

Origin of Manganese Carbonates in the Janggun Mine, South Korea

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Abstract: Mn-Pb-Zn-Ag deposits of the Janggun mine are hosted in the Cambro-Ordovician Janggun limestone mostly along the contacts of the Jurassic Chunyang granite. The deposits are represented by several ore pipes and steeply dipping lenticular bodies consisting of lower Pb-Zn-Ag sulfide ores and upper manganese carbonate and oxide ores. The former consists mainly of arsenic, antimony, silver, manganese, and tin-bearing sulfides, whereas the latter are characterized by hypogene rhodochrosite, and superficial manganese oxides including todorokite, nsutite, pyrolusite, cryptomelane, birnesite and janggunite. Origin of the upper manganese ore deposits has been a controversial subject among geologists for this mine: hydrothermal metasomatic vs. syngenetic sedimentary origin. Syngenetic advocates have proposed a new sedimentary rock, rhodochrostone, which is composed mainly of rhodochrosite in mineralogy. In the present study, carbon, oxygen and sulfur isotopic compositions were analyzed obtaining results as follows: Rhodochrosite minerals, (Mn, Ca, Mg, Fe) CO₃, from hydrothermal veins, massive sulfide ores and replacement ores in dolomitic limestone range in isotopic value from -4.2 to -6.3‰ in δ¹³C(PDB) and +7.6 to +12.9‰ in δ¹⁸O(SMOW) with a mean value of -5.3‰ in δ¹³C and +10.7‰ in δ¹⁸O. The rhodochrosite bearing limestone and dolomitic limestone show average isotopic values of -1.5‰ in δ¹³C and +17.5‰ in δ¹⁸O, which differ from those of the rhodochrosite mentioned above. This implies that the carbon and oxygen in ore fluids and host limestone were not derived from an identical source. δ³⁴S values of sulfide minerals exhibit a narrow range, +2.0 to +5.0‰ and isotopic temperature appeared to be about 288~343°C. Calculated initial isotopic values of rhodochrosite minerals, δ¹⁸O_{H₂O} = +6.6 to +10.6‰ and δ¹³C_{CO₂} = -4.0 to -5.1 ‰, strongly suggest that carbonate waters should be deep seated in origin. Isotopic data of manganese oxide ores derived from hypogene rhodochrosites suggest that the oxygen of the limestone host rock rather than those of meteoric waters contribute to form manganese oxide ores above the water table.

INTRODUCTION

Janggun mine is located within the southeastern part of the Taebaegsan metallogenic belt, where there are some large productive tungsten-base metal ore deposits, South Korea (Fig. 1). Since 1940, the mine has been producing high grade manganese ore. From 1945 to 1975 the mine produced 3,000 tons per year of manganese

ore of average Mn 30 to 35 percent. This amount covered 75% of total production of Mn in South Korea. After 1975, the mine hit by lead-zinc-silver orebody beneath the manganese orebody, however, have changed into lead-zinc-silver mine and have produced about 4,200 ton/month of crude ores of average grade: 5.5 percent Pb, 5.0 percent Zn, 0.2 percent Cu, 100g Ag per ton and 1g Au per ton.

The Janggun ore deposits can be grouped into upper manganese and lower sulfide orebodies

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by mineral assemblages. Of the two kinds of orebodies, the manganese orebodies have been a controversial subject among geologists: syngenetic sedimentary (Kim, 1975, 1968, 1972, 1979), hydrothermal replacement, or hydrothermal metasomatic (Lee, 1967; Whang, 1968; Whang et al., 1975; Lee, 1980; Imai and Lee, 1980), and syngenetic and hydrothermal in part, (Whang and Reedman, 1968) in origin.

Recently base metal ore deposits were described as hydrothermally metasomatic in origin even by syngenetic advocators. Kim (1975) proposed a new sedimentary rock, rhodochrostone, which is composed mainly of rhodochrosite minerals.

In this study, data on the stable isotope compositions of manganese carbonates (rhodochrosite), calcite, host limestone and sulfide minerals which are coexisted and associated with manganese carbonates is presented and discussed in terms of origin and depositional condition of ore fluids in the Janggun manganese-lead-zinc-silver ore deposits.

GEOLOGIC SETTING

The general geology of the Janggun mine area has been summarized by Kim(1962), Lee(1953), Whang (1968), Whang and Reedman (1975), Kim (1975, 1979) and Lee (1980). The mineralogy and ore geneses of manganese carbonate ore deposits in this mine are well studied and summarized in Kim (1968, 1974, 1975, 1977, 1979). In complex sulfides ores, Lee(1980) and Imai and Lee (1980) have described in detail.

Wonnam formation and Yuli groups of the Precambrian basement consist dominantly of meta-sediments, schist, gneiss and phyllite. Jangsan quartzite, Dueumri schist formation and Janggun limestone formation (about 800m thick) of Cambro-Ordovician age covered above Precambrian formations unconformably. On the Permian-Carboniferous Dongsugok and Jaesan formations is a mica schist and phyllite lying unconfor-

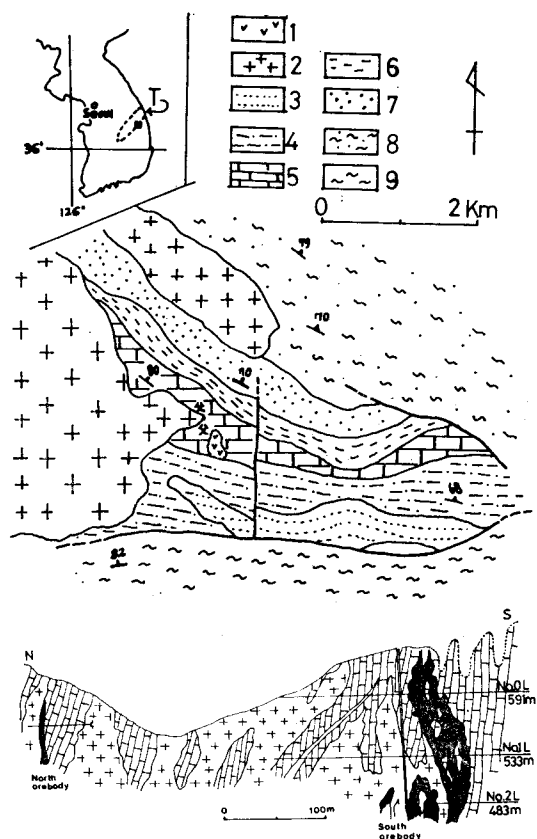


Fig. 1 Geologic map and section of the Janggun mine (Imai and Lee, 1978).

1. Andesitic rock
2. Chunyang granite
3. Jaesan formation
4. Dongsugok formation
5. Janggun limestone formation
6. Dueumri formation
7. Jangsan formation
8. Yuli formation
9. Wonnam formation

mably. Jaesan formation consist mainly of metamorphosed black sandstone and shale with coal seams (Fig.1.).

General trend of the formations strike $N 70^{\circ} E$ and dip $80^{\circ} NW$. According to Imai and Lee (1980), the metamorphic rocks experienced the intermediate P-T metamorphism during Jurassic Daebo-orogeny and belong to the greenschist to lower amphibolite facies.

Janggun limestone formation, which is the host rock of the ore deposits, consists predominantly of dolomitic limestone, thin bedded limestone, dolomite and massive crystalline lime-

stone. Characteristics of carbon and oxygen isotopic compositions and lithology of the Janggun carbonate rocks are similar to those of Cambro-Ordovician limestone of the Great Limestone Series in the Taebaegsan basin (Kim 1980). Chunyang two mica granite of Jurassic age intruded into the above formations.

The manganese ore deposits developed along and near the contact of the Cambro-Ordovician Janggun limestone and Chunyang granite of Jurassic age. Nearly all the production of the ores has come from the small chimney type orebody, small breccia pipes and veins filling calcite, sulfides and rhodochrosite. East-west Jaesan and north-south faults do not directly relate to the mineralization (Lee 1980).

ORE DEPOSITS

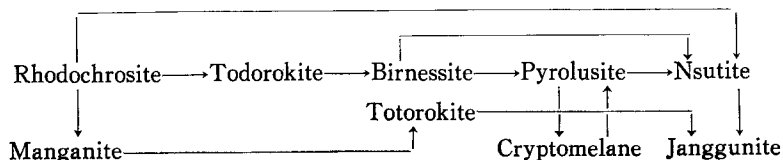
Manganese-lead-zinc deposits of the Janggun mine have been emplaced in the Cambro-Ordovician Janggun limestone mostly along the contacts of the Jurassic Chunyang granite (133my. Kim, 1971; 180 ± 2 my. Lee, 1980). Most ores in this mine are mined from South A orebody characterized by chimney or small pipe types. Mineralization age is estimated to be late Cretaceous (78 my. Lee, 1980) corresponding to the Bulguksa granite (late Cretaceous to early Tertiary) in South Korea.

The deposits are classified into lower sulfide dominant ores and upper manganese carbonates and manganese oxide ores. Much of sulfide ore is represented as massive, coarse grained and banded replacement ores occurring in small pipes that average 20 by 30m in width and dipping 70° SSE.

Major sulfide minerals are galena, sphalerite, pyrrhotite, arsenopyrite, and pyrite which are accompanied by minor bismuth, manganese and tin bearing sulfide minerals and sulfosalts. The manganese deposits of the mine can be classified into two genetic types; hydrothermal (hypogene)

and superficial. The former is characterized by hypogene rhodochrosite in small pipes and hydrothermal vein. The latter formed residual concentration and by supergene oxidation-enrichment of preexisting rhodochrosite minerals near or at the surface. Replacement texture formed by alternation of sulfide and manganese carbonate minerals around ore pipes have sometimes been missed while reading sedimentary texture.

Superficial manganese oxides formed by supergene processes have given rise to the economically workable manganese deposits in the upper level of the pipes. Entirely localized above the water table, they consist of todorokite, nsutite, pyrolusite, cryptomelane, birnesite and janggunite (Kim 1979). Kim (1979) concluded that the manganese carbonates including rhodochrosite, were formed from manganese rich water in the stagnant environment of a restricted marine basin and manganese oxide ores were formed in the supergene enrichments based on ore texture, mineralogy and chemistry of the ores. He attached importance to the banded ore texture with alternating sulfide and rhodochrosite minerals to interpret the genesis and origin of ores. The writer's opinion, however, is that the banded textures were observed replacement textures, not sedimentary ones in the field and laboratory works (Fig. 2). Manganese carbonates are characterized by rhodochrosite [$(\text{Mg}_{0.045} \text{Ca}_{0.068} \text{Fe}_{0.049} \text{Mn}_{0.838}) \text{CO}_3$], showing pale pinkish color (Fig. 3). In general, the ratios of CaCO_3 vs MnCO_3 in solid solution of rhodochrosite in this mine revealed 1 : 7 on the basis of CO_2 volume percent yielded by reaction of H_3PO_4 . Mn content of sulfide minerals which are coexisting with rhodochrosite are 0.05 in sphalerite and 0.02 in stannite in atomic weight percent by EPMA analyses (Lee, 1980). By wall rock alteration and chemical data, Lee (1980) suggested that rhodochrosite represents the final product of manganese enrichment from



carbonate in dolomite and calcite type structures by hydrothermal replacement. In ore genesis of manganese oxide ores, it is clear that all geologist's idea is convergent to supergene enrichment and oxidation of the preexisting manganese carbonate ores. Manganese oxide minerals were formed in the above paragenetic sequence (Kim, 1979).

This study was begun in an effort to interpret the origin of primarily manganese carbonate minerals, such as rhodochrosite, in the light of carbon and oxygen isotope compositions. Manganese oxide minerals are made up of low temperature higher oxide minerals e.g., todorokite, nsutite, and pyrolusite such as those at Moanda Gabon Africa, Butte, Montana USA, Piedras Negras Mexico and Toyoguchi mine Iwate prefecture, Japan.

STABLE ISOTOPE STUDY

Powdered samples of carbonate minerals were reacted at 25°C with 100% H₃PO₄ (McCrea, 1950) during 5 days for rhodochrosite, 3 days for dolomite, 1 hour for limestone and vein calcite. The fractionation data are referenced in



Fig. 2 Banded replacement texture of sulfide and carbonate minerals.

the following: CO₂-calcite and CO₂-H₂O, Bottinga (1969) and Bottinga and Craig (1969), sulfide-sulfide, Kajiwara and Krouse (1971) and Ohmoto and Rye (1979). Rhodochrosite-water fractionation was approximated using the calcite-water data (O'Neil et al., 1969). All isotope values are reported as parts per mil deviation, (‰) = $\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000$ where R is ¹³C/¹²C or ¹⁸O/¹⁶O and ³⁴S/³²S from the standards: SMOW for oxygen (Craig 1957, 1961), PDB (Pee Dee Belemnite) for carbon (Craig 1953, 1957) and Canon Diablo troilite for sulfur (Thode et al., 1961). Ranges of isotopic composition of ores derived from deep seated origin in the world are compared with those of the Janggung. Carbon and oxygen isotopic composition of the hydrothermal fluids responsible for the formation of the Janggung manganese ores were estimated from calculations based on analyses of isotopic composition of minerals presumed to have been in equilibrium with the hydrothermal fluids.

Manganese carbonates

The carbon and oxygen isotopic compositions were determined for 14 limestone, dolomitic limestone and dolomite, 10 vein calcite and 20 rhodochrosite samples (Table 1 and 2). Isotopic values for sulfide and rhodochrosite ore bearing limestone and dolomites range from -2.6 to +0.1‰ in δ¹³C and +10.9 to +21.9‰ in δ¹⁸O with a mean value of -1.6‰ in δ¹³C and +17.8‰ in δ¹⁸O. There are no isotopic differences in samples collected near the contact, inbetween or far from the orebody. Rhodochrosite (MnCO₃) of the south A orebody have isotopic composition of -4.2 to -6.3‰ in δ¹³C and of +2.9 to +12.7‰ in δ¹⁸O with an average value of -5.8‰ in δ¹³C and +10.6‰ in δ¹⁸O. Average

Table 1 Carbon and oxygen isotopic compositions of carbonate rocks from the Janggum mine.

Sample	Location (See Fig. 1)	Description	Minerals	$\delta^{13}\text{C}$ (PDB) ‰	$\delta^{18}\text{O}$ (SMOW) ‰
K31	No.0(591m)L. 50m portal	grey limestone	LS	-1.0	+21.0
K32	ditto	ditto	LS	+0.1	+10.7
K33	No.0 L. 80m portal	grey limestone	LS	-0.7	+16.4
K37	No.0 L. near orebody	grey limestone	LS	-1.6	+18.1
K38	No.1 L. (533m)	grey limestone	LS	-1.0	+13.3
K41	No.1 L.	light grey crystalline limestone	LS	-2.6	+13.2
K42	ditto	grey crystalline limestone	LS	-1.9	+19.8
K43	No.0 L. near orebody	grey limestone	LS	-0.8	+18.8
K44	ditto	ditto	LS	-2.0	+14.4
K46	No.1 L.	dolomitic limestone	do LS	-1.7	+20.4
K48	No.1 L.	dolomite	do	-2.4	+19.9
K49	No.1 L.	grey crystalline limestone	LS	-2.6	+21.5
K50	ditto	ditto	LS	-2.2	+20.0
K51	ditto	dolomite	do	-2.0	+21.9
average				-1.6	+17.8
K34	No.0 L. near orebody	calcite vein in vug	C	-5.0	+14.5
K36	No.0 L. in orebody	calcite associated with rhodochrosite	C	-4.4	+13.3
K39	ditto	calcite vein	C	-4.2	+12.8
K40	ditto	calcite associated with sulfide ores	C	-6.3	+20.4
K52	ditto	calcite associated with sulfide ores	C	-5.4	+20.2
K53	No.1 L.	calcite vein in sulfide ores	C	-5.9	+22.9
K54	No.1 L.	ditto	C	-5.7	+16.8
K55	No.1 L.	calcite associated with rhodochrosite	C	-4.0	+17.6
K45	North orebody	calcite vein in sulfide ores	C	-2.3	+ 8.2
K47	ditto	ditto	C	-0.3	+10.1
average				-4.4	+14.7

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the vein calcite are -4.4‰ and $+14.7\text{‰}$ respectively. Considering the isotopic data with mean values of -1.1‰ in $\delta^{13}\text{C}$ and $+16.0\text{‰}$ in $\delta^{18}\text{O}$, of Cambro-Ordovician limestone in the Taebaegsan basin presented by Kim (1980), the Janggum limestone formation may be correlated with the Paleozoic limestone formation in the Taebaegsan basin. All Paleozoic carbonate rock samples from Taebaegsan basin fall into normal marine limestone range according to Keith and Weber (1964). Carbonate rocks in South Korea show distinctive isotopic ranges to their depositional environments, marine and nonmarine (Fig. 3). Average isotopic depletions between host carbonate rocks and rhodo-

chrosite ore minerals show 4.27‰ in $\delta^{13}\text{C}$ and 7.1‰ in $\delta^{18}\text{O}$, due to decarbonation processes during mineralization, and different sources of carbon and oxygen (Fig. 4). Rhodochrosite ores coexisting and/or associated sulfides in dolomitic limestone, which show stratiforms or veins, have a nearly identical isotope values. Specifically, rhodochrosite of well stratified manganese carbonate rock samples regarded as rhodochrosite, have -4.2‰ in $\delta^{13}\text{C}$ and $+10.55\text{‰}$ in $\delta^{18}\text{O}$. CO_2 gases of CaCO_3 and MnCO_3 of solid solution of rhodochrosite $(\text{Mn, Ca})\text{CO}_3$ were obtained by different reaction time: $\text{CO}_{2\text{CaCO}_3}$ for 1 or 2 hours and $\text{CO}_{2\text{MnCO}_3}$ for 5 days. Volume percent of $\text{CO}_{2\text{MnCO}_3}/\text{CO}_{2\text{CaCO}_3}$ of rhodochrosite revealed

Table 2 Carbon and oxygen isotopic composition of rhodochrosite from the South A orebody of the Janggun mine.

Sample	Location	Description	Rhodochrosite(Mn,Ca)CO ₃				Content of CaCO ₃ to MnCO ₃
			CaCO ₃		MnCO ₃		
			δ ¹³ C‰	δ ¹⁸ O‰	¹³ C‰	¹⁸ O‰	
12	No.0 L. near orebody	pinkish rhodochrosite	-4.7	+13.2	-5.0	-12.6	
13	ditto		—	—	-4.5	+12.5	
14	No.0 L. stope	crystalline rhodochrosite	-5.2	+12.7	-5.6	+11.2	
15	No.0 L. stope	pinkish rhodochrosite	—	—	-5.4	+10.8	1 : 7
16	ditto	ditto	—	—	-6.1	+11.9	1 : 7
17	ditto	rhodochrosite coexisted with limestone	-4.3	+12.2	-5.3	+10.2	1 : 1
18	ditto	pinkish rhodochrosite	—	—	-6.1	+12.0	1 : 11
19	No.1 L. stope	rhodochrosite contacted with limestone	—	—	-4.2	+ 9.6	1 : 11
20	ditto	rhodochrosite coexisted with sulfide ores	-5.3	+10.2	-6.1	+ 9.1	—
21	ditto	ditto	-5.4	+14.6	-5.4	+ 8.7	1 : 1
24	No.1 L. near orebody	pinkish rhodochrosite	—	—	-5.0	+12.7	1 : 6
25	ditto	ditto	—	—	-5.1	+12.1	1 : 5
26	ditto	ditto	-6.0	+11.1	-5.9	+ 7.9	1 : 5
27	No.2 L. stope	pinkish rhodochrosite	-6.0	+14.3	-5.8	+ 8.2	1 : 6
28	No.1 L. near orebody	ditto	—	—	-6.3	+ 8.8	1 : 8
29	No.0 L. stope	rhodochrosite coexisted with sulfide ores	-6.4	+18.2	-6.0	+12.6	1 : 2
30	ditto	rhodochrosite coexisted with calcite	-4.6	+12.8	-4.6	+12.2	1 : 7
31	ditto		—	—	-5.4	+ 9.8	1 : 9
average					-5.8	+10.6	
SK-1	rhodochrosite	of well stratified ore			-4.14	+10.5	
H30	surface stope	black manganese oxide ore	-7.7	+22.7	- 8.6	+20.6	
H31	ditto	ditto	-7.9	+22.8	- 8.4	+20.5	
311	Yeonwha I Mine	pinkish rhodochrosite	—	—	- 5.0	+10.2	1 : 12

about 1 : 7 which is a reasonably good agreement of the data of EPMA analysis of the mineral grains of rhodochrosite. δ¹³C values of CO_{2CaCO₃} and CO_{2MnCO₃} are nearly identical or slightly light in CO_{2CaCO₃}. In δ¹⁸O, however, CO_{2MnCO₃} concentrated more heavy isotopes than CO_{2CaCO₃}, implying CO_{2MnCO₃} in unequilibrium with CO_{2CaCO₃} isotopically.

Sulfur isotopes

Twenty four samples of sulfide minerals, including sphalerite, galena, pyrite and arsenopyrite were analyzed, of which four sphalerite-galena mineral pairs can avail the isotope temperature.

Most samples of sulfide minerals are intergrown with rhodochrosite and calcite. As shown in Table 3, δ³⁴S value of the sulfides ranges from -0.3 to +5.2‰ which fall into the sulfur isotopic range, +2 to +5‰ of 186 sulfide minerals, South Korea which were interpreted as deep seated origins (Kim and Nakai 1980).

Using isotopic fractionation of Kajiwarra and Krouse (1969) and Ohmoto and Rye (1979), isotopic temperature appeared to be 288~343°C for the South A orebody. This temperature is slightly higher than fluid inclusion homogenization temperature of quartz, 200 to 350°C (Lee

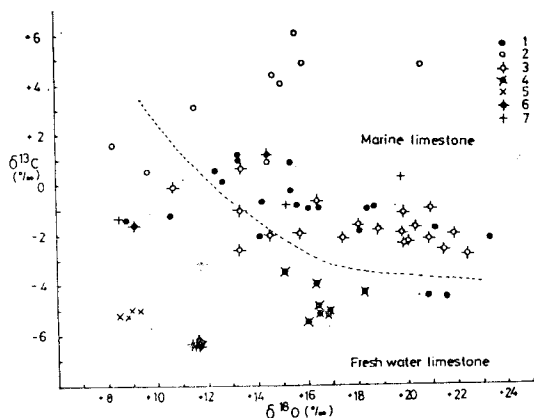


Fig. 3 Distribution of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for carbonate rocks from different depositional environment and geologic age in South Korea (Kim, 1985).

1. Great Limestone Series in Yongweol district (Paleozoic, marine)
2. Okchon geosynclinal zone (Precambrian marine)
3. Janggun limestone (Paleozoic, marine)
4. Hongjom Series in Jeungun district (Paleozoic, marine with fresh water inflow)
5. Yonchon system (Precambrian)
6. Kyongsang basin (Mesozoic, nonmarine)
7. Jeungun limestone (Paleozoic, marine)

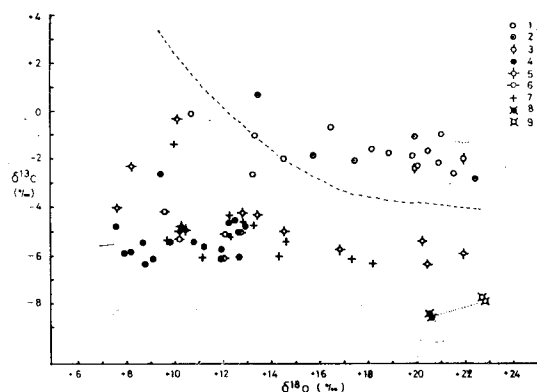


Fig. 4 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of rhodochrosite, calcite, manganese oxide minerals and host carbonate rocks in the Janggun mine.

1. limestone
2. limestone (Kim, 1980)
3. dolomite
4. rhodochrosite (MnCO_3)
5. vein calcite
6. stratified manganese carbonate rocks
7. rhodochrosite (CaCO_3)
8. manganese oxides (MnCO_3)
9. manganese oxides (CaCO_3)

1980). Mineral paragenesis indicate early sulfide and a later carbonate sequence. In general, judging from the mineral paragenesis, formation temperature of the carbonate may be lower than those of sulfide mineralization. In this regard, temperature of the carbonate formation is assumed to be about 200~300°C and slightly lower.

DISCUSSION

Generally, manganese deposits classified genetically into the following types viz, hydrothermal (hypogene) syngenetic sedimentary (volcanogenic and nonvolcanogenic, including deep sea manganese nodules) and superficial (residual and supergene). In attempts to determine the genetic types of the manganese deposits, mineralogical, chemical, tectonic and experimental aspects are considered by Roy (1968), Huebner (1969), Park (1956), Hewett (1966), Varentsov (1964), Borchet (1970), Watanabe et al. (1970), Hewtt and Fleishen (1960), Hariya (1961), Sivaprakash (1980), Lahri (1971), Fron del and Baum (1974), and Wright and Mc-Curry (1970). Rhodochrosite minerals are common in both hypogene and sedimentary manganese mineral deposits. Janggun manganese deposits are not beyond these sophisticated genetic problems. Recently $\delta^{13}\text{C}$ values of deep seated CO_2 in magmatic systems are considered to range from -5.0 to -7.0 per mil based on the $\delta^{13}\text{C}$ data for hydrothermal gangue assemblages, carbonatite, CO_2 of geothermal areas and fluid inclusion CO_2 (Rye, 1966; Taylor et al., 1967; Deine, 1968; Osaki, 1973; Landis and Rye, 1974; Bethke and Rye, 1979; Casadevall and Ohmoto, 1977; and Ohmoto, 1979). Isotopic data of rhodochrosite, however, are rare because the carbon isotopic data do not indicate a unique source for carbon. And the $\delta^{13}\text{C}$ values of CO_2 may vary in hydrothermal systems due to changes in P, T, f_{O_2} and pH of the ore fluids. Some isotopic data of rhodochrosite in association with base metal ore

Table 3 $\delta^{34}\text{S}$ values and descriptions of samples of the South A orebody from the Janggung mine.

sample	Location	Description	Minerals	$\delta^{34}\text{S}$ CDT (‰)	Isotope Temperature
1	No. 0 L.	massive sulfide ore	sp	+3.1	343° C
2	No. 0 L.	sulfide ore coexisted with manganese carbonates	gn	+3.3	
3	No. 0 L.	ditto	sp	+3.8	
4	No. 1 L.	massive ore	gn	+2.8	
5	No. 0 L.	ditto	sp	+3.4	
6	No. 0 L.	mineral pairs of sphalerite and galena	sp	+4.5	
7	ditto	ditto	gn	+2.6	
8	North orebody	ditto	sp	+4.1	
9	ditto	ditto	gn	+2.2	
11	North orebody	sulfide ore veins	sp	+1.9	
12	No. 0 L.	massive ores	sp	+4.2	
13	ditto	ditto	gn	+1.9	
14	No. 1 L.	ore	sp	+4.5	
15	ditto	banded ore	gn	+4.0	314° C
16		banded ore	sp	+4.5	
17	No. 1 L.	ore veins	gn	+2.9	
18	No. 1 L.	ore veins	sp	+4.6	
19	ditto	ditto	gn	+2.5	
72	No. 0 L.	cubic pyrite in vug	py	+3.7	314° C
81	ditto	pyrite coexisted with rhodochrosite and calcite	py	+3.2	
82	ditto	ditto	py	+3.8	
87	North orebody	sulfide ore vein	Arspy	+5.2	314° C
88	No. 2 L.	massive ores	py	-0.3	
	No. 1 L.	arsenopyrite coexisted with rhodochrosite	Arspy	+4.5	

sp; sphalerite, gn; galena, py; pyrite, Arspy; arsenopyrite

* Coexisting mineral pairs are indicated by brackets.

deposits were available to interpret the source of carbonate ore fluids. In this work, the origin of rhodochrosites was considered in the light of carbon and oxygen isotope compositions. In addition, the $\delta^{34}\text{S}$ were also analyzed for the sulfide minerals in association with manganese carbonates. Average $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of rhodochrosites in Janggung mine are -5.8‰ and $+10.6\text{‰}$ respectively. On the other hand, rhodochrosite ore bearing limestone and dolomitic limestone have average values of -1.6‰ in $\delta^{13}\text{C}$, and $+17.8\text{‰}$ in $\delta^{18}\text{O}$. These isotope values of rhodochrosites of the Janggung mine were compared with those of rhodochrosites originating as deep seated such as Sunnyside mine, Colorado, Creede mining district, Colorado, Pasto Buena, Peru, and Oe, Inakuraishi and Jokoku mine,

Japan (Fig. 5). The $\delta^{13}\text{C}$ value of CO_2 in the manganese carbonate fluids ranges from -4.0 to -5.1 per mil when calculated from rhodochrosite of the Janggung mine, the carbon isotopic fractionation factors between CaCO_3 and CO_2 (Bottinga, 1968) and assumed temperature of about 250°C by fluid inclusion data. The $\delta^{13}\text{C}$ values are within the isotopic range of deep seated origin interpreted in some base metal deposits and some geothermal area (Fig. 6). The carbon isotope data of vein calcites ($\delta^{13}\text{C} = -4.4\text{‰}$ in average) are consistent with the above conclusion. The initial $\delta^{18}\text{O}$ value of the H_2O calculated on the basis of formation temperature, isotopic composition of rhodochrosite and fractionation factors by O'Neil et al., (1969) is $+2.03$ to $+6.0\text{‰}$ which suggests that the carbonate ore

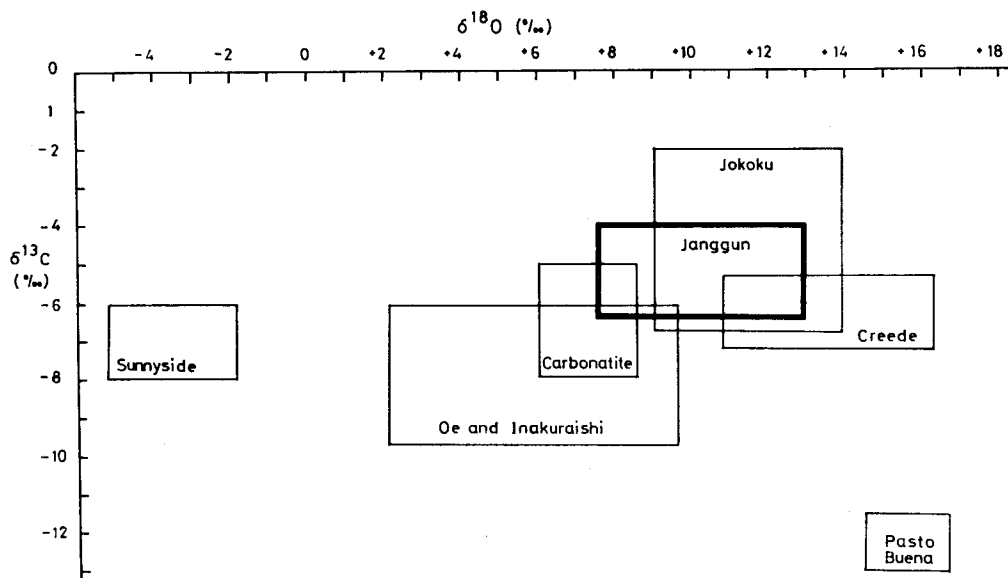


Fig. 5 Carbon and oxygen isotopic compositions of some rhodochrosite minerals. Isotope data from Sunnyside mine (Casadevall and Ohomoto, 1977). Oe, Inakuraishi and Jokoku mine (Osaki, 1973), Creede mining district (Betheke and Rye, 1979) Pasto Buena (Landis and Rye, 1974) and Carbonatite (Taylor et al., 1967)

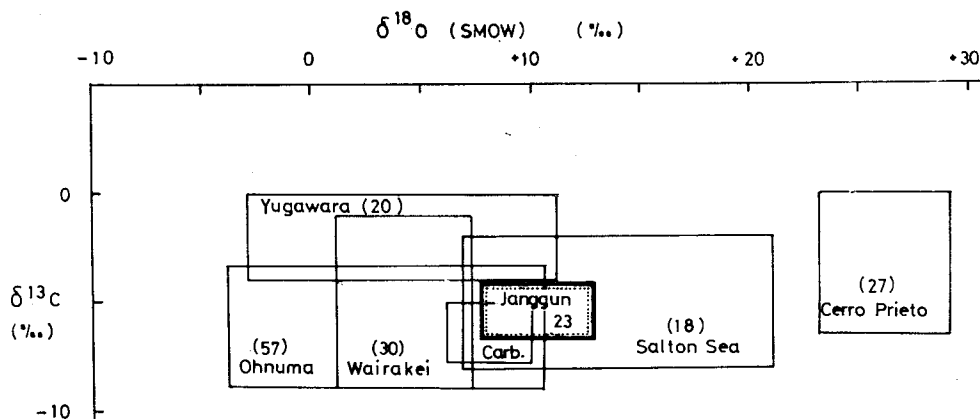


Fig. 6 Carbon and oxygen isotopic compositions of some hydrothermal carbonate from geothermal areas. Isotope data from Yugawara (Watanabe et al., 1977), Ohnuma (Yamamoto, 1981), Cerro Prieto (Olson, 1979), Salton Sea (Clayton et al., 1968), Wairakei (Clayton and Steiner, 1975) and Carbonatite (Taylor et al., 1967).

fluid originated from deep seated or mixture of deep seated one and local meteoric water. Present meteoric water of the Janggung mine are -8.9% in $\delta^{18}\text{O}$ and -64.65% in δD (Kim and Nakai, 1981). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of rhodochrosite differ considerably from host limestone and dolomitic limestone even in the very contact of

the orebody, perhaps imply substantially different source of carbon and oxygen. Salinity of the liquid was estimated at 0.9 to 5.0 NaCl wt. % (Imai and Lee, 1980). Carbonate ore fluids estimated at -4.0 to -5.0% in $\delta^{13}\text{C}$ and $+2\sim+6.0\%$ in $\delta^{18}\text{O}$ fall into the same ranges of isotopic composition ($\delta^{13}\text{C} = -5.1$ to -4.0% ,

$\delta^{18}\text{O} = +4.2$ to $+9.47\%$) in the Creede mining district, Colorado.

As shown in Fig. 6, isotope compositions of carbonate fluids, hydrothermal carbonates and gases of geothermal area including Yugawara, Ohnuma, Japan, Wairakei, New Zealand, Salton Sea, and Cerro Prieto converge into carbonatite area. Specifically, the isotope values of the manganese carbonate of Janggung mine are plotted on the center of these ranges.

Manganese oxide ores have isotopic composition of -8.6 to -8.4% in $\delta^{13}\text{C}$ and $+20.6$ to $+20.5\%$ in $\delta^{18}\text{O}$. These low values in $\delta^{13}\text{C}$ were subjected to isotopic fractionation occurring during oxidation between meteoric water and/or atmospheric CO_2 gas and manganese carbonate (rhodochrosite). Heavy $\delta^{18}\text{O}$ values also were resulted from oxygen shift from the limestone and dolomitic limestone. In this regard, carbon of meteoric water and oxygen of limestone strongly contribute to formation of manganese oxide minerals on the water table in the deposits. Narrow range of $\delta^{34}\text{S}$ value, -0.3 to $+5.2\%$, also strongly suggest the deep seated origin of ore fluids. Therefore, the Janggung manganese carbonate ore fluids presumably originated from deep seated, and were magmatic in origin which might be closely related to Jurassic Chunyang granite.

Ohmoto (1972) demonstrated that the mode of variation $\delta^{13}\text{C}$ values and $\delta^{34}\text{S}$ values coexisting sulfide and carbonate minerals in a given deposits indicate the relative oxidation state of the ore fluid. In the South A orebody of the Janggung mine, uniform values in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ are shown suggesting a depositional condition of ore fluid of intermediate $f\text{O}_2$, approximately -35 to -38 of log $f\text{O}_2$.

In addition to isotopic evidence, geological evidence to support the hypogene origin is as follows:

1) As shown in the profile of the orebodies,

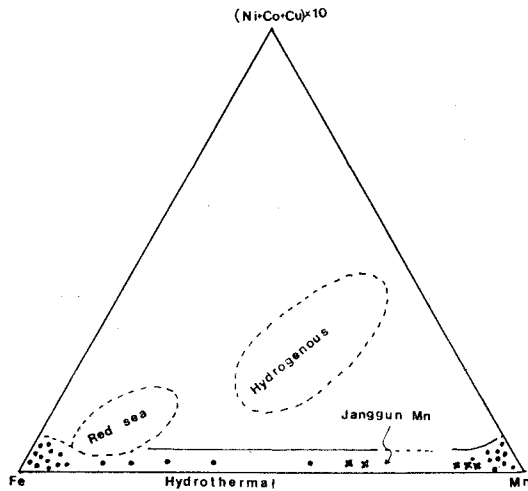


Fig. 7 Ratio Fe—Mn—(Cu + Ni + Co) in metaliferous sediments from the ocean floor (Banatti et al., 1976).

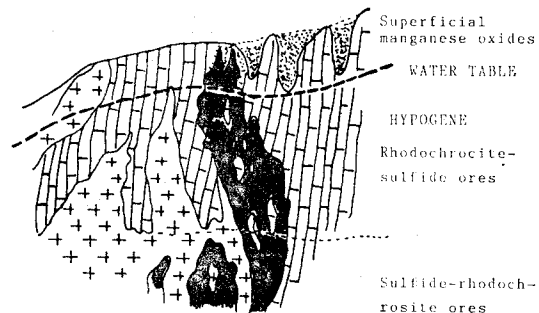


Fig. 8 Schematic model of ore pipes of the Janggung mine.

there is no continuity of orebed in the same horizon of the carbonate rock beds. Mineralization and alteration are limited only around the ore pipes and veins.

2) Iron-manganese association and braunite minerals characterized by exhalative sedimentary types do not appear in this mine.

3) Chemical composition of manganese ore are plotted on the hydrothermal field in Fe—Mn—(Cu+Ni+Co) diagram (Fig. 7).

4) Crystalline rhodochrosite dominantly occurred through the orebodies except near surface manganese oxide orebodies. Mineral zoning of the South A orebody appeared sulfides-rhodoch-

rosite, rhodochrosite-sulfides and manganese oxides in ascending order due to ascending hydrothermal solution (Fig. 8). This mineral zoning is coincidence with those of Wolam orebody of Yonwha I Mine (Yun, 1979), and of the Chichibu mine, Japan (Miyazawa, 1977).

CONCLUSIONS

1. The manganese carbonate ores, mostly represented by rhodochrosite ores, of the Janggun mine are hypogene hydrothermal in origin in the light of occurrence, mineralogy, carbon, oxygen and sulfur isotope compositions.

2. The initial $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of manganese carbonate fluids and $\delta^{34}\text{S}$ values of sulfides in association with the manganese carbonate ores indicate the deep seated origin of carbon and sulfur.

3. Depositional conditions of the ore fluid are estimated as intermediate, approximately -35 to -38 of $\log f\text{O}_2$, based on variations of $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ values of coexisting sulfide and carbonate minerals.

4. Manganese oxide ores superficially formed by ascending hydrothermal ore fluids mingling with meteoric water, and by supergene oxidation enrichment of preexisting hypogene manganese carbonates at or near surface, mainly above the water table. On the basis of isotopic data of rhodochrosite, manganese oxides and local meteoric water it leads me to conclude that oxygen of the limestone host rock rather than those of meteoric water highly affect manganese oxide minerals.

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將軍鑛山產 망간광물의 成因에 關한 研究

金奎漢*

要約: 將軍鉛·亞鉛·망간鑛床은 캄브로-오도비스紀의 將軍石灰岩과 春陽花崗岩과의 接觸부에 發達하는 接觸交代鑛床이다. 鑛體는 脈狀 및 광洞형 광체로 상부에는 酸化망간 및 炭酸망간석을 주로 하는 망간광물이 우세하고 하부에는 閃亞鉛石-方鉛石-黃鐵石-유비철석(탄산망간석) 등의 黃化鑛物이 우세하게 발달하고 있다. 그중 망간광상의 성인에 대하여 熱水交代와 同時堆積起源으로 그 해석을 달리하고 있으며 炭酸망간석(rhodochrosite)이 동시 퇴적기원이란 근거에서 장미암(rhodochrostone)으로 명명된 堆積岩이 제안되었다(김, 1975). 본 연구에서는 탄산망간석의 기원을 규명하고 이들 鑛物의 침전환경을 추정하기 위하여 모암인 탄산염암류와 탄산망간석, 산화망간, 방해석 등의 炭素安定同位元素($\delta^{13}\text{C}$)와 酸素동위원소($\delta^{18}\text{O}$)를 분석하고 이에 수반되는 黃化鑛物의 黃同位元素($\delta^{34}\text{S}$)를 분석검토하였다. 모암인 석회암 및 돌로마이트질석회암은 $\delta^{13}\text{C} = -2.6 \sim +0.1\%$ (평균 -1.5%), $\delta^{18}\text{O} = +10.9 \sim +21.9\%$ (평균 $+17.5\%$)이고 탄산망간석은 $\delta^{13}\text{C} = -4.2 \sim -6.3\%$ (평균 -5.3%), $\delta^{18}\text{O} = +7.6 \sim +12.9\%$ (평균 $+10.3\%$)이다.

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10.7%)로 이들 사이에는 현저한 동위원소값의 차이를 나타내고 있다. 이는 鑛化溶液의 炭素 및 酸素가 母岩인 炭酸鹽岩의 것과는 同一起源이 아님을 가르킨다. 黃同位元素($\delta^{34}\text{S}$)의 값도 +2.0~+5%로 좁은 범위를 나타내며 火成起源의 黃으로 해석된다. 黃同位元素地質溫度計에 의해 추정된 鑛床生成溫度는 288~343°C이다. 炭酸망간석을 鑛床生成 鑛化溶液의 $\delta^{18}\text{O}_{\text{H}_2\text{O}} = +6.6 \sim +10.6\%$, $\delta^{13}\text{C}_{\text{CO}_2} = -4.0 \sim -5.1\%$ 로 深部起源(火成起源)으로 해석된다. 따라서 炭酸망간석은 마그마성 열수기원에서 鑛床生成된 것이다. 그러나 망간산화물은 모두 地下水面 상부에서 炭酸망간석의 酸化에 의해 二次的으로 형성된 表成酸化망간이며 산화망간광물의 산소는 순환수의 산소보다 石灰岩의 산소와 同位元素交換이 우세하게 일어난 것으로 해석된다.



Fig. 9. Banded replacement texture of sulfide and silicate minerals.