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INESITE FROM THE KOKURIKI MINE, HOKKAIDO, JAPAN

by

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(with 4 text-figures and 4 tables)

Abstract

Inesite occurs in veinlet cutting hematite ore from the Kokuriki mine, eastern Hokkaido. Its associated minerals are rhodochrosite, barite and quartz.

The inesite forms fine prisms up to 1 mm long and is pale orange in color. Refractive indices are: $\alpha = 1.618(3)$, $\beta = 1.639(3)$ and $\gamma = 1.656(3)$. Biaxial, negative. $2V(meas.) = 67\text{-}70°$.

The composition is as follows: SiO_2 45.94, Al_2O_3 0.02, Fe_2O_3 0.57, MnO 37.50, MgO 0.10, CaO 8.60, Na_2O 0.04, K_2O 0.04, H_2O 8.90, Total 101.71 wt.%. The H_2O content was determined by a thermogravimetric analysis. The empirical formula is calculated as: $(Ca_{1.97}Na_{0.02}K_{0.01})_{\Sigma 2.00}(Mn_{6.80}Mg_{0.03})_{\Sigma 6.83}(Si_{9.84}Fe^{3+}_{0.09}Al_{0.01})_{\Sigma 9.94}O_{35.00}H_{12.72}$.

Unit-cell parameters based on morphological cell were determined by X-ray powder diffraction as follows: $a = 8.938(4)$, $b = 9.259(5)$, $c = 11.959(5)$ Å, $\alpha = 91.96(7)°$, $\beta = 132.72(3)°$, $\gamma = 94.36(6)°$.

Crystal field spectra indicate that the orange color of the inesite may be caused by Mn^{3+} converted from a part of Mn^{2+}.

Introduction

Inesite has been reported from a number of metamorphosed manganiferous deposits as a late vein-forming mineral (Glass and Schaller, 1939; Takasu, 1955; Yoshimura and Momoi, 1960; Ryall and Threadgold, 1968; Abrecht, 1984).

In Hokkaido, an occurrence of inesite has been reported from the Todoroki mine (Yoshimura, 1932).

In the present study, inesite associated with hematite ores of the Kokuriki mine, Hokkaido, is described in detail.

Occurrence

The Kokuriki mine is located in Hiyoshi, about 20 km north of Kitami City, southern part of the Tokoro district, eastern Hokkaido, Japan (Text-fig. 1). The mine is not operated at present. The hematite ores of the Kokuriki mine occur in a member of the Nikoro Group which consists mainly of Jurassic greenstones and small amounts of chert and limestone, lying between a pillow basalt and a radiolarian chert (Bamba, 1984; Research Group of Tokoro Belt, 1984).

The ore specimens studied were collected from the dump of the mine. Inesite occurs in veinlet cutting hematite ore and is associated with rhodochrosite, barite and quartz (Text-fig. 2). In other specimens, Mn^{3+} dominant pumpellyite and piemontite occur in veinlets (Togari and Akasaka, in prep).

Contribution from the Department of Geology and Mineralogy, Faculty of Science, Hokkaido University, No. 1864.

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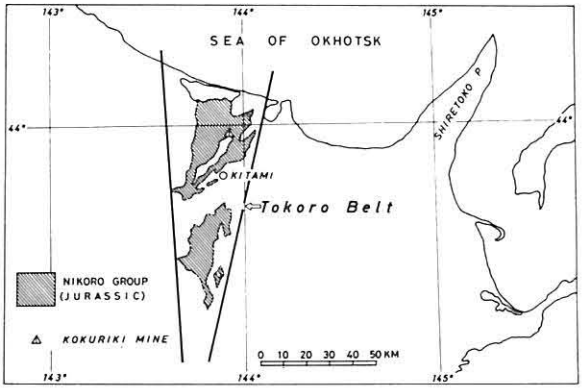
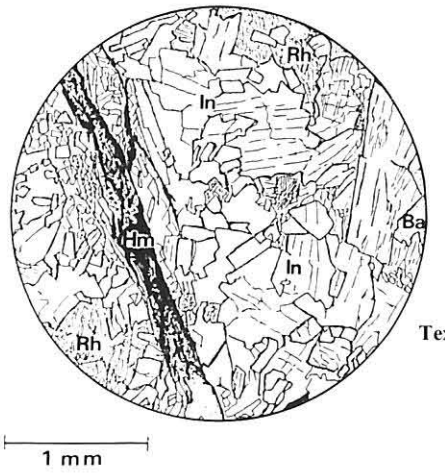


Text-fig. 1 Index map showing the location of the Kokuriki mine.



Text-fig. 2 Microscopic sketch of a thin section of inesite in the hematite ore from the Kokuriki mine.
In: inesite, Hm: hematite, Rh: rhodochrosite, Ba: barite.

Optical properties

This mineral is fine prisms up to 1 mm long, forming aggregates in network veinlets. It is transparent and pale orange in color, showing a vitreous lustre. The dominant wave length is 591 nm. Saturation and refractivity are calculated as 27.4% and 30.5%, respectively.

Optical properties are: biaxial and negative, 2V (meas.) 67-70°, 2V (calc.) 83°. Refractive indices measured by the immersion method are: $\alpha = 1.618(3)$, $\beta = 1.639(3)$ and $\gamma = 1.656(3)$. Cleavage {100} and {010}.

Chemical analysis

Chemical analysis was carried out with a HITACHI XMA-5A electron microprobe at 15 kV with beam current of 0.02 μA and beam diameter of 5 μm. The data were corrected by the method of Bence and Albee (1968) and Albee and Ray (1970) using following standards: wollastonite (Ca, Si), synthetic spinel (Mg, Al), synthetic MnO (Mn), synthetic rutile (Ti), synthetic magnetite (Fe), and anorthoclase (Na, K). H_2O

content was determined by thermogravimetric analysis as indicated later.

The compositions of inesite are listed in Table 1 with the results obtained by other workers (Glass and Schaller, 1939; Richmond, 1942; Kitahara, 1950; Takasu, 1955; Yoshimura and Momoi, 1960; Ryall and Threadgold, 1968; Abrecht, 1984). The structural formula of the present inesite is as follows: $(Ca_{1.97}Na_{0.02}K_{0.01})_{\Sigma 2.00}(Mn_{6.80}Mg_{0.03})_{\Sigma 6.83}(Si_{9.84}Fe^{3+}{}_{0.09}Al_{0.01})_{\Sigma 9.94}O_{35.00}H_{12.72}$. This is in close agreement with the simple formula, $Ca_2Mn_7Si_{10}O_{28}(OH)_2 \cdot 5H_2O$ (Richmond, 1942; Ryall and Threadgold, 1968; Abrecht, 1984), rather than that, $Ca_2Mn_7Si_{10}O_{28}(OH)_2 \cdot 6H_2O$ (Takasu, 1955; Yoshimura and Momoi, 1960).

Table 1 Compositions of inesite

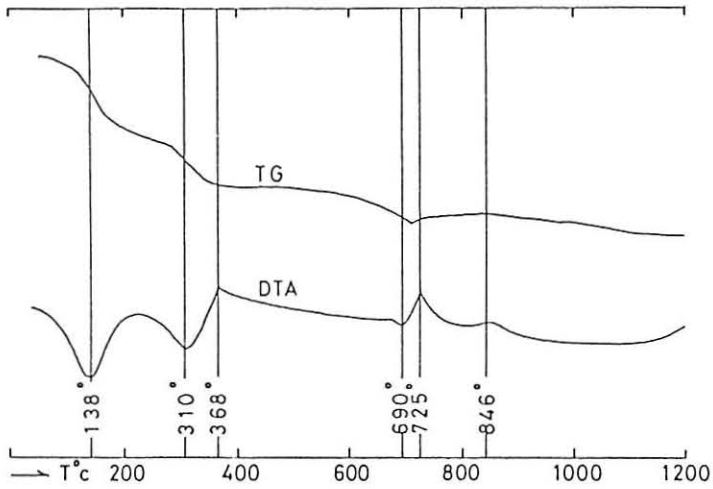
	1	2	3 (a)	3 (b)	4	5	6	7 (a)	7 (b)
SiO_2	45.94 (38)	45.64	44.71	44.89	43.67	45.67	45.48	45.71	45.60
Al_2O_3	0.02 (2)	—	0.20	0.29	0.34	—	0.19	0.03	0.07
Fe_2O_3	0.57 (11)	—	0.15	0.18	0.21	—	—	—	—
FeO	—	0.27	—	—	—	0.92	3.03	0.21	0.23
MnO	37.50 (43)	36.77	37.12	36.80	36.92	35.10	33.24	37.72	38.42
MgO	0.10 (9)	0.68	0.42	0.23	0.87	0.86	0.23	0.25	0.23
CaO	8.60 (36)	8.34	7.31	8.49	8.30	9.33	8.73	8.32	7.57
Na_2O	0.04 (2)	—	—	—	—	—	0.30	0.00	0.00
K_2O	0.04 (2)	—	—	—	—	—	0.18	0.02	0.01
H_2O	8.90	7.82	9.42	9.07	8.81	8.66	8.73	7.70	7.70
Total	101.71	99.52	99.33	99.95	99.12	100.54	100.11	100.03	99.72
Structural formula*									
Si	9.84	10.07	9.98	10.07	9.89	10.01	9.87	10.08	10.08
Al	0.01	—	0.05	0.08	0.09	—	0.05	0.01	0.01
Fe^{3+}	0.09	—	0.03	0.03	0.04	—	—	—	—
Fe^{2+}	—	0.05	—	—	—	0.17	0.55	0.04	0.04
Mn	6.80	6.87	7.02	6.99	7.08	6.51	6.11	7.05	7.19
Mg	0.03	0.22	0.14	0.08	0.29	0.28	0.07	0.08	0.08
Ca	1.97	1.97	1.75	2.04	2.01	2.19	2.03	1.97	1.79
Na	0.02	—	—	—	—	—	0.13	0.00	0.00
K	0.01	—	—	—	—	—	0.05	0.01	0.01
H	12.72	11.51	14.04	13.19	13.31	12.66	12.65	11.32	11.36

1 Kokuriki mine, Japan (present study). Standard deviations are in the parenthesis. Total iron as Fe_2O_3.
2 Innai mine, Japan (Kitahara, 1950)
3 (a) Rendaiji mine, Japan (Takasu, 1955)
3 (b) Rendaiji mine, Japan (Yoshimura and Momoi, 1960)
4 Kacho mine, Japan (Yoshimura and Momoi, 1960)
5 Quinault, USA (Glass and Schaller, 1939; Richmond, 1942)
6 Broken Hill Lode, Australia (Ryall and Threadgold, 1968)
7 (a), (b) Hale Creek mine, USA (Abrecht, 1984)

*Structural formulae of Nos. 1, 2, 5, 6, 7 (a) and 7 (b) were calculated on a basis of 35 oxygens, and those of Nos. 3 (a), 3 (b) and 4 on a basis of 36 oxygens.

Thermal analysis

The results of a differential thermal analysis-thermogravimetric (DTA-TG) study are shown in Text-fig. 3 and Table 2. Powdered inesite, 26 mg in weight, was heated at



Text-fig. 3 DTA and TG curves of inesite in air. Heating rate 10°C/min. Pt/Pt-13Rh thermocouple.

Table 2 DTA peak temperature of inesite

Endothermic	Exothermic
138 (s)	
310 (ms)	
	368 (mw)
690 (w)	
	725 (ms)
	846 (w)

Relative intensity of peaks: s = strong; ms = medium strong; m = medium; mw = medium weak; w = weak

a rate of 10°C/min in a tiny platinum crucible.

Both the DTA and TG-curves are very similar to those given by Ito (1961), Ryall and Threadgold (1968) and Abrecht (1984), whereas DTA peak temperatures are in good agreement with those by Abrecht rather than those by Ito or Ryall and Threadgold.

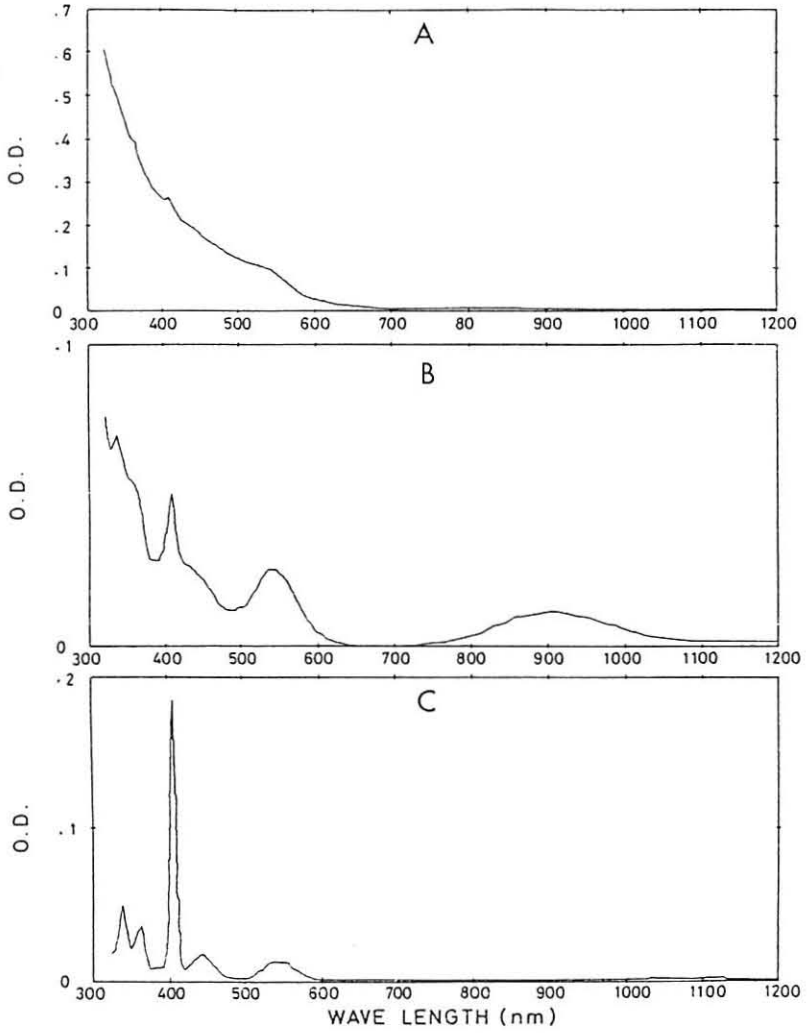
Water content of inesite has been determined as 8.9 wt.% after heating up to 1,200°C. In the range of 20 to 200°C, 4 wt.% H_2O was released, and in the range 200 to 400°C, 2.8 wt.% H_2O. This result is completely consistent with that by Abrecht. Although (OH) water released in the range 600 to 800°C cannot be determined directly by TG because of the oxidation of Mn (Ito, 1961), it is estimated to be 2.1 wt.% by subtraction of H_2O content of coordinated water from total water content.

The X-ray powder diffraction pattern of the product heated up to 1,200°C could be attributed to bustamite and cristobalite.

X-ray powder diffraction

The X-ray powder diffraction pattern was obtained by using Cu radiation. The X-ray powder data given in Table 3 are indexed based on the morphological cell by Ryall and Threadgold (1968). However we modified a part of the indexed powder data by Ryall and Threadgold, because some indices are inconsistent with their unit-cell parameters.

The unit-cell parameters calculated from the indexed X-ray powder data are listed in Table 4. The inesites from the Kokuriki mine and from the Broken Hill Lode have similar unit-cell parameters each other (Table 4. Nos. 1a and 2). Other unit-cell



Text-fig. 4 Crystal-field spectra for inesite.
A: Inesite from the Kokuriki mine.
B: Inesite from the Rendaiji mine.
C: Rhodochrosite from the Yakumo mine.

Table 3 X-ray powder diffraction pattern of inesite

	Broken Hill Lode, Australia*					kokuriki	mine
d (cal)	d (obs)	I/Io	H	K	L	d (obs)	I/Io
9.159	9.16	100	0	1	0	9.17	100
6.716	6.69	10	0	$\bar{1}$	1		
6.515	6.54	40	1	0	$\bar{1}$	6.52	13
6.172	6.15	5	1	1	$\bar{1}$		
5.081	5.09	40	$\bar{1}$	$\bar{1}$	2		
4.580	4.59	50	0	2	$\bar{2}$	4.59	20
4.434	4.44	5	2	0	2		
4.378	4.38	5	0	0	$\bar{1}$	4.37	6
4.260	4.27	30	0	2	1	4.26	6
4.126			0	$\bar{1}$	2	4.13	5
4.100	4.10	10	2	0	$\bar{1}$		
4.098			2	$\bar{1}$	2		
4.004	4.01	50	1	2	$\bar{2}$	4.01	55
3.892	3.89	10	2	1	2	3.89	5
3.794	3.79	10	1	0	$\bar{3}$		
3.595	3.62	10	1	1	3		
3.542	3.55	10	1	$\bar{1}$	1		
3.267			1	2	1	3.269	10
3.258	3.26	10	2	0	0		
3.206	3.20	10	2	$\bar{1}$	$\bar{2}$	3.206	10
3.086			2	2	2	3.090	5
3.053	3.05	5	0	3	0	3.057	10
2.990			0	$\bar{3}$	1	2.994	8
2.949			2	1	0	2.951	10
2.917	2.92	80	1	$\bar{3}$	0	2.921	57
2.877	2.88	10	$\bar{3}$	0	2	2.881	8
2.843	2.84	80	1	0	2	2.841	82
2.838			2	$\bar{2}$	0		
2.730	2.73	70	$\bar{3}$	0	4	2.734	10
2.701	2.70	30	1	0	$\bar{4}$		
2.691			0	1	3	2.693	8
2.634	2.63	20	$\bar{3}$	1	4	2.637	8
2.634			1	3	0		
2.572			1	2	2	2.571	10
2.561	2.56	30	3	2	3	2.558	40
2.555			3	2	2		
2.542			3	1	1	2.542	10
2.394	2.39	10	2	3	3	2.395	5
2.365			2	1	1	2.365	2
2.342			0	2	3	2.340	6
2.332	2.33	20	3	2	2	2.333	10
2.197			3	3	3	2.199	10
2.188	2.19	60	4	1	4	2.190	35
2.172	2.17	40	1	1	3	2.175	15
2.172			3	0	0		
2.171			2	3	4		
2.167			1	0	3	2.165	6
2.130	2.13	10	0	4	2		
2.122	2.12	10	3	2	1		
2.121			1	4	1		
2.068			4	1	5	2.068	6
2.053	2.05	10	3	1	0	2.051	6
2.051			4	1	2		
2.051			1	1	3		
2.050			4	0	2		
2.049			4	2	4		

*Modified based on data by Ryall and Threadgold (1968)

Table 4 Unit-cell parameters of inesite

No.	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
1a	8.938 (4)	9.259 (5)	11.959 (5)	91.96 (7)	132.72 (3)	94.36 (6)
1b	8.835 (3)	9.259 (4)	11.959 (5)	88.13 (5)	131.99 (3)	97.01 (4)
2	8.927	9.245	11.954	91.80	132.58	94.37
3	8.89	9.14	12.14	87.63	132.50	97.02
4	8.968 (3)	9.265 (2)	11.956 (4)	88.20 (1)	132.71 (1)	96.41 (1)
5	8.889 (2)	9.247 (2)	11.975 (3)	88.15 (2)	132.07 (2)	96.64 (2)
6	8.862 (2)	9.258 (2)	11.972 (2)	88.08 (1)	132.02 (1)	96.64 (2)

Standard deviations are in the parenthesis.
1 Kokuriki mine, Japan (present study).
a; Morphological cell (Ryall and Threadgold, 1968)
b; Richmond's cell (Richmond, 1942)
2 Broken Hill Lode, Australia (Ryall and Threadgold, 1968)
3 Quinault, USA (Richmond, 1942)
4 Hale Creek mine, USA (Abrecht, 1984). Richmond's cell.
5 Hale Creek mine, USA (Van and Ghose, 1978). Richmond's cell.
6 Crescent mine, USA (Van and Ghose, 1978). Richmond's cell.

parameters of inesite from the Kokuriki mine (Table 4. No. 1b) were calculated in terms of the Richmond's cell, which can be derived by transforming morphological HKL to Richmond's HKL by the matrix $\bar{1}0\bar{1}/0\bar{1}0/001$ (Richmond, 1942). These values are in fair agreement with those of inesites from other localities (Table 4. Nos. 3, 4, 5 and 6).

Crystal-field spectra

Crystal-field spectra for powdered specimens were taken in the wavelength range of 325-1,200 nm at room temperature, by Beckman model DK-2A automatic recording spectrophotometer with reflection technique using an integration sphere. The reflection spectra obtained from 2 cm ϕ circular area were plotted against optical density (O.D.) scale in Text-fig. 4 (Ikeda, 1984). Al_2O_3 was used as the working standard. Crystal-field spectra of rhodochrosite from Yakumo mine and inesite from the Rendaiji mine are also shown for comparison. The spectrum of pink inesite from the Rendaiji mine, which shows the bands at wavelength 340 nm (29,412 cm^{-1}), 360 nm (27,778 cm^{-1}), 410 nm (24,390 cm^{-1}), 440 nm (22,727 cm^{-1}) and 545 nm (18,349 cm^{-1}), is very similar to that of rhodochrosite. Thus pink color of inesite from the Rendaiji mine is caused by Mn^{2+}-cations in the octahedral site as expected from the results of chemical analysis. Although this inesite has been reported not to contain Fe^{2+} from the wet chemical analysis, it seems to contain a very small amount of Fe^{2+}, because the weak and broad band at wavelength 920 nm (10,870 cm^{-1}) may be assigned to Fe^{2+} spin-allowed transitions in the octahedral site (cf. Burns 1970). On the other hand, the spectrum of inesite from the Kokuriki mine is very different from that of the Rendaiji mine, although the weak bands at wavelength 340 nm, 360 nm, 410 nm, 440 nm and 545 nm are assigned to Mn^{2+} in the octahedral site. In this spectrum, it seems that the

bands at 390 nm (25,640 cm^{-1}), 430 nm (23,256 cm^{-1}) and 490-500 nm (20,000-20,600 cm^{-1}) are added to the spectrum of inesite from the Rendaiji mine. According to the previous studies on the minerals containing Mn^{3+}-cations (Abs-Wurmbach et al., 1981; Smith et al., 1982; Langer et al., 1982), the bands at wavelength 430 nm and 490-500 nm seem to be assigned to Mn^{3+} in the octahedral site, and that at wavelength 390 nm may be assigned to Mn^{2+}-Mn^{3+} charge transfer. Thus the orange color of inesite from the Kokuriki mine may be caused by Mn^{3+} converted from a part of Mn^{2+}.

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