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New characterization of takanelite

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ABSTRACT

In a study of the hexagonal 7-Å phyllomanganate minerals, the Mn^{2+} analogue of rancieite, takanelite, has been discovered at the Janggun mine, Korea. This takanelite occurs as massive or colloform bands in the nsutite-rich ores of the supergene oxidation zone of rhodochrosite. Color is brownish gray to dark gray, with dull luster and dark brown streak. The hardness ranges from 2.5 to 3.0, and the measured and calculated densities are 3.43 and 3.436, respectively.

Under reflected light it is anisotropic and shows no internal reflection. Electron-microprobe and wet-chemical analyses give MnO_2 74.01, MnO 10.42, CaO 3.64, MgO 0.59, K_2O 0.33, Fe_2O_3 0.26, H_2O 11.50, for a total of 100.75 wt%. The empirical chemical formula for the mineral is $(Mn^{2+}_{0.15}Ca_{0.07}Mg_{0.02}K_{0.01})Mn^{4+}_{0.88}O_{2.00}\cdot 0.66H_2O$, whereas the idealized formula is $(Mn^{2+},Ca)_{2x}Mn^{4+}_{1-x}O_2\cdot 0.66H_2O$ ($x = 0.12$). The mineral has a hexagonal unit cell with $a = 2.830(1)$ and $c = 7.240(3)$ Å, $Z = 1$, and $a{:}c = 1{:}2.558$. The X-ray diffraction lines are 7.25(s) (001), 3.619(wb) (002), 2.451(m) (100), 2.347(w) (101), 1.429(m) (110). The DTA curve shows endothermic peaks at 190, 610, 790, and 920 °C. After heating at 200 °C for 24 h, $d(001)$ decreased from 7.25 to 6.90 Å. The IR absorption spectrum shows absorption bands at 3440, 1635, 1070, 670, 570, 510, and 460 cm^{-1}.

Analysis and comparison of these data with those for takanelite given by Nambu and Tanida (1971) show that the samples described by them were actually rancieite.

INTRODUCTION

The presumed Mn^{2+} analogue of rancieite from the Nomura mine, Japan, was named takanelite by Nambu and Tanida (1971) and approved by the IMA. It is, however, curious that it has the same X-ray diffraction pattern as rancieite. The $d(001)$ values of takanelite and rancieite are both 7.57 Å, but their reported chemical formulas are $(Mn^{2+},Ca)Mn^{4+}_4O_9\cdot 1.3H_2O$ (Nambu and Tanida, 1971) and $(Ca,Mn^{2+})Mn^{4+}_4O_9\cdot 3H_2O$ (Richmond et al., 1969), respectively.

During a study of the phyllomanganate minerals, many samples that have $d(001)$ values between 7.1 and 7.6 Å were collected. To determine the cause of this variation in $d(001)$, these samples have been analyzed chemically. A crystal-chemical study of these materials has revealed that the 001 spacings of 7-Å phyllomanganate minerals depend on the nature of interlayer cations and H_2O molecules in interlayers between $[MnO_6]$ octahedral layers.

Among the 7-Å phyllomanganate minerals studied, samples were found that are Mn^{2+} dominant and that therefore correspond chemically to takanelite. However, X-ray diffraction analysis shows a considerable difference between the 001 spacings of these minerals: 7.57 Å for takanelite (Nambu and Tanida, 1971) and 7.25 Å for Mn^{2+}-dominant samples. Considering the difference in ionic radii of Ca^{2+} (0.99 Å) and Mn^{2+} (0.80 Å) (Rösler and Lange, 1972), it is improbable that takanelite, a supposed Mn^{2+}-rich mineral, would have d-values similar to those observed for our Mn^{2+}-rich material (7.25 Å), but that a value as large as 7.57 Å might correspond to the Ca-rich material. These Mn^{2+}-dominant samples have therefore been characterized and the data compared with those of Nambu and Tanida (1971). This has shown that the data given by Nambu and Tanida for supposed takanelite are at least in part for rancieite.

MINERALOGICAL DATA FOR A Mn^{2+} ANALOGUE OF RANCIEITE

Occurrence and physical properties

A presumed Mn^{2+} analogue of rancieite has been found at the Janggun mine, Bonghwa, Korea. It occurs as massive or colloform bands in nsutite-rich ores of the supergene zone derived through oxidation of rhodochrosite. It is usually replaced by nsutite or pyrolusite along the colloform bands or in a random fashion, showing gradational contacts (Fig. 1). The manganese ore containing this mineral is gray in color and very hard because of the presence of abundant nsutite. It is characterized by small, gray shiny or greasy colloform areas. The physical properties of this takanelite are summarized and compared with those of rancieite in Table 1. Density was measured using heavy liquids.

Chemical composition

A review of the crystal chemical relations of phyllomanganate minerals (Kim, in preparation) shows that all

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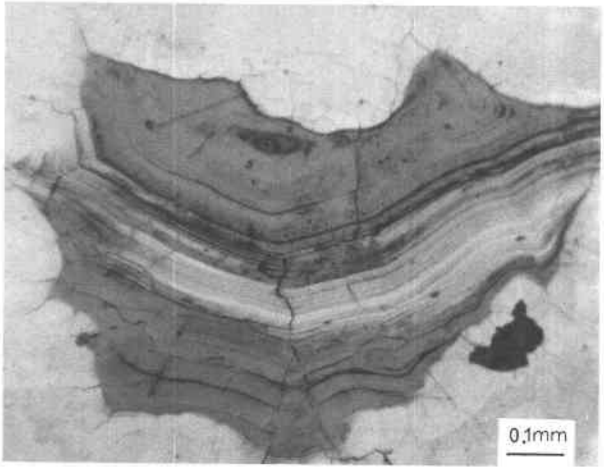

Fig. 1. A polished section showing takanelite from the Janggun mine, Korea. The mineral (gray, colloform) is replaced by nsutite (light gray) along the edge of the sample and within colloform layers.

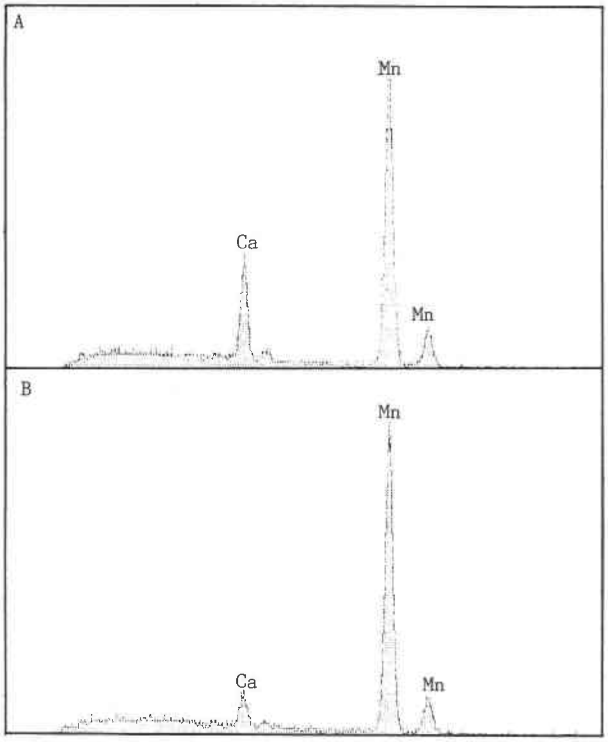

Fig. 2. Comparison of X-ray energy dispersive spectra of rancieite (**A**) from Oriente Province, Cuba, and the takanelite (**B**) from the Janggun mine, Korea.

the hexagonal 7-Å phyllomanganate minerals, including rancieite, birnessite, and related phases, have layer structures that consist of alternating layers of edge-sharing [MnO_6] octahedra and sheets of H_2O molecules. Mono- and divalent cations are arranged above and below the vacancies in the octahedral layers, as suggested by Giovanoli et al. (1970), Chukhrov et al. (1978, 1979), and Burns and Burns (1979). The vacant octahedral sites are randomly distributed, as suggested by Chukhrov et al. (1978, 1979). Chemical compositions of these minerals suggest that statistically one out of nine octahedral sites is vacant in the hexagonal 7-Å phyllomanganate minerals. This structural model led to the derivation of a new general formula, $R_{2x}Mn^{4+}_{9-x}O_{18}\cdot nH_2O$, where $R = Mn^{2+}$, Ca^{2+}, Mg^{2+}, Na^+, K^+, and x is the total number of vacant sites per 18 O atoms. This formula is for the contents of nine unit cells. Therefore, one unit cell has the contents $R_{2x}Mn^{4+}_{1-x}O_2\cdot nH_2O$, where x is the fraction of vacant octahedral sites.

A chemical analysis of the takanelite from the Janggun mine was carried out using an ARL electron microprobe. Mn and H_2O were analyzed by wet-chemical methods.

Table 1. Comparative data for rancieite and takanelite

	Rancieite*	Takanelite**
Formula	$(Ca, Mn^{2+})_{2x}Mn^{4+}_{1-x}O_2\cdot 0.72H_2O$ ($x = 0.10$)	$(Mn^{2+}, Ca)_{2x}Mn^{4+}_{1-x}O_2\cdot 0.66H_2O$ ($x = 0.12$)
Symmetry	hexagonal	hexagonal
a (Å)	2.841	2.830(1)
c (Å)	7.540	7.240(3)
Habit	massive, very fine grained, scaly	massive, colloform, friable
Color	silver gray, brown, brownish black	brownish gray, dark gray
Streak	purplish dark brown	dark brown
Luster	dull	dull
Mohs hardness	2.5–3	2.5–3 (HV = 26)
D_{meas}	3.0–3.2	3.425
D_{calc}	3.078	3.436
	Microscopic appearance in polished section	
Color	light gray	light gray to gray
Reflection pleochroism	none	none
Anisotropism	distinct (yellowish white, gray)	distinct (brownish gray, gray, dark gray)
Extinction	wavy	parallel
Internal reflection	none	none
Reflectance	low	low

* Data from Richmond et al. (1969).
** From the Janggun mine, Korea.

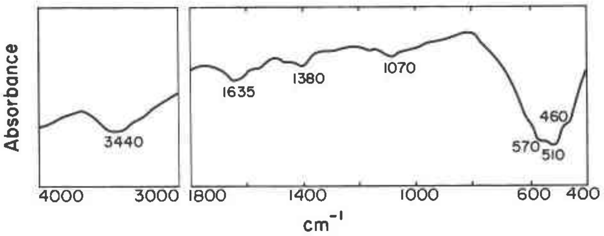

Fig. 3. Infrared absorption spectrum of takanelite from the Janggun mine, Korea.

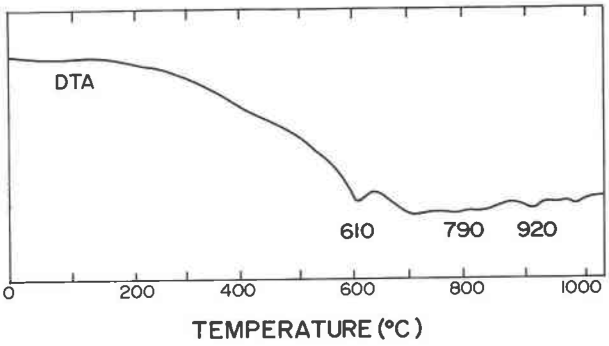

Fig. 4. DTA curve of takanelite from the Janggun mine, Korea.

Available O, determined by the oxalate titration method, was allotted to MnO_2 and the remaining Mn was calculated as MnO. Traces of Ba and Al were detected and Si was not detected by emission spectroscopic analysis.

Chemical analyses of rancieite from Oriente Province, Cuba, takanelite from the Janggun mine, Korea, takanelite of Nambu and Tanida from Nomura mine, Japan, and rancieite and takanelite from other localities are given in Table 2. The chemical formulas calculated on the basis of the structural model described above are $(Ca_{0.15}Mn^{2+}_{0.05}Na_{0.01}K_{0.01})Mn^{4+}_{0.90}O_{2.00}\cdot 0.72H_2O$, or ideally $(Ca,Mn^{2+})_{2x}Mn^{4+}_{1-x}O_2\cdot 0.72H_2O$ ($x = 0.10$) for rancieite from Oriente Province, Cuba, and $(Mn_{0.15}Ca_{0.07}Mg_{0.02}K_{0.01})Mn^{4+}_{0.88}O_{2.00}\cdot 0.66H_2O$, or ideally $(Mn^{2+},Ca)_{2x}Mn^{4+}_{1-x}O_2\cdot 0.66H_2O$ ($x = 0.12$) for takanelite from the Janggun mine, Korea.

On the basis of 18 O atoms, rancieite and takanelite have the formulas $(Ca,Mn^{2+})_{2x}Mn^{4+}_{9-x}O_{18}\cdot nH_2O$ and $(Mn^{2+},Ca)_{2x}Mn^{4+}_{9-x}O_{18}\cdot nH_2O$, respectively. The value of x varies from 0.81 to 1.28 in the studied samples and, therefore, the formulas are close to the stoichiometric formula $CaMn_4O_9\cdot 3H_2O$ given by Fleischer and Richmond (1943) and Perseil (1967) and to the formula $CaMn_4O_9\cdot 4H_2O$ given by Bardóssy and Brindley (1978) and Barrese et al. (1986). Differences between chemical compositions of rancieite and takanelite from the Janggun mine are seen in the X-ray energy dispersive spectra (Fig. 2) that were obtained using energy dispersive spectrometer attached to JEOL 733 Superprobe. The ranceite has a higher Ca peak, as expected.

X-ray powder diffraction data

X-ray powder diffraction data for rancieite and takanelite, measured from powder patterns obtained with a Gandolfi camera and Mn-filtered Fe$K\alpha$ radiation, are given in Table 3. The powder pattern of takanelite from the Janggun mine was indexed on a hexagonal cell with $a = 2.830(1)$ and $c = 7.240(3)$ Å, $a{:}c = 1{:}2.558$, $Z = 1$.

Infrared absorption spectra and DTA data

Infrared absorption spectra of takanelite from the Janggun mine, Korea, obtained by the KBr pellet technique, show absorption bands at 3440 (m), 1635 (m), 1070 (w), 670 (vw), 570 (vs), 510 (vs), and 460 (vs) cm^{-1}. Absorption bands at 3440 and 1635 cm^{-1} are attributed to H_2O molecules in the structure (Fig. 3). The DTA curve (Fig. 4) of takanelite shows endothermic peaks at 190, 610, 790, and 920 °C. After heating at 200 °C for 24 h $d(001)$ of takanelite decreased from 7.25 to 6.90 Å.

CRYSTAL-CHEMICAL RELATIONS

As mentioned above, rancieite and takanelite have layer structures that consist of alternating layers of edge-sharing

TABLE 2. Chemical analyses of rancieite and takanelite samples

	(1)	(2)	(3)	(4)	(5)		(1)	(2)	(3)	(4)	(5)
MnO_2	75.04	64.8	74.01	66.66	70.39	Mn^{4+}	0.90	0.91	0.88	0.86	0.87
MnO	3.31	3.0	10.42	16.07	13.06	Mn^{2+}	0.05	0.05	0.15	0.25	0.20
CaO	8.10	6.1	3.64	1.05	2.66	Ca	0.15	0.12	0.07	0.02	0.05
MgO	0.16	0.32	0.59	0.23	0.22	Mg	0.00	0.01	0.02	0.01	0.01
Na_2O	0.12	0.11	—	0.16	0.05	Na	0.01	0.00	—	0.01	—
K_2O	0.26	0.12	0.33	0.09	0.05	K	0.01	0.00	0.01	0.00	—
Fe_2O_3	0.12	2.9	0.26	0.86	1.34	O	2.00	2.00	2.00	2.00	2.00
Al_2O_3	0.12	2.6	—	0.83	1.70	H_2O	0.72	0.83	0.66	0.65	0.16
SiO_2	0.62	0.7	—	2.62	3.61						
Others	0.12	0.31	—	1.47	—						
H_2O	12.62	13.69	11.50	10.83	7.14						
Total	100.50	97.65	100.75	100.87	100.22						

Note: Fe_2O_3, SiO_2, and Al_2O_3 are assumed to be due to impurities such as goethite, kaolinite and quartz. Numbers in parentheses indicate the following: (1) rancieite from Oriente Province, Cuba (Richmond et al., 1969); (2) rancieite from Itéa, Greece (Bardóssy and Brindley, 1978); (3) takanelite from the Janggun mine, Korea (this work); (4) takanelite from the Anson Betts mine, Plainfield, Massachusetts, U.S.A. (Frondel et al., 1960), originally described as birnessite; (5) takanelite from the Nomura mine, Japan (Nambu and Tanida, 1971).

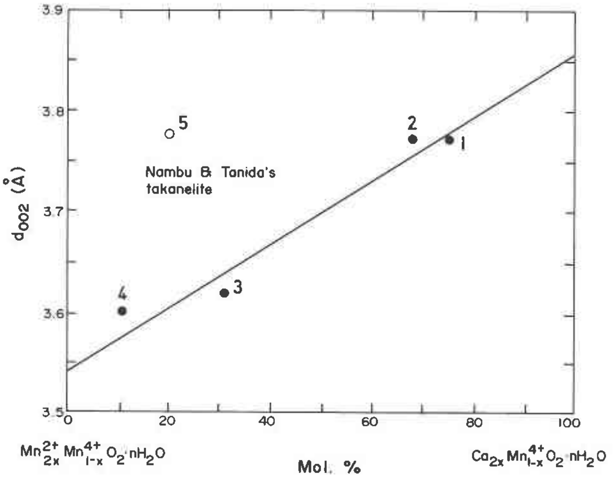

Fig. 5. Plot of *d*(002) vs. chemical composition for the hexagonal 7-Å phyllomanganate minerals of formula $R_{2x}Mn^{4+}_{1-x}O_2 \cdot nH_2O$, where $R = Mn^{2+}$, Ca. Numbers are the same as in Tables 2 and 3.

[MnO_6] octahedra and sheets of H_2O molecules, with Ca and Mn^{2+} arranged above and below the vacancies in the octahedral layers. In order to determine if takanelite is derived from rancieite by substitution of Mn^{2+} for the Ca^{2+} in the interlayer positions of rancieite, *d*(002) has been plotted vs. chemical composition for rancieite and takanelite specimens for a system consisting of two end-members: $Ca_{2x}Mn^{4+}_{1-x}O_2 \cdot nH_2O$ and $Mn^{2+}_{2x}Mn^{4+}_{1-x}O_2 \cdot nH_2O$ in Figure 5. Data for rancieite and takanelite samples from other localities are also shown. Figure 5 is consistent with a solid solution series between the two end-members. Considering the difference in the ionic radii of Ca^{2+} (0.99 Å) and Mn^{2+} (0.80 Å) (Rösler and Lange, 1972), it may be expected that substitution of Ca^{2+} by Mn^{2+} in the interlayer will cause a decrease in the basal spacings, as shown in Figure 5.

DISCUSSION

Takanelite, defined by Nambu and Tanida (1971) as the Mn^{2+} analogue of rancieite, was approved by the IMA. According to Nambu and Tanida (1971), takanelite has the same X-ray pattern as rancieite (Table 3) and has the formula $(Mn_{0.89}Ca_{0.23}Mg_{0.03})Mn^{4+}_{3.94}O_{9.00} \cdot 1.3H_2O$. According to results of the present study, it should lie on the trend for the series $(Ca,Mn^{2+})_{2x}Mn^{4+}_{1-x}O_2 \cdot nH_2O$ shown in Figure 5. However, it plots at a position far from the trend.

Takanelite from the Janggun mine gives an X-ray diffraction pattern similar to that of rancieite but with smaller *d*-values. This variation (in particular, the difference in 001 interplanar spacings) is reasonable in view of the difference in the ionic radii of Ca^{2+} and Mn^{2+}. The 001 *d*-values of the phyllomanganate minerals under discussion vary systematically with the Mn^{2+}:Ca ratio and the H_2O content. It is unlikely that Nambu and Tanida's takanelite with $Mn^{2+}/R = 0.77$ has the same *d*(001) value (7.57 Å) as rancieite with $Mn^{2+}/R = 0.23$, where $R = Mn^{2+}$, Ca, Mg, Na, K.

The parameters for the hexagonal cell of Nambu and Tanida's takanelite ($a = 8.68$ Å, $c = 9.00$ Å) apparently were determined incorrectly, as pointed out by Chukhrov et al. (1979). The powder data can be indexed on a hexagonal cell with $a = 2.843$ and $c = 7.53$ Å, which corresponds to the parameters of rancieite. In addition, the number of H_2O molecules is too small. It is difficult to explain these discrepancies. It therefore seems likely that Nambu and Tanida's type specimen of takanelite may actually be rancieite containing impurities such as todorokite and braunite, as Nambu and Tanida themselves (1971) showed in their X-ray data. The fact that their takanelite sample gives the same *d*-values as rancieite strongly suggests such a possibility.

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TABLE 3. Comparative X-ray powder diffraction data of rancieite and takanelite

Rancieite					Takanelite					
(1)			(2)		(3)		(4)		(5)	
I	*d* (Å)	*hkl*	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)
s	7.57	001	100	7.56	s	7.25	s	7.31	100	7.57
m	3.77	002	20	3.77	wb	3.619	w	3.60	25	3.765
mw	2.46	100	12	2.46	m	2.451	m	2.44	15	2.462
m	2.34	101	10	2.35	w	2.347			20	2.349
m	2.06	102	10	2.06					10	2.065
m	1.76	103	8	1.76					7	1.754
m	1.423	110	7	1.42	m	1.429	m	1.418	17	1.420
		111	5	1.40						

Note: Numbers in parentheses indicate the following: (1) Oriente Province, Cuba (Richmond et al., 1969); (2) Itéa, Greece (Bardóssy and Brindley, 1978); (3) Janggun mine, Korea (this work); (4) Anson Betts mine, Plainfield, Ma., U.S.A. (Frondel et al., 1960), originally described as birnessite; (5) Nomura mine, Japan (Nambu and Tanida, 1971).

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