

# Chemistry and Dehydration Behavior of (Ca, Mg)-buserite from the Janggun Mine, Korea

장군광산에서 산출되는 (Ca, Mg)-부서라이트의  
화학조성과 탈수현상에 관한 연구

Hunsoo Choi (최헌수) · Soo Jin Kim (김수진)

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

**ABSTRACT:** The natural (Ca, Mg)-buserite has been identified from the manganese oxide ores of the Janggun mine, Korea, which have been formed by supergene weathering of sedimentary-metamorphic rhodochrosite. It occurs together with rancieite forming one very fine-grained buserite-rancieite flake. This (Ca, Mg)-buserite-rancieite occurs as microcrystalline flaky crystals. It precipitated around the fine-grained takanelite aggregate. Electron microprobe analyses give the formula  $(Ca_{0.98}Mg_{0.07}Mn_{0.95}^{2+})Mn_{0.99}^{4+}O_2 \cdot 1.46H_2O$  for (Ca, Mg)-buserite.

The dehydration experiments by relative humidity control and heating as well as rehydration experiment by relative humidity control show that (Ca, Mg)-buserite dehydrates completely at 90°C and rehydrates up to 27% of the original state. The dehydration at 26% RH (corresponding to heating to about 40°C) is characterized by the decrease in the intensity of 9.86 Å peak with slight shifting to 9.60 Å. It is due to the loss of very weakly bound water molecules in the interlayer. The dehydration from 40°C to 90°C is characterized by the gradual shifting of 001 peak from 9.60 Å to 7.42 Å. It is due to the loss of weakly bound water molecules in the interlayer.

**요약:** 장군광산의 산화망간광석에서 자연산 (Ca, Mg)-부서라이트를 발견하였는바, 이는 퇴적 또는 변성기원의 능망간석의 표성 풍화에 의해 형성되었다. 부서라이트는 란시아이트와 함께 세립의 부서라이트-란시아이트 엽편을 이룬다. 이 (Ca, Mg)-부서라이트-란시아이트는 엽상의 작은 결정으로 산출된다. 이는 세립의 다카넬라이트 집합체 주위에 침전되어 있다. 전자현미분석 결과, 장군광산의 (Ca, Mg)-부서라이트는  $(Ca_{0.98}Mg_{0.07}Mn_{0.95}^{2+})Mn_{0.99}^{4+}O_2 \cdot 1.46H_2O$ 의 화학식을 갖는다.

상대습도의 조절 및 가열에 의한 탈수실험과 상대습도 조절에 의한 재수화 실험에 의하면, (Ca, Mg)-부서라이트는 90°C에서 완전히 탈수되며 27%만이 재수화된다. 상대습도 26%에서의 (40°C로 가열한 경우와 일치하는) 탈수현상은 9.86 Å 회절선의 9.60 Å으로의 감소 및 강도의 감소로 특징지워진다. 이는 층간의 매우 약하게 결합된 물분자의 방출에 기인한다. 40°C에서 90°C까지의 가열에 의한 탈수현상은 001 회절선이 9.60 Å에서 7.42 Å까지 점이적 이동으로 특징지워진다. 이는 층간에 약하게 결합되어 있는 물분자의 방출에 의한 것이다.

## INTRODUCTION

Buserite is the name given by Giovanoli et al. (1971) to the 10-Å phase in the sea-floor manganese nodules, which was assumed to have the same structure as synthetic "10 Å manganate"

(Giovanoli et al., 1970). It has been reported from marine manganese nodules by Arrhenius and Tsai (1981), Chukhrov et al. (1984), and Oswald and Dubrawski (1987), as well as from the terrestrial manganese oxide deposit by Kim and Chang (1989). The mineral name buserite was approved

by the Commission on New Minerals and Mineral Names, International Mineralogical Association (Hey and Embrey, 1974), but it is not listed in Fleischer's "Glossary of Mineral Species" (1991).

Buserite has two interlayer water molecules between  $[\text{MnO}_6]$  octahedral sheets, which are different from rancieite group mineral (rancieite, takanelite and birnessite) having one interlayer water (Stouff and Boulègue, 1988). On the basis of dehydration experiment for Ca-buserite from Dongnam Mine, Kim and Chang (1989) suggested that buserite be a hydrated form of rancieite.

Dehydration of buserite was studied by the relative humidity control for synthetic buserite (Tejedor-Tejedor and Paterson, 1979) and heating for natural buserite (Kim and Chang, 1989). Tejedor-Tejedor and Paterson (1979) showed that the stability of the 10-Å phase in synthetic buserite is determined by the nature of interlayer cation and that the collapse of 10-Å phase is irreversible except Ca-buserite. Heating experiment by Kim and Chang (1989) revealed that Ca-buserite dehydrates at 90°C to become rancieite. This fact suggests that Ca-buserite has the same composition as rancieite except the water contents.

Synthetic Na-buserite is formulated as  $[\text{Mn}^{3+}(\text{Mn}^{2+})\text{O}_{12}]^+ [\text{Na}_x(\text{OH})_x(\text{H}_2\text{O})_x]^-$  (Giovanoli and Arrhenius, 1988), but the chemistry of natural buserite has been uncertain. The major cation in the interlayer of buserite from Dongnam mine is Ca (Kim and Chang, 1989). Crystal chemistry of rancieite group minerals supposed to have structure similar to that of buserite has been studied by Kim (1990, 1991). He gives the chemical formula for rancieite group minerals  $\text{R}_2\text{Mn}^{3+}_2\text{O}_{12} \cdot n\text{H}_2\text{O}$  by Kim (1990, 1991).

This paper aims to report the chemistry and dehydration behavior of the natural (Ca, Mg)-buserite from the Janggun mine.

## OCCURRENCE

Geology of the Janggun mine area consists of the Jangsan quartzite, the Dueumri Formation and the Janggun limestone of Cambrian in one age. Manganese oxide ores were formed by supergene oxidation of rhodochrosite or other manganese carbonates (Kim, 1979).

(Ca, Mg)-Buserite usually occurs together with rancieite in one very fine-grained buserite-rancieite flake. Both phases are microscopically not distinguishable to each other. The (Ca, Mg)-buserite-rancieite flakes are precipitated around the fine-grained takanelite aggregate. They are light grey to white in color, and show distinct bireflectance and anisotropism in reflected light. Their sizes are less than 0.05mm (Fig. 1).

## METHODS

Polished sections of the manganese oxide ores from the Janggun mine were prepared for electron microprobe analysis and textural study. The buserite-rancieite flakes were carefully collected by hand picking under the stereomicroscope, and agitated in water by ultrasonic cleaner



Fig. 1. Microphotograph of (Ca, Mg)-buserite-rancieite (B) and takanelite (T) from Janggun mine, Korea.

for X-ray analysis and dehydration experiment.

Chemical analysis of the samples was carried out by the wave dispersive method using a JEOL Superprobe 733 at Seoul National University, at 20KV with beam current of 20nA and beam diameter of 1  $\mu$ m.

The dehydration experiments of the samples were carried out by stepwise lowering of relative humidity or by heating. In order to control the relative humidity of the samples, we used the newly manufactured cylindrical chamber, a modified model of Churchman (1970). It was directly attached to the sample holder of X-ray goniometer. The relative humidity was controlled by the saturated salt solutions or sulfuric acid solution of known concentration (Weast, 1988). Heating experiment was carried out using Rigaku high temperature attachment and programmed temperature controller, PTC-10A. X-ray intensity data were collected with automated Rigaku Geigerflex by the step-scan mode, using Ni-filtered  $\text{CuK}\alpha$  radiation at 40KV/30mA.

## RESULTS

### X-ray Diffraction Study

X-ray diffraction analysis was performed for the flaky sample which was carefully collected under the stereomicroscope. The result shows that the flaky mineral has characteristic 9.86Å and 7.60Å peaks. Peaks at 9.86Å and 7.60Å are for (001) reflections of 10-Å phase (buserite) and 7-Å phase (rancieite), respectively. Therefore, it became evident that the flaky mineral is in fact a mixture of the buserite and rancieite. This fact is also supported by the observation that the relative intensity of two peaks are variable from sample to sample. An endeavor to find the single 10-Å phase was failed. It might be due to the easy dehydration of 10-Å phase to 7-Å phase at low temperature.

### Chemical Composition

The buserite-rancieite flakes are not abundantly found in manganese oxide ores. They were analysed by electron probe microanalyser. Chem-

ical analyses of the buserite-rancieite flakes were regarded as those of buserite only. It is based on the assumption that buserite has the similar layer structure and chemistry as rancieite except the contents of water molecules. Dehydration experiments (Tejedor-Tejedor and Paterson, 1979; Kim and Chang, 1989) also revealed such a conclusion.

Since  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  are not separated in the electron microprobe analysis, both values have been theoretically calculated from total Mn using the general formula of rancieite by Kim (1990, 1991). Kim (1990, 1991) suggested that the general formula of rancieite group for 9 unit cells be  $\text{R}_{2x}\text{Mn}_{8-x}^{4+}\text{O}_{18} \cdot n\text{H}_2\text{O}$ , where  $\text{R}=\text{Ca}, \text{Mn}^{2+}, \text{Mg}, \text{K}$  and  $\text{Na}$  and  $x$  is approximately one. Therefore, if  $x=1$ , the formula becomes  $\text{R}_2\text{Mn}_8^{4+}\text{O}_{18} \cdot n\text{H}_2\text{O}$ .  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  were calculated by using this formula. The total number of cations in analyses was recalculated to 10, and 8 out of 10 was allowed to  $\text{Mn}^{4+}$  and the remaining 2 to R. From this allocation, the proportion of  $\text{Mn}^{2+}$  was calculated from total R. From the values of  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$ , weight percentages of  $\text{MnO}_2$  and  $\text{MnO}$  were calculated. Water content was calculated by difference.

The resulting chemical compositions of the buserite-rancieite flakes are given in Table 1. The contents of Ca,  $\text{Mn}^{2+}$  and Mg are variable from sample to sample (Fig. 2). However, the chemical analyses are mostly concentrated in the (Ca, Mg)-rich field. The average chemical analyses show that the flaky mineral is (Ca, Mg)-buserite having the formula  $(\text{Ca}_{.05}\text{Mg}_{.07}\text{Mn}_{.46}^{2+}\text{K}_{.01})\text{Mn}_{.49}^{4+}\text{O}_{18} \cdot 1.46\text{H}_2\text{O}$ . The number of Ca varies from 0.05 to 0.15 on the basis of 2 oxygens. The number of water molecules of (Ca, Mg)-buserite is expected to be larger than 1.46, since the sample is actually a mixture of (Ca, Mg)-buserite and (Ca, Mg)-rancieite.

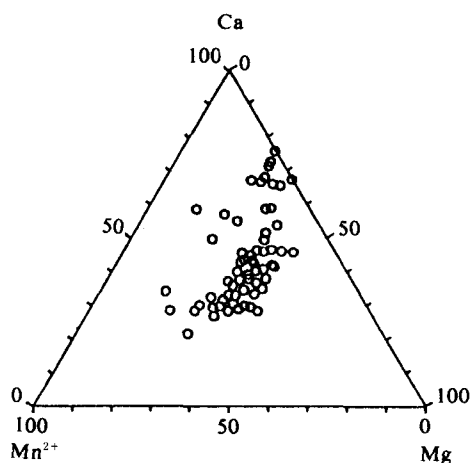
### Dehydration Experiment by Relative Humidity Control

Dehydration experiments were performed for the (Ca, Mg)-buserite-rancieite sample by lowering the relative humidity (RH) from 93% to 6% at about 10% intervals. Four X-ray diffraction profiles for different relative humidities are shown in Figure 3. The intensity of initial 001 peak at 9.86Å decreased gradually with decrease-

**Table 1.** Electron microprobe analyses of (Ca, Mg)-buserite-rancieite from Janggun mine, Korea.

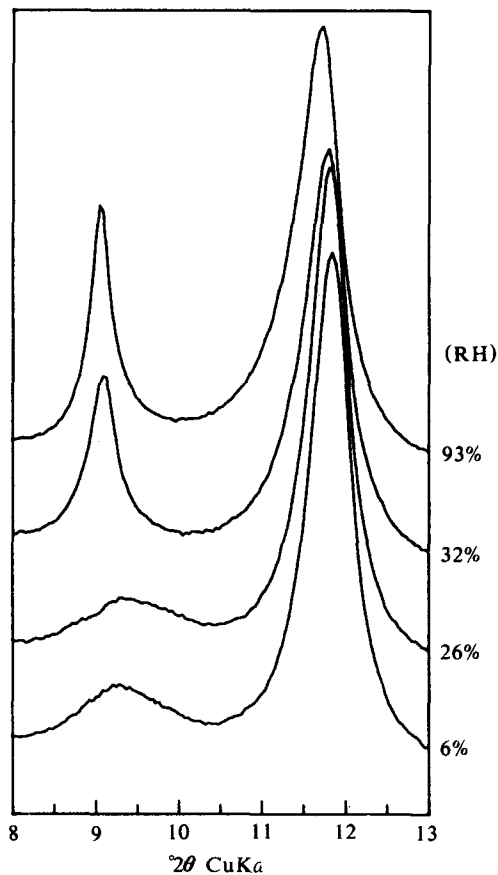
	1	2	3	4	5	6	7*
MnO <sub>2</sub>	62.99	64.00	64.85	68.11	67.90	65.72	66.91
MnO	0.33	1.19	1.86	3.34	4.02	5.56	3.01
CaO	7.00	5.88	5.20	3.08	2.99	2.17	4.17
MgO	1.69	2.25	2.34	3.14	2.69	2.06	2.49
FeO	0.15	0.19	0.15	0.09	0.11	0.07	0.13
ZnO	0.00	0.00	0.00	0.03	0.02	0.06	0.03
K <sub>2</sub> O	0.20	0.19	0.27	0.40	0.60	0.53	0.35
Na <sub>2</sub> O	0.10	0.00	0.06	0.18	0.12	0.24	0.10
H <sub>2</sub> O	27.53	26.30	25.28	21.63	21.54	23.59	22.74
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
cation numbers on basis of 18 oxygens							
Mn <sup>4+</sup>	8.019	8.010	8.018	8.033	8.038	8.045	8.025
Mn <sup>2+</sup>	0.052	0.183	0.282	0.482	0.583	0.835	0.454
Ca	1.381	1.140	0.996	0.563	0.549	0.411	0.775
Mg	0.465	0.607	0.623	0.799	0.688	0.544	0.644
Fe	0.023	0.028	0.022	0.013	0.016	0.011	0.019
Zn	0.000	0.000	0.000	0.004	0.003	0.007	0.004
K	0.047	0.044	0.061	0.087	0.132	0.120	0.077
Na	0.036	0.000	0.020	0.061	0.038	0.083	0.033
H <sub>2</sub> O	16.913	15.884	15.085	12.320	12.305	13.937	13.172
Mn/R** %	2.6	9.1	14.1	24.0	29.0	41.5	22.6
Ca/R%	68.9	56.9	49.7	38.0	27.3	20.5	38.6
Mg/R%	23.2	30.3	31.1	39.8	34.2	27.0	32.1

\* average of 79 data for (Ca, Mg)-buserite-rancieite.

\*\* R = Mn<sup>2+</sup> + Ca + Mg + Fe + Zn + K + Na**Fig. 2.** Ca-Mn<sup>2+</sup>-Mg triangular diagram for (Ca, Mg)-buserite-rancieite from Janggun mine.

ing relative humidity and the crest of the peak gradually shifted from 9.86 Å at 93% RH to 9.52 Å at 6% RH. The 001 peak of (Ca, Mg)-buserite at 93% RH was considerably sharp and symmetrical, but it became broader and asymmetrical with lowering the relative humidity.

On lowering the relative humidity from 93% down to 32%, the 001 peak decreased only 14% in intensity and from 9.86 Å to 9.73 Å in d-spacing. With prolonged time under the constant condition of 26% RH, the intensity of 001 peak decreased drastically by 62% with respect to initial intensity and d-spacing of 001 peak decreased from 9.73 Å to 9.60 Å, whereas the intensity of 7.6 Å peak of (Ca, Mg)-rancieite increased by 25% (Fig. 4). However, further lowering of the relative humidity down to 6% resulted in no further change in the

**Fig. 3.** X-ray diffraction patterns of (Ca, Mg)-buserite-rancieite sample in equilibrium with different relative humidities (RH).

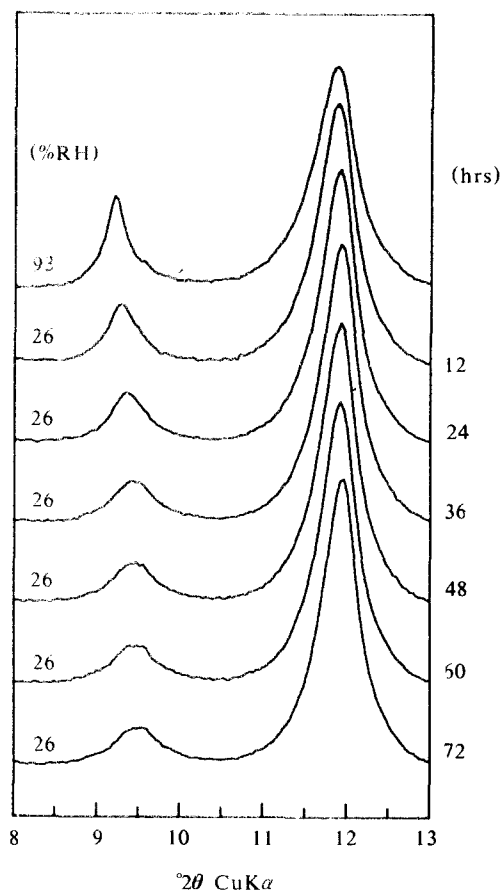


Fig. 4. X-ray diffraction patterns showing the dehydration of (Ca, Mg) buserite-rancieite sample at constant 6% RH with various lengths of time.

intensity. It is significant to mention that between 93% and 32% RH no additional peak appeared between 9.6 Å and 7.6 Å peak (Fig. 3), but the 001 peak became asymmetrical below 26% RH suggesting the presence of some minor intermediate peaks.

### Dehydration Experiment by Heating

Dehydration experiment of (Ca, Mg)-buserite-rancieite sample was carried out by increasing temperature from 40°C to 90°C with an interval of 5°C or 10°C and at a heating rate of 1°C/min. X-ray diffraction patterns were obtained after heating for one hour at each temperature of 40,

50, 60, 70, 80 and 90°C (Fig. 5). With increasing temperature, the basal reflection of (Ca, Mg)-buserite gradually shifted from 9.60 Å at 40°C to 7.42 Å at 90°C. The intensity of basal reflection of (Ca, Mg)-rancieite increased gradually with increasing temperature.

### Rehydration Experiment by Relative Humidity Control

Rehydration experiment was also carried out for the dehydrated sample by raising the relative humidity and then immersing it in water (Fig. 6). By raising up to 93% RH, the basal reflection of buserite increased slightly (13%) in intensity and sharpness. This slightly rehydrated sample was

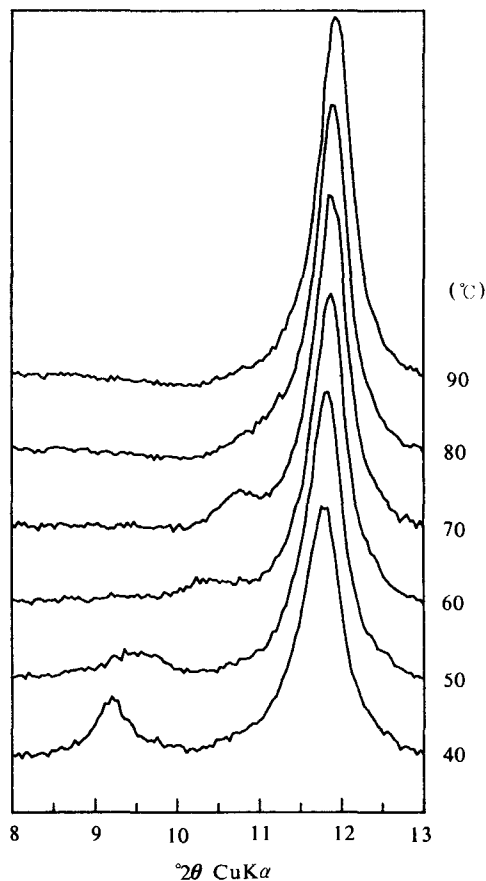
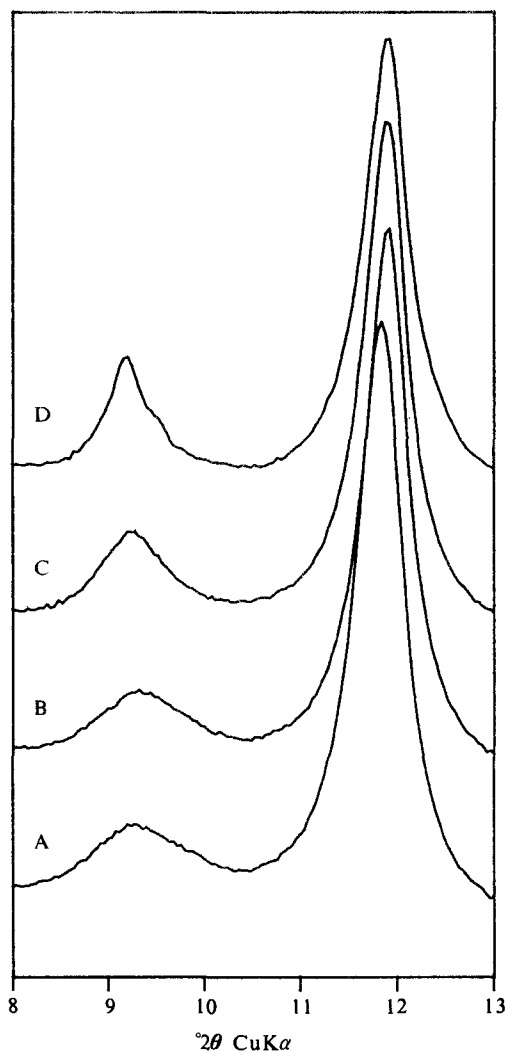


Fig. 5. X-ray powder diffraction patterns of (Ca, Mg)-buserite-rancieite sample at different temperatures.

## DISCUSSION



**Fig. 6.** X-ray diffraction patterns showing the rehydration of the dehydrated (Ca, Mg)-buserite-rancieite sample by controlling the relative humidity. A: dehydrated at 6% RH. B: rehydration at 32% RH. C: rehydration at 93% RH. D: immersion of sample (C) in water for 5 months.

immersed in water for 5 months for further hydration. It turned out from this experiment that the sample was further hydrated resulting in the increase (27%) in intensity and sharpness of the 001 peak. However, the complete rehydration was not achieved.

The occurrence of natural buserite was reported by several workers as mentioned above. But the chemistry of buserite has not been clearly defined yet. Ca-buserite from the Dongnam mine was qualitatively characterized by energy dispersive spectrum (Kim and Chang, 1989). The present paper may be the first report of the chemistry and dehydration behavior of natural (Ca, Mg)-buserite.

The sample studied in this work is actually mixture of (Ca, Mg)-buserite and (Ca, Mg)-rancieite. Dehydration experiment shows that the sample is completely dehydrated at 90°C. This fact indicates that the 10-Å phase in the studied sample is not todorokite but buserite, because todorokite is stable up to about 30°C (Bish and Post, 1989; Kim and Chang, 1989).

The chemical analyses of this sample can be regarded as those of (Ca, Mg)-buserite disregarding the water content as mentioned already. The number of water molecules in the formula of buserite is actually the average content of water molecules of (Ca, Mg)-buserite and (Ca, Mg)-rancieite. It, therefore, is expected that the actual content of water molecules of (Ca, Mg)-buserite may be larger than that calculated from the analysis of (Ca, Mg)-buserite-rancieite sample.

The results of dehydration by controlling the relative humidity as well as by heating show that there are two types of water molecules in (Ca, Mg)-buserite, that is, the very weakly bound water molecules and the weakly bound water molecules. The very weakly bound water molecules dehydrate very easily above about 26% RH and the weakly bound water molecules dehydrate gradually up to 90°C. Tejedor-Tejedor and Pateron (1979) show that synthetic Ca- and Mg-buserite are dehydrated to 7 Å phase at 33% RH and 3% RH, respectively, and that synthetic Ca-buserite is dehydrated again by increasing the relative humidity. The dehydration and rehydration phenomena of the (Ca, Mg)-buserite are in accordance with the combination of dehydration phenomena of synthetic Ca- and Mg-buserite.

It can be concluded that the dehydration of

(Ca, Mg)-buserite at 26% RH is due to the loss of very weakly bound water molecules, whereas dehydration from 40°C to 90°C is due to the loss of weakly bound water molecules in the interlayer.

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