

Mechanisms of Formation of Manganese Oxide Minerals in the Manganese Deposits of the Taebaeg Mt. Region, Korea

太白山地區 망간鑛床에 있어서 酸化망간鑛物의 生成機構

Soo Jin Kim (金洙鎭) · Hyen Goo Cho(曹鉉丘) · Hun soo Choi(崔憲洙)

Department of Geological Sciences, Seoul National University, Seoul 151-742, Korea
(서울대학교 지질과학과)

ABSTRACT: The manganese oxide ores in the Taebaeg Mt. region have been formed by supergene weathering of the primary hydrothermal or sedimentary manganese ores. The supergenesis is controlled by the physical chemistry of the descending groundwater in the supergene zone. It includes the fundamental geological processes, such as dissolution, oxidation, transportation, precipitation, and crystallization and recrystallization. However, the fundamental mechanisms for the formation of various manganese oxide minerals are 1) replacement, 2) precipitation from solution, and 3) solid state crystallization and recrystallization. Various textures and structures of ores have been formed by these processes. Detailed paragenetic sequence of manganese oxide minerals in each ore deposit is summarized.

요약: 太白山地區의 主要 망간鑛床에서 產出하는 酸化망간 鑛物들은 一次的으로 生成된 炭酸 망간 또는 珪酸망간의 表成風化作用에 依하여 生成되었다. 이들 酸化망간 鑛石의 生成에 關여된 地質作用에는 溶解作用, 酸化作用, 運搬作用, 沈澱作用, 晶出作用 및 再結晶作用 등이 있다. 그러나 簡便의 酸化망간 鑛物 生成은 交代作用, 溶液으로부터의 晶出作用 및 固體狀態에서의 晶出 및 再結晶作用 등에 依하여 이루어졌다. 이들 鑛物生成作用에 依하여 多樣的인 名種 鑛石의 組職이 形成되었으며, 母鑛石의 鑛物組成과 風化環境에 따라 特徵的인 鑛物 및 鑛物共生關係가 形成되었다. 그러나 一般的으로 風化殘留鑛床 中の 酸化망간 鑛物들은 $Mn^{2+} \rightarrow Mn^{3+} \rightarrow Mn^{4+}$ 의 方向으로 生成되었다.

INTRODUCTION

Various manganese oxide mineral species are found in the manganese oxide deposits of the Taebaeg Mt. region. They were derived from the various kinds of protore and manganese rocks in the supergene environment. They also show various ore textures that reflect their process of formation.

The detailed textural analysis of the manganese oxide ores from different ore deposits shows that different paragenetic sequences of minerals exist with different ore deposits. This paper is the summary of the mineral-forming processes and paragenesis of manganese oxide minerals in the manganese oxide ores of

Taebaeg Mt. Region.

EXPERIMENTAL

The manganese oxide ores collected in the field were cut with diamond saw and impregnated with araldite and polished on one surface. The polished sections were studied under the ore microscope, in order to identify the constituent mineral species of ores. But exact identification of manganese oxide minerals was possible only by X-ray diffraction analysis using Debye-Scherrer camera. After the X-ray identification, polished sections were restudied for detailed textural analysis. Understanding of the mechanisms of forma-

tion of manganese oxide minerals was possible by the detailed textural analysis.

RESULTS

Mechanisms of Formation

The geological processes in the supergene weathering zone include dissolution, oxidation, transportation, precipitation, and crystallization and recrystallization. However, the fundamental mechanism for the formation of various manganese oxide minerals are replacement, precipitation from solution and solid state crystallization and recrystallization (Kim, 1984).

(A) Replacement

The minerals of protores or early-formed minerals react with the surrounding groundwater percolating down through or stagnant in the ores, to be stable in the given physicochemical environment. By this reaction various minerals are newly formed at the expense of earlier ones. Replacement textures are formed as results of such processes. Therefore, replacement textures are common in the manganese oxide ores which have been formed in the supergene weathering environment. Modes of formation of manganese oxide minerals resulted from replacement are summarized in the following.

- a) Minerals formed by replacement of manganiferous carbonates: eg. vernadite, manganite, nsutite, todorokite
- b) Minerals formed by replacement of manganese silicates: eg. birnessite
- c) Minerals formed by replacement of earlier oxides: eg. manganite, birnessite, nsutite
- d) Minerals formed by replacement of non-manganiferous minerals: eg. pyrolusite, nsutite

Various physicochemical processes resulting in the replacement textures have been found from this study. They are summarized in the following.

- a) Hydroxidation with anion exchange:

- eg. rhodochrosite-vernadite
- b) Oxidation with cation exchange: eg. vernadite-birnessite
- c) Oxidation with dehydration: eg. manganite-nsutite
- d) Oxidation with cation exchange and dehydration: eg. pyrolusite-nsutite
- e) Reduction with hydration: eg. pyrolusite-nsutite
- f) Reduction with cation exchange: eg. birnessite-todorokite
- g) Complete exchange: eg. calcite-todorokite

B) Precipitation from solution

Manganese oxide minerals formed by precipitation from solution occur in the forms of cavity-filling or lining. There are two modes of minerals which have been formed by precipitation from solution. They are:

- a) Crystallization from non-colloidal solution and
- b) Colloidal deposition.

Various types of precipitation textures are formed with crystallization or precipitation from solution in cavities of manganese oxide ores. They include dendritic or arborescent (eg. nsutite, cryptomelane), fibrous (eg. todorokite), granular (eg. pyrolusite, nsutite), comb or geode (eg. pyrolusite, janggunit), globular (eg. todorokite), cryptocrystalline massive (eg. todorokite) and colloform (eg. birnessite). The crystallinity of minerals are highly crystalline, microcrystalline, cryptocrystalline or amorphous. Granular massive texture is frequently found in the manganese oxide ores which were formed by precipitation from non-colloidal solution. Cryptocrystalline massive texture is frequently found in todorokite which was formed by colloidal precipitation.

Colloform textures have been considered by many works to be formed by colloidal precipitation. But many features of some colloform bands suggest the direct crystallization from non-colloidal solution. Under high magnification, the individual bands in colloform bands are seen to consist of many fi-

brous or columnar crystals which are developed perpendicular to the banding, and their smooth surfaces or boundaries between bands are seen to be rugged, showing fibrous or columnar crystals. In this case, smooth surfaces of colloform bands are an indication of a large number of nuclei and spatially uniform growth of crystals and not a definite indication of colloform precipitation. Some of the surface textures of colloform bands are quite similar to the coarse-grained radiating crystal aggregates, if the scale is disregarded (Kim, 1979).

On the other hand, Some of colloform bands which consist of nearly amorphous manganese oxides probably have been formed by colloidal precipitation. A rather smooth surface as seen under high magnification probably indicates a colloidal origin. It is believed that there is a gradation boundary between colloidal and non-colloidal phases in the formation of manganese oxide ores.

C) Solid State Crystallization and Recrystallization

Almost all colloform ores which have been formed originally as gels become more or less crystalline with aging. Solid state crystallization of amorphous gel ores and their recrystallization is very important for the formation of fabrics of manganese oxide ores. Crystalline character of colloform or massive types of ores of colloidal origin results from crystallization in solid state. Such "Umkrystallization" is frequently found in todorokite and cryptomelane. Some porphyroblastic fabric in the massive todorokite ores results from recrystallization of microcrystalline or cryptocrystalline todorokite. Nsutite is partly recrystallized to coarser grains along the cracks or in the colloform bands.

Paragenetic Sequence

The textural relations of manganese oxide ores from each manganese deposit of the Taebaeg Mt. region show that the manganese oxide minerals of each deposit were formed in a certain characteristic Paragenetic Sequence.

A pair of minerals in the paragenetic sequence suggests one of processes including oxidation, reduction and simple sequence. The paragenetic sequence of manganese oxide minerals in each manganese deposit of Taebaeg Mt. region are summarized in Table 1.

The sequence from rhodochrosite to poorly-crystallized todorokite or nsutite in the Janggun mine indicates the oxidation from Mn^{2+} to Mn^{4+} , and that from rhodochrosite through manganite to todorokite indicates the oxidation from Mn^{2+} through Mn^{3+} to Mn^{4+} . The direct oxidation of Mn^{2+} to Mn^{4+} without passing through Mn^{3+} stage is indicated by the frequent replacement of rhodochrosite by nsutite. This phenomenon may be explained in another way, that is, Mn^{2+} has been oxidized to Mn^{3+} , and then Mn^{3+} completely to Mn^{4+} . Direct oxidation of Mn^{2+} to Mn^{4+} also can be explained by the disproportionation reaction. The sequence from poorly-crystallized todorokite to ordinary todorokite represents disorder-order transformation of structure with concurrent dehydration.

The later formed minerals generally have higher oxidation coefficients than the earlier ones, but that is not always the case as indicated by the janggunite which is late in the sequence but has a low oxidation coefficient.

CONCLUSIONS

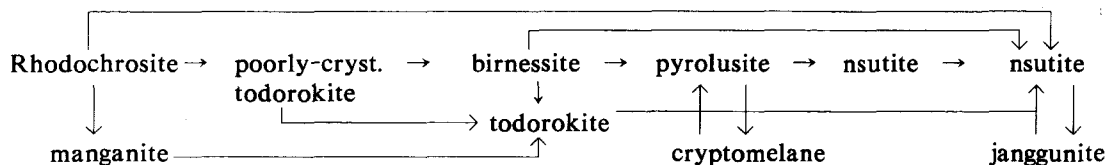
The manganese oxide ores in the Taebaeg Mt. region have been formed by mechanisms including replacement, precipitation from solution and solid state crystallization and recrystallization in the supergene weathering environment.

Replacement of earlier minerals by later ones is due to the processes including oxidation, reduction and hydroxidation with one of anion exchange, cation exchange, hydration, and dehydration. A complete exchange of one mineral by another is also one of replacement processes in manganese oxide ores.

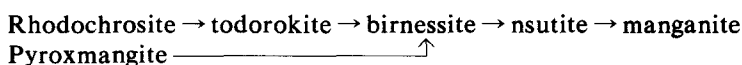
Precipitation from colloidal or non-colloidal solution has resulted in ore textures including dendritic or arborescent, fibrous,

Table 1. Paragenetic sequences of manganese oxide minerals in the manganese deposits of Taebaeg Mt. region.

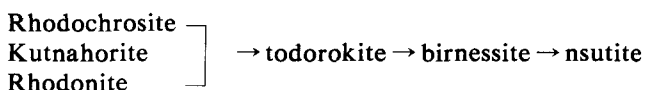
Janggun mine (Kim, 1979)



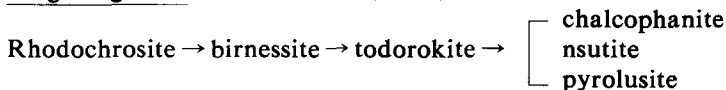
Buncheon mine (Kim and Son, 1984)



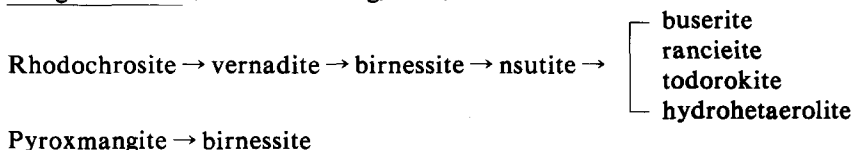
Yeonhwa mine (Choi, 1984)



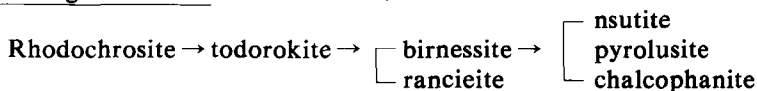
Jangseong mine (Kim and Yoon, 1986)



Dongnam mine (Kim and Chang, 1989)



Eosangcheon mine (Kim and Kim, 1982)



granular, combor geode, globular, massive or colloform. Large part of colloform textures has been formed by non-colloidal solution. Crystallization of amorphous gel ores and subsequent recrystallization are also an important process for the formation of fabrics of manganese oxide ores.

Paragenetic sequences of manganese oxide minerals for all the manganese deposits suggest the formation of minerals in the order, $Mn^{2+} \rightarrow Mn^{3+} \rightarrow Mn^{4+}$, although there are some exceptions to this rule. A pair of minerals in

the paragenetic sequence suggests one of several processes including oxidation, reduction or simple sequence.

Acknowledgments: This work was supported by the Korea Science and Engineering Foundation (project no. 86-0709-02).

REFERENCES

Choi, H. (1984) Mineralogy and genesis of manganese ores in the Yeonhwa 1 Mine,

- Korea. Master thesis, Seoul National University.
- Kim, S.J. (1979) The stratabound Manganese Carbonate Deposits of the Janggun Mine Area, Korea. Monograph series on Mineral Deposits, No. 18, Gebriider Borntraeger, pp.1-79.
- Kim, S.J. (1984) Syngenetic and epigenetic textures of manganese oxide ores in the supergene weathering zone. In: Wauschkuhn et al. (ed.) Syngensis and Epigenesis in the Formation of Mineral Deposits, 12-17, Springer Verlag.
- Kim, S.J. and Kim, S.H. (1982) Mineralogy and genesis of manganese ores in the Eosangcheon Mine, Korea. Jour. Korea Inst. Mining Geol., 15, 205-219.
- Kim, S.J. and Son, B.K. (1984) Mineralogy and genesis of manganese ores from the Buncheon Mine, Korea. Jour. Korea Inst. Mining Geol., 17, 273-282.
- Kim, S.J. and Yoon, H.O. (1986) Mineralogy and genesis of manganese ores in the Jangseong manganese deposits, Korea. Jour. Korea Inst. Mining Geol., 19, 265-276.
- Kim, S.J. and Chang, S. (1989) Mineralogy and genesis of manganese deposits in the Dongnam Mine, Korea. Jour. Min. Soc. Korea, 2, 73-80.