

Mineralogy and Genesis of Manganese Ores in the Dongnam Mine, Korea

東南鑛山の 망간鑛石에 對한 鑛物學的 및 成因의 研究

Soo Jin Kim (金 洙 鎭) and Se-Won Chang (張 世 沅)¹⁾

Department of Geological Sciences, Seoul National University, Seoul 151-742, Korea

(서울대학교 자연과학대학 지질학과)

ABSTRACT: Manganese deposits at the Dongnam mine occur as vein in the Pungchon limestone of Ordovician age. Manganese ore veins consist of the hydrothermal manganese carbonate ores in the deeper part and the supergene manganese oxide ores in the shallow part. Manganese carbonate ores consist mainly of rhodochrosite, with minor amount of pyroxmangite, garnet, calcite, quartz, pyrite, galena and sphalerite. Manganese oxide ores consist of rancieite, buserite, birnessite, vernadite, todorokite, pyrolusite, nsutite, hydrohetaerolite and goethite. Manganese oxide minerals were formed in the following sequences; 1) rhodochrosite → vernadite → birnessite → nsutite → pyrolusite, 2) pyroxmangite → birnessite, 3) Buserite → rancieite. Todorokite, buserite and hydrohetaerolite were precipitated from solution in the later stage. The natural analogue of synthetic buserite has been discovered from the mine. It has been disclosed that buserite transforms to rancieite by dehydration, and that distinction between buserite and todorokite is possible by X-ray diffraction studies combined with dehydration experiment. Minerals identified from the mine have been characterized using various methods including polarizing microscopy, X-ray diffraction, thermal analysis, infrared spectroscopy, X-ray diffraction, thermal analysis, infrared spectroscopy, electron microscopy and dehydration experiment.

要約: 東南鑛山の 망간鑛石은 朝鮮系 大石灰岩統의 豊村石灰岩內에 母岩의 構造를 橫斷하면서 脈狀으로 産出한다. 망간鑛石은 熱水起源의 炭酸망간鑛石과 表成起源의 酸化망간鑛石으로 構成되어 있다. 炭酸망간鑛石은 主로 菱망간石으로 構成되어 있지만 파이록스만자이트, 柘榴石, 方解石, 石英, 黃鐵石, 方鉛石, 閃亞鉛石을 少量 含有한다.

酸化망간鑛石은 란시아이트, 부서라이트, 버네사이트, 버나다이트, 토도로카이트, 軟망간石, 엔스타이트, 하이드로헤테롤라이트 및 針鐵石으로 構成되어 있다.

酸化망간鑛物들은 炭酸망간鑛物 및 硅酸망간鑛物의 酸化作用, 溶液으로부터의 沈澱作用에 依하여 生成되었으며 生成順序는 1)菱망간石→버나다이트→버네사이트→엔스타이트→軟망간石, 2)파이록스만자이트→버네사이트, 3)부서라이트→란시아이트이다. 부서라이트, 토도로카이트, 하이드로헤테롤라이트는 溶液으로부터 沈澱作用에 依하여 生成되었다. 이 鑛山에서 産出되는 各鑛物에 對하여 현미경, X-선, IR, DTA, TG, 電子현미경에 依한 鑛物學的 特性이 研究되었다.

INTRODUCTION

The Dongnam mine is located in Neungeon, Mureung-ri, Nam-myeon, Jeongseon-gun, Gang-

weon-do, Korea (Lat. 37° 16'90"N, Long. 128° 47'30"E). The mine is firstly known for its magnetite ore deposit. However, manganese ore deposits are also found in the northern and sou-

1) Present address: Korea Institute of Energy and Resources, P.O. Box 5, Taejon 302-343, Korea
(한국동력자원연구소 석재·산업자원연구실)

thern vicinity of the magnetite deposit.

This work aims to study the mineralogy of manganese ores and their genesis.

METHODS OF STUDY

Occurrence of manganese ores has been studied in the field. Various types of ores were sampled in the field for a systematic work in the laboratory.

Detailed mineralogical characterization has been made for all the mineral species of the manganese ores. For this purpose, the stereomicroscope, polarizing microscope, and ore microscope studies as well as various analyses including X-ray diffraction, infrared, DTA, TG, and transmission electron microscopy were made.

GEOLOGY OF ORE DEPOSITS

The Dongnam mine area consists of the Jangsan quartzite and Myobong Formation of Cambrian

age, the Pungchon limestone and Hwajeol Formation of Cambrian age, the Pungchon limestone and Hwajeol Formation of Ordovician age in the ascending order. These formations are intruded by the age-unknown granodiorite and quartz porphyry. Granodiorite occurs in the central part of quartz porphyry. Faults trending NE are found in the area (Fig. 1).

The manganese deposits occur as veins in the Pungchon limestone cutting its general structures. They are developed in the northern and southern vicinity of the magnetite deposit which is generally developed in the mass of quartz porphyry and partly in the skarn zone. Molybdenite occurs as disseminated particles or veinlets in granodiorite and associated skarn zone.

The manganese ore veins show the strike of NS-N25°E, and the dip of 70°-90°SE. The veins are approximately 0.5-1.5 m in thickness. Total nine manganese ore veins are found in the area. The manganese ore veins consist chiefly of manganese oxides in the shallow depth and manganese carbonate in the deeper part. Manganese silicate ores are found in the contact zone of sulfide veins and country rocks.

RESULTS

Nature of Mineralization

The manganese carbonate ores including minor amount of silicate minerals occur in veins trending NS-N25°E cutting the structures of country rocks. The manganese carbonate veins grade to sulfide veins in depth. The manganese silicates are generally found as narrow zones with the manganese carbonate or sulfide veins. The manganese oxide minerals occur in the supergene oxidation zone of the hydrothermal manganese carbonate ores. The depth of oxidation zone is less than 20 m.

The minerals identified from the manganese carbonate veins are rhodochrosite, calcite, pyroxmangite, garnet, knebelite, chlorite, pyrite, galena, and sphalerite. The manganese oxide ores consist of rancieite, buserite, birnessite, vernadite, todorokite, pyrolusite, nsutite, hydrohetaerolite, and goethite.

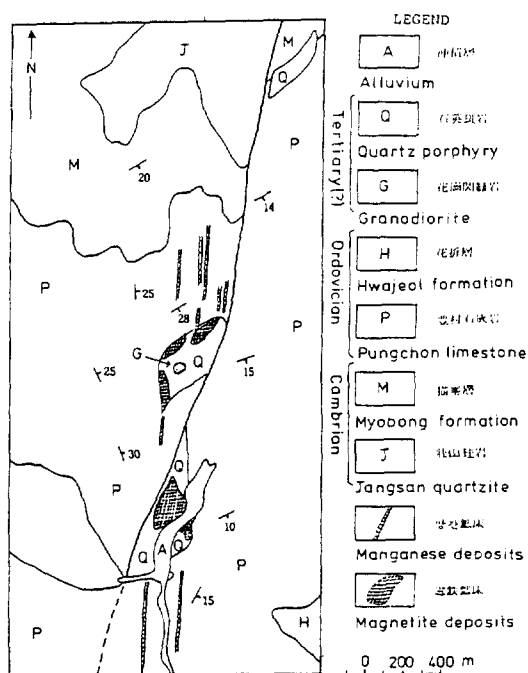


Fig. 1. Geologic map of Dongnam mine area (Kim, 1982)

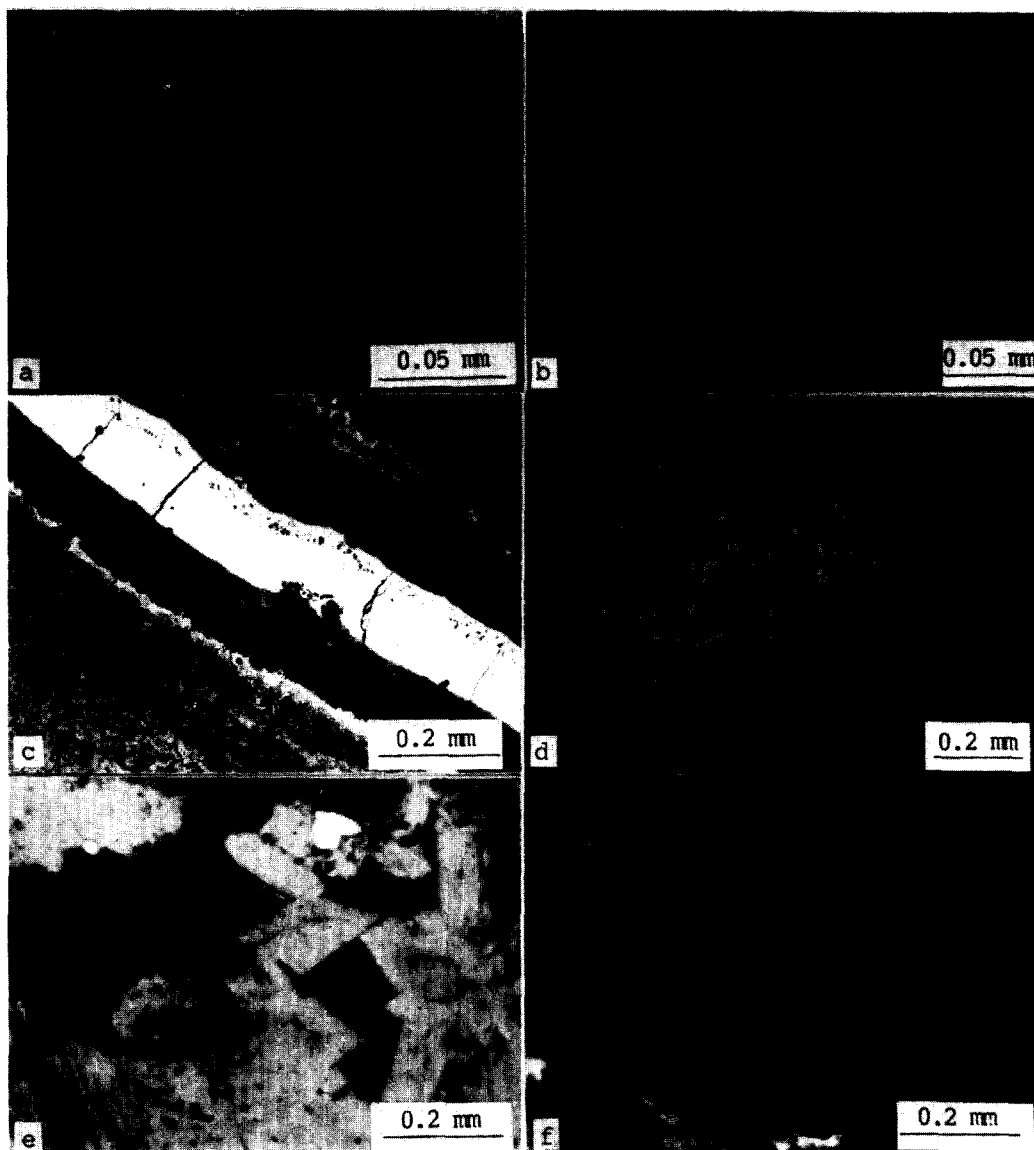


Fig. 2. Photomicrographs of manganese oxide minerals from Dongnam mine, Korea. (a) Platy buserite rancieite, (b) Acicular buserite rancieite, (c) Colloform birnessite, (d) Birnessite pseudomorph after pyroxmangite, (3) Vernadite pseudomorph after rhodochrosite, (f) Fibrous todorokite.

Mineralogy

Phylломanganate minerals: The phylломanganate minerals refer to the manganese oxide minerals of layer structures which consist of sheets of edge-shared $[\text{MnO}_6]$ octahedra and sheets

of water molecules. Mono- and divalent cations are present above and below the vacancies in the octahedral sheets. Phylломanganates include buserite, lithiophorite, chalcophanite, rancieite, birnessite, and vernadite. Among these, buserite, rancieite, birnessite, and vernadite

Mineralogy and Genesis of Manganese Ores

Table 1. Comparison of physical and optical properties of phylломanganate minerals from the Dongnam mine, Korea.

	Buserite-rancieite	Birnessite	Vernadite
Physical properties			
Color	brownish black to bluish black	greyish black to black	greyish black to bluish black
Streak	brown	black	black
Luster	submetallic	submetallic	submetallic
Hardness	low	moderate	moderate
Optical properties			
Color	grey to white	yellowish white	grey to white with creamy tinge
Bireflectance	distinct	weak	weak
Anisotropism	distinct	weak	weak
Extinction	(?)	—	—
Internal reflection	reddish brown	not present	not present
Reflectance	moderate	moderate	moderate

Table 2. X-ray diffraction data of buserite, rancieite, birnessite, vernadite, and todorokite from Dongnam mine, Korea.

Buserite			Rancieite		Birnessite		Vernadite		Todorokite	
I	d(Å)	hkl	d(Å)	hkl	I	d(Å)	I	d(Å)	I	d(Å)
m	9.69	001	7.57	001	m	7.34			m	9.69
w	4.85	002	3.72	002					w	4.86
m	2.44	100	2.34	100	w	2.43	m	2.44	w	2.46
			2.06	102	w	2.15	w	2.16		
			1.76	103	w	1.66				
					vw	1.49				
m	1.42	110	1.42	110	vw	1.42	w	1.41	w	1.42

have been identified from the manganese oxides of the Dongnam mine.

Buserite and rancieite occur in close association with each other. Both minerals are usually found in the same grain. X-ray diffraction analysis of the sample always shows diffraction patterns of both minerals with varying relative ratio. This is attributed to the formation of rancieite by dehydration of interlayer water within buserite. Detailed relationship of both minerals will be discussed in a separate paper. Buserite and rancieite are abundant minerals in the manganese oxide ore. They occur as fine-grained aggregates or encrustation on the limestone. They are very fine-grained and flaky in habit. Under the microscope, they occur as 1)

platy aggregates (Fig. 2a) and 2) acicular aggregates (Fig. 2b). They are closely associated with todorokite, birnessite, goethite, calcite, and quartz.

Birnessite occurs as two types; 1) colloform birnessite (Fig. 2c), and 2) birnessite pseudomorph after pyroxmangite. Colloform birnessite occurs as colloform bands alternating with nsutite (Fig. 2d). It is also partly replaced by nsutite. Birnessite formed by replacement from pyroxmangite occurs as acicular or short prismatic pseudomorphs (Fig. 2d).

Vernadite occurs as the direct oxidation product of rhodochrosite. Under the microscope, it occurs as rhombic pseudomorphs after rhodochrosite (Fig. 2e). They consist of very fine-

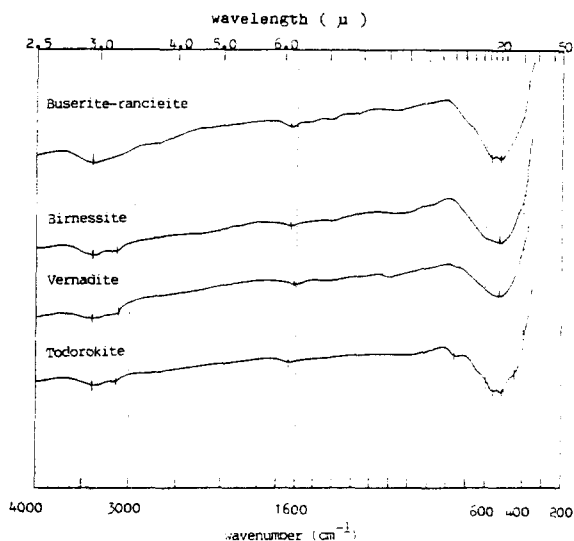


Fig. 3. Infrared absorption spectra for phyllos manganese minerals and todorokites.

Table 3. Infrared absorption bands of manganese oxide minerals from Dongnam mine, Korea.

Buserite-Rancieite		Birnessite		Vernadite		Todorokite	
cm ⁻¹	I	cm ⁻¹	I	cm ⁻¹	I	cm ⁻¹	I
445	s					450	
500	s						
640	sh	525	s	525	s	520	s
670	sh					765	
1630	w	1640	w	1620	w	1650	w
3440	m	3440	m	3450	m	3400	m

grained anhedral aggregates.

Comparison of physical and optical properties of buserite, rancieite, birnessite, and vernadite are given in Table 1.

X-ray powder diffraction data of buserite, rancieite, birnessite, and vernadite from Dongnam mine, are given in Table 2. The diffraction lines at 2.43-2.46 and 1.41-1.42 Å are common to all these manganese oxide minerals. These two lines represent diffraction of X-rays from atomic planes of hexagonally close-packed oxygens containing Mn⁴⁺ ions in octahedral

coordination with oxygen in which the [MnO₆] octahedra share edges (Burns and Burns, 1979). Vernadite is a highly disordered phase of birnessite (Giovanoli, 1980).

Infrared absorption spectra of buserite-rancieite, birnessite, and vernadite are shown in Fig. 3. Infrared absorption bands are given in Table 3.

Tunnel structured manganese mineral (Todorokite): It has been known that todorokite has the tunnel structure, although it has the similar X-ray diffraction pattern as buserite. Todorokite is a major constituent mineral of the manganese oxide ore from the Dongnam mine. It occurs as spherulitic or fine-grained needle-like aggregates (Fig. 2f) in association with pyrolusite, nsutite, hydrohetaerolite, rancieite, birnessite, and goethite.

Comparison of physical and optical properties of todorokite with other manganese oxide minerals is given in Table 1. X-ray powder diffraction data of todorokite are given in Table 2. Infrared absorption spectrum of todorokite is shown in Fig. 3. It is distinguished from other spectra by absorption band at 765 cm⁻¹.

From the above X-ray, infrared, thermal and dehydration studies, it became evident that the buserite in this study is the natural analogue of the synthetic buserite which was prepared by Giovanoli et al. (1975). Buserite is unstable in the natural environment thus readily loses its interlayer water, resulting in the formation of rancieite. The difference in d-values of rancieite and birnessite is due to the difference in the interlayer cations, that is, Ca in the rancieite and Na, Ca in the birnessite. Detailed discussion on the problem will be made in the separate paper.

X-ray diffraction pattern of buserite is the same as that of todorokite. However, it has been known that buserite has layer structure, where as todorokite has tunnel structure (Turner and Buseck, 1981). Inequality of buserite and todorokite is evidenced by the difference in infrared and thermal properties. Todorokite is considerably stable up to 300 – 500°C but buserite is very unstable, thus readily dehydrates to form rancieite.

Vernadite having two diffuse reflections at 2.4 and 1.4 Å is assumed to be a highly disordered birnessite as evidenced by X-ray diffraction, infrared absorption band and thermal behaviour.

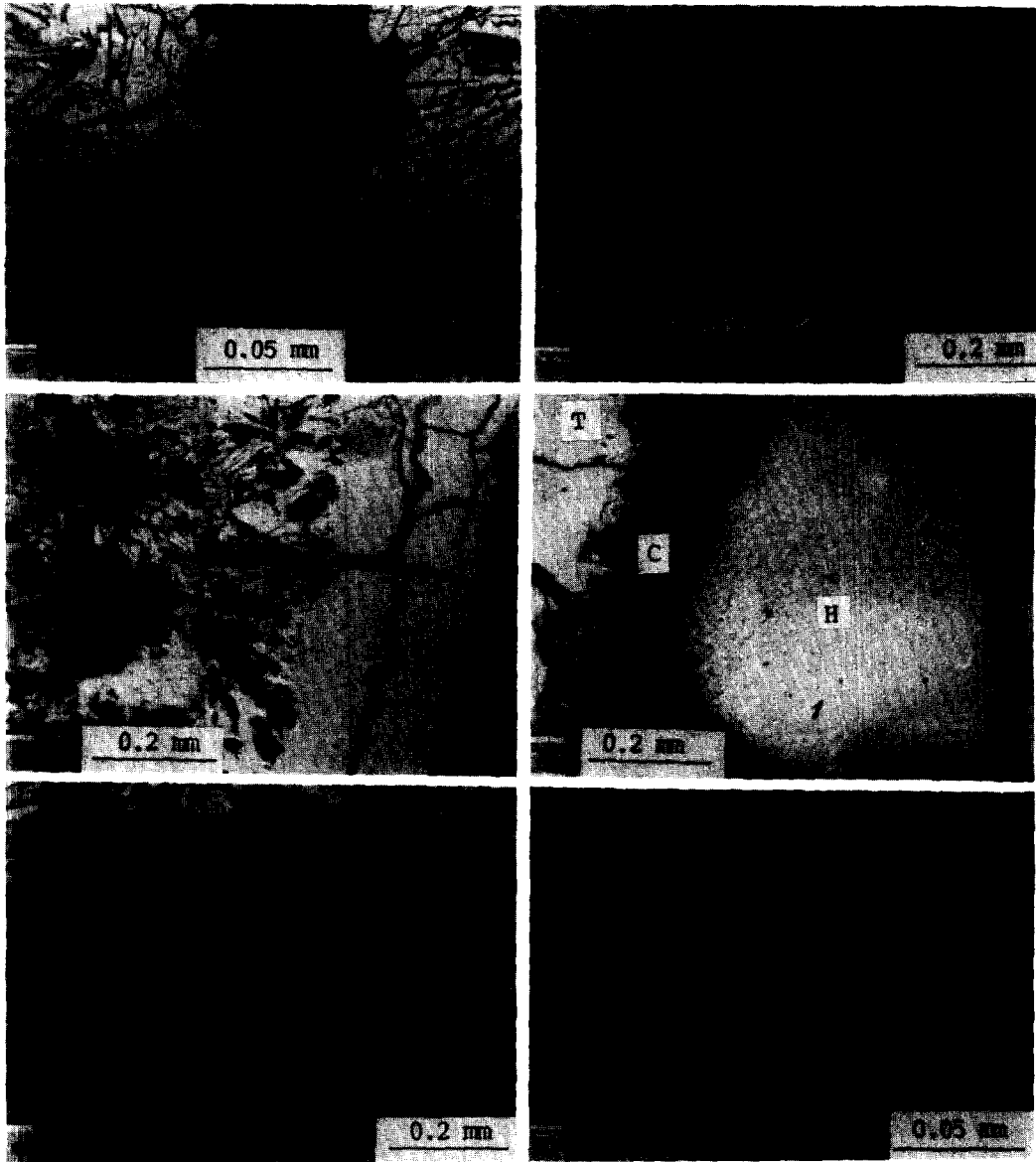


Fig. 4. Photomicrographs of manganese oxide minerals from Dongnam mine, Korea.
 (a) Pyrolusite crystals. Grey area is polyester. Polished section.
 (b) Pyrolusite formed by replacement from rhodochrosite. Polished section.
 (c) Colloform bands of nsutite(white) and goethite(grey). Left half consists of pyrolusite crystals. Polished section.
 (d) Ball-shaped hydrohetaerolite(H) in association with calcite(C) and todorokite(T). Polished section.
 (e) Prismatic pyroxmangite and quartz vein. Thin section. Open nicols.
 (f) Pyroxmangite in association with rhodochrosite(dark) and quartz(white grey). Thin section. Crossed nicols.

Other manganese oxide minerals: Pyrolusite shows well-developed crystals, or columnar and radiating aggregates along the walls of cavities (Fig. 4a). They were probably precipitated or crystallized from the noncolloidal solution. In some ores, it replaces birnessite and nsutite, and preserves rhombic cleavages which indicate the replacement from rhodochrosite (Fig. 4b). It also occurs as veinlets in nsutite which has been formed by replacement from birnessite. It is associated with nsutite, todorokite, goethite, birnessite, calcite, and quartz.

It is iron black in color, black in streak, metallic in luster, and low in hardness. In the reflected light, it is yellowish white in color, and

Table 4. X-ray powder diffraction data of manganese oxide minerals (FeK α /Mn)

Pyrolusite			Nsutite		Hydrohetaerolite		
I	d(\AA)	hkl	I	d(\AA)	I	d(\AA)	hkl
vs	3.077	110	m	3.94	m	2.996	112
s	2.387	101	w	2.56	w	2.847	200
w	2.193	200	m	2.41	s	2.638	103
m	2.097	111	w	2.33	vs	2.450	211
w	1.963	210	vw	2.23	w	2.239	004
vs	1.619	211	vs	2.12	m	2.023	220
m	1.554	220	w	2.06	w	1.761	204
m	1.432	002	s	1.635	w	1.708	105
w	1.391	310	m	1.603	m	1.677	312
s	1.302	301	vw	1.478	w	1.610	303
vw	1.250	311	w	1.370	s	1.564	321
w	1.202	202	vw	1.368	vs	1.503	224
w	1.161	212	w	1.255	s	1.433	400
vw	1.1235	321			vw	1.416	314
vw	1.0957	400			vw	1.306	305
m	1.0562	222			vw	1.294	332
w	1.0387	330			vw	1.281	420
w	0.9990	411			m	1.262	413
					vw	1.233	422
					vw	1.211	404
					w	1.154	316
					vw	1.138	501
					vwm	1.126	008
					w	1.114	424
					w	1.101	415
					w	1.092	512
					m	1.072	503
					w	1.063	521
					w	1.045	208
					m	1.015	440

it shows moderate to high reflectance, distinct bireflectance, strong anisotropism, and no internal reflection.

X-ray powder diffraction data for pyrolusite are given in Table 4. The d-values are indexed on a tetragonal unit cell with parameter $a=4.397$, $c=2.816\text{\AA}$. The axial ratio $a:c$ is 1:0.651. They have been refined by the lattice constant least squares refinement program, LCISQ(MIV) (Burnham, 1970). No systematic correction term has been used.

Infrared absorption spectrum for pyrolusite is shown in Fig. 5, and the characteristic infrared absorption bands are 415,560, and 710 cm^{-1} .

Nsutite occurs as colloform bands alternating with birnessite and goethite, and it is usually associated with pyrolusite, todorokite, quartz, and calcite. It shows shrinkage cracks (Fig. 4c). It has been formed by replacement from birnessite and todorokite, and it is replaced by pyrolusite. In cases, nsutite veinlet cuts birnessite which was formed from pyroxmangite. It also shows colloform layers alternating with goethite, filling or lining the cavities.

It is greyish black in color, black in streak, metallic in luster, and high in hardness. In the reflected light, it is white in color and shows very high reflectance, distinct bireflectance, strong anisotropism, and no internal reflection. Sometimes, it looks like isotropic when it is cryp-

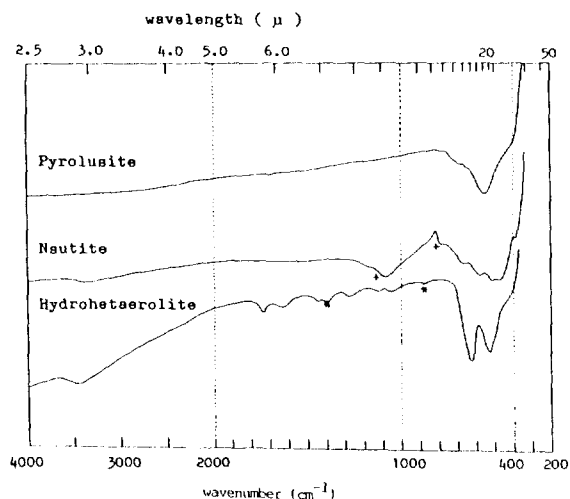


Fig. 5. Infrared absorption spectra for pyrolusite, nsutite, and hydrohetaerolite from Dongnam mine. +: Due to quartz. *: Due to calcite.

to crystalline.

X-ray powder diffraction data for nsutite are given in Table 9. Infrared absorption spectrum for nsutite is shown in Fig. 5. It shows absorption bands at 395, 465, 515, 575, 685, and near 3400 cm⁻¹.

Hydrohetaerolite occurs as fine, earthy filling the cavities in calcite. It is associated with todo-

Table 5. X-ray powder diffraction data of pyroxmangite, knebelite, goethite, and rhodochrosite(FeK α /Mn)

Pyroxmangite		Knebelite			Goethite		
I	d(Å)	I	d(Å)	hkl	I	d(Å)	hkl
vw	6.358	m	3.59	111	vw	4.937	020
w	4.719	s	2.85	130	vs	4.127	110
w	4.228	w	2.64	40	w	3.358	120
w	3.662	m	2.59	131	s	2.679	130
vw	3.554	m	2.53	112	w	2.600	040
vw	3.458	w	2.44	200,041	m	2.440	111
w	3.115	w	2.34	122,140	m	2.242	121
vs	2.954	m	1.80	222	m	2.186	140
m	2.868	w	1.69	061	vw	1.803	211
w	2.758	w	1.66	133	m	1.720	221
vw	2.677	w	1.65	152	w	1.688	240
vw	2.595				vw	1.598	231
w	2.514	Rhodochrosite			m	1.563	151
vw	2.310				w	1.507	002,250
w	2.274	I	d(Å)	hkl	w	1.459	061
s	2.172				vw	1.419	112
w	2.115	w	3.599	012	w	1.390	330
w	2.066	vs	2.819	104	w	1.361	170
vw	2.013	w	2.371	110	w	1.319	132
w	1.977	m	2.158	113	vw	1.293	042
vw	1.893	m	1.990	202	vw	1.268	331
w	1.865	w	1.822	024	w	1.143	410
w	1.721	s	1.759	018,116	w	1.127	242
vw	1.697	vw	1.550	211			
m	1.661	m	1.526	122			
w	1.584	w	1.447	214			
w	1.489	vw	1.418	208			
w	1.476	m	1.375	030			
s	1.428	w	1.300	0, 0, 12			
vw	1.345	vw	1.245	0, 2, 10			
vw	1.329	w	1.218	128			
w	1.202	vw	1.143	1, 1, 12			
w	1.097						
vw	1.092						

rokitite. It shows ball-shape (Fig. 4d).

It is brownish black to dark brown in color, brown in streak, submetallic in luster, and low to moderate in hardness. It is yellowish white in color in the reflected light. It shows weak birefractance, strong anisotropism, and no internal reflection.

X-ray powder diffraction data for hydrohetaerolite are given in Table 5. They are indexed on a tetragonal unit cell with parameter a=5.734, c=8.990Å. The axial ratio a:c is 1:1.568. They have been refined by the lattice constant least squares refinement program, LCISQ (MIV). No systematic correction term has been used.

Infrared absorption spectrum for hydrohetaerolite is shown in Fig. 5. Positions of absorption bands are 430, 540, 630, 1075, 1125, 1280, 1455, 1645, 1740, and near 3500 cm⁻¹.

Iron hydroxide: Goethite is frequently found in manganese oxide and manganese carbonate ores.

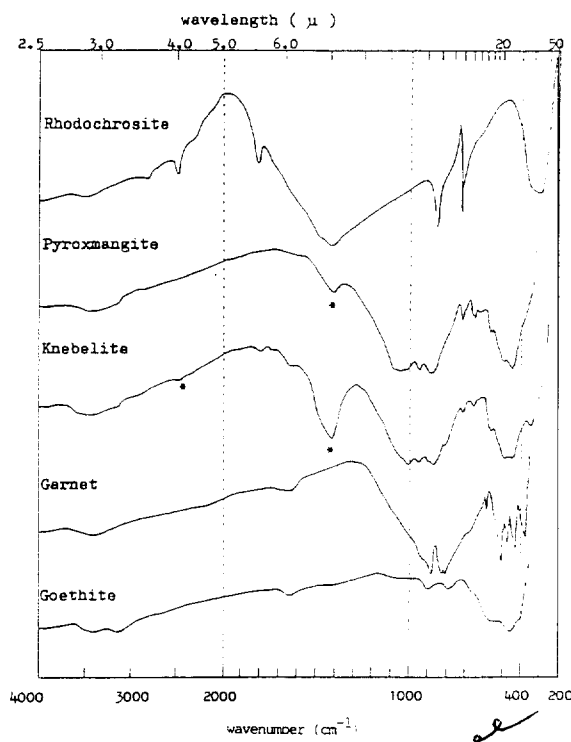


Fig. 6. Infrared absorption spectra for rhodochrosite, pyroxmangite, knebelite, garnet, and goethite from Dongnam mine.

*: Due to rhodochrosite.

It occurs as pseudomorphs after pyrite in manganese oxide ores, and the relict of pyrite is preserved. It also shows colloform layers together with nsutite. It is also found in limestone as colloform bands in open spaces.

It is reddish to black in color, moderate in hardness, and submetallic in luster. In the reflected light, it is grey in color, and it shows weak bireflectance, distinct anisotropism, and reddish brown internal reflection.

X-ray powder diffraction data for goethite are given in Table 5. They are indexed on an orthorhombic unit cell. $a=4.607$, $b=9.962$, $c=3.021\text{\AA}$. The axial ratio $a:b:c=0.462:1:0.303$. They have been refined by the lattice constant least square refinement program, LCLSQ (MIV). No systematic correction term has been used.

Infrared absorption spectrum for goethite is shown in Fig. 6. Positions of absorption bands are 410, 465, 575, 670, 790, 905, near 1070, 1650, near 3150, and near 3450 cm^{-1} .

Hydrothermal minerals: Rhodochrosite is found not only in manganese carbonate ores, but also in manganese silicate ores. In manganese carbonate ores, it is associated with pyrite. It occurs as fine aggregates in thin section. In manganese silicate ores, it is closely associated with knebelite and pyroxmangite. It is oxidized to vernadite in the weathered zone.

Rhodochrosite from the Dongnam mine is grey to pink in color. It is moderate in hardness and vitreous in luster. In thin section, it is colorless and pale pleochroic and shows undulatory extinction.

X-ray powder diffraction data for rhodochrosite are given in Table 5. Infrared absorption spectrum for rhodochrosite is shown in Fig. 6. Positions of absorption bands are 320, 725, 865, 1430, 1815 and 2498 cm^{-1} .

Pyroxmangite is a main constituent mineral of the manganese silicate ore. It occurs as short prismatic crystals or coarse crystals (Fig. 4e, f). It is closely associated with quartz, rhodochrosite, knebelite, and chlorite. It is replaced by birnessite.

It is pinkish in hand specimen, high in hardness, and pearly to vitreous in luster. In thin section, it is colorless and shows inclined extinction.

X-ray powder diffraction data for pyroxmangite are given in Table 5. Infrared absorption spectrum for pyroxmangite is shown in Fig. 6. 1050 cm^{-1} .

mineral	hypogene process	supergene process	
		oxidation	precipitation
knebelite	-----	-----	-----
pyroxmangite	-----	-----	-----
rhodochrosite	-----	-----	-----
vernadite	-----	-----	-----
todorokite	-----	-----	-----
birnessite	-----	-----	-----
nsutite	-----	-----	-----
pyrolusite	-----	-----	-----
hydrohetaerolite	-----	-----	-----
rancieite	-----	-----	-----

Fig. 7. The paragenetic sequence of manganese minerals in Dongnam mine.

Positions of absorption bands are 450, 500, 555, 572, 623, 655, 700, 720, 885, 950, and near 1050 cm^{-1} .

Knebelite manganoan fayalite is found in the manganese silicate ores. It is consistently associated with pyroxmangite and quartz. It occurs as very fine-grained aggregate. It is greenish in hand specimen, high in hardness, and vitreous in luster. Color is pale greenish in thin section. It shows weak pleochroism. X-ray powder diffraction data are given in Table 5. Infrared absorption spectrum for knebelite is shown in Fig. 6.

Paragenetic sequence: The textural study of the manganese ores from the Dongnam mine shows that the manganese minerals were formed from the hydrothermal minerals in the following paragenetic sequence.

Pyroxmangite \rightarrow birnessite

Rhodochrosite \rightarrow vernadite \rightarrow birnessite \rightarrow nsutite \rightarrow pyrolusite

Todorokite, rancieite, and hydrohetaerolite were precipitated from solution in the later stage.

SUMMARY AND CONCLUSIONS

The conclusions reached from the study on the mineralogy and genesis of manganese oxide minerals in the Dongnam mine are summarized in the following.

1) The manganese ore deposits occur as veins developed in the Ordovician Pungchon limestone and they consist of manganese carbonate, manganese silicate, and manganese oxide ores.

- 2) The manganese oxide ores were formed by oxidation of manganese carbonate and silicate ores, and precipitation from solution in supergene weathering environment. The trends of oxidation area; i) Rhodochrosite → vernadite → birnessite → nsutite → pyrolusite ii) Pyroxmangite → birnessite, iii) Buserite → rancieite Buserite, rancieite, todorokite, and hydrohetaerolite have been formed mainly by precipitation from solution.
- 3) The natural buserite has been discovered from this study. It has the same layer structure as the rancieite, as evidenced from infrared spectra and X-ray diffraction pattern.
- 4) Buserite is different from todorokite in structure as evidenced by infrared spectra although the two have the similar X-ray diffraction pattern. Distinction between two minerals is possible only by combined tests of X-ray diffraction and dehydration.

Acknowledgement: This research was supported by grant (No. 86-0709-02) from the Korea Science and Engineering Foundation.

REFERENCES

- Burns, R. and Burns, V.M. (1979) Manganese oxides: in *Marine Mineralogy*, 1-46. Litho-Craf., Inc., Chelsea, Michigan.
- Giovanoli, R. Burki, P. and Giuffredi, M. (1975) Layer structured manganese oxide hydroxides. IV: The buserite Group: Structure stabilization by transition elements. *Chimia*, 29, 517-520.
- Giovanoli, R. (1980) Vernadite is randomstacked birnessite. *Mineral. Deposita*, 15, 251-253.
- Turner, S. and Buseck, P.R. (1981) Todorokite: A new family of naturally occurring manganese oxides. *Science*, 212, 1024-1027.