

Mineralogy and Genesis of Manganese Ores from the Eosangcheon Mine, Korea

Soo Jin Kim* and Seong Hoon Kim*

Abstract: The Eosangcheon manganese ore deposits occur as supergene weathering deposits along quartz porphyry dikes developed in the Ordovician Heungweolri dolomite and Samtaesan limestone formations. The manganese ores are composed of manganese oxide minerals and associated other minerals. Rancieite and todorokite are abundantly found, and birnessite, nsutite, pyrolusite and chalcophanite are found in minor quantities. Associated other minerals are calcite, gypsum, goethite, lepidocrosite, quartz, and sericite. Microscopic, chemical, X-ray powder diffraction, infrared absorption spectroscopic and differential thermal analyses have been made for manganese oxide minerals and associated other minerals. The relationship of birnessite and rancieite was studied by means of X-ray powder diffraction and infrared absorption spectroscopic analyses. It is assumed that these minerals are closely related to each other in crystal structure, but separate species.

The manganese oxide minerals were formed mainly by replacement, precipitation from solution, and recrystallization in the supergene weathering environment. The trend of formation of manganese oxide minerals is: (Rhodochrosite)-(todorokite)-(birnessite, rancieite)-(nsutite, pyrolusite, chalcophanite).

Introduction

The Eosangcheon mine is located in Eosangcheonmyeon, Danyang-gun, Chungcheongbugdo, about 13 Km southeast of Jaechon City, Chungcheongbug-do, and lies at $37^{\circ}05'30''$ - $37^{\circ}06'30''$ N in latitude and $128^{\circ}21'$ - $128^{\circ}22'$ E in longitude.

The mine produced several thousand tons of manganese oxide ores from 1977 to 1979. But it is no longer in production.

This manganese deposit is characterized by the abundant occurrence of rancieite and todorokite in supergene veins.

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A) Purpose and Scope of Study

This study aims to clarify the mineralogy and genesis of the manganese ores in the Eosangcheon

mine.

B) Procedures and Methods of Study

This study was made by means of field investigations and laboratory works. Systematic sampling was difficult because of poor exposures and caved pits. However, it was possible to collect enough samples for this study from dumps and exposures. Laboratory works were made as follows:

Polarizing and ore microscopic observation :

The 30 thin sections and 80 polished sections were prepared to study the occurrences, associations and textures of minerals.

Manganese ores are usually friable and soft, and have many pores. Therefore, a special technique was needed to prepare good polished sections. Samples cut with thin diamond saw were impregnated in polyester and placed in the vacuum jar for 5 minutes and then they were polished carefully (Sorem and Foster, 1973).

X-ray powder diffraction analysis : In order to

*Department of Geological Sciences, Seoul National University

identify the mineral species, X-ray powder diffraction analyses were made. X-ray powder diffractometer and Debye-Scherrer powder camera methods were used for identification of all minerals. A JEOL model JDX-5P generator was used to produce X-ray radiation. A JEOL model JDX-CP comparator was used to measure d spacings, and intensities of lines were estimated visually. Microsamples for X-ray photograph were prepared under the ore microscope.

Infrared absorption spectroscopic analysis : Infrared absorption spectroscopic analyses were made to clarify the mineralogy of manganese oxides.

Infrared spectra were obtained with a Perkin-Elmer model 283B spectrophotometer on approximately 2 mg of powdered sample (-300mesh) dispersed in KBr pellets for the 4000 cm^{-1} to 200 cm^{-1} region. Pellets of 12 mm diameter were pressed for 4 minutes at 1.2Kbar under vacuum.

Infrared spectra were calibrated with polystyrene film.

Thermal analysis : Rancieite was studied for

its thermal behavior. Differential thermal analysis (DTA) curve was obtained with a Shimadzu model 20B thermal analyzer. Aluminium oxide (Al_2O_3) was used as inert standard. DTA curve recorded at $20^\circ\text{C}/\text{min}$.

Chemical analysis : Wet chemical analysis was made for rancieite. Samples were prepared by hand picking under the binocular microscope.

Chemical analysis of other manganese oxides was not possible because of difficulty in preparing the enough pure sample due to minute intergrowth with other minerals.

C) Previous Works

The general geology of the Eosangcheon mine district was investigated by the Geological Investigation Corps of Taebaegsan Region (1962).

Hwang(1981) studied the geology and genesis of these manganese ore deposits on the geochemical view point.

General Geology

The geology of the Eosangcheon mine area consists of the Samtaesan Formation and the

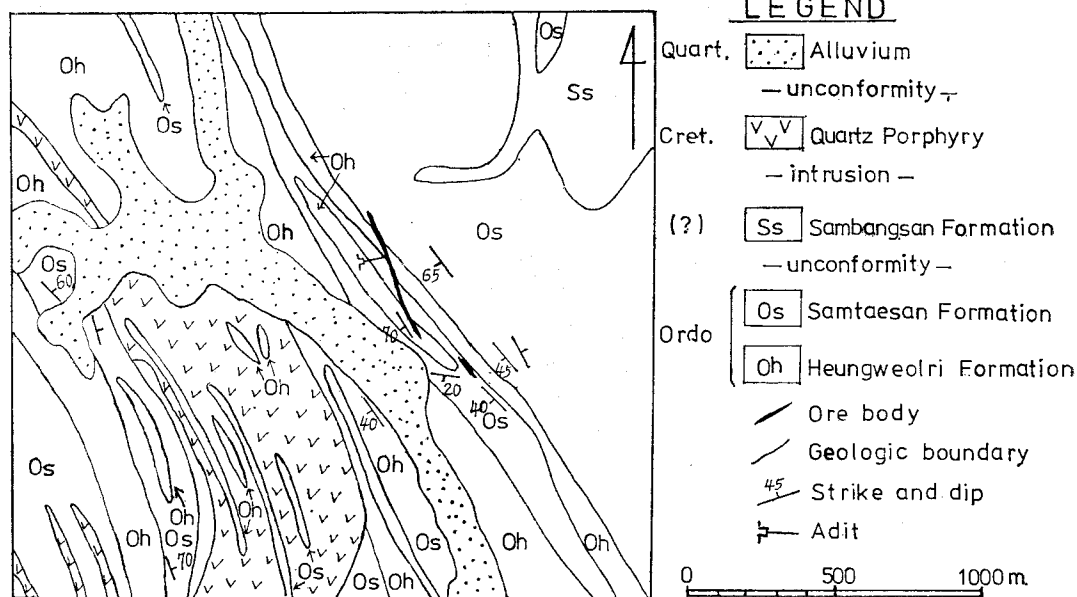


Fig. 1. Geological map of Eosangcheon mine area

Heungweolri Formation of Ordovician age, the Sambangsan Formation of Permian age, and quartz porphyry of Cretaceous age (Fig. 1).

The Heungweolri Formation consists of white to grey dolostone intercalated with thin limestone. The Samtaesan Formation consists of grey limestone. The Sambangsan Formation lies on the Samtaesan Formation unconformably. The Sambangsan Formation consists of dark grey and green shales, and intercalated quartzite and limestone. Quartz porphyry intrudes the above formations. It shows prophyritic texture. The phenocrysts consist of quartz, orthoclase and plagioclase. The groundmass is composed of quartz, sericite and plagioclase. Chalcedony showing spherulitic texture is also found in the rock.

The general strikes of the formations are N20–40°W. The Heungweolri and Samtaesan Formations show dip of 20–70°SW or 60–80°NE in places. The Sambangsan Formation shows dip of 30–40°NE. Minor folds are developed in the Samtaesan Formation.

Manganese Ore Deposits

The manganese ore deposits are found along two quartz porphyry dykes showing the strike of N15°W and N25°W, respectively, cutting the Heungweolri and Samtaesan Formations (Fig. 1). The main manganese ore vein is 450 m in extension and 0.5–2 m in thickness.

On outcrops and in pits, no other manganese minerals than manganese oxides were found. But rhodochrosite was reported from drill cores 400 m below the surface made by the Geological and Mineralogical Institute of Korea (now the Korea Institute of Energy and Resources) in 1975 (Hwang, 1981). This fact together with field relations, mineral assemblages and textures of ores suggests that the primary rhodochrosite ores have been oxidized to a considerable depth under the supergene weathering environment. A close associa-

tion of manganese ores with quartz porphyry dykes suggests a close connection of primary manganese mineralization with quartz porphyry in genesis.

Manganese Ores

A) Manganese and Associated Minerals

Manganese ores found on the surface and in pits are all composed of manganese oxides and other minerals. Manganese oxide minerals identified are rancieite, todorokite, birnessite, nsutite, pyrolusite and chalcophanite. Other minerals in the manganese oxide ores are quartz, calcite, goethite, lepidocrosite, sericite and gypsum. Rancieite and todorokite are most abundant manganese oxide minerals in the ores. Birnessite, nsutite, pyrolusite and chalcophanite are found in minor quantities.

B) Megascopic Characters of Ores

Manganese oxide ores from the Eosangcheon mine are megascopically characterized by their considerable low hardness and high porosity. The low hardness of the ores is attributed to the high content of soft rancieite and the high porosity.

Megascopic types of manganese oxide ores are

- 1) massive ore,
- 2) network ore,
- 3) colloform ore, and
- 4) wad.

Massive type of ore consists mainly of rancieite and todorokite. Network type of ore is mainly developed in the matrix of weathered quartz porphyry. This type of ore is well observed in underground workings. It consists mainly of todorokite with minor rancieite. Colloform type of ore is found near the surface, and consists mainly of nsutite and birnessite. Wad is mainly found in the surface cover of the manganese deposits. Wad is a soil-like dark material consisting of nsutite, todorokite and pyrolusite.

C) Mineralogical Types of Ores

Mineralogical types of manganese oxide ores are classified on the basis of main mineral assemblages of ores. Associated other minerals are neglected. Mineralogical types of manganese oxide ores are:

- 1) Todorokite ore,
- 2) Rancieite ore,
- 3) Todorokite-birnessite ore,
- 4) Todorokite-rancieite ore,
- 5) Rancieite-birnessite ore, and
- 6) Chalcophanite-pyrolusite ore.

Mineralogy of Manganese and Associated Minerals

A) Todorokite

Occurrence: Todorokite is abundantly found in the manganese oxide ores from the Eosangcheon mine. It is the main constituent mineral of the massive and network types of ores.

Todorokite occurs as microcrystalline fibers or flakes (Photo 1) in open spaces or isotropic masses.

Todorokite replaces dolomite or calcite along grain boundaries or cleavages, and quartz grains in veinlets along the contact of manganese oxide ores and country rocks.

Todorokite formed by replacement from probably rhodochrosite is in turn replaced by chalcophanite or by rancieite. Todorokite is also replaced by birnessite, nsutite or goethite. It is also observed that todorokite is cut by nsutite or pyrolusite veinlets.

Todorokite formed by precipitation from solution occurs as colloform bands in cavities or massive bodies. Todorokite is associated with rancieite in colloform bands. Todorokite also occurs as mixtures with sericite.

Physical and Optical Properties: Todorokite is brownish black to black in color, dark brown to black in streak, and submetallic to earthy in luster. Hardness is low, but higher in the compact todorokite associated with nsutite.

Todorokite is opaque. In the reflected light,

it is grey to whitish grey. It shows weak bireflectance, strong anisotropism, and undulatory extinction. No internal reflection is observed. Massive todorokite is nearly isotropic.

X-ray Powder Diffraction Data: X-ray powder diffraction data of todorokite from the Eosangcheon mine are shown in Table 1.

Infrared Absorption Spectra: Infrared absorption spectra of todorokite from the Eosangcheon mine are shown in Fig. 2 and absorption bands are given in Table 2.

Todorokite shows characteristic absorption bands at 440–450, 515–520, 555, and 3200 cm^{-1} . Above first three bands are due to the vibrations related to the MnO_6 octahedral arrangement. Absorption band at 3200 cm^{-1} is due to water molecules.

B) Rancieite

Occurrence: Rancieite is the most abundant manganese oxide mineral in this mine. It has been formed by precipitation from solution or by replacement.

Rancieite formed by precipitation from solution occurs as 1) flaky crystals, 2) cryptocrystalline masses, and 3) colloform bands.

Flaky rancieite is mainly found in the open spaces within manganese oxide ores. Divergent, subparallel or random arrangement of rancieite flakes in open spaces suggests crystallization from solution. Some of rancieite flakes in the polished sections look like a fibers (Photo 2). Flaky nature of rancieite is easily observed under the stereomicroscope or even with naked eye in cases. Flaky rancieite is closely intergrown with fibrous todorokite.

Cryptocrystalline massive rancieite is also found as the cavity-fillings, or as replacement product of todorokite. It is usually relatively compact.

Colloform rancieite is found in the colloform ores as cryptocrystalline aggregates together with todorokite or birnessite. Rancieite in colloform

Table 1. X-ray powder diffraction data of manganese oxide minerals from the Eosangcheon mine (Fe /Mn)

Todorokite			Rancieite (massive)			Rancieite (flaky)			Birnesite		Nsutite		Pyrolusite			Chalcophanite									
I	d(Å)	hkl	I	d(Å)	hkl	I	d(Å)	hkl	I	d(Å)	I	d(Å)	I	d(Å)	hkl	I	d(Å)	hkl	I	d(Å)	hkl	I	d(Å)	hkl	
s	9.40		s	7.49	002	s	7.60		s	7.10	wb	3.94	vs	3.02	110	w	6.96		vw	1.796		vw	1.118		
m	6.71		w	3.70	004	m	3.71		m	3.56	w	1.61	s	2.33	101	vs	6.60		w	1.742		w	1.106		
m	4.60		w	2.45	024								vw	2.14	200	vw	6.23		vw	1.663		vw	1.093		
vw	3.91		vw	2.35	122								m	2.06	111	w	4.00		w	1.618		m	1.056		
vw	3.40		vw	2.06	124								w	1.92	210	s	3.90		m	1.554		vw	1.035		
m	2.38		m	1.420	140								s	1.59	211	vw	3.61		vw	1.488			1.030		
w	2.33												m	1.53	220	mb	3.36			1.467		m	1.000		
m	2.17												w	1.41	002	vw	3.19		m	1.397					
m	1.40												vw	1.368	310	vw	3.00		w	1.380					
													m	1.286	301	m	2.67		w	1.372					
													vw	1.228	311	m	2.48		w	1.296					
													vw	1.188	202	m	2.37		w	1.253					
													vw	1.151	212	w	2.32		vw	1.187					
													w	1.114	321	s	2.16		vw	1.172					
													m	1.050	222	w	2.06		vw	1.158					
													m	1.035	330	m	1.846		vw	1.130					

b: broad

bands is replaced by nsutite or goethite.

Physical and Optical Properties: Flaky rancieite is purplish brown in color, metallic in luster, and very low in hardness. It has perfect cleavage in one direction. It is usually translucent and distinctly iridescent. It shows distinct birefractance, strong anisotropism, reddish brown internal reflection and low reflectance.

Massive rancieite is dark brown in color, brown in streak, submetallic in luster and low in hardness. It is grey with reddish tinge in the reflected light. Other optical properties of massive rancieite are similar to those of flaky rancieite.

X-ray Powder Diffraction Data: X-ray powder diffraction data of rancieite from the Eosangcheon mine are given in Table 1. Hexagonal cell has been indexed for rancieite.

Infrared Absorption Spectra: Infrared absorption spectra of rancieite from the Eosangcheon mine are shown in Fig. 2, and absorption bands are given in Table 2.

Rancieite shows characteristic absorption bands

at 415–520, 495, 535, 620, and 670–680 cm^{-1} which are distinguishable from birnessite. These bands are due to the vibrations related to the MnO_6 octahedral arrangement. Absorption bands at 1610–1615 and 3400 cm^{-1} are due to water molecules and (OH) in the structure. The band near 680 cm^{-1} is the characteristic band of rancieite (Potter and Rossman, 1979).

Differential Thermal Analysis: DTA curve of rancieite from the Eosangcheon mine is shown in Fig. 3. Endothermic peak at 100°C is due to dehydration of adsorption water and interlayer water, endothermic peak at 200–220°C due to dehydration of (OH) and oxidation to MnO_2 , and another endothermic peak at 730°C due to the transformation of MnO_2 to Mn_2O_3 phase.

Chemical Composition: The chemical formula of the original rancieite by Richmond et al. (1969) was $(\text{Ca}, \text{Mn})\text{O} \cdot 4\text{MnO}_2 \cdot 3\text{H}_2\text{O}$.

Bardóssy and Brindley (1978) reported the formula $(\text{Ca}_{0.55}\text{Mn}_{0.22}^{2+}\text{Mg}_{0.04})\text{O} \cdot 4\text{MnO}_2 \cdot 3.66\text{H}_2\text{O}$ for a rancieite from Itéa, Greece. Chukhrov et al.

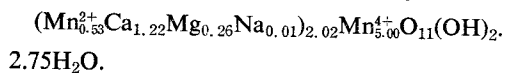
Table 2. Infrared absorption bands of manganese oxide minerals from the Eosangcheon mine, Korea

Todorokite (fibrous)	Todorokite (massive)		Rancieite (massive)	Rancieite (flaky)		Birnessite		Chalcophanite		Nsutite		Pyrolusite	
	cm ⁻¹	I		cm ⁻¹	cm ⁻¹	I	cm ⁻¹	I	cm ⁻¹	I	cm ⁻¹	I	cm ⁻¹
295	295	w				265	vw			260	sh		
315	315	w						315	w			325	sh
			345	340	sh	345	vw	340	sh		sh		
			415	420	vs					375		405	sh
540	440	s	450	435	vs	435	sh	440	vs		sh		
						470	sh	470	vs	475			
495	485	sh	495	495	vs			495	vs		vs		
515	520	vs				520	vs	535	vs	525	s	535	vs
			535	535	sh					560	s		
555	555	vs				565	sh	615		570			
615	625	sh	620	620	sh			645	s				
						650	sh		sh	700	sh	655	sh
			670	680	sh			1625	m		w	715	sh
760	750	m				760	sh			1610			
			875	—	w						m		
			1410	—	w								
1620	1620	w	1615	1610	m	1620	w	3315	s				
3200	3200	m	3400	3300	s	3400	m	3400	s	3400			

vs: very strong s: strong; m: medium; w: weak sh: shoulder

(1979) proposed a general formula of rancieite and birnessite from electron microprobe analytical data of some rancieites and birnessites from different localities. The general formula proposed by them is $(R^+, R^{2+}, R^{3+})_2 Mn_6^{4+} O_{14 \pm x} \cdot x(H_2O)_n$, where $R^+ = Na^+, K^+$; $R^{2+} = Mn^{2+}, Ca^{2+}, Mn^{2+}$ and others; $R^{3+} = Mn^{3+}$ and others. Recent crystal-chemical study by Kim(1980), however, shows that the general formula for rancieite and birnessite should be $(R)_{2-2x} Mn_{5+x}^{4+} O_{11}(OH)_2 \cdot nH_2O$, where $R = Mn^{2+}, Ca, Mg, Na, K$; n is approximately 3 for rancieite and 1.5 or less for birnessite.

Chemical analysis of rancieite made by wet method is given in Table 3. Fe_2O_3 , and SiO_2 were treated as impurities. Chemical formula of rancieite determined from the analysis is



C) Birnessite

Occurrence: Birnessite is found in small quantities. It occurs as cryptocrystalline, nearly isotropic masses.

It is found that birnessite replaces todorokite or rhodochrosite. Relicts of rhombic cleavages of rhodochrosite are preserved in birnessite. Birnessite is replaced by nsutite (Photo 3), rancieite, or goethite. It is cut by calcite or nsutite veinlets.

Birnessite is also found in colloform bands, alternating with rancieite or nsutite. Birnessite in colloform bands is also replaced by nsutite.

Physical and Optical Properties: Birnessite is greyish black to black in color, black in streak, and earthy in luster. Hardness is moderate. It is opaque to translucent.

Birnessite is grey with greenish tinge in the polished section. It shows weak anisotropism to nearly isotropism. No internal reflection is ob-

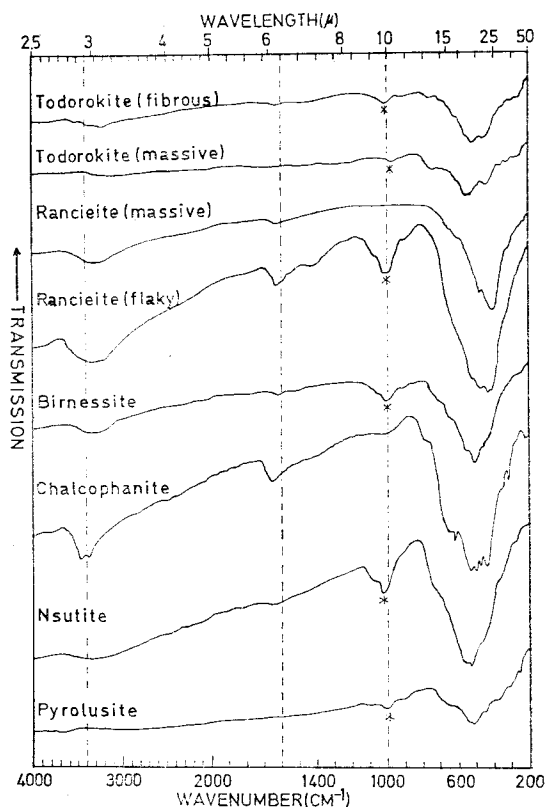


Fig. 2. Infrared absorption spectra of manganese oxide minerals from the Eosangcheon mine, Korea. Asterisk indicates the absorption band caused by quartz impurity.

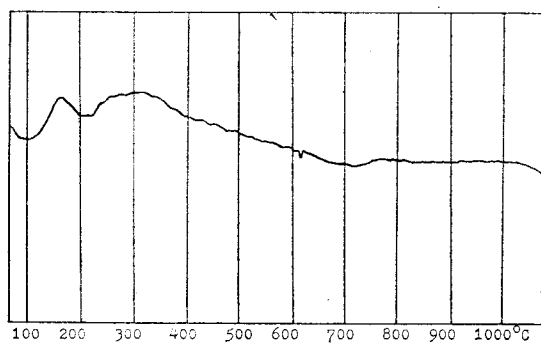


Fig. 3. DTA curve of rancieite from the Eosangcheon mine.

served.

X-ray Powder Diffraction Data: X-ray powder diffraction data of birnessite from the Eosangcheon mine are given in Table 1.

Table 3. Chemical analysis of rancieite from the Eosangcheon mine

1		2		3	
	wt%		wt%		
MnO ₂	53.90	MnO ₂	53.90	Mn ⁴⁺	5.00
MnO	4.65	MnO	4.65	Mn ²⁺	0.53
CaO	8.48	CaO	8.48	Ca	1.22
MgO	1.28	MgO	1.28	Mg	0.26
Na ₂ O	0.03	Na ₂ O	0.03	Na ⁺	0.01
K ₂ O	1.57	K ₂ O	0.01	K ⁺	—
SiO ₂	10.80	H ₂ O(+)	8.38	(OH) ⁻	2.00
Fe ₂ O ₃	2.50	goethite	2.78	O ²⁻	11.00
Al ₂ O ₃	5.08	quartz	4.81	H ₂ O	2.75
H ₂ O(+)	9.26	sericite	13.23		
total	97.55	total	97.55		

1: analysis; 2: recalculation for impurities;
3: coefficients

Infrared Absorption Spectra: Infrared absorption spectra of birnessite are shown in Fig. 2, and the absorption bands are given in Table 2. Birnessite shows characteristic absorption bands at 435, 470, 520, 565, 650 and 760 cm⁻¹. The absorption bands at 1620 and 3400 are due to water molecules and hydroxide ions. Bands between 200–800 cm⁻¹ suggest that birnessite has a layer structure, but relatively low degree of order in this case.

D) Nsutite

Occurrence: Nsutite occurs as massive isotropic, massive granular, or colloform masses.

Massive nsutite replaces rancieite, todorokite, birnessite, or goethite. It also replaces calcite along grain boundaries or cleavages. It is also observed that nsutite is developed in the matrix of rancieite as veins. It is also found that colloform bands of birnessite and nsutite are diffusely replaced by later nsutite (Photo 3).

Nsutite in colloform bands alternates with birnessite, rancieite, or goethite. Colloform bands are developed in cavities by filling or lining the open spaces.

Shrinkage cracks are usually developed in nsutite by dehydration (Zwicker et al., 1962; Kim,

1975)

Physical and Optical Properties: Nsutite is greyish black in color, black in streak, metallic in luster. Nsutite is very hard. It is hardest among all manganese oxide minerals. It is opaque.

In the reflected light, nsutite is white in color, and very high in reflectance. In granular type, it shows distinct bireflectance and strong anisotropism. Some cryptocrystalline nsutite is nearly isotropic.

X-ray Powder Diffraction Data: X-ray powder diffraction data of nsutite from the Eosangcheon mine are given in Table 1.

X-ray powder film shows only two lines. It is assumed that nsutite from this mine is considerably disordered in structure.

Infrared Absorptions Spectra: Infrared absorption spectra of nsutite from the Eosangcheon mine are shown in Fig. 2, and absorption bands are given in Table 2. Nsutite shows characteristic absorption bands at 375, 475, 525, 565, 570, 700, 1610 and 3400 cm^{-1} .

E) Pyrolusite

Occurrence: Pyrolusite occurs as random or radiating columnar crystals, crystal aggregates, or massive masses (Photo 4).

Pyrolusite replaces todorokite, and cuts dolomite, calcite, or chalcophanite as veinlets. It is cut by nsutite or goethite veinlets.

Physical and Optical Properties: Pyrolusite is iron black with dark bluish tint in color, black in streak, and metallic in luster. Hardness of pyrolusite is low in massive type, and high in crystal aggregates.

Pyrolusite is opaque. In the reflected light, it is yellowish white in color and shows very high reflectance, distinct bireflectance and strong anisotropism. Internal reflection is not found.

X-ray Powder Diffraction Data: X-ray powder diffraction data of pyrolusite are given in Table 1. Unit cell dimensions of pyrolusite are $a_0=4.404\text{\AA}$, $c_0=2.875\text{\AA}$. It is tetragonal. Axial ratio $a:c=1:$

0.653.

Infrared Absorption Spectra: Infrared absorption spectra of pyrolusite are shown in Fig. 2. Pyrolusite shows absorption bands at 325, 405, 535, 655, and 715 cm^{-1} . Absorption band at 535 cm^{-1} is characteristic Mn-O stretching vibration of pyrolusite.

F) Chalcophanite

Occurrence: Chalcophanite occurs as massive fine-grained aggregates or tiny prismatic crystals (Photo 5). It is a rare mineral in the manganese oxide ores in the mine.

Chalcophanite replaces todorokite which has been formed by replacement of rhodochrosite. It is cut by nsutite veinlets.

Tiny prismatic crystals of chalcophanite are found in the massive chalcophanite matrix. In some cases, chalcophanite is associated with pyrolusite in the massive chalcophanite matrix. (Photo 4). Chalcophanite and pyrolusite crystals in this case are assumed to have been formed from solution nearly at the same time.

Physical and Optical Properties: Chalcophanite is dark brown in color. Its color is similar to, but lighter than that of rancieite. It is reddish brown in streak, and low in hardness. It is opaque.

In the reflected light, chalcophanite is grey in color, and shows low reflectance, strong bireflectance, strong anisotropism and red internal reflection. Internal reflection is not observed in crystals.

X-ray Powder Diffraction Data: X-ray powder diffraction data of chalcophanite from the Eosangcheon mine are given in Table 1.

Infrared Absorption Spectra: Infrared absorption spectra of chalcophanite from the Eosangcheon mine are shown in Fig. 2. Infrared absorption bands of chalcophanite are given in Table 2.

Chalcophanite shows absorption bands at 315, 340, 440, 470, 495, 535, 615, 645, 1625, 3315 and 3400 cm^{-1} . Last three sharp absorption

bands are due to the crystallographically ordered water molecules, and four bands from 550cm^{-1} to 400cm^{-1} are diagnostic of chalcophanite (Potter and Rossman, 1979).

G) Mineral X

An unidentified mineral X is found in the manganese oxide ores. It occurs as very small grains having distinct cleavage in one direction (Photo 6). It is associated with pyrolusite, rancieite and goethite.

Under the microscope, mineral X is grey in color, and shows very low reflectance, very weak bireflectance, and very weak anisotropism to nearly isotropism. Internal reflection is not observed. Optical properties suggest that it be a manganese oxide mineral.

Size of mineral X is too small to get sample for X-ray powder camera or infrared analysis. Electron microprobe analysis is needed to know the chemistry of this mineral.

H) Goethite

Goethite is widely distributed in manganese oxide ores. It occurs as pseudomorphs after pyrite, as veinlets or colloform globules or bands in manganese oxide ores.

Pseudomorphic goethite shows zonal structure in many cases. Colloform goethite alternates with manganese oxide minerals in bands. Goethite replaces manganese oxide minerals, or vice versa.

I) Lepidocrosite

Lepidocrosite occurs as very fine-grained platy crystals in association with sericite and gypsum in manganese oxide ores. It is not abundantly found.

J) Calcite

Calcite of supergene origin occurs as cavity- or fissure-fillings in manganese oxide ores.

K) Quartz

Quartz in manganese oxide ores is derived from the original manganese carbonate ores. Therefore, most of quartz in manganese oxide ores are residual quartz that have escaped chemical weathering during the formation of manganese oxide

ores from the primary manganese carbonate ores by the supergene oxidation and precipitation. Quartz is replaced by manganese oxide minerals.

L) Sericite

Sericite is the main constituent mineral of the weathered quartz porphyry constituting the host or wall rock of manganese oxide ore deposits. It is also associated with manganese oxide ores themselves.

M) Gypsum

Gypsum occurs as very fine-grained crystals in association with sericite and lepidocrosite in manganese oxide ores.

Relationship between Rancieite and Birnessite

Birnessite was named by Jones and Milne (1956), and rancieite has been considered as a quite different mineral from birnessite by Richmond et al. (1969) and others. These two minerals were reported from many places and studied by many workers. On the basis of X-ray powder diffraction data, Bardóssy and Brindley (1978) have suggested that rancieite structure differs from the birnessite structure only in the identity of the interlayer cation, and they raised the possibility that rancieite and birnessite might better be considered as minerals of the same group. Chukhrov et al. (1979) also have suggested that rancieite and birnessite are members of the same isomorphous series of minerals of the chalcophanite structure type. But recently, Kim (1980) studied the relationship between birnessite and rancieite on the basis of crystal chemistry, and proposed the general formula $(\text{R})_{2-2x}\text{Mn}_{5+x}^{4+}\text{O}_{11}(\text{OH})_2 \cdot n\text{H}_2\text{O}$; for rancieite ($n \doteq 3$) and birnessite ($n \doteq 1.5$), giving two solid solution series; the rancieite series and the birnessite series.

In this study, the relationship of rancieite and birnessite was studied by means of X-ray powder diffraction and infrared absorption spectroscopic analyses. X-ray diffraction and infrared absorp-

tion data are given in Table 1 and 2, respectively.

X-ray powder patterns of rancieite and birnessite are generally similar, although the birnessite from the Eosangcheon mine is considerably disordered or poorly crystalline. The main difference in X-ray data of two minerals is in the d_{002} value; 7.60Å in rancieite and 7.10Å in birnessite in this study. Variation of d_{002} value in two minerals has been explained crystalchemically by Kim (1980). Difference of d_{002} values of rancieite and birnessite with the same atoms in (R) site is attributed to the degree of hydration or dehydration. Chemical analysis and infrared absorption spectra also suggest that rancieite has more water than birnessite.

Infrared absorption spectra suggest that rancieite and birnessite have the layer structure closely related to each other, but show significant difference in the arrangement of their octahedral frameworks (Potter and Rossman, 1979). The infrared absorption bands near 3400 and 1610 cm^{-1} are found in both minerals, but bands of 200 to 800 cm^{-1} are different in both minerals. Infrared absorption bands at 420, 495, 535, 620 and 670–680 cm^{-1} of rancieite are not found in birnessite. Infrared absorption bands at 470, 520, 565, 650 and 760 cm^{-1} of birnessite are not found in rancieite. Such differences might be attributed to the difference in MnO_6 octahedral arrangement in two minerals. Our infrared study also supports Potter and Rossman's conclusion (1979) that rancieite and birnessite should be considered as separate minerals.

Textures and Structures of Ores

A) Hypogene Primary Features

The primary rhodochrosite ores with some sulfides of hypogene origin have been so deeply oxidized that they are found in 400 meters depth below the surface by drilling. Therefore, it was not possible to have enough samples of primary

ores for detailed study of their textures and structures in this study.

B) Supergene Features

Oxidation Textures: Since almost all rhodochrosite ores have been nearly completely oxidized to manganese oxide ores, the oxidation texture of rhodochrosite is not found. However, pseudomorphic forms of manganese oxides after rhodochrosite are remained in the manganese oxide ores. Rhombic shapes and cleavages of original rhodochrosite are remained in the manganese oxide ores.

Precipitation Textures: The textures suggesting the precipitation from colloidal or noncolloidal solution are colloform bands, dendritic, fibrous, massive, granular, and geode. Minerals showing characteristic textures are as follows:

Colloform: todorokite, rancieite, birnessite, nsutite.

Dendritic: todorokite

Fibrous: todorokite

Massive: todorokite, rancieite, chalcophanite

Granular: pyrolusite

Geode: rancieite, todorokite

Replacement Textures: Early formed manganese oxide ores are replaced by later oxides. The fundamental mechanisms of such type of replacement are the further oxidation of early formed manganese oxides and the substitution of silicates or carbonates by manganese oxides.

Important replacement textures are:

- a) Pseudomorphic replacement of rhodochrosite by todorokite.
- b) Replacement of todorokite by rancieite, birnessite, nsutite, pyrolusite, or chalcophanite.
- c) Replacement of birnessite by nsutite, (Photo 3), or rancieite.
- d) Replacement of carbonates or silicates by manganese oxides.
- e) Replacement of manganese oxides by goethite or vice versa.

Recrystallization Textures: Significant recrystallization texture is the recrystallization of

- a) cryptocrystalline todorokite to fibrous aggregate.

Formation of Minerals

A) Paragenetic Sequence

The textural relations of the manganese oxide ores from the Eosangcheon mine show that the manganese oxides were formed in the paragenetic sequence shown in Fig. 4, and more detailed paragenetic relations of all minerals associated are shown in Fig. 5. The sequence from rhodochrosite to todorokite indicates the oxidation from Mn²⁺ to Mn⁴⁺, that from todorokite to nsutite indicates further oxidation reaction.

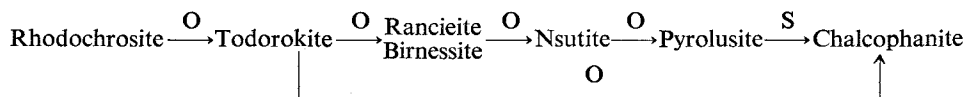


Fig. 4. Paragenetic sequence of manganese oxide minerals at the Eosangcheon mine. O: oxidation; S: simple sequence.

cesses the manganese oxide minerals have been formed. The fundamental processes of formation of manganese oxide minerals are replacement, precipitation from solution, and solid state crystallization and recrystallization.

Todorokite has been formed predominantly by replacement and subordinate precipitation from solution. Rancieite and birnessite have been formed by replacement or precipitation. Nsutite has been formed predominantly by replacement, and pyrolusite and chalcophanite by precipitation from solution.

Distribution of Minerals

The distribution of manganese oxide minerals could not be studied in detail because of poor exposures and destruction of pits. However, the general outline of distribution of minerals could be understood.

- a) Early formed minerals such as todorokite,

The oxidation coefficient, $Mn^{4+}/(Mn^{4+} + Mn^{2+})$ of manganese oxide minerals increases from the early formed ones to later ones, but that is not always the case as indicated by the chalcophanite which is late in the sequence but has a low oxidation coefficient. Such a phenomenon is attributed to the lower oxidation potential in certain part of the circulating groundwater than other parts.

The paragenetic sequence and the stability relations of minerals indicate that todorokite is not stable, and that rancieite and birnessite are considerably stable in the present environment except near the surface in the Eosangcheon mine.

B) Mechanisms of Formation

Textures of ores tell that by what kinds of pro-

rancieite, and birnessite are mainly found in the less porous ores below the surface.

Minerals	Primary	Supergene Process	
		Early	Late
Rhodochrosite			
Quartz			
Todorokite		-----	
Rancieite		-----	
Birnessite		-----	
Nsutite		-----	
Pyrolusite			-----
Chalcophanite			-----
Mineral X			-----
Goethite		-----	
Sericite		-----	
Gypsum		-----	
Lepidocrosite		-----	

Fig. 5. Paragenetic chart of manganese and associated minerals in the Eosangcheon mine.

- b) Later formed minerals such as nsutite, pyrolusite, and chalcophanite are found in ores near the surface.
- c) Flaky rancieite and todorokite crystals are found as cavity-fillings in ores.

Genesis of Manganese Ore Deposits

Field occurrence, mineralogy and textures of manganese oxide ores indicate that they were formed from the manganese carbonate ores of hydrothermal origin by supergene weathering processes.

The primary manganese carbonate ores accompanying some sulfides were formed along the contact of carbonate rocks and quartz porphyry dyke. The manganese carbonate mineralization is assumed to have been connected with quartz porphyry in genesis.

The oxidation of rhodochrosite along the fissures, grain boundaries or cleavages was the beginning of the formation of manganese oxide ores. Oxidation of rhodochrosite proceeded downward, causing migration of dissolved manganese toward the fissures in quartz porphyry and manganese ores. Reticulated or veinlet manganese oxide ores in quartz porphyry were formed by precipitation of manganese from the groundwater passing through the oxidized zone.

All the modes of manganese oxide mineralization indicate that the oxidation of manganese carbonates and further oxidation of early formed oxides as well as the migration of dissolved manganese, played the very important role in the formation of manganese oxide deposits. Movement of groundwater along the contact of quartz porphyry and ore veins or country rocks accelerated the formation of manganese oxide deposits.

Summary and conclusions

The conclusions reached from the study on the mineralogy and genesis of the manganese oxide

ores in the Eosangcheon mine are summarized as follows:

- 1) The geology of the Eosangcheon mine area consists of the Ordovician Heungweolri Formation and Samtaesan Formation, Permian, Sambangsan Formation, and Cretaceous quartz porphyry which intruded the above formations. The rocks around the ore deposits show the strike of N 20–40° W and the dip of 60–80° NE.
- 2) The manganese ore deposits occur as supergene weathering deposits along quartz porphyry dikes developed in the Ordovician sedimentary rocks.
- 3) The manganese oxide ores are composed of todorokite, rancieite, birnessite, nsutite, pyrolusite and chalcophanite with associated other minerals such as goethite, calcite, quartz, sericite, gypsum and lepidocrosite. Of these minerals chalcophanite is first reported in Korea from the Eosangcheon mine.
- 4) Microscopic, chemical, X-ray, infrared and DTA studies were made for manganese oxide minerals and associated other minerals.
- 5) The relationship of birnessite and rancieite was studied by means of X-ray powder diffraction and infrared absorption spectroscopic analyses. The structure of birnessite and rancieite is closely related to each other, but different as evidenced by infrared absorption spectra.
- 6) An unidentified opaque mineral is found in the intensively weathered manganese oxide ores, and it is assumed to be a manganese oxide mineral. More advanced method is needed to clarify the mineralogy of this mineral.
- 7) The manganese oxide ores were formed by replacement, precipitation from solution, and recrystallization in the supergene weathering environment.
- 8) The trend of formation of manganese oxides

is as follows: (Rhodochrosite)-(todorokite)-
(birnessite, rancieite)-(nsutite, pyrolusite,
chalcophanite).

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Photo 1. Todorokite flakes. Polished section. Open Nicols. X480.



Photo 2. Fibrous rancieite. Polished section. Open nicols. X120.

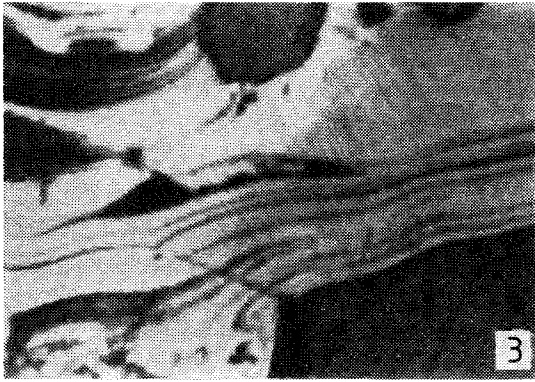


Photo 3. Colloform bands of birnessite (black) and nsutite (white). Nsutite replaces these bands diffusely. Polished section. Open nicols. X60.

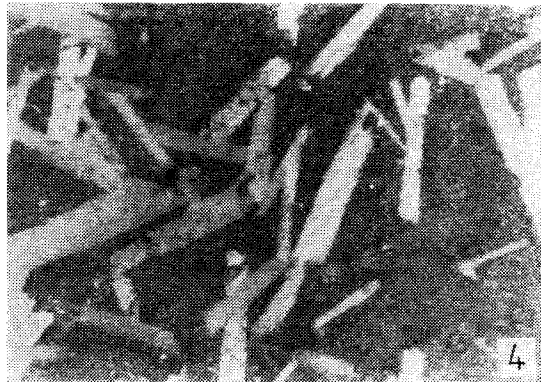


Photo 4. Columnar crystals of pyrolusite in massive chalcophanite. Polished section. Open nicols. X480.



Photo 5. Tiny prismatic crystals of chalcophanite, Polished section. Open nicols. X480

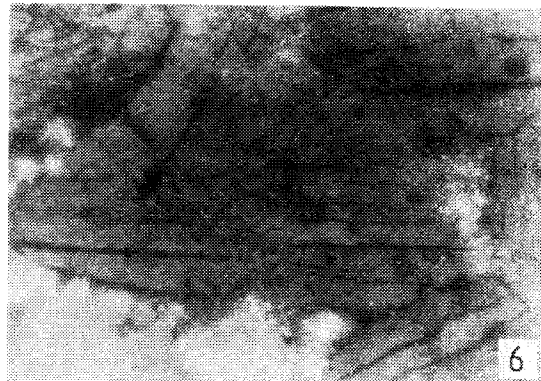


Photo 6. Mineral X showing distinct cleavage in one direction. Polished section. Open nicols. X1200. Oil immersion.

魚上川鑛山の 망간鑛石에 對한 鑛物學的 및 成因的研究

金洙鎭* · 金性勳*

요약 : 어성천 망간광상은 고생대 오르도비스기의 홍월리 돌로마이트층과 삼태산 석회암층에 관입한 석영 반암맥을 따라 산출되는 표성광상이다.

망간광석은 산화망간광물들과 이에 수반되는 맥석광물들로 구성되어 있다. 산화망간광물들 중 란시사이트와 토도로카이트는 다량으로 산출되며, 비어네사이트, 엔스타이트, 연망간석, 켈코파나이트는 소량으로 산출된다. 맥석광물로는 방해석, 석고, 침철석, 레피도크로사이트, 석영, 견운모등이 산출된다.

산화망간광물들과 맥석광물들의 연구에는 현미경 관찰, 화학분석, 엑스선회절분석, 적외선흡수분광분석, 시차열분석 방법등이 이용되었다.

비어네사이트와 란시사이트의 관계가 엑스선회절분석과 적외선흡수분광분석법에 의하여 연구되었다. 이 두 광물들은 구조적으로 상당히 밀접한 관계가 있으나 서로 다른 광물종임이 적외선 흡수 스펙트럼연구에 의하여 확실시된다.

산화망간광물들은 표성환경하에서 교대작용, 용액으로부터의 침전, 재결정작용등에 의하여 생성되었다. 산화망간광물들의 생성순서는 다음과 같은 경향을 보여준다 : (능망간석)—(토도로카이트)—(비어네사이트, 란시사이트)—(엔스타이트, 연망간석, 켈코파나이트).

*서울대학교 自然科學大學 地質科學科