

Mineralogical Characterization of Buserite from the Janggun and Dongnam Mines, Korea

장군광산과 동남광산에서 산출되는 부서라이트의 광물학적 특성

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ABSTRACT : X-ray diffraction (XRD), Electron microprobe analyses (EPMA) and heating experiments were used for mineralogical characterization of natural buserites collected from the Janggun and Dongnam mines. They are closely associated with 7-Å phase (usually rancieite) in manganese oxide ores of the supergene oxidation zones of manganese carbonate deposits. Electron microprobe analyses give the average formula $(\text{Ca}_{0.78}\text{Mg}_{0.64}\text{Mn}^{2+}_{0.45})\text{Mn}^{4+}_{8.03}\text{O}_{18} \cdot 13.2\text{H}_2\text{O}$ and $(\text{Zn}_{0.81}\text{Ca}_{0.77}\text{Mg}_{0.26})\text{Mn}^{4+}_{8.00}\text{O}_{18} \cdot 10.9\text{H}_2\text{O}$ for buserite from the Janggun and the Dongnam mine, respectively. The basal reflection of buserite from the Janggun mine shifts continuously from 9.86 Å at 40°C to 7.60 Å at 90°C, but the buserite from the Dongnam mine shows tendency of decreasing intensity in the 9.67 Å peak and of increasing intensity in the 7.53 Å peak in the range of 40~90°C, showing no gradual shifting of peaks.

Key words : buserite, manganese oxide ore, Janggun mine, Dongnam mine, rancieite

요약 : 장군광산과 동남광산에서 산출되는 부서라이트에 대한 광물학적 특성을 연구하기 위하여 X-선 회절분석, 전자현미분석, 열분석 실험을 실시하였다. 장군 광산과 동남 광산에서의 부서라이트는 망간 탄산염광상의 표성 산화 작용에 의해 형성된 산화망간 광석 내에 란시아이트와 함께 산출된다. 전자현미분석결과 장군광산 부서라이트의 화학 조성은 $(\text{Ca}_{0.78}\text{Mg}_{0.64}\text{Mn}^{2+}_{0.45})\text{Mn}^{4+}_{8.03}\text{O}_{18} \cdot 13.2\text{H}_2\text{O}$ 이며 동남광산에서 산출되는 부서라이트는 $(\text{Zn}_{0.81}\text{Ca}_{0.77}\text{Mg}_{0.26})\text{Mn}^{4+}_{8.00}\text{O}_{18} \cdot 10.9\text{H}_2\text{O}$ 이다. 장군광산의 부서라이트의 저면 격자 간격은 40°C에서 9.86 Å이며, 90°C에서는 7.60 Å로 온도가 상승함에 따라 점진적으로 감소한다. 그러나 동남광산에서 40°C부터 90°C까지의 온도가 변화함에 따라 점진적인 회절선의 이동은 나타나지 않고 9.67 Å의 회절선의 강도는 감소하고 7.53 Å의 회절강도는 증가하는 경향을 보여준다.

주요어 : 부서라이트, 산화망간광석, 장군광산, 동남광산, 란시아이트

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INTRODUCTION

Mn-oxide minerals, as the major constituents of marine Mn deposits (Usui 1979; Mellin and Lei 1993; Glasby *et al.*, 1996; Usui and Glasby 1998), molecular sieves (Shen *et al.*, 1993, 1994, 1996; Wasserman *et al.*, 1995; Tian *et al.*, 1997) and catalysts (Wong and Cheng 1992; Cao and Suib 1994; Ching and Suib 1997; Ramamouthy *et al.*, 1999) are interested in recent investigates. The hydrothermal treatment of the busserite and its Co and Fe-doped products were carried out for 4 days in pure water in the temperature range from 120 to 200°C (Kumagai *et al.*, 2005). According to Manceau *et al.* (1997), synthetic busserite is a powerful oxidant and often has been used for studying surface redox reactions. Definitions and terminology for describing Mn-oxide minerals are still somewhat confusing. The X-ray diffraction (XRD) pattern of busserite was found to be equivalent to that of the synthetic 10 Å-phyllomanganate (Bilinski, *et al.*, 2002).

Busserite has not yet been accepted as a mineral by the Commission on New Minerals and Mineral Names (CNMMN) but the compound has been listed in The Mineral Name Index of the Powder Diffraction File (1997). The chemistry of natural 10 Å-phyllomanganates has not been defined correctly, because they have a fine grained habit and occurs as a mixture with other manganese oxides. Although some authors gave a formula for the natural busserite (Dubrawski and Ostwald, 1987; Choi and Kim, 1992), a general formula for 10 Å-phyllomanganates has not been defined. The ideal composition of busserite has been uncertain. Giovanoli and Arrhenius (1988) suggested that synthetic Na-busserite be formulated as $[\text{Mn}_5^{4+}(\text{Mn}^{2+}, \text{Mn}^{3+})\text{O}_{12}]^+ \cdot [\text{Na}_2(\text{OH})_3(\text{H}_2\text{O})_9]$. Although the occurrence of natural busserite has been widely reported, its chemistry has been scarcely reported. Dubrawski and Ostwald (1987) analyzed busserite from the Pacific Ocean nodules and gave the formula to $\text{Na}_3\text{MgMn}_{14}\text{O}_{32} \cdot 21\text{H}_2\text{O}$, and Ito *et al.* (1998) identified busserite in marine Mn nodules in the Pacific and Atlantic Oceans. The structural model of busserite was proposed by Arrhenius and

Tsai (1981) and Chukhrov *et al.* (1984). Water plays a very important role in the structure and chemistry of minerals, particularly with regard to the topological properties of their bond networks. Thus, the dimensionality of the structural unit in a mineral is primarily controlled by the amount and role of water in the structure (Hawthorne, 1992, Lanson *et al.*, 2000).

The Janggum mine has been developed for the manganese oxide ores since 1943, but has been exploited for the lead-zinc-silver deposit from 1975. Many authors have reported the geology of the Janggum mine area (Kim *et al.*, 1962; Lee *et al.*, 1990), genesis of manganese ores (Kim, 1970), and mineralogy (Kim, 1969, 1975). Geology of the Janggum mine area consists of quartzite, the schist and limestone of Cambrian age (Lee *et al.*, 1990). Manganese ore deposits consist of manganese oxide ores and manganese carbonate ores. Manganese oxide ores were formed by supergene oxidation of rhodochrosite or other manganese carbonates (Kim, 1970).

The Dongnam mine was developed for magnetite and manganese oxide ores from early 1950's, but now it is closed. Mineralogy of manganese oxide minerals of the Dongnam mine area were studied by Chang (1983). Geology of the Dongnam mine area consists of slate of Cambrian age, limestone of Ordovician age, the age-unknown porphyritic granite and monzodiorite and quartz porphyry of Cretaceous age (Chang, 1983). Manganese ore deposits consist of manganese oxide, manganese carbonate and manganese silicate ores. Manganese oxide ores were formed by supergene oxidation of rhodochrosite or other manganese carbonates and manganese silicates, and precipitation from solution in supergene weathering environment (Chang, 1983).

The purpose of this work is to investigate the mineralogical characterization of busserite from Janggum and Dongnam mine. Natural busserites were investigated to know the exact configuration of interlayer waters and their roles in the 10 Å-phyllomanganate minerals, by the methods of XRD, and chemical analysis.

EXPERIMENTAL METHODS

Sampling

From Janggun and Dongnam mine, many hand specimens were collected and studied under the stereomicroscope, but natural buserite were limitedly found. The natural buserites were carefully collected by hand picking under the stereomicroscope, and agitated in water by ultrasonic cleaner for further experiments. These hand-picked samples were checked by X-ray powder diffraction. Polished sections were also prepared for electron microprobe analysis and textural study.

X-ray Diffraction

Preliminary X-ray diffraction analysis was carried out to identify the manganese mineral. X-ray source was Ni filtered CuK α radiation 40 kV/30 mA using a Rigaku Geigerflex. The intensity data were collected using Rigaku RAD3-C automatic diffractometer in continuous scanning mode. Powder samples were packed in the aluminum holder. Slit set was 0.5°–0.15 mm⁻¹, and scanning speed was 1° 2 θ /min.

Chemical Analysis

The natural buserite samples were too small to be analyzed by wet method. Therefore, chemical analysis and compositional distribution map of natural buserite was carried out by the wave dispersive method using the electron microprobe analyzer (EPMA), a JEOL Superprobe 733, at 20 kV with beam current of 20 nA and beam diameter of 1 μ m. Data correction was performed using a ZAF correction procedure with a Link automation system. Since Mn⁴⁺ and Mn²⁺ are not separated in the electron microprobe analysis, both values have been theoretically calculated from total Mn using the general formula of rancieite group by Kim (1991).

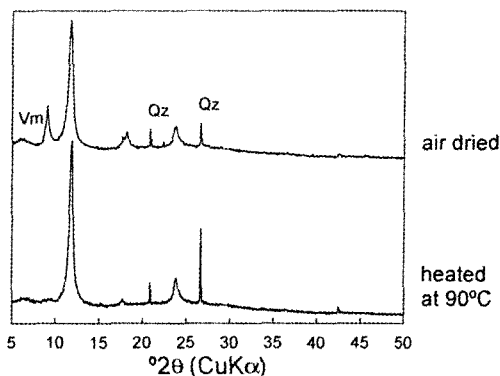


Fig. 1. X-ray diffraction patterns of untreated and heated buserite from the Janggun Mine. Vm: vermiculite, Qz: quartz.

RESULTS

Janggun Mine

Buserite usually occurs together with rancieite in one very fine-grained buserite-rancieite flake. Both phases are microscopically not distinguishable to each other. The buserite-rancieite flakes are precipitated around the fine-grained takanelite aggregate. They are also associated with quartz and vermiculite.

X-ray diffraction analysis was performed for the flaky sample which was oriented on the slide glass. The results show that they have characteristic 9.86 Å and 7.60 Å peaks. The relative intensities of two peaks are variable from sample to sample. It means that this flaky sample is a mixture of 10-Å and 7.6-Å phases. But an endeavor to find the single 10-Å phase was failed. A 7.6-Å phase manganate was identified as rancieite, but a 10-Å phase manganate was not certain whether it is due to buserite or todorokite. Therefore, flaky sample was heated at 90°C to distinguish buserite from todorokite. Peaks at 9.86 Å disappeared in heated sample at 90°C (Fig. 1). Therefore, peaks at 9.86 Å, 4.91 Å and 3.28 Å have been assigned for 001, 002 and 003 reflections of buserite, respectively, and peaks at 7.60 Å and 3.76 Å are for 001 and 002 reflections of rancieite, respectively. In the intercalation

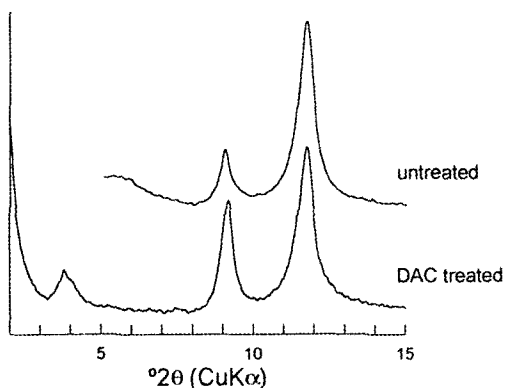


Fig. 2. X-ray diffraction patterns of untreated and DAC intercalated busserite from the Janggung mine.

experiment with dodecylammonium chloride (DAC), natural busserite from the Janggung mine was not intercalated (Fig. 2).

Busserite is closely associated with rancieite. Furthermore, these flakes are not abundantly found in manganese oxide ores. It is impossible to analyze the pure busserite sample by wet method. Since, the 10-Å phase become the 7-Å phase by collapse of the basal spacing in the vacuum under the electron microscope, the chemical analysis was actually performed on the 7-Å phase which has been dehydrated from 10-Å phase. The resulting chemical compositions of the busserite flakes are given in Table 1. The average

Table 1. Electron microprobe analyses of busserite from the Janggung and Dongnam mine

Composition	MnO ₂	MnO	CaO	MgO	FeO	ZnO	K ₂ O	Na ₂ O	H ₂ O	Total
Janggung Mine	66.91	3.01	4.17	2.49	0.13	0.03	0.35	0.10	22.74	100.00
Dongnam Mine	68.12	0.00	4.22	1.04	0.29	6.48	0.16	0.41	19.21	100.00

Unit: wt.%, H₂O: calculated by difference

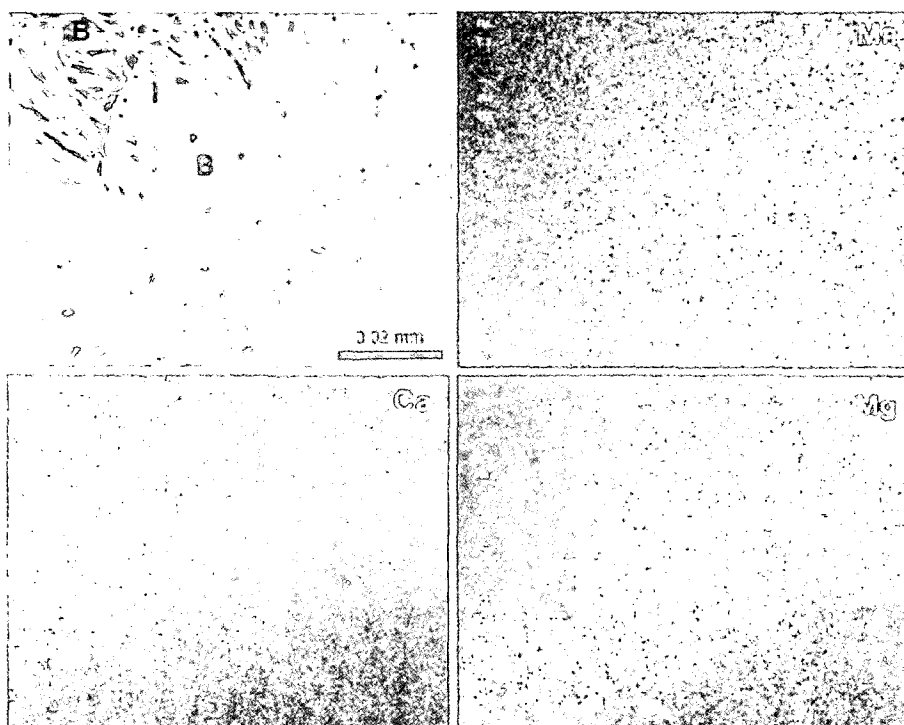


Fig. 3. Secondary electron image and wave dispersive X-ray image of busserite aggregates from the Janggung mine.

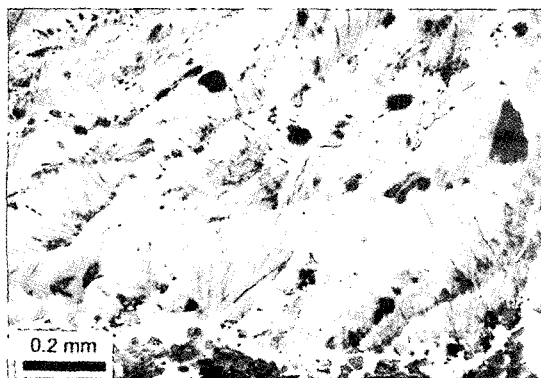


Fig. 4. Microphotograph of buserite aggregates from the Dongnam mine.

chemical analyses show that the buserite from the Janggun mine is (Ca, Mg)-dominant, having the formula $(\text{Ca}_{0.78}\text{Mg}_{0.64}\text{Mn}^{2+}_{0.45})\text{Mn}^{4+}_{8.03}\text{O}_{18} \cdot 3.2\text{H}_2\text{O}$. The number of Ca varies from 0.41 to 1.38 on the basis of 18 oxygens. Fig. 3 shows secondary electron image (SEI) and wave dispersive X-ray image of buserite aggregates from the Janggun mine. The contents of Ca, Mn^{2+} and Mg are variable from sample to sample.

Dongnam Mine

Buserite is closely associated with rancieite. Buserite-rancieite flake occurs as minute crystal aggregates in open spaces within manganese oxide ores and along the wall (limestone) of veins. Buserite-rancieite is light brown to dark brown in color in the flaky aggregates, whereas bluish black in fan-like or massive aggregates. It occurs as radiating, fan-like or subparallel groups of flaky particles under the microscope (Fig. 4). The mineral is associated with todorokite, birnessite, nsutite, pyrolusite, vernadite, and hydrohaerterolite with minor goethite and calcite.

Heating experiments show that the diffraction line at 9.67 Å disappears at 70~90°C completely and the intensities of lines at 7.53 Å and 3.77 Å are in some measure strong (Fig. 5). It is supposed that flake is a mixture of buserite and rancieite. In the intercalation experiment with dodecylammonium chloride (DAC), natural buserite from the Dongnam mine was partially intercalated (Fig. 6).

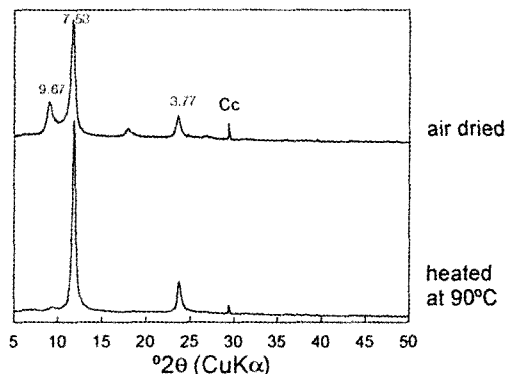


Fig. 5. X-ray diffraction patterns of untreated and heated buserite from the Dongnam mine. Cc: calcite.

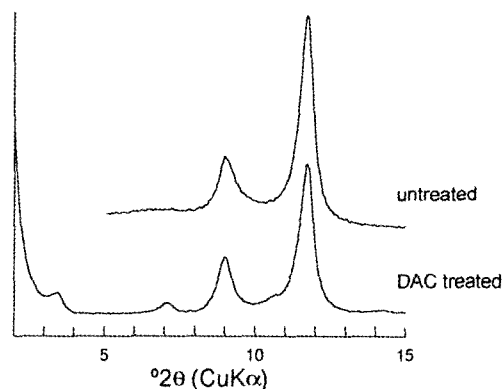


Fig. 6. X-ray diffraction patterns of untreated and DAC intercalated buserite from the Dongnam mine.

The chemical analyses of the buserite flakes are given in Table 1. The average chemical analyses show that the buserite from the Dongnam mine is (Zn, Ca)-dominant, giving the formula $(\text{Zn}_{0.81}\text{Ca}_{0.77}\text{Mg}_{0.26})\text{Mn}^{4+}_{8.00}\text{O}_{18} \cdot 10.9\text{H}_2\text{O}$. The numbers on the basis of 18 oxygens of Zn and Ca vary from 0.12 to 1.56 and 1.49 to 0.15, respectively. Secondary electron image and wave dispersive X-ray image shows that Ca is dominant at the rim of flake and Zn is dominant in the core, and some flakes are Ca-dominant and others are Zn-dominant (Fig. 7).

SUMMARY

Natural buserites were collected from the Jang-

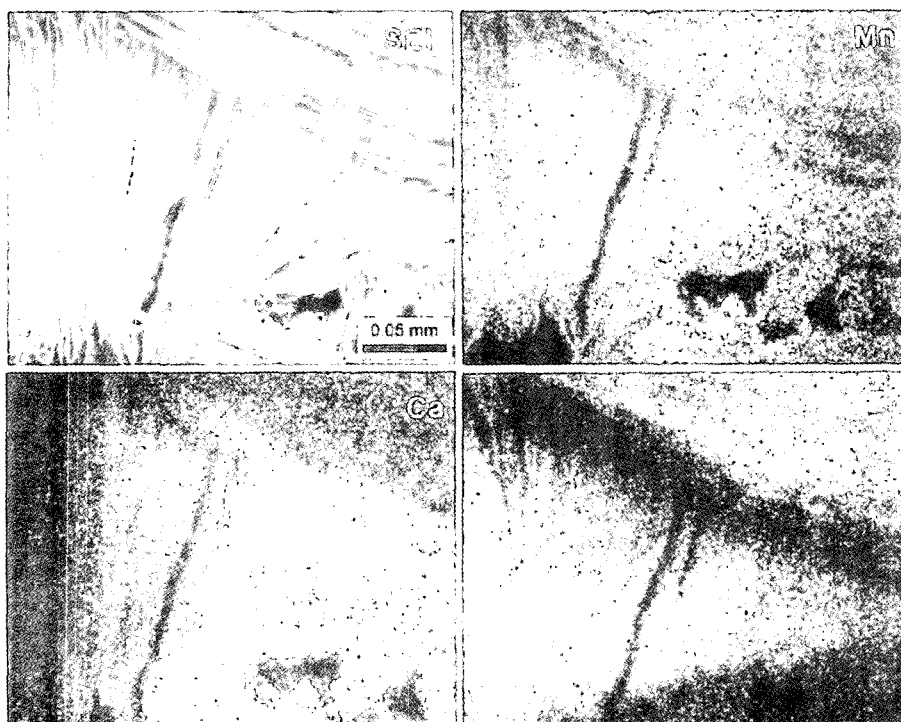


Fig. 7. Secondary electron image and wave dispersive X-ray image of busserite aggregates from the Dongnam mine.

gun and Dongnam mines. Both minerals were identified from one and the same flakes. The intensity ratios of 10 Å to 7 Å peaks are variable from sample to sample, showing a tendency to decrease with dehydration. Electron microprobe analyses give the average formula $(\text{Ca}_{0.78}\text{Mg}_{0.64}\text{Mn}^{2+}_{0.45})\text{Mn}^{4+}_{8.03}\text{O}_{18} \cdot 13.2\text{H}_2\text{O}$ and $(\text{Zn}_{0.81}\text{Ca}_{0.77}\text{Mg}_{0.26})\text{Mn}^{4+}_{8.00}\text{O}_{18} \cdot 10.9\text{H}_2\text{O}$ for busserite from the Janggung and the Dongnam mine, respectively.

The natural busserites from the Janggung and Dongnam mines show different dehydration behaviors on heating experiments. The basal reflection of busserite from the Janggung mine shifts continuously from 9.86 Å at 40°C to 7.60 Å at 90°C, but from the Dongnam mine shows tendency of decreasing intensity in the 9.67 Å peak and increasing intensity no gradual shifting of peaks in the 7.53 Å peak in the range of 40~90°C. The natural busserite from the Dongnam mine was partially intercalated, but that from the Janggung mine was not.

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