

Buserite and Its Relationship to Rancieite in Dongnam Mine, Korea

東南鑛山에서 發見된 부서라이트 및 이 鑛物의 란시아이트와의 關係

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ABSTRACT: The terrestrial Ca-buserite has been found from Dongnam mine, Korea. It occurs in close association with rancieite in the manganese oxide ores which were formed by supergene leaching of hydrothermal rhodochrosite in veins. A study on this mineral using X-ray diffraction, infrared, polarizing and electron microscopes and dehydration experiment shows that the natural Ca-buserite (10 Å phase) is more or less unstable, transforming partly to rancieite (7.5 Å phase) in the natural environment, and upon heating, its 10 Å line shifts to 7.5 Å at 70-90°C. The Ca-buserite is the hydrate of rancieite.

요약: 천연산 Ca-부서라이트가 東南鑛山에서 發見되었는 바, 이 鑛物은 脉狀으로 産出하는 熱水起源의 菱錳 鑛석이 表成 風化作用을 받아 生成되었다. X線 廻折장치, 赤外線分光器, 偏光顯微鏡, 電子顯微鏡 및 脫水實驗을 利用하여 이 鑛物에 對하여 研究한 結果, 이 천연산 Ca-부서라이트(10Å 相)는 自然環境에서 多少 不安定하여 部分的으로 란시아이트(7.5Å 相)으로 遷移하며 加熱하면 10Å 廻折線이 70~90°C에서 7.5Å으로 移動한다는 것이 밝혀졌다. 즉, Ca-부서라이트는 란시아이트의 舍水型이라 할 수 있다.

INTRODUCTION

Buserite and rancieite are the typical phyllo-manganate minerals and belong to 10 Å phase and 7.5 Å phase, respectively. The nature of buserite and its relationship to rancieite have not yet been clearly elucidated.

Buserite is originally a synthetic material which was prepared by oxidation of aqueous Mn(OH)₂ suspensions in cold aqueous NaOH solution by molecular oxygen. It was firstly synthesized by Marti (1944) and then Wadsley (1950). Giovanoli *et al.* (1970) resynthesized the Marti's or Wadsley's phase and proposed the name sodium manganese (II, III) manganate (IV) hydrate or "10 Å manganite".

Giovanoli *et al.* (1971) proposed that the 10 Å phase in manganese nodules be called buserite, in honor of W. Buser, and suggested that buserite has the same crystal structure as synthetic "10 Å

manganite". Buserite was accepted as a mineral name by the Commission on New Minerals and Mineral Names, I.M.A., when evidence was submitted that todorokites are a mixture of buserite and its decomposition products birnessite and manganite (γ -MnOOH) (Hey and Embrey, 1974). Other varieties (Co, Ni, Cu, etc.) are obtained from Na-buserite by cation exchange in solution of the corresponding nitrates (Giovanoli, 1980).

Giovanoli and his coworkers also recommended that todorokite should be discredited as a valid mineral (Giovanoli and Brutsch, 1979 a, b, and Giovanoli, 1980). However, recent experimental evidences derived from infrared spectroscopy (Potter and Rossman, 1979), electron diffraction (Chukhrov *et al.*, 1978, 1979 a, b, 1981; Siegel, 1981), high resolution transmission electron microscopy (Turner and Buseck, 1979, 1981; Turner *et al.*, 1983) and extended X-ray

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absorption fine structure measurement (Crane, 1981) verify the integrity of todorokite (Burns *et al.*, 1983). Giovanoli (1985) has reconsidered his earlier assertion that todorokite is not a valid mineral species.

On the other hand, no satisfactory data exist for the natural occurrence of phases analogous to synthetic busserite (Chukhrov *et al.*, 1979). Burns *et al.* (1983) also mentioned that busserite has yet to be positively identified in the natural environment. However, busserite has been reported from marine manganese nodules by Arrhenius and Tsai (1981), by Chukhrov *et al.* (1983, 1984), Andreev *et al.* (1984) and Oswald and Dubrawski (1987). Chukhrov *et al.* (1984) show that there are two types of busserite; busserite I in which single vacant octahedral sites are randomly distributed, and busserite II in which in addition to single vacant octahedra, chains of 2, 3 or more vacant octahedra are present. Terrestrial occurrence of busserite has not yet been reported (Oswald and Dubrawski, 1987). In addition, the name busserite is absent from Fleischer's (1980, 1983, 1986) "Glossary of Mineral Species".

In the course of study on the phyllosulfate minerals, the authors identified the natural Ca-busserite from the terrestrial manganese oxide ores of Dongnam mine, Korea, although it has been partly transformed to rancieite.

This paper aims to report the occurrence of the natural Ca-busserite and elucidates its relationship to rancieite.

OCCURRENCE

The geology of the Dongnam mine area where the Ca-busserite and rancieite were found, consists of the Myobong slate of Cambrian age, the Pungchon limestone and Hwajeol Formation of Ordovician age and granodiorite and quartz porphyry of Tertiary(?) age.

The Ca-busserite and rancieite are found in the oxidation zone of the hydrothermal manganese carbonate veins trending NS-N25°E, and cutting the Pungchon limestone. Manganese ore veins are developed in the peripheral zone around the magnetite deposits which are developed along the contact between limestone and quartz porphyry.

The Ca-busserite and rancieite are important constituent minerals of the manganese oxide ores in the Dongnam mine. Both minerals are present in one and the same flakes. Therefore, the term "Ca-busserite-rancieite" is necessary to describe such flakes. Ca-busserite-rancieite occurs as minute crystal aggregates in open spaces within manganese oxide ores and along the wall (limestone) of veins. It is very fine-grained, but relatively well crystallized, so that its flaky habit is easily seen with naked eye in many places. It is light brown to dark brown in color in the flaky aggregates, whereas bluish black in fan-like or massive aggregates.

Under the microscope, Ca-busserite-rancieite occurs as radiating, fan-like or subparallel groups of flaky (Fig. 1) or acicular crystals,



Fig. 1. The natural Ca-busserite-rancieite flakes from Dongnam mine, Korea. (A) Radiating or subparallel groups of flaky crystals in polished section. Open nicols. (B) Flaky crystals under SEM.

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or massive aggregates. Fan-like aggregates show colloform surface. The size of the buserite-rancieite is 0.12 mm in length for the largest but usually less than 0.05 mm. The flakes are elongated parallel to the cleavage and flattened probably on (001). In reflected light, it is grey to white in color and shows distinct anisotropism.

The mineral is associated with todorokite, birnessite, nsutite, pyrolusite, vernadite, and hydroheterolite. Goethite and calcite are also associated.

EXPERIMENTAL

The manganese oxide ores were studied under the ore microscope to know the general mineral composition as well as their physical and optical properties.

Each pure mineral sample was collected under the microscope for X-ray diffraction, infrared and thermal analyses. Collected samples were carefully crushed to powder between two glass slides under the microscope so that their crystal structures are not destroyed.

X-ray powder patterns were obtained with the JEOL model JDX-5P X-ray diffractometer using 114.6 mm Debye-Scherrer camera or diffractometer. Infrared absorption spectra were obtained with the Perkin-Elmer model 283B spectrophotometer on the KBr pellets for the 4000 to 200 cm^{-1} region. Thermal analysis (DTA, TG and DTG) was made using the Rigaku Thermoflex and the model PTC-10A temperature controller. Heating experiment was made using the Hitachi model IRC-2 temperature controller and digital thermocouple.

RESULTS

X-ray Diffraction Study

X-ray powder diffraction pattern of the sample suggested that it be a mixture of 10 Å phase and rancieite, because it showed characteristic lines at 9.67 Å and 7.53 Å (Table 1). But a very interesting phenomenon was found in the X-ray powder patterns of different samples of the same material. The relative intensities of 10 Å and 7.5 Å lines are variable from sample to sample. Sample in which 10 Å line is predominantly developed is also found.

In order to know the cause of such variation, dehydration experiment has been made for the

Table 1. Comparison of X-ray powder diffraction data of the natural Ca-buserite, synthetic Ca-buserite, and todorokite

Partly dehydrated natural Ca-buserite (this study)			Synthetic Ca-buserite (Giovanoli, 1980)		Todorokite (Kim, 1979)	
I	d		I	d	I	d
s	9.69	B	10	10.06	s	9.60
vs	7.53	R	1	7.70	vw	7.05
m	4.85	B	6	5.01	m	4.78
s	3.74	B+R			vw	4.27
			3	2.57	w	2.83
			3	2.49		
m	2.45	B+R	3	2.43	s	2.39
m	2.34	B+R	1	2.34		
			1	2.30		
			1	2.21	m	2.20
			2	2.17		
vw	2.06	B+R				
			1	1.95	w	1.97
vw	1.76	B+R	2	1.93	vw	1.75
			1	1.84	vw	1.62
			1	1.83	vw	1.54
			1	1.71		
			2	1.47		
m	1.42	B+R	2	1.45	s	1.42
					vw	1.29

B: natural Ca-buserite, R: rancieite

sample. A powder sample mount has been continuously heated with temperature controller and the temperature was carefully checked with digital thermocouple. X-ray powder diffraction patterns have been obtained for the same powder mount heated for half an hour at each designated temperature between 25° and 110°C (Fig. 2) and d-values have been determined with quartz standard. X-ray powder diffraction data for the original material and its heat-treated products are given in Table 2.

Heating experiments show that the diffraction line near 10 Å (actually 9.67 Å) disappears at 70-90°C completely and the intensities of lines at 7.5 Å and 3.77 Å increase to a considerable degree. It indicates that the 10 Å phase trans-

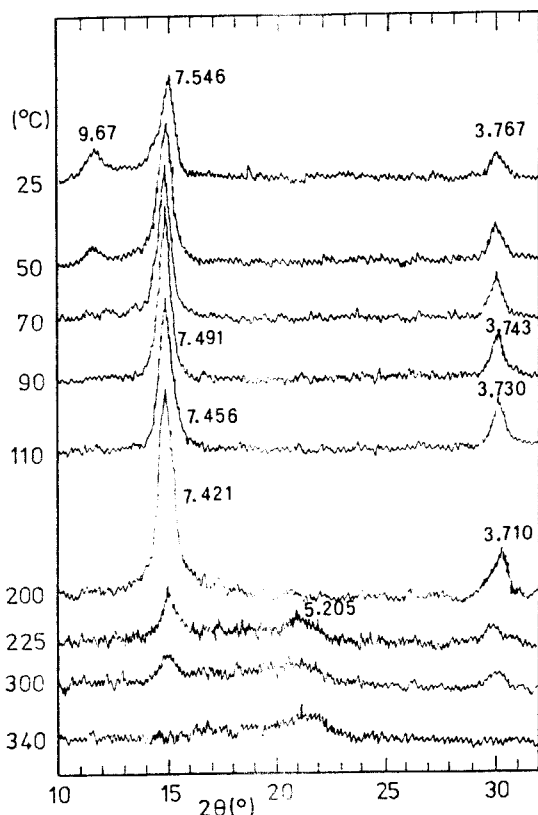


Fig. 2. X-ray powder diffraction patterns of partly dehydrated natural Ca-buserite from Dongnam mine, Korea and its heat-treated products. Heated for 30 minutes at each temperature between 25° and 110°C.

Table 2. X-ray powder diffraction data of partly dehydrated Ca-buserite and their heat-treated products

room temp.			200°C			300°C	
I	d	phase	I	d	hkl	I	d
w	9.67	B					
s	7.57	R	s	7.51	001	m	7.55
vw	4.82	B				m	5.21
m	3.72	B+R	m	3.73	002		
w	2.44	B	w	2.45	100	w	2.44
w	2.34	B+R	w	2.33	101		
vw	2.06	B+R					
vw	1.76	B+R					
w	1.42	B+R	w	1.42	110	m	1.42
vw	1.39	B					
vw	1.37	R	vw	1.34	111	w	1.37

B: Ca-buserite, R: rancieite

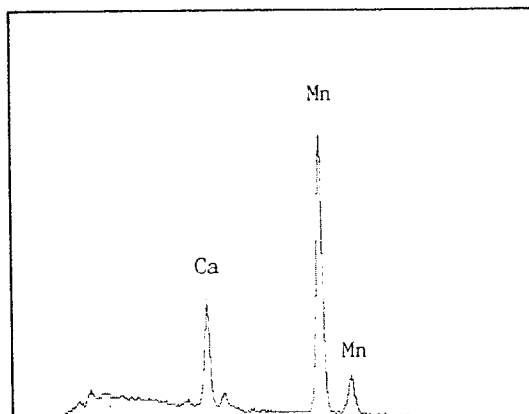


Fig. 3. Energy dispersive spectrum of Ca-buserite-rancieite under vacuum of electron microprobe.

formed to 7.5 Å phase by dehydration. Such a phenomenon suggests that the 10 Å phase corresponds to buserite which is distinguished from todorokite which is stable up to 300-500°C. Energy dispersive spectral analysis (Fig. 3) shows that it is Ca-buserite in which calcium is dominant as the interlayer cations in the layer structure. X-ray data of the sample are compared with those of synthetic Ca-buserite and todorokite in Table 1.

X-ray pattern of 7.5 Å phase corresponds to that of rancieite. 7.5 Å phase is stable up to about 200°C. The intensity of 7.5 Å (actually 7.54 Å) (001) line increases to maximum at about 175°C (not shown in Fig. 2), and then gradually decreases, shifting toward 7.40 Å. This line together with its (002) line (3.7 Å) disappears at 300-340°C. A new line at 5.2 Å begins to appear at 200-250°C. At 340°C, only 5.2 Å line is present. This line might be produced by the collapse of (001) basal plane. All the above phenomena are reproducible in every dehydration experiment.

The frequent coexistence of 10 Å and 7.5 Å phases in nature is due to the easy dehydration property of Ca-buserite at moderate temperature. Paterson (1981) suggests that d-spacing of line near 10 Å of synthetic buserite varies with the humidity. Oswald and Dubrawski (1987) reports that heating of 10 Å phyllosilicate from marine ferromanganese crust to 100°C for 4 hours results in formation of the 7 Å birnessite structure. Their 10 Å phase might be Na-buserite.

Infrared Study

The infrared absorption spectra of heat-treated samples show no significant difference in the positions of absorption bands up to 230°C as compared with those of the original sample as shown in Figure 4. Comparison of infrared absorption bands of natural Ca-buserite and rancieite is given in Table 3. It indicates that no significant structural rearrangement occurs

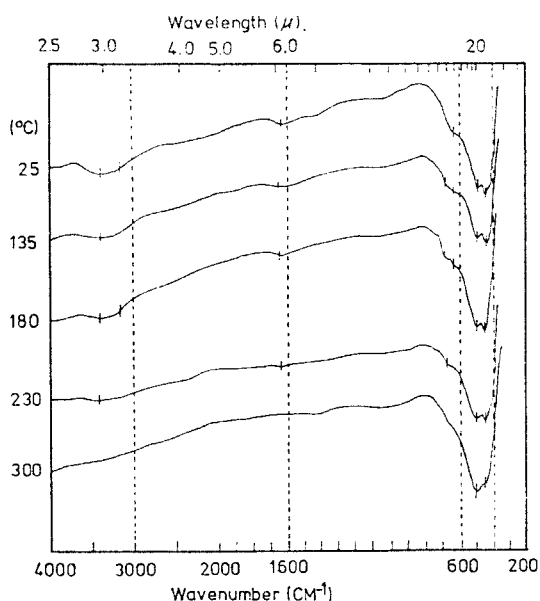


Fig. 4. Infrared absorption spectra of partly dehydrated Ca-buserite and its heat-treated products.

Table 3. Positions of infrared absorption bands for natural Ca-buserite and rancieite

partly dehydrated natural buserite		Rancieite	
cm ⁻¹	I	cm ⁻¹	I
445	vs	420	sh
		435	vs
495	vs	495	vs
		535	sh
650	sh	620	sh
		680	sh
1645	w	1610	m
3400	mb	3400	m

sh: shoulder, b: broad

during dehydration from 10 Å phase to 7.5 Å phase except the interlayer water. Spectra at high temperature show an increase in band energy of the major bands. Similar results were obtained for the synthetic buserite and its dehydration products by Potter and Rossman (1979).

Thermal Study

DTA, TG, and DTG curves of partly dehydrated Ca-buserite are shown in Figure 5. They show five main reactions at or near 65°, 180°, 500°, 690°, and 1020°C. The first reaction at 65°C is due to the loss of adsorbed and interlayer water of buserite. It is well correlated with the disappearance of 10 Å line and the increase in intensity of 7.5 Å line at 70-90°C in dehydration experiment. Relatively low value of weight loss (2.97%) from 25-90°C suggests that the sample has been considerably dehydrated to 7.5 Å phase (rancieite) under the natural environment. The DTA curve above 90°C well agrees with that of rancieite by Bardossy and Brindley (1978). Weight loss (2.30%) from 90-150°C is probably due to weakly bound water of crystallization in rancieite structure. Weight loss (11.04%) from 150-490°C is probably due to dehydration of the tightly bound water. The combined weight loss (6.62%) from 205-1025°C is net loss of oxygen. Three stages of weight loss from 25-500°C are well correlated with the structural change in the sample as evidenced by the X-ray powder patterns of heat-treated samples.

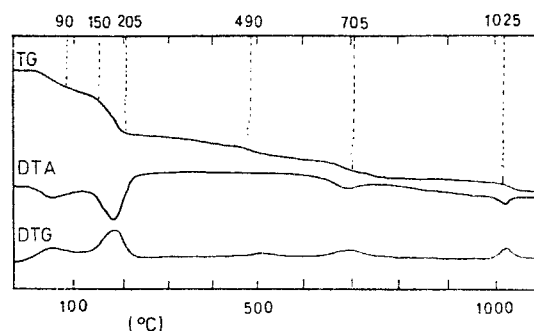


Fig. 5. DTA, TG and DTG curves of partly dehydrated natural buserite. Heating rate: 10°/min.

DISCUSSION

Although marine busserite was reported by several workers as mentioned above, no one reported the occurrence of terrestrial busserite. This is perhaps the first report on the terrestrial Ca-busserite. In addition, although the relationship of marine busserite (may be Na-busserite) and birnessite was studied by several workers (Arrhenius and Tsai, 1981; Chukhrov *et al.*, 1984; Oswald and Dubrawski, 1987), no one mentioned on the relationship of busserite and rancieite.

The present study shows that the natural Ca-busserite loses its characteristic 10 Å diffraction line at 70-90°C by dehydration of its interlayer water molecules, resulting in the formation of 7.5 Å phase (rancieite). Such a phenomenon and the easy observation of Ca-busserite phase transformed partly to rancieite, suggest that Ca-busserite is unstable in the natural environment. However, busserite phase is present in the cool temperature and moderate humidity in the Dongnam mine.

In the case of Ca-busserite and rancieite from Dongnam mine, Korea, both minerals have the same chemistry except the content of water molecules. Both minerals have Ca as the dominant cation in the interlayers as shown in energy dispersive spectrum in Figure 3. It is assumed that two layers of water molecules are present in busserite, whereas one layer of water molecule in rancieite as in birnessite. The difference of rancieite and birnessite is the kinds of mono- and divalent cations between $[\text{MnO}_6]$ octahedral layers and sheets of interlayer water; Ca is dominant in rancieite, whereas Na is dominant in birnessite. Distinction between rancieite and birnessite is often obscure in the literature, leading to the misunderstanding of the crystal chemistry of 7 Å phyllo manganese minerals. Detailed crystal chemistry of 7 Å phyllo manganese minerals including rancieite and birnessite will be discussed in the separate paper.

Transformation from busserite to rancieite is not a gradual but abrupt change in the structure as shown in Figure 2. The gradual shifting of the peak at 9.67 Å toward 7.546 Å is not observed in the dehydration experiment. It implies that although both have the similar layer structures, some difference in structures between busserite and rancieite exists, as has been suggested by Arrhenius and Tsai (1981) and Chukhrov *et al.*

(1984). The principal difference in their structures is the presence of additional weakly bound molecular water in the interlayer space of busserite, making it unstable as Chukhrov *et al.* (1984) suggested in the case of busserite-birnessite transition. The gradual dehydration in rancieite (Fig. 2) revealed by the gradual shifting of peak at 7.546 Å toward 7.421 Å during heating up to 200°C suggests the stronger hydrogen bond in the water molecules in the interlayer spaces.

Above discussion shows that Ca-busserite and rancieite are different to each other in (001) dimensions and contents of interlayer water. The present author proposes that the Ca-busserite be a valid mineral.

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