

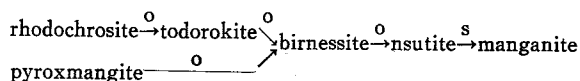
Mineralogy and Genesis of Manganese Ores from the Buncheon Mine, Korea

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Abstract: The Buncheon manganese ore deposits occur in vein along the fault of N20°E, cutting the foliation of Yulri Series. The deposits consist of primary manganese silicate ores in the deeper part and superficial manganese oxide ores near the surface. The spatial distribution of manganese oxide ores with respect to the manganese silicate ores suggests that the manganese oxide ores are the supergene oxidation product of the manganese silicate ores.

Manganese silicate ores consist mainly of fine- to coarse-grained pyroxmangite with minor rhodochrosite, quartz, sulfides and chlorite. Manganese oxide ores are composed of supergene manganese oxides such as nsutite, birnessite, manganite and todorokite, and other associated minerals.

Paragenetic sequence of formation of the manganese minerals are as follows:



(o: oxidation, s: simple sequence)

In order to elucidate the mineralogy of the manganese minerals, microscopic, X-ray, IR spectroscopic, and thermal studies were made for manganese and associated minerals.

INTRODUCTION

The Buncheon manganese deposits lie at Jugmi Mt. about 2 Km south of Buncheon railroad station in Socheon-myeon, Bonghwa-gun, Gyeongsangbugdo. The deposits are located about 5 Km north of the Janggun mine.

The Buncheon manganese deposits are characterized by the abundant occurrence of manganese silicate mineral (pyroxmangite).

Manganese ores at the Buncheon mine consist of primary manganese silicates and supergene secondary manganese oxides.

The deposits were studied by Koh and Yoo (1971). The manganese oxide ores were produced from the mine in the past, but no mining operation is being made now.

GENERAL GEOLOGY

Geology of the Buncheon mine area consists

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of the Yulri Series and the Buncheon granite gneiss of Precambrian age, the Chunyang granite and pegmatite of Jurassic, and acidic dyke rocks of Cretaceous age (Fig. 1).

The Yulri Series consists of the metamorphosed argillaceous sediments such as muscovite-chlorite schist, andalusite-muscovite schist, andalusite-biotite schist, andalusite-mica-chlorite schist, muscovite schist, andalusite-cordierite-muscovite schist, the metamorphosed arenaceous sediments such as micaceous sandstone, and thin crystalline limestone.

The Buncheon granite gneiss intrudes the Yulri Series in the northeastern part of the area. It is massive coarse-grained rock with some schistose structure. The Chunyang granite intrudes the Yulri Series. Pegmatite is found in the Yulri Series and the Chunyang granite. Acidic dyke rock intrudes the Yulri Series and the Buncheon granite gneiss.

The general strike of the Yulri Series is NE-

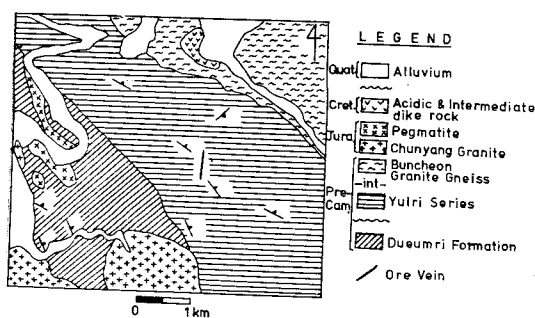


Fig. 1 Geological map of the Buncheon mine area. SW.

MANGANESE ORE DEPOSITS

The Buncheon manganese deposits consist of the primary manganese silicate ores and the secondary supergene manganese oxide ores. The latter ores have been formed by supergene oxidation and enrichment from the former ores. Both ores occur in one and the same vein in schists of the Yulri Series. The manganese oxide ores are developed as the weathering zone near the surface just above the manganese silicate ores.

The main ore vein is assumed to extend about several hundred meters showing the strike of $N20^{\circ}E$ and the thickness of 0.5~5 meters. Although other veins are also reported to occur in the area, they have not been found in this study, except a small outcrop of manganese oxides along the contact of schists and the Buncheon granite gneiss. It is significant to mention that this manganese oxide ores also contain pyroxmangite as the primary manganese mineral.

MANGANESE SILICATE ORES

Manganese and Associated Minerals

The manganese silicate ores, the primary ores in the Buncheon mine, consist mainly of pyroxmangite with minor rhodochrosite, quartz, and sulfides (pyrite, sphalerite, galena, chalcopyrite, and alabandite) (Fig. 5C, D, E).

Ore Textures

The manganese silicate ores are light pink with greyish tone in color, and fine- to medium-grained. The ores partly contain sulfides and/or chlorite as disseminated particles or veinlets when viewed with naked eye.

Under the microscope, pyroxmangite is fine- to coarse-grained and shows granular or prismatic habit. It is often found that the prismatic crystals of pyroxmangite are curved. It is surrounded by rhodochrosite in places, but it is generally found that the rhodochrosite is admixed with pyroxmangite. Such texture is resulted from the irregular replacement of pyroxmangite by rhodochrosite. Pyroxmangite occurs as euhedral crystals in the quartz-rich parts which have been formed by filling of quartz in pyroxmangite geodes.

Sulfides such as pyrite, sphalerite, chalcopyrite, and galena are sparsely disseminated in the pyroxmangite matrix. Alabandite is found as the filling material in the cavity in pyroxmangite ore. Successive precipitation of rhodochrosite and then alabandite is well observed with naked eye.

Rock fragments consisting mainly of chlorite are often included in the manganese silicate ores. They are probably derived from the country rock. Some of chlorites are remobilized to form veinlets or networks in the manganese silicate ores.

Mineralogy

Pyroxmangite

Pyroxmangite is the main constituent mineral of the manganese silicate ores. It is pink or lilac in color, in hand specimen, and colorless or slightly pleochroic in thin section. It turns to dark brown or black on the fresh surface when it is exposed to the air for a long time. Such a tarnishing is due to the rapid oxidation. It is partly replaced by rhodochrosite (Fig. 5E, F).

X-ray powder diffraction data of pyroxmangite from the Buncheon mine are given in Table 1, and infrared absorption spectral curve is shown in Fig. 2. The infrared absorption bands of Si—O stretching vibrations appear between 1100 and 900 cm^{-1} , and those of Si—O bending vibrations between 400 and 500 cm^{-1} . The small bands from 800 to 500 cm^{-1} are interpreted as due to the structure with a unit repeat of seven twisted tetrahedra. Pyroxmangite studied by Ryall and Threadgold (1966) shows seven peaks between 550 and 750 cm^{-1} , confirming the claim by Lazarev and Tenisheva (1961) that the number of peaks in this region provides information as to the number of tetrahedra in the repeat unit of a single chain silicate.

DTA curve of pyroxmangite was obtained from 20° to 1500°C. The curve shows no change up to 1100°C. It shows melting about at 1100°C.

Rhodochrosite

Rhodochrosite occurs as veinlets in the matrix of pyroxmangite, or minor constituent of pyroxmangite ore (Fig. 5E). Rhodochrosite is white to pink in color in hand specimen, and colorless to pale pink in thin section. It shows pleochroism in thin section, and internal reflection in polished section.

X-ray powder diffraction data of rhodochrosite

Table 1 X-ray powder diffraction data of pyroxmangite and rhodochrosite from the Buncheon mine, Korea

Pyroxmangite			Rhodochrosite		
I	d(Å)	hkl	I	d(Å)	hkl
vw	4.62	101	m	3.66	012
m	3.10	210, $\bar{2}41$	vvs	2.84	104
vs	2.94	102	w	2.38	110
w	2.66		m	2.17	113
w	2.61		m	2.00	202
m	2.21		w	1.82	024
s	2.17		vs	1.768	018
w	2.05		m	1.540	122
			m	1.377	032

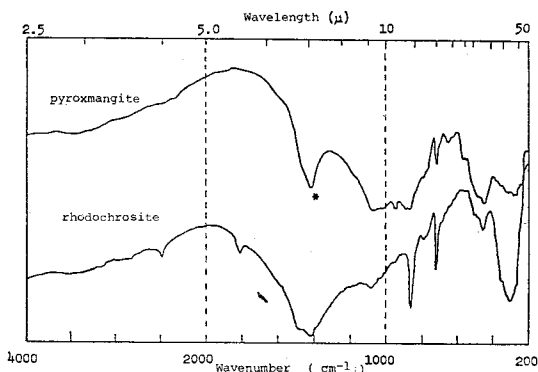


Fig. 2 Infrared absorption spectra of pyroxmangite and rhodochrosite from the Buncheon mine.

* Caused by rhodochrosite impurity.

from the Buncheon mine are given in Table 1, and infrared absorption spectral curve is shown in Fig. 2. Infrared absorption spectral curve of rhodochrosite from the Buncheon mine shows characteristic strong absorption bands at 1420, 865 and 725 cm^{-1} , and other weak bands at 2500 and 1810 cm^{-1} .

Alabandite

Alabandite is not abundantly found. It occurs as fillings in the rhodochrosite geodes. It shows exsolution texture with pyrrotite.

Alabandite is black in color and adamantine in luster. X-ray powder diffraction pattern of alabandite shows characteristic peaks at 2.61, 1.85 and 1.51 Å.

Chlorite

Chlorite is abundantly found in manganese oxide ores. It occurs as inclusions or networks in the manganese silicate ores. Chlorite inclusions in manganese silicate ores are the chloritization product of mica schist inclusions, whereas chlorite networks are the remobilization or remineralized products.

Chlorite is dark green to green in hand specimen. It shows green or greenish color and weak pleochroism in thin section.

MANGANESE OXIDE ORES

Manganese Oxides and Associated Minerals

The manganese oxide ores consist mainly of birnessite, nsutite, manganite, and todorokite, with other associated minerals such as kaolinite, goethite and quartz. Birnessite and nsutite occur abundantly, but manganite and todorokite in small amounts.

Types of Manganese Oxide Ores

The manganese oxide ores are generally moderately hard, porous and low in grade. Clay and goethite are abundantly included in the ores.

[Mineralogical Types]

Manganese oxide ores can be classified into the following types on basis of mineralogical assemblages.

- 1) birnessite ore,
- 2) birnessite-todorokite ore,
- 3) nsutite ore, and
- 4) nsutite-manganite ore.

[Genetic Types of Ores]

Textural study shows that manganese oxide ores have been formed by several different processes. The ore types classified on basis of main mineral-forming processes are:

- 1) ores formed by replacement, and
- 2) ores formed by precipitation from solution.

Ores formed by replacement is usually moderately compact, but porous. Most of manganese oxide ores have been formed by replacement. This process includes the oxidation of manganese silicate and carbonate, further oxidation of early-formed oxides, and transformation from one phase to another.

Ores formed by precipitation from solution are characterized by fine colloform bands or comb structure.

Ores formed by replacement consist of birnessite, todorokite and nsutite, whereas those by precipitation from solution consist of manganite,

birnessite and nsutite.

Mineralogy

Todorokite

Todorokite from the Buncheon mine is a poorly-crystalline type. It occurs as the pseudomorphs after rhodochrosite. Therefore, it generally replaces rhodochrosite, and is replaced by birnessite (Fig. 6A). Todorokite is very fine-grained. It shows twinning in places. Very fine-grained particles are intimately intergrown to each other. This intergrowth is well observed when the analyzer is slightly shifted from the exact crossed nicols.

Todorokite is brownish grey in color and submetallic in luster on polished surface. Under the microscope, it is greyish white, and shows moderate reflectance, weak bireflectance and anisotropism. Internal reflection is not found.

Todorokite occurs in too small particles to take X-ray photomicrograph. Infrared absorption spectra of todorokite from the Buncheon mine are shown in Fig. 3.

Birnessite

Birnessite is abundantly found in manganese oxide ores. It has been formed by replacement or precipitation from solution. It replaces pyroxmangite and todorokite, and is replaced by nsutite or goethite. It often occurs as prismatic or acicular pseudomorphs after pyroxmangite (Fig. 5D), and rhombic pseudomorphs after rhodochrosite (Fig. 6A). It also occurs as replacement relicts in nsutite. Occasionally, it occurs in fissures of quartz or cleavage of muscovite.

Birnessite formed by precipitation from solution occurs as colloform bands alternating rhythmically with nsutite (Fig. 6C). It is cut by nsutite or goethite. Networks of nsutite or goethite are found in birnessite.

Birnessite is usually black and often brown in color in hand specimen. It is grey to dirty grey in polished section. It shows weak anisotropism and undulose extinction and no internal reflection.

Table 2 X-ray powder diffraction data of manganese oxide minerals from the Buncheon mine.

Birnessite		Nsutite			Manganite		
I	d(Å)	I	d(Å)	hkl	I	d(Å)	hkl
s	7.27	s	4.025	110	vs	3.37	210
s	2.42	vw	2.557	130	m	2.62	020
m	1.42	vs	2.427	021	w	2.61	120
		m	2.119	121	s	2.40	202
		s	1.631	221	m	2.25	220
		vw	1.467	300	m	2.18	212
		w	1.413	320	s	1.78	222
		w	1.372	061	w	1.700	420
					vs	1.666	213
					w	1.633	230
					m	1.496	032
					m	1.431	004
					m	1.323	214
					vw	1.296	503
					vw	1.281	304
					w	1.262	513
					vw	1.247	530
					w	1.215	531
					w	1.182	142
					w	1.159	702
					m	1.138	105
					w	1.117	433
					w	1.099	134
					w	1.079	043
					w	1.027	730
					w	1.015	343
					w	0.991	542

X-ray powder diffraction data of birnessite from the Buncheon mine are given in Table 2. Infrared absorption spectra of birnessite are shown in Fig. 3, and the absorption bands are given in Table 3.

Nsutite

Nsutite occurs as massive or colloform types. It replaces birnessite (Fig. 6A) and partly quartz. Goethite is frequently associated with nsutite. Nsutite in colloform bands alternates with birnessite (Fig. 6C), manganite, or goethite (Fig. 6D). It replaces colloform bands of birnessite diffusely. It also occurs as veinlets in birnessite. Shrinkage cracks and pores are

Table 3 Infrared absorption bands of manganese oxide minerals from the Buncheon mine.

Todorokite		Birnessite		Nsutite		Manganite	
cm ⁻¹	I	cm ⁻¹	I	cm ⁻¹	I	cm ⁻¹	I
290	w						
320	w	365	sh				
370	vw			370	w		
						380	s
				390	w		
440	s			435	sh	435	s
				460	sh		
470	s	465	sh				
						480	s
500	s			520	s	500	s
530	s	535	s				
570	sh	560	s				
		580	s	580	s		
		600	sh			590	s
670	sh						
				695	sh		
790	w	740	sh			770	w
890	m						
						1085	m
						1150	m
1630	w	1630	w	1625	w		
						2000	m
		3400	m	3400	w	2550	m
3300	s						

found in nsutite. These cracks and pores are the results of decrease in volume due to dehydration. Pseudomorphic rhombic shape of original rhodochrosite is often preserved in nsutite.

Nsutite is completely opaque. It is black to greyish black in color and metallic in luster. It is hardest among the manganese oxide minerals. In the reflected light, it is white with a faint creamy tint and shows high reflectance. It shows distinct bireflectance and strong anisotropism, but sometimes isotropism. It also shows undulatory extinction and no internal reflection.

Nsutite is a natural form of γ -MnO₂. X-ray powder diffraction data of nsutite from the Buncheon mine are given in Table 2. Although the X-ray pattern of nsutite has been indexed

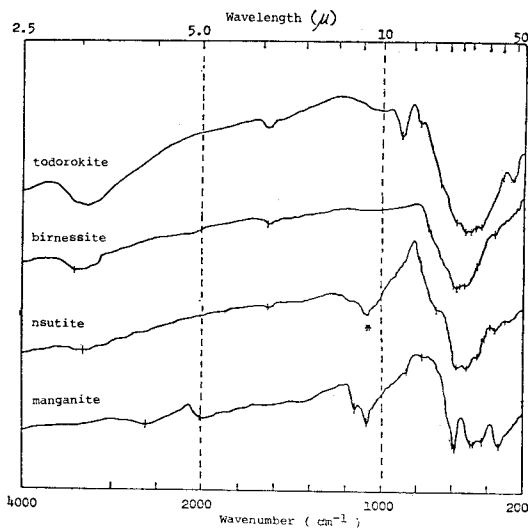


Fig. 3 Infrared absorption spectra of manganese oxide minerals from the Buncheon mine. Asterisk indicates the peak due to quartz impurity.

on hexagonal symmetry by Faulring (1965), they can also be indexed on an orthorhombic symmetry as shown in Table 2. An orthorhombic unit cell calculated for the nsutite from the Buncheon mine is as follows:

$$a=4.430\text{\AA}, b=9.511\text{\AA}, c=2.814\text{\AA}$$

$$\text{Volume of unit cell: } 118.542 \times 10^{-24} \text{cm}^3$$

$$\text{Axial ratio: } a:b:c = 0.466:1:0.296$$

Infrared absorption spectra of nsutite are shown in Fig. 3, and the absorption bands are given in Table 3.

DTA, TG and DTG curves for nsutite from the Buncheon mine are given in Fig. 4. DTA

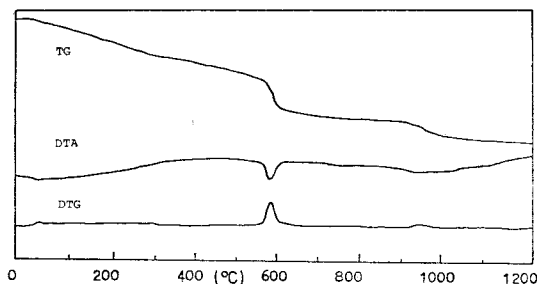


Fig. 4. TG, DTA and DTG curves of nsutite from the Buncheon mine.

curve of nsutite shows endothermic peaks at 580°C due to transformation to Mn_2O_3 , and 964°C due to transformation of Mn_2O_3 to Mn_3O_4 .

Manganite

Manganite occurs as lining on the wall of cavities, or colloform bands with nsutite. Manganite crystals grow perpendicular to the wall surface (Fig. 6B).

Manganite is brownish black in color, and not completely opaque but translucent red in the very thin parts. In polished section, it is grey to white in color and shows distinct anisotropism.

X-ray powder diffraction data for manganite from the Buncheon mine are given in Table 2. Infrared absorption spectra of manganite from the Buncheon mine are given in Fig. 3, and the absorption bands are given in Table 3. In the low-frequency region approximately between 700 and 350 cm^{-1} , infrared spectra of manganite show intense absorption bands. The bands occurring between 1150 and 1085 cm^{-1} are Mn-OH deformation and O-H valence vibrations. Since only a single hydrogen bond length exists in crystal lattice, the multiple OH bands could be possible due to a coupling effect (Schwarzmann and Marmann, 1965, 1966). Two weak bands at 2000 and 2800 cm^{-1} are due to O-H valence vibration.

Other minerals

Goethite is widely distributed in the manganese oxide ores. It is the oxidation product of pyrite. Goethite formed by precipitation from solution occurs as colloform bands, alternating with nsutite. It cuts colloform birnessite bands.

Ore Textures and Structures

Megascopic Fabric

Magascopically, the manganese oxide ores from the Buncheon mine are characterized by their highly porous fabric without precipitation

of carbonates in the pores.

Replacement Textures

Replacement textures are widely found in the manganese oxide ores from the Buncheon mine.

Replacement process includes the oxidation of protores to manganese oxides and further oxidation of early formed manganese oxides to later manganese oxides.

Pseudomorphic replacement textures of pyroxmangite by birnessite or of rhodochrosite by todorokite are abundantly found in the early-formed manganese oxide ores. Minerals showing the replacement textures are summarized in the following.

pyroxmangite.....→birnessite
 rhodochrosite→todorokite
 birnessite.....→nsutite
 todorokite→birnessite
 quartz, feldspar.....→birnessite, nsutite
 pyrite, chalcopyrite→goethite

Precipitation Textures

Precipitation texture is not abundantly found in the manganese oxide ores from the Buncheon mine.

Characteristic precipitation textures are:

- a) Colloform bands of birnessite and nsutite in cavities in the manganese oxide ores.
- b) Manganite crystals growing on the walls of fissures or pores.

Genesis of Ores

Paragenetic Sequence

The textural relations of the manganese oxide ores from the Buncheon mine show that the manganese oxide minerals were formed in the paragenetic sequence as shown in the following.

rhodochrosite \xrightarrow{o} todorokite \xrightarrow{o} birnessite \xrightarrow{o} nsutite
 pyroxmangite \xrightarrow{o} birnessite \xrightarrow{s} manganite

(o: oxidation; s: simple sequence)

Mechanism of Formation

Textures of ores show that the fundamental

processes of formation of manganese oxide minerals are replacement and precipitation from solution. Replacement of minerals took place in the order of increasing oxidation coefficient.

Todorokite is the first oxidation product from rhodochrosite. Birnessite is the first oxidation product from pyroxmangite. Birnessite has been oxidized to nsutite. All these processes are expressed as the replacement texture. In such replacement process, addition or removal of cations took place.

Birnessite, nsutite and manganite also have been formed by precipitation from colloidal or noncolloidal solution which was formed by dissolution of preexisting or early-formed manganese minerals.

SUMMARY AND CONCLUSIONS

The conclusions of the study on the mineralogy and genesis of the manganese ores in the Buncheon mine are summarized as follows:

- 1) The geology of the Buncheon mine area consists of the Dueumri formation, the Yulri series, the Buncheon granite gneiss, pegmatite of Precambrian and porphyry of Cretaceous age.
- 2) The manganese ore deposits are developed as vein along the fault plane, showing the strike of N20°E, cutting the foliation of Yulri series. The deposits consist of primary manganese silicate ores in the deeper part and superficial manganese oxide ores near the surface.
- 3) The manganese and other associated minerals have been studied by the methods of microscopic, X-ray, IR spectroscopic, thermal and chemical analyses.
- 4) Manganese silicate ores consist mainly of fine- to coarse-grained pyroxmangite with minor rhodochrosite, quartz, sulfides and chlorite.
- 5) Manganese oxide ores are composed of supergene manganese oxides such as nsutite, birnessite, manganite and todorokite, and

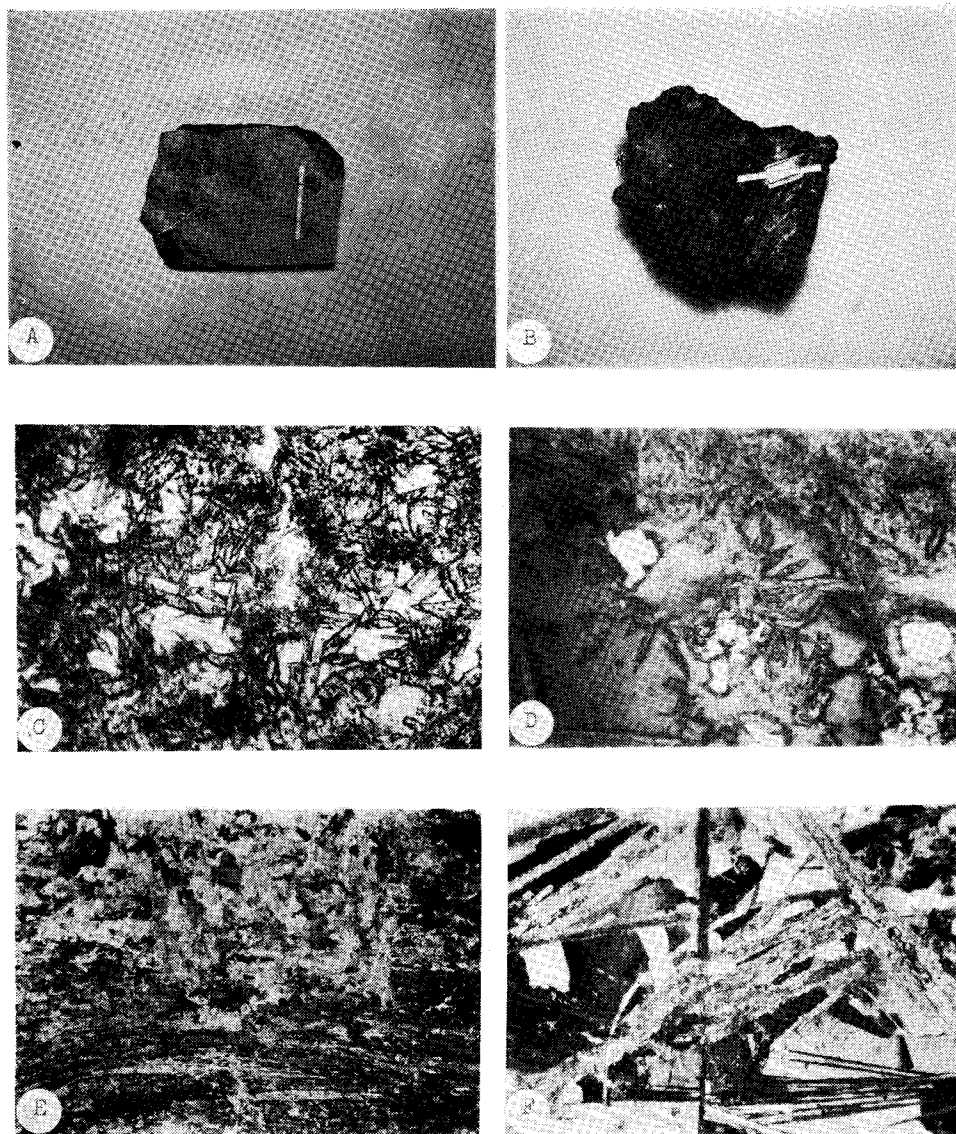


Fig. 5 Surface characters and photomicrographs of manganese ores from the Buncheon mine.

- A) Manganese silicate ore including sulfides and chlorite fragments. Note the oxidation film on the surface.
- B) Manganese oxide ore.
- C) Pyroxmangite aggregate with interstitial quartz in the manganese silicate ores. $\times 70$. Thin section.
- D) Pseudomorph of birnessite (grey) after pyroxmangite. White parts are the relicts of galena which escaped from oxidation. $\times 70$. Polished section.
- E) Replacement of pyroxmangite (grey) by rhodochrosite. $\times 70$. Thin section.
- F) Acicular rhodochrosite (dirty grey) in quartz aggregate. $\times 70$. Thin section.

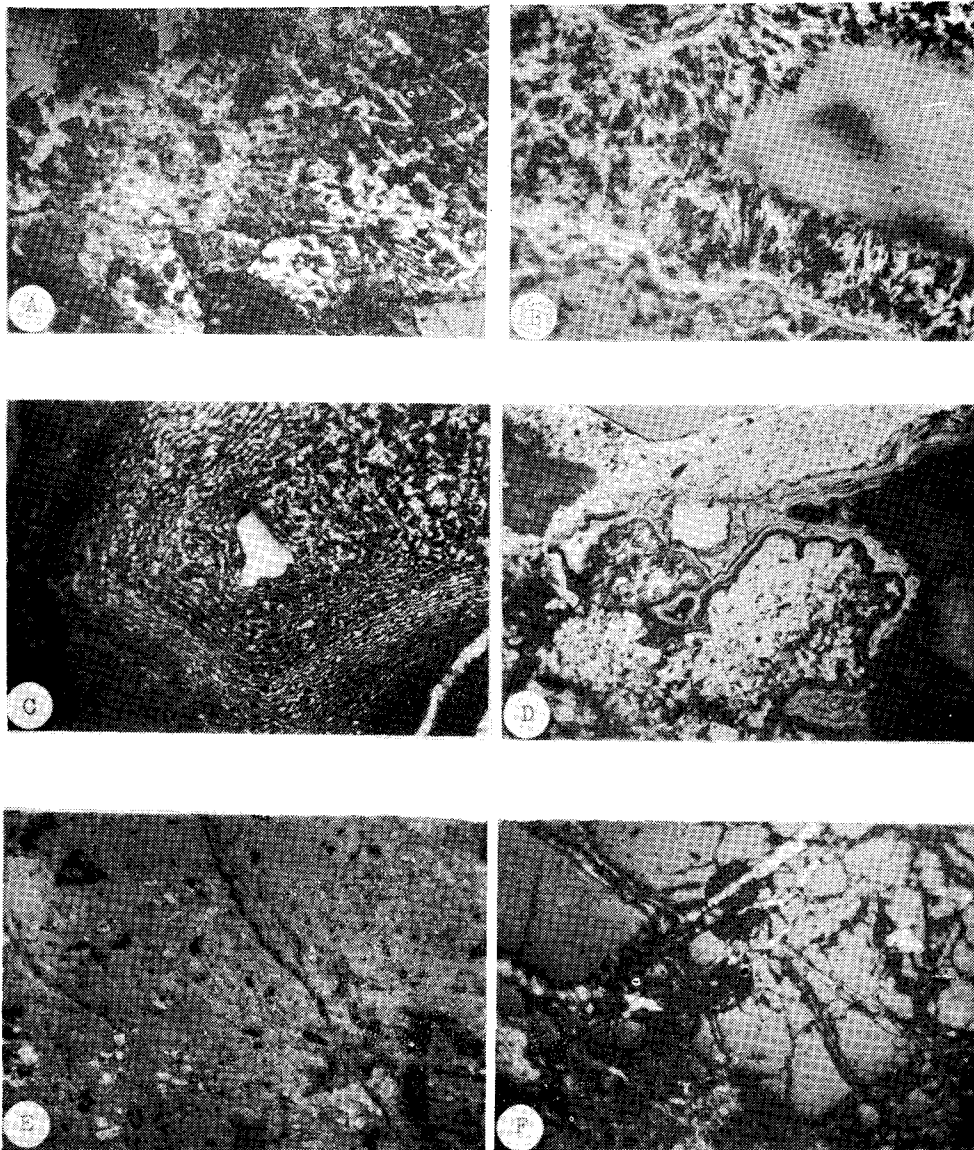
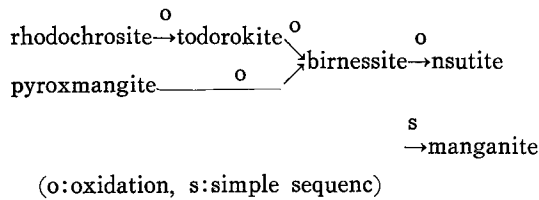


Fig. 6 Photomicrographs of manganese oxide ores from the Buncheon mine.

- A) Sequential replacement of rhodochrosite→todorokite (light grey)→birnessite (dark)→nsutite (white). Note the relict cleavages of rhodochrosites. $\times 70$. Polished section.
- B) Manganite crystals growing on the wall of cavity in manganese oxide ore. $\times 70$. Polished section.
- C) Colloform bands of nsutite (white) and birnessite (dirty grey and black). $\times 70$. Polished section.
- D) Colloform goethite (grey). White part is nsutite. $\times 70$. Polished section.
- E) Goethite (grey) formed by oxidation of pyrite (white). $\times 70$. Polished section.
- F) Replacement of quartz (grey) by birnessite (dirty grey) and nsutite (white). $\times 70$. Polished section.

associated other minerals such as goethite, kaolinite, quartz, plagioclase and muscovite.

6) The study on textures of manganese oxide ores shows that various manganese oxide minerals have been formed by oxidation of pyroxmangite or phodochrosite, precipitation from solution and further oxidation of earlier formed minerals. Paragenetic trend of formation of the manganese minerals are as follows:



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汾川鑛山の 망간鑛石에 對한 鑛物學的 및 成因的 研究

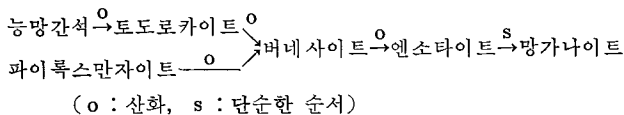
金 洙 鎮* · 孫 炳 國*

요약 : 분천 광산의 망간 광상은 선캠브리아기 울리통의 변성암류의 열상 구조를 횡단하는 N20°E 방향의 단층면을 따라 열수 용액이 충전하여 형성된 열수 기원의 규산 망간 광석과 이의 표성 산화작용에 의하여 생성된 산화 망간 광석으로 구성되어 있다.

규산 망간 광석은 주로 파이록스만자이트로 구성되어 있으며 소량의 능망간석, 석영, 녹니석 및 황화광물(황철석, 황동석, 십아연석, 방연석, 알라반다이트, 자류철석)등이 포함되어 있다.

산화 망간 광석은 엔소타이트, 버네사이트, 토도로카이트, 망가나이트 등으로 구성되어 있다.

파이록스만자이트와 능망간석의 산화과정 및 광물생성 순서는 다음과 같다.



망간 광석을 구성하고 있는 광물들은 광학적, X선적, 적외선 흡수분광학적, 열분석에 의하여 감정 연구되었다.

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