

## Crystal Chemistry of Hexagonal 7 Å Phyllomanganate Minerals

### 7 Å 層狀構造型 酸化망간鑛物의 結晶化學

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**ABSTRACT:** Crystal-chemical study of hexagonal 7 Å phyllomanganate minerals reveals that they have hexagonal layer structures with variable c dimensions which depend on the nature of interlayer cations and content of water molecules between edge-sharing  $[\text{MnO}_6]$  octahedral layers.

Approximately one out of nine octahedral sites is statistically vacant, leading to the general unit cell formula  $\text{R}_{2x}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$ , where  $\text{R} = \text{Ca}, \text{Mn}^{2+}, \text{Mg}, \text{K}, \text{Na}$ ;  $x = 0.09-0.14$ ;  $n = 0.37-0.84$ ,  $Z = 1$ . The minerals of this formula fall under the name of rancieite group. It includes Ca-dominant (rancieite),  $\text{Mn}^{2+}$ -dominant (takanelite), Na-dominant (birnessite), and Mg-dominant members. Minerals of the rancieite group occur predominantly in two different hydration states, i.e., n shows the values around 0.35 and 0.75. It is suggested that minerals of higher hydration state be called as species (i.e., rancieite, etc.) and those of lower hydration state be called as dehydrated varieties (i.e., dehydrated rancieite, etc.).

**요약:** 육방정계의 7 Å 층상망간광물들에 대한 결정화학적 연구에 의하면 이 광물들은 층을 공유하고 있는  $[\text{MnO}_6]$  팔면체층 사이에 존재하는 층간 양이온의 성질과 그리고 물분자의 함량에 따라 c 축의 길이가 변하는 층상구조를 가지고 있다. 이들 광물의 화학조성과 구조에 대한 연구결과 팔면체 site 9개마다 약 1개의 site가 비어 있어서 단위포에 대한 화학식은  $\text{R}_{2x}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$ 와 같이 된다. 여기서  $\text{R} = \text{Ca}, \text{Mn}^{2+}, \text{Mg}, \text{K}, \text{Na}$ ,  $x = 0.09-0.14$ ,  $n = 0.37-0.84$ ,  $Z = 1$ 이다. 이 화학식으로 표현될 수 있는 광물은 “란시아이트군” 광물로 부를 때 여기에 란시아이트 (Ca 멤버), 다카넬라이트( $\text{Mn}^{2+}$  멤버), 버네사이트 (Na 멤버) 및 Mg 멤버가 속한다. 란시아이트와 다카넬라이트는 고용체계열을 이루고 있으며 광물들은 주로  $n = 0.35$  및 0.75의 두 함수상태로 산출된다. 높은 함수상태에 있는 광물을 종(예: 란시아이트), 낮은 함수상태에 있는 광물을 탈수변종(예: 탈수 란시아이트)으로 부르는 것이 합당하다. 7 Å 층상망간광물의 정확한 감정을 위해서는 X-선회절분석 및 화학분석이 꼭 필수적이다.

## INTRODUCTION

Hexagonal 7 Å phyllomanganate minerals refer to hexagonal manganese oxide minerals that are characterized by layer structure with basal  $d(001)$  spacing in the range of 7.1–7.6 Å. The minerals include rancieite, birnessite and related phases and show widespread occurrence in marine and terrestrial manganese deposits.

Our present knowledge on these minerals is considerably limited due to the scarcity of precise characterization works available, owing to their

poor crystalline nature and common occurrence as mixtures with other phases. The relationship of 7 Å phyllomanganate minerals has not yet been studied in detail.

Although the name birnessite was originally given to the Na-dominant member of the 7 Å phyllomanganate minerals (Jones and Milne, 1956), it has been also applied to other cation-dominant members with  $d(001) = 7.1-7.4$  Å regardless of their chemistry in many previous works. Such an ambiguous application of the terminology has led to a considerable confusion in

the current understanding of phylломanganate minerals. Confusion is also arising in the differentiation of birnessite and rancieite. For instance, the phylломanganate mineral with  $d(001) = 7.4 \text{ \AA}$  was named birnessite by Frondel et al. (1960) and Yoshimura (1967), whereas rancieite by Sorem and Gunn (1967). Further confusion has arisen from takanelite which has same X-ray diffraction pattern as rancieite. All these confusions have been raised from the poor understanding of crystal chemistry of 7 Å phyllo-manganate minerals.

During the study on manganese ores, the present author was able to collect many different samples of 7 Å phylломanganate minerals from different localities. X-ray and chemical analyses of these samples were carried out to know the range and the cause of variation in chemistry and X-ray data which are generally encountered in these minerals.

Based on the data collected by the author and those by others, hexagonal 7 Å phyllo-manganate minerals are reviewed and then their crystal chemical nature is discussed in this paper.

## REVIEW OF PREVIOUS WORKS

Since the birnessite was first named by Jones and Milne (1956) from Birness, Scotland, it has been reported from many localities. Birnessite from Birness has the formula  $(\text{Na}_{0.7} \text{Ca}_{0.3}) \text{Mn}_7 \text{O}_{14} \cdot 2.8\text{H}_2\text{O}$  (Jones and Milne, 1956) and shows four powder diffraction lines. Electron microprobe analysis of birnessite from Boron, California gives the formula  $\text{Na}_{0.54} \text{Ca}_{0.51} \text{Mn}_{0.65}^{42+} \text{Mn}_{0.34}^{4+} \text{O}_{14.1} \cdot 2.9\text{H}_2\text{O}$  (Brown et al., 1971). The formula of birnessite from Finland is  $(\text{Ca}, \text{Na}, \text{K}) (\text{Mn}, \text{Fe}, \text{Al}, \text{Mg})_7 \text{O}_{14} \cdot n\text{H}_2\text{O}$  (Koliijonen et al., 1976). Birnessite from Cumington (actually Plainfield), Massachusetts, shows a considerably high MnO content (16.07%), but low content of  $\text{Na}_2\text{O}$  and  $\text{CaO}$  (Frondel et al., 1960). They gave the formula  $(\text{Ca}, \text{Mg}, \text{Na}_2, \text{K}_2)_x (\text{Mn}^{4+}, \text{Mn}^{2+}) (\text{O}, \text{OH})_2$ . It has been revealed by the present author that it is not birnessite, but a mineral related to takanelite as will be discussed later in this paper. Birnessite from the bottom beds of the Caribbean Sea shows

high Mg content as shown in the formula  $(\text{Na}, \text{K}, \text{Ca})_{0.83} \text{Mg}_{1.04} \text{Mn}_{5.96} (\text{Fe}, \text{Co}, \text{Ni}, \text{Cu})_{0.61} \text{O}_{13.6} \cdot 3.8\text{H}_2\text{O}$  (Glover, 1977). Recently Chukhrov et al. (1985) proposed the structural formula  $[\text{Mn}_{0.13} \text{Na}_{0.06} \text{K}_{0.06} \text{Ca}_{0.01} (\text{OH})_{0.22} (\text{H}_2\text{O})_{0.56}]^+ [\text{Mn}_{0.66} \text{Mg}_{0.21} \text{O}_{1.37} (\text{OH})_{0.63}]^-$  for the birnes-site from the Pacific Ocean.

Crystal structure of birnessite has not been determined because of its minute grain sizes. However, Feitknecht and Marti (1945), Buser et al. (1954) and Frondel et al. (1960) discussed the layer structure of 7 Å phylломanganates. More pertinent information on its structure has been derived from electron diffraction analysis of synthetic compounds by Giovanoli et al. (1970 a, b) and Giovanoli and Stahli (1970). According to them, the structure of synthetic birnessite,  $\text{Na}_4 \text{Mn}_{14} \text{O}_{27} \cdot 9\text{H}_2\text{O}$ , consists of alternating layers of edge-shared  $[\text{MnO}_6]$  octahedra and sheets of water molecules by analogy with chalcophanite structure (Wadsley, 1955). One out of six octahedral sites in the layer of linked  $[\text{MnO}_6]$  is vacant as compared with one out of seven in chalcophanite.

According to Chukhrov et al. (1978), the magnitude of the parameters of the hexagonal cell of birnessite under TEM are  $a = 2.87$ ,  $c = 7 \text{ \AA}$ , while the XRD data show  $c = 7.16 \text{ \AA}$ . The difference in  $c$  dimensions is probably due to a partial dehydration which might have taken place in vacuum and thereby contracted the mineral structure. They also show that the distribution of vacant positions in the octahedral layers of birnessite are apparently disordered as compared to chalcophanite. Burns and Burns (1977, 1979) reviewed the structure of the synthetic and natural birnessites. Recent EXAFS study on synthetic 10 Å and 7 Å phylломanganates by Stouff and Boulegue (1988) supports a model of the phylломanganates structure by Giovanoli (1969).

The name 'rancieite' dates back to Leymerie (1859). The name was later used by Lacroix (1910) and Hintze (1930) as a synonym of psilomelane. Fleischer and Richmond (1943) showed that rancieite should not be included in the psilomelane group, and proposed the formula  $(\text{Ca}, \text{Mn}^{2+}) \text{Mn}_4^{4+} \text{O}_9 \cdot 3\text{H}_2\text{O}$  for rancieite from Cuba. Perseil (1967) studied the material from the type

locality at Pyrene and gave the formula  $\text{RO} \cdot 4\text{MnO}_2 \cdot 4\text{H}_2\text{O}$ . Richmond et al. (1969) made a systematic study on materials from USA, Cuba, France and Bulgaria, and presented the formula  $(\text{Ca}, \text{Mn}^{2+})\text{O} \cdot 4\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ . Bardóssy and Brindley (1978) studied rancieite from a Greek occurrence and proposed the empirical formula  $(\text{Ca}_{0.55}\text{Mn}_{0.22}\text{Mg}_{0.04})\text{O} \cdot 4\text{MnO}_2 \cdot 3.66\text{H}_2\text{O}$ , which is close to that of mineral from Cuba. Chukhrov et al. (1979) calculated the formula of rancieite in correspondence with the formula  $\text{Ca}_2\text{Mn}_6^{4+}\text{O}_{14} \cdot 6\text{H}_2\text{O}$ . Barrese et al. (1986) characterized the rancieite from Italy, and gave the formula  $\text{CaMn}_4\text{O}_9 \cdot 4\text{H}_2\text{O}$ .

Rancieite has a hexagonal cell with  $a=2.841$   $c=7.540$  Å (Richmond et al., 1969) for the sample from Oriente Province, Cuba, and  $a=2.83(4)$ ,  $c=7.55$  Å for that from Greece (Bardóssy and Briandley, 1978). Rancieite has the hexagonal cell with  $a=2.88$ ,  $c=7$  Å under the electron microscope (Chukhrov et al., 1979). The decrease of the magnitude of  $c$ , as compared to that of the natural state, is the result of dehydration and redistribution of water in the structure under the influence of the vacuum of the electron microscope. The structure of rancieite was studied by Chukhrov et al. (1970, 1985) using electron diffraction and showed that the electron diffraction pattern of the (001) basal plane of rancieite contain only the rare intense network of reflections, which can be associated with the disordered distribution of vacancies in the octahedral layers, and that all the  $\text{R}^{2+}$  occupies interlayer positions. The layer type structure of rancieite that Giovanoli (1969) referred to as "the birnessite family" was also suggested by Bardóssy and Brindley (1978).

Although it has been generally accepted that birnessite and rancieite have similar layer structures as suggested by Giovanoli et al. (1970 a, b), Bardóssy and Brindley (1978), Potter and Rossman (1979), and Burns and Burns (1979), the relationship of two minerals has not been studied in detail.

Electron diffraction studies by Giovanoli et al. (1969), and Chukhrov et al. (1978; 1979) suggest that birnessite and rancieite have hexagonal cells in which the vacant octahedral sites are disor-

dered leading to  $c=7.0-7.5$  Å. However, Potter and Rossman (1979) concluded from their infrared study that birnessite and rancieite have similar layer structures, but significant differences in the arrangement of octahedral frameworks.

Detailed study on the relationship of birnessite and rancieite was discussed first by Chuhrov et al. (1979) and Kim (1980). Chukhrov et al. (1979) carried out electron diffraction and chemical studies, and insisted that rancieite and birnessites are members of the same isomorphous series of minerals of the chalcophanite structure type and that the difference between rancieite and birnessite lies in dissimilar interlayer cations. Kim (1980) showed that solid solution series exist between the Ca- and  $\text{Mn}^{2+}$ -dominant members and that main difference between two series lies in the difference of interlayer cation and the content of water molecules.

## CHEMICAL COMPOSITION

Chemical analyses of minerals were carried out using the electron-microprobe A. R. L. instrument (for cations) and by wet-chemical method (for Mn and  $\text{H}_2\text{O}$ ). Standards for electron-microprobe analysis include pure metals, synthetic and natural minerals. In order to differentiate  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  from total Mn, The available oxygen was determined by the titration (Furman, 1966). Available oxygen is allotted to  $\text{MnO}_2$  from the total Mn, and the remaining Mn is calculated as MnO.  $\text{H}_2\text{O}$  is total water. Total water was regarded as the interlayer water molecules. This is based on the present observation that on heating the rancieite and related phases the water started to escape already at  $50-60^\circ\text{C}$ , resulting in the decrease in the basal spacings of the hexagonal 7 Å phyllosulfate minerals.

Chemical analyses of selected hexagonal 7 Å phyllosulfate minerals including rancieite, birnessite, takanelite and other related phase, are given together with some of reported data in Table 1.

Examination of Table 1 reveals that when  $\text{O} = 18$ ,  $\text{Mn}^{4+}$  varies from 7.72–8.19 and averages 8.01 suggesting that the  $[\text{MnO}_6]$  octahedral layer has roughly  $\text{Mn}_8\text{O}_{18}$  composition due to

vacancies in octahedral sites. It suggests that approximately one out of nine octahedral sites is statistically vacant leading to  $\text{Mn}_{9-x}^{4+}\text{O}_{18}$  ( $x=0.81-1.28$ ) as the composition of octahedral layer in the 7 Å phyllosilicate minerals. The excess negative charges due to vacancy in octahedral sites are balanced by the mono- and divalent cations in the interlayers. The total number of

interlayer cations (R) varies from 1.72–2.60 approaching the value of  $2x$  in each mineral.

The above structural model led to the derivation of new general formula,  $\text{R}_{2x}\text{Mn}_{9-x}^{4+}\text{O}_{18} \cdot n\text{H}_2\text{O}$ , where  $\text{R}=\text{Mn}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+$ ;  $x$  is the total number of vacant sites per 18 oxygens;  $2x$  is the total number of interlayer cations per 18 oxygens, and  $n$  is 3–8. Assuming that  $x$  is

**Table 1.** Chemical analyses of hexagonal 7 Å phyllosilicate minerals of  $\text{R}_{2x}\text{Mn}_{9-x}^{4+}\text{O}_{18} \cdot n\text{H}_2\text{O}$  and their interpretation.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
MnO <sub>2</sub>	75.04	64.8	69.56	66.66	74.01	79.08	54.24	75.8
MnO	3.31	3.0	6.75	16.07	10.42	11.21	4.66	—
CaO	8.10	6.1	7.78	1.05	3.64	0.30	1.65	0.39
MgO	0.16	0.32	0.10	0.23	0.59	—	—	6.2
Na <sub>2</sub> O	0.12	0.11	0.02	0.16	—	0.04	2.17	1.9
K <sub>2</sub> O	0.26	0.12	0.08	0.09	0.33	1.40	—	1.8
H <sub>2</sub> O	12.62	13.69	7.21	10.83	11.50	7.97	10.87	10.34
Fe <sub>2</sub> O <sub>3</sub>	0.12	2.9	8.50	0.86	0.26	—	2.88	1.1
Al <sub>2</sub> O <sub>3</sub>	0.12	2.6	—	0.83	—	—	3.32	—
SiO <sub>2</sub>	0.61	0.7	—	2.62	—	—	18.92	0.9
others	0.12	0.31	—	1.47	—	—	0.28	1.57
total	100.50	97.65	100.87	100.87	100.75	100.00	98.99	100.00
Mn <sup>4+</sup>	0.896	0.906	0.870	0.858	0.881	0.910	0.906	0.892
Mn <sup>2+</sup>	0.049	0.049	0.104	0.253	0.152	0.058	0.095	—
Ca	0.150	0.124	0.151	0.021	0.067	0.005	0.043	0.007
Mg	0.004	0.010	0.003	0.006	0.015	—	—	0.157
Na	0.007	0.004	0.001	0.006	—	0.002	0.102	0.063
K	0.006	0.002	0.002	0.002	0.007	0.040	—	0.039
O	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
H <sub>2</sub> O	0.724	0.830	0.371	0.648	0.659	0.443	0.754	0.580
R	0.215	0.189	0.260	0.289	0.242	0.195	0.240	—
Ca/R	0.70	0.65	0.58	0.07	0.28	0.04	0.18	—
Mn <sup>2+</sup> /R	0.23	0.27	0.40	0.88	0.63	0.78	0.40	—
x	0.104	0.094	0.130	0.142	0.119	0.090	0.095	—
For 9 (R <sub>2x</sub> Mn <sub>9-x</sub> <sup>4+</sup> O <sub>18</sub> · n H <sub>2</sub> O)								
n	6.512	7.470	3.339	5.835	5.947	3.988	6.784	5.218
R	1.935	1.720	2.337	2.599	2.129	1.915	2.154	2.064
x	0.940	0.850	1.168	1.281	1.056	0.807	0.805	—

Note: Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were interpreted as due to impurities such as goethite, kaolinite and quartz.

- (1) Rancieite from Oriente Province, Cuba (Richmond et al., 1969).
- (2) Rancieite from Itéa, Greece (Bardóssy and Brindley, 1978).
- (3) Rancieite (dehydrated) from Anson Betts mine, Plainfield, Ma., U. S. A. (this work).
- (4) Takanelite from Anson Betts mine, Plainfield, Ma., U. S. A. (Fronzel et al., 1960).
- (5) Takanelite from Janggun mine, Korea (this work).
- (6) Takanelite (dehydrated) from Anson Betts mine, Plainfield, Ma., U. S. A. (this work).
- (7) Birnessite from Birness, Scotland (Jones and Milne, 1956).
- (8) Mg analogue of birnessite from Caribbean Sea (Glover, 1977). Electron microprobe data.

1, the formula becomes  $\text{RMn}_4^{4+}\text{O}_9 \cdot n\text{H}_2\text{O}$ , which has the same form as  $\text{CaMn}_4\text{O}_9 \cdot 3\text{H}_2\text{O}$  by Fleischer and Richmond (1943),  $(\text{Ca}, \text{Mn}^{2+})\text{O} \cdot 4\text{MnO}_2 \cdot 3\text{H}_2\text{O}$  by Richmond et al. (1969), and  $\text{CaMn}_4\text{O}_9 \cdot 4\text{H}_2\text{O}$  by Barrese et al. (1986). Fleischer and Richmond's (1943) formula is another expression of the same formula as  $\text{R}_{2x}\text{Mn}_{9-x}^{4+}\text{O}_{18} \cdot n\text{H}_2\text{O}$ , assuming  $x=1$ .

The formula  $\text{R}_{2x}\text{Mn}_{9-x}^{4+}\text{O}_{18} \cdot n\text{H}_2\text{O}$  is for the multiple cell consisting of nine unit cells. Therefore, the unit cell has the formula  $\text{R}_{2x}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$ , where  $x=0.09-0.14$ , and  $n=0.37-0.83$ . According to this new interpretation of chemical analyses, birnessite from Birness, Scotland (Jones and Milne, 1956) has the formula  $(\text{Na}_{0.10}\text{Mn}_{0.10}^{2+}\text{Ca}_{0.04})\text{Mn}_{0.91}^{4+}\text{O}_2 \cdot 0.75\text{H}_2\text{O}$ , whereas that from Plainfield, Ma., U. S. A. (Frondelet et al., 1960) has the formula  $(\text{Mn}_{0.25}^{2+}\text{Ca}_{0.02}\text{Na}_{0.01})\text{Mn}_{0.86}^{4+}\text{O}_2 \cdot 0.65\text{H}_2\text{O}$ .

On the basis of the dominant cations in the interlayer, the hexagonal  $7\text{\AA}$  phyllosilicate minerals are chemically divided into the following four members.

$(\text{Ca}, \text{Mn}^{2+})_{2x}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$	Rancieite
$(\text{Mn}^{2+}, \text{Ca})_{2x}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$	Takanelite
$(\text{Mg}, \text{Mn}^{2+})_{2x}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$	Mg analogue
$(\text{Na}, \text{Mn}^{2+})_{2x}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$	Birnessite

Among the above four members, rancieite, takanelite and birnessite are already existing species, whereas remaining Mg analogue of rancieite has not yet been described. Excluding the Na-dominant member (birnessite) and Mg-dominant member, we have the minerals in which Ca and  $\text{Mn}^{2+}$  are the dominant cations in the interlayer. Chemistry of these minerals suggests that a solid solution series exists between two end members;  $\text{Ca}_{2x}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$  and  $\text{Mn}_{2x}^{2+}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$ . The various ratios of the dominant cation to the total interlayer cations ( $\text{Mn}^{2+}/\text{R}$  and  $\text{Ca}/\text{R}$ ) (Table 1) also display such a relation.

The content of water molecules of the hexagonal  $7\text{\AA}$  phyllosilicate minerals is considerably variable from sample to sample and even in one species. The number of water molecules per each formula unit in the minerals studied ranges from 0.37 to 0.83. However, excluding the Na- and Mg-dominant members, both Ca-

and  $\text{Mn}^{2+}$ -dominant members show a discontinuity between  $n=0.44$  and  $0.65$ . Both members occur predominantly in two different hydration states;  $n=0.37-0.44$  and  $0.65-0.83$  in nature.

## X-RAY DIFFRACTION DATA

X-ray diffraction data were obtained from powder films using 114.6mm Gandolfi camera and  $\text{FeK}\alpha/\text{Mn}$  radiation. The original birnessite of Jones and Milne (1956) has 4 diffraction lines at 7.27, 3.60, 2.44, and  $1.412\text{\AA}$ . An examination of X-ray powder patterns of birnessites so far reported, shows that there is a wide variation in their interplanar spacing, especially in those of the first two lines. Such a variation is also observed in the X-ray powder patterns of rancieites.

The X-ray powder data of hexagonal  $7\text{\AA}$  phyllosilicate minerals in this study were indexed on hexagonal cells. The X-ray powder diffraction data and unit cell parameters of each member of  $7\text{\AA}$  phyllosilicate minerals are given in Table 2. The unit cell content (Z) is one.

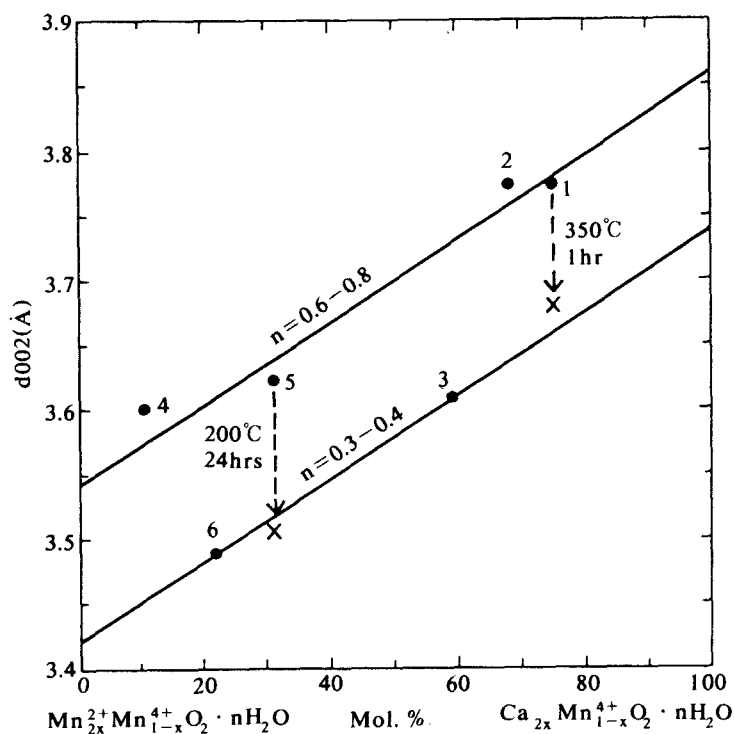
## CRYSTAL CHEMISTRY

Among the four members that are based on the dominant cation in the interlayer of  $7\text{\AA}$  phyllosilicate minerals,  $\text{Mn}^{2+}$  member has not been studied in detail so far. In order to know the crystal-chemical relation between Ca- and Mg-dominant members,  $d(002)$  vs. chemical composition were plotted in Fig. 1 in terms of a system consist of two end members;  $\text{Ca}_{2x}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$  and  $\text{Mn}_{2x}^{2+}\text{Mn}_{1-x}^{4+}\text{O}_2 \cdot n\text{H}_2\text{O}$ . Considering the difference in ionic radii of  $\text{Ca}^{2+}$  ( $0.99\text{\AA}$ ) and  $\text{Mn}^{2+}$  ( $0.80\text{\AA}$ ), it is expected that ionic substitution in the interlayer results in the distribution pattern of points with high gradient as shown in Fig. 1. In calculating the mole percentage of  $\text{Mn}^{2+}$  and Ca, minor Mg was added to  $\text{Mn}^{2+}$ , and Na to Ca, since Mg is similar to  $\text{Mn}^{2+}$ , and  $\text{Na}^+$  and K to Ca in ionic radii. K is nearly negligible because of its small amount.

However, a close examination of Fig. 1 shows that minerals are plotted along two parallel curves; upper curve with  $n=0.65-0.83$  and lower curve with  $n=0.37-0.44$ . Minerals with  $n$  between

**Table 2** X-ray powder diffraction data of hexagonal 7 Å phylломanganate minerals. Numbers in ( ) are the same as in Table 1.

(1)			(3)		(4)		(5)			(6)		(7)	
Rancieite (Oriente Province, Cuba; Richmond et al., 1969)			Rancieite (dehydrated form) (Anson Betts mine, Ma., U. S. A.; this work)		Takanelite (Anson Betts Mine, Ma., U. S. A.; Fronzel et al., 1960)		Takanelite (Janggun mine, Korea; this work)			Takanelite (dehydrated form) (Anson Betts mine, Ma., U. S. A.; this work)		Birnessite (Birness, Scotland ; Jones and Milne, 1956)	
I	d(Å)	hkl	I	d(Å)	I	d(Å)	I	d(Å)	hkl	I	d(Å)	I	d(Å)
s	7.57	001	s	7.37	s	7.31	s	7.25	001	s	6.98	s	7.27
m	3.77	002	w	3.61	w	3.60	w	3.619	002	w	3.49	w	3.60
w	2.46	100	m	2.424	m	2.44	m	2.451	100	s	2.461	m	2.44
m	2.34	101	w	2.347			w	2.347	101				
m	2.06	102											
m	1.76	103											
m	1.423	110	m	1.411	m	1.418	m	1.429	110	s	1.422	m	1.412
a=2.841 Å			a=2.799 Å		a=2.818 Å		a=2.830 Å			a=2.842 Å		a=2.818 Å	
c=7.540 Å			c=7.22 Å		c=7.20 Å		c=7.240 Å			c=6.98 Å		c=7.20 Å	



**Fig. 1.** Variation of d(002) spacings as a function of composition of the solid solution series consisting of two end members;  $\text{Ca}_{2x}\text{Mn}_{1-x}\text{O}_2 \cdot n\text{H}_2\text{O}$  and  $\text{Mn}_{2x}\text{Mn}_{1-x}\text{O}_2 \cdot n\text{H}_2\text{O}$ . The upper curve is for the rancieite and takanelite, and the lower curve is for both's dehydrated phases.

0.44 and 0.65 have not yet been identified. More detailed study is necessary to prove the presence of such a gap in the content of water molecules in the  $\text{Mn}^{2+}$ - and Ca-dominant members. It can be said, however, that  $\text{Mn}^{2+}$ - and Ca-dominant mem-

bers are rather stable in both ranges of hydration states. The upper curve is for the more hydrated minerals, while the lower curve for the less hydrated minerals.

In order to know the relationship between

**Table 3.** Summary of crystal-chemical data of some hexagonal 7 Å phyllo-manganate minerals of formula  $R_{2x}Mn_{1-x}^{4+}O_2 \cdot nH_2O$ , and expected d(001) spacing for each mineral.

Mineral	For specimens studied				Expected	
	Dominant cation in R	x	n	d(001) (Å)	d(001) (Å)	
Rancieite	Ca	0.09-0.10	0.72-0.83	7.56-7.57	7.40-7.72	
Dehydrated rancieite	Ca	0.13	0.37	7.37	7.16-7.48	
Takanelite	Mn <sup>2+</sup>	0.12-0.14	0.65-0.66	6.98-7.31	7.08-7.40	
Dehydrated takanelite	Mn <sup>2+</sup>	0.09	0.44	6.98	6.84-7.16	
Birnessite	Na	0.10	0.75	7.27		

two curves, dehydration experiments on rancieite and Mn<sup>2+</sup> analogue of rancieite were carried out. On heating at 350°C for one hour, d(001) spacing of rancieite (sample No.1 in Fig. 1) from Oriente Province, Cuba, collapsed from 7.57 to 7.14 Å. On heating at 200°C for 24 hours, d(001) spacing of Mn<sup>2+</sup> analogue (sample No.5 in Fig. 1) of rancieite from the Janggun mine, Korea, collapsed from 7.25 to 6.90 Å. The dehydrated samples of this experiment are plotted near the lower curve in Fig. 1. It suggests that the major difference in d(001) spacings between two curves is due to the content of water molecules. In other words, the minerals on the lower curve are the dehydrated forms of those on the upper curve.

Crystal-chemical data of phyllo-manganate minerals studied as well as the expected d(001) spacings of each species and its dehydrated phase which were calculated from Fig. 1 are summarized in Table 3.

Chukhrov et al. (1985) suggested that Mn is present as Mn<sup>4+</sup> and Mn<sup>3+</sup> and (OH) is present in both the octahedral layer and interlayer in the birnessite from Pacific. In order to examine Chukhrov's model for all the 7 Å phyllo-manganate minerals, the actual 2x/x ratios in the formula  $R_{2x}Mn_{1-x}^{4+}O_2 \cdot nH_2O$  were measured for both cases when Mn in the interlayer is present as Mn<sup>3+</sup> or Mn<sup>2+</sup>, on the assumption that (OH) is present only in the interlayer. The results are given in Table 4.

The number of interlayer cation, theoret-

**Table 4.** The, measured 2x/x ratios in the formula  $R_{2x}Mn_{1-x}^{4+}O_2 \cdot nH_2O$  in different states of Mn in the interlayer R site.

Mineral	Measured 2x/x ratio	
	Mn <sup>3+</sup>	Mn <sup>2+</sup>
(1) Rancieite	1.65	2.07
(2) Rancieite	1.50	2.01
(3) Dehydrated rancieite	1.56	2.01
(4) Takanelite	1.38	2.04
(5) Takanelite	1.48	2.03
(6) Dehydrated takanelite	1.44	2.17
(7) Birnessite	1.74	2.67

tically, should be twice the number of vacancies (x) in the [MnO<sub>6</sub>] octahedral layer. Table 4 shows that when Mn in the interlayer is present as Mn<sup>2+</sup>, the 2x/x ratios nearly approach to 2.0 for rancieites and takanelites, but when it is present as Mn<sup>3+</sup> they deviate from 2.0. These facts suggest that the formulas based on (Mn<sup>4+</sup>, Mn<sup>2+</sup>) are reasonable in rancieites and takanelites, whereas those based on (Mn<sup>4+</sup>, Mn<sup>3+</sup>) are reasonable in birnessite. Determination of exact content of (OH) in minerals studied was not possible. Therefore, the possible content of (OH) has been included in the values of the interlayer water molecules.

## DISCUSSION

One of the current problems in manganese oxides is about the 7 Å phyllo-manganate minerals. Much confusion was raised in using the terms birnessite and rancieite, because the nature and relationship of both minerals have not been clearly known so far. Especially the name 'birnessite' has been used for all the manganese oxide minerals which have diffraction pattern similar to that of the original birnessite without considering the chemical composition.

A more confusing point is that the validity of rancieite has been questioned by Perseil and Giovanoli (1979) from their electron diffraction work. They show that the electron diffraction pattern and calculated magnitude of the unit cells of rancieite under vacuum of the electron microscope are close to that of birnessite as has suggest-

ed by Chukhrov et al.(1979). According to the dehydration experiment by the present author, dehydrated products of rancieite and its  $Mn^{2+}$  analogue are plotted respectively near the lower curve of Fig. 1. This is in accordance with the electron diffraction data. However, all these observations do not indicate that rancieite and birnessite are the same mineral species, but do suggest that both minerals have similar structures. The rancieite which was renamed as  $Mn^{2+}$ -birnessite by Perseil and Giovanoli (1979) might correspond to the  $Mn^{2+}$  analogue of rancieite in the present work. Although hexagonal 7 Å phylломanganate minerals have the same layer structures as discussed already, they show significant differences in the unit cell dimensions, the contents of cations and water molecules.

From the present study on the nature of hexagonal 7 Å phylломanganate minerals, it has been suggested that they have the common formula  $R_{2x}Mn_{1-x}^{4+}O_2 \cdot nH_2O$ , and are divided into four members; that is, Ca-dominant (rancieite),  $Mn^{2+}$ -dominant (takanelite), Na-dominant (birnessite), and Mg-dominant members. In addition, it has been known that Ca- and  $Mn^{2+}$ -dominant members form two separate solid solution series, each having the different hydration states.

Takanelite was newly characterized by the present author (Kim, in press). Takanelite,  $(Mn^{2+}, Ca) Mn_4^{4+}O_6 \cdot nH_2O$  ( $n=1.3$ ) which has been named by Nambu and Tanida (1971) as the  $Mn^{2+}$  analogue of rancieite and approved by IMA, becomes the subject of serious discussion. The fact that it has the same X-ray powder diffraction pattern as that of rancieite is not reasonable, considering the difference of ionic radii of Ca and  $Mn^{2+}$ . It should be plotted toward the  $Mn^{2+}$ -end member side of the upper curve in Fig. 1. It is not similar to the  $Mn^{2+}$  analogue of rancieite of the present study in various aspects. Considering the powder diffraction data of takanelite, it is unreasonable that it has high  $Mn^{2+}$  and low  $H_2O$  content. The fact that X-ray powder data of takanelite match those of rancieite quite well, suggests that it might be rancieite containing impurities such as todorokite and braunite, as

Nambu and Tanida (1971) shows in their X-ray data. The takanelite suggested in this study may be the true  $Mn^{2+}$  analogue of rancieite rather than the Nambu and Tanida's takanelite.

The Mg analogue of birnessite in this study was also originally called birnessite for the sample from Carribean Sea by Glover (1977). However, according to the present interpretation of its chemistry it might be the Mg analogue of birnessite. The structural and chemical characters of this mineral were also confirmed by the present author for sample which was sent from Dr. E. D. Glover. However, a problem is that it is considerably well crystallized giving 14-17 diffraction lines. It seems that more study is needed for justification of Mg analogue of birnessite.

It became clear from this study that the basal spacings of hexagonal 7 Å phylломanganate minerals depend on the nature of interlayer cations and the content of interlayer water between edge-sharing  $[MnO_6]$  octahedral layers. Since each species occurs showing wide variation in hydration state, it is reasonable that minerals with higher hydration be called species (i. e., rancieite, etc.) and those with lower hydration be called hydrarated varieties (i. e., dehydrated rancieite, etc.). Ideally, fully hydrated hexagonal 7 Å phylломanganate minerals might have  $n=1$  in the formula. The expected  $d(001)$  values of each species and dehydrated species are given in Table 3.

It is difficult to identify the mineral species of 7 Å phylломanganate minerals only by X-ray diffraction, because both the higher hydrated and the lower hydrated curves are overlapped in  $d(001)$  spacings. For instance, a mineral with  $d(002)=3.60 \text{ \AA}$  may be either the  $Mn^{2+}$  analogue of rancieite (sample No.4) or dehydrated rancieite (sample No. 3). Therefore, as far as the identification of 7 Å phylломanganate minerals is concerned, data from both X-ray diffraction and chemical analysis of the mineral are indispensable. Otherwise, exact identification is not possible.

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