

## MANGANESE MINERALS IN CLAYS: A REVIEW

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**Abstract**—Vernadite ( $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ ) is a mineral with a poorly ordered structure. Its synthetic analogue is designated  $\delta\text{-MnO}_2$ . Birnessite and vernadite are independent mineral species and cannot be described further under the same name. They have similar hexagonal unit-cell parameters,  $a_0$ , but different  $c_0$  parameters. Rancieite has a structure similar to that of birnessite. Calcium bearing, 14-Å birnessite occurring in nature was first described by the authors. In addition to the todorokite having the parameters  $a_0 = 9.75 \text{ \AA}$ ,  $b_0 = 2.84 \text{ \AA}$ , and  $c_0 = 9.59 \text{ \AA}$ , other species of natural todorokite are known having  $a_0$  parameters that are multiples of 4.88 Å equal to 14.6 and 24.40 Å, the  $b_0$  and  $c_0$  parameters being the same.

**Key Words**—Birnessite, Ca-birnessite, Manganese, Rancieite, Todorokite, Vernadite.

### INTRODUCTION

Like iron oxides, manganese oxides in the form of various mineral species are typical constituents of many clays and are formed by the oxidation of  $\text{Mn}^{2+}$  contained in low-temperature solutions or in hypergene minerals. The determination of the properties and compositions of manganese minerals that occur as microcrystalline aggregates with other minerals presents considerable difficulties. Consequently, our knowledge of these materials is far from complete. The following review of some of the most important manganese minerals in clays is based on both published and unpublished data obtained by X-ray diffraction (XRD), infrared spectroscopic (IR), and analytical electron microscopic techniques.

### VERNADITE

Vernadite was described first and named by Betekhtin (1940) who gave it the formula  $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ . As demonstrated by the authors (Chukhrov *et al.*, 1978a), vernadite is a common manganese mineral formed by weathering and during the formation of certain sedimentary rocks. X-ray powder diffraction patterns of natural vernadite are similar to those of the synthetic manganese oxide designated  $\delta\text{-MnO}_2$ , which, like vernadite, also contains much water. The composition of natural vernadite may be expressed by the formula  $\text{MnO}_2 \cdot m(\text{R}_2\text{O}, \text{RO}, \text{R}_2\text{O}_3) \cdot n\text{H}_2\text{O}$ , where R = mono-, di-, and trivalent cations. Some scientists describe natural vernadite as  $\delta\text{-MnO}_2$  or as birnessite.

The diffraction patterns of synthetic  $\delta\text{-MnO}_2$  and vernadite have  $d$  spacings at  $\sim 2.4$  and  $\sim 1.4 \text{ \AA}$ ; however, birnessite yields additional reflections at 7.0–7.2 Å, 3.5–3.6 Å, and other spacings (Table 2). According to Buser *et al.* (1954), crystallites of  $\delta\text{-MnO}_2$  are as thick as 2–3 atomic layers. Bricker (1965) considered the  $\delta\text{-MnO}_2$  particles to be two-dimensional.

Most natural vernadites formed by precipitation from solution by the micro-organism oxidation of  $\text{Mn}^{2+}$ . This process has been repeated in special laboratory experiments (Figure 1). Vernadite is formed also by replacement of todorokite (Figure 2) which appears to be stable in a less oxidizing environment. The important prerequisite for vernadite precipitation is a very rapid oxidation of  $\text{Mn}^{2+}$ , which prevents the formation of more stable minerals. Enormous amounts of vernadite are found in deep-sea ferro-manganese nodules and micronodules confined to deep-sea muds.

The fullest picture of the structural features of vernadite may be deduced from electron diffraction patterns of the lath-particles of this mineral. The spot patterns display hexagonal symmetry with  $a_0 = 2.86 \text{ \AA}$  similar to the  $a_0$  value found for birnessite. A  $c_0$  value of  $\sim 4.7 \text{ \AA}$  has been determined from electron diffraction patterns of vernadite laths tilted with respect to the electron beam; some reflections of these patterns at  $d \sim 2.20 \text{ \AA}$  lie near the 100,  $1\bar{1}0$ , and 010 reflections, but further from the axis of tilting than the latter. They may be considered as the 101,  $1\bar{1}1$ , and 011 reflections. The 101 reflection is often recognized in the ring electron diffraction patterns of tangled flaky aggregates. Basal reflections from the bent edges of vernadite flakes have not been observed. The  $a_0$  parameter of vernadite (2.86 Å) is approximately equal to the edge length of the  $\text{MnO}_6$ -octahedron, and the  $c_0$  parameter ( $\sim 4.7 \text{ \AA}$ ) is equal to the thickness of a double layer of close packed oxygen ions.

The vernadite structure is rather disordered. It can be represented as a double layer of hexagonally close packed oxygen ions and water molecules, in which statistically less than half of the octahedra are occupied by manganese ions. The octahedron occupation coefficient is supposedly dependent on the percentage of molecular water,  $\text{Mn}^{2+}$  or  $\text{Mn}^{3+}$ , and other cations in the total composition. By its diffraction features ver-

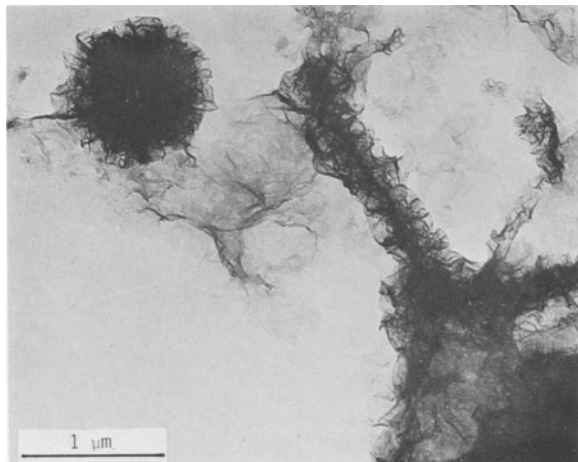


Figure 1. Transmission electron micrograph of vernadite as a product of bacterial synthesis.

vernadite is generally similar to  $\delta'$ -FeOOH (feroxyhite). However, according to the structural model of  $\delta'$ -FeOOH, the electron diffraction patterns should contain a 102 reflection at  $d = 1.69 \text{ \AA}$ , which is much more intense than the 101 reflection. Vernadite does not yield a 102 reflection. In contrast, both the 101 reflection of the synthetic  $\delta'$ -FeOOH and the 101 reflection of natural feroxyhite are much stronger than the 102 reflection, a difference that can be explained by spatial disorders in  $\delta'$ -FeOOH (feroxyhite). The presence of water molecules and of other elements (Na, K, Ca, etc.) in addition to manganese in the structure of vernadite increases its deviation from the ideal model, and consequently reduces the intensity of the 102 reflection so much that it cannot be located in the patterns.

The IR spectrum of vernadite is characterized by an intense band with maxima at  $500$  and  $435 \text{ cm}^{-1}$  (the valent oscillations of Mn–O bonds). The maxima are not well resolved, and their intensities are similar (the intensity of the maximum at  $435 \text{ cm}^{-1}$  is somewhat higher). The absorption bands of vernadite bands are similar in shape and habit to those of birnessite indicating that the occupation of octahedral layers of both minerals is similar.

As shown by electron diffraction data, vernadite contains iron mainly in the form of a mechanical admixture of feroxyhite or goethite, and more rarely, lepidocrocite. Vernadite developed from todorokite commonly displays relic inclusions.

Chemical analyses of homogeneous vernadites are given in Table 1. The empirical formulae are as follows: from the Kurchatov fracture zone:  $\text{MnO}_2 = 1.000$ ;  $\text{R}_2\text{O} = 0.043$ ;  $\text{RO} = 0.325$ ;  $\text{R}_2\text{O}_3 = 0.140$ ;  $\text{H}_2\text{O}^+ = 0.721$ ;  $\text{H}_2\text{O}^- = 1.920$ ;  $\text{MnO}_2/(\text{R}_2\text{O} + \text{RO} + \text{R}_2\text{O}_3) = 1.84$ ; from Lepkhe-Nelm:  $\text{MnO}_2 = 1.000$ ;  $\text{R}_2\text{O} = 0.006$ ;  $\text{RO} = 0.263$ ;  $\text{R}_2\text{O}_3 = 0.082$ ;  $\text{H}_2\text{O}^+ = 0.255$ ;  $\text{H}_2\text{O}^- = 1.160$ ;  $\text{MnO}_2/(\text{R}_2\text{O} + \text{RO} + \text{R}_2\text{O}_3) = 2.84$ .

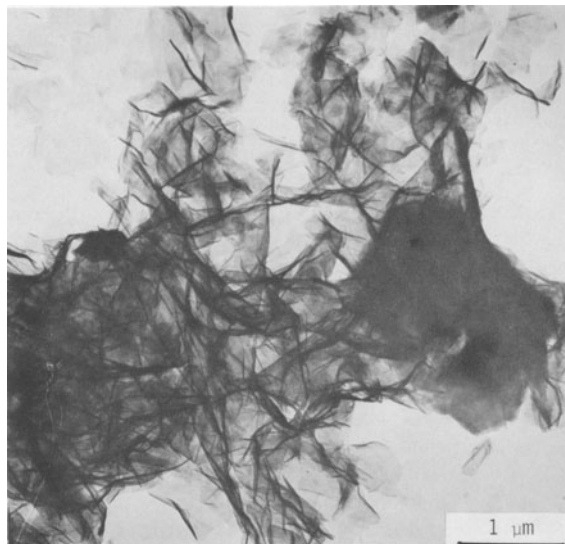


Figure 2. Transmission electron micrograph of vernadite after todorokite. Chiatura deposit in Georgia.

### BIRNESSITE

Birnessite was described by Jones and Milne (1956) from pebbles collected in the vicinity of Birness in Scotland. In X-ray powder diffraction pattern (Table 2) it gave four lines. Its formula is  $\text{Na}_{0.7}\text{Ca}_{0.3}\text{Mn}_7\text{O}_{14} \cdot 2.8 \text{ H}_2\text{O}$ . Electron microprobe analysis of monomineralic fractions of birnessite from Boron, California (Brown *et al.*, 1971), which appeared under the electron micro-

Table 1. Chemical analyses of vernadites.

	Kurchatov Fracture Zone, Pacific Ocean (wt. %)	Lepkhe-Nelm, Kola Peninsula (wt. %)
SiO <sub>2</sub>	0.80	1.30
TiO <sub>2</sub>	1.50	—
MnO <sub>2</sub>	46.47	56.45
P <sub>2</sub> O <sub>5</sub>	—	1.30
Al <sub>2</sub> O <sub>3</sub>	1.00	1.00
Fe <sub>2</sub> O <sub>3</sub>	10.47	7.00
MnO	1.09	4.81
MgO	2.62	0.28
CoO	3.41	—
PbO	0.34	—
CaO	2.15	5.17
SrO	—	0.33
BaO	—	1.93
NiO	0.95	—
Na <sub>2</sub> O	2.29	0.12
K <sub>2</sub> O	0.60	0.23
CO <sub>2</sub>	—	3.70
H <sub>2</sub> O <sup>+</sup>	6.94	3.00
H <sub>2</sub> O <sup>-</sup>	18.50	13.53
Cl	1.19	—
Total	100.32	100.15

Table 2. Diffraction characteristics of birnessites.

Scotland (Jones and Milne, 1956)		Massachusetts (Frondel <i>et al.</i> , 1960)		Mexico (Levinson, 1962)		Washington (Sorem and Gunn, 1971)		California (Brown <i>et al.</i> , 1971)	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
7.27	strong	7.31	10	7.2	10	7.2	100	7.24 ± 0.07	strong
3.60	weak	3.60	5	3.60	5	3.6	50	3.55 ± 0.07	medium-weak
2.44	medium	2.44	7	2.40	6	2.45	10	2.46 ± 0.01	medium
1.412	medium	1.418	8	1.42	1	1.42	10	1.42 ± 0.04	medium
Pyrenees (Perceil <i>et al.</i> , 1974)		Finland (Koljonen <i>et al.</i> , 1976)		Caribbean Sea (Glover, 1977)		Pacific Ocean (present account)			
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	(hkl)	
7.18	strong	7.28 ± 0.05	100	7.08	100	7.16	strong	001	
3.60	medium	3.63 ± 0.02	10	3.547	28	3.57	medium	002	
2.45	weak	2.44 ± 0.01	10	2.468	17	2.48	weak	100	
				2.333	43	2.35	medium-weak	101	
				2.031	24	2.02	weak	102	
				1.775	1			004	
				1.711	29	1.72	very weak	103	
1.42	weak	1.414 ± 0.004	5	1.426	17	1.435	medium	110	
				1.398 <sup>1</sup>	10			111	

<sup>1</sup> Reflections with d below 1.398 Å are not included.

scope to be composed of slightly bent platelets about 0.2 μm thick, corresponds to the formula  $\text{Na}_{0.54}\text{Ca}_{0.51}\text{Mn}^{2+}_{0.65}\text{Mn}^{4+}_{6.34}\text{O}_{14.1} \cdot 2.9\text{H}_2\text{O}$ . The formula of birnessite from the fluvio-glacial deposits in Finland is as follows:  $(\text{Ca}, \text{Na}, \text{K})(\text{Mn}, \text{Fe}, \text{Al}, \text{Mg})_7\text{O}_{14} \cdot n\text{H}_2\text{O}$  (Koljonen *et al.*, 1976).

The chemical analysis of birnessite from Cumington, Massachusetts, shows a considerably greater  $\text{MnO}_2$  content (16.07%) than birnessite from Boron, whereas the percentages of  $\text{Na}_2\text{O}$  and  $\text{CaO}$  are lower. The maximum amount of iron (12.3%  $\text{Fe}_2\text{O}_3$ ) has been found in birnessite from Mexico containing some admixed pyrolusite (Levinson, 1962). Several birnessite species contain no iron (Jones and Milne, 1956; Finkelman *et al.*, 1974).

Glover (1977) described birnessite from the bottom beds of the Caribbean Sea in the form of nodules less than 1 mm in diameter. This material has the formula  $(\text{Na}, \text{K}, \text{Ca})_{0.83}\text{Mg}_{1.04}\text{Mn}_{5.96}(\text{Fe}, \text{Co}, \text{Ni}, \text{Cu})_{0.16}\text{O}_{13.6} \cdot 3.8\text{H}_2\text{O}$ . In addition to the higher amount of K, Mg, Ca, and Na, this birnessite has a considerably higher degree of structural order and gives as many as 17 XRD lines, whereas the diffraction patterns of other birnessites display only the strongest lines. Giovanoli *et al.* (1970) concluded that birnessite has a structure related to that of chalcophanite  $(\text{Zn}_2\text{Mn}^{4+}_6\text{O}_{14} \cdot 6\text{H}_2\text{O})$ .

In electron micrographs, birnessite appears as thin laths up to 0.3 μm long (Figure 3). The d-spacings of birnessite from the Pacific Ocean, studied by the present authors are compared with data for other birnessites in Table 2. Selected area electron diffraction (SAD) patterns from the basal faces of birnessite microcryst-

tallites show a hexagonal net of spot reflections. The bent edges of the laths yield basal 001 reflections corresponding to  $d(001) = 7.03\text{--}7.05$  Å. The diffraction pattern of the laths tilted to the electron beam show 101, 102, and 103 reflections with spacings at ~2.34, 2.05, and 1.72 Å, respectively, in addition to hk0 and 001 reflections. The electron diffraction measurements have made it possible to determine the dimensions of the birnessite hexagonal unit cell as  $a_0 = 2.87$  Å and  $c_0 = 7.05$  Å. According to the XRD data, the birnessite from the Pacific Ocean floor has a somewhat higher value of  $c_0 = 7.16$  Å ( $d(001) = 7.16$  Å). The difference is probably due to a partial dehydration which might have taken place in vacuum and thereby contracted the mineral structure. Table 3 contains the electron microprobe data of the birnessite from the Pacific Ocean. From the analytical data, a formula of the chalcophanite type is obtained as follows:  $(\text{Na}_{0.650}\text{Ca}_{0.303}\text{K}_{0.116})(\text{Mg}_{0.542}\text{Co}_{0.005}\text{Zn}_{0.001}\text{Mn}^{3+}_{0.382}\text{Fe}_{0.001})\text{Mn}_{6.000}\text{O}_{13.808} \cdot (\text{H}_2\text{O})_{5.197}$ .

In view of the structural similarity of birnessite and chalcophanite, it has been supposed that the octahedra contain four-valent manganese atoms only, and that other cations ( $\text{Mn}^{3+}$  or  $\text{Mn}^{2+}$ , Mg, Ca, Na, etc.) occupy the space between the octahedral layers and the layers of  $\text{H}_2\text{O}$ . In calculating the formula it has been assumed that there are  $\text{Mn}^{3+}$  ions in the interlayer positions. The amount of oxygen has been deduced from the sum of cation charges in the formula on the assumption that a part of manganese occurs in the form of  $\text{Mn}^{3+}$ . A comparison of  $F^2(00\ell)$  for the structural model with the experimental intensities for 001 reflections supports the proposed model.



Figure 3. Transmission electron micrograph of birnessite from the Chiatura deposit in Georgia.

Unlike chalcophanite, birnessite includes interlayer cations of varying valence, which according to the values of the ionic radii can be subdivided into two groups: ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ) and ( $\text{Co}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ). The octahedral layers of birnessite appear less imperfect than those of chalcophanite. Birnessite is notably deficient in water; the structural positions of the water molecules may be occupied by oxygen atoms. The main structural feature of birnessite that distinguishes it from chalcophanite is a random distribution of defective octahedra and associated interlayer cations. Therefore birnessite is characterized by a hexagonal unit cell with minimal values of  $a_0 = 2.84 \text{ \AA}$  (approximately equal to the edge length of the  $\text{MnO}_6$  octahedron base) and  $c_0 = 7 \text{ \AA}$  equal to the distance between adjacent octahedral layers (Chukhrov *et al.*, 1978b).

Of particular interest is a possible relation between birnessite and vernadite. The crystalline particles of vernadite and birnessite are discernible only under an electron microscope and appear as very minute (tens of Ångstrom units) laths, which are coiled, bent, or twisted so that they look like filaments. Compared with birnessite, the particles of vernadite are considerably thinner and smaller. The IR spectra of birnessite dis-

Table 3. Chemical analysis of birnessite from the Pacific Ocean.

Components	wt. %
$\text{SiO}_2$	0.06
$\text{MnO}_2$	77.64
$\text{Fe}_2\text{O}_3$	0.12
$\text{MgO}$	3.06
$\text{CoO}$	0.05
$\text{CaO}$	2.38
$\text{K}_2\text{O}$	0.76
$\text{ZnO}$	0.01
$\text{Na}_2\text{O}$	2.82
$\text{H}_2\text{O}$ (from difference to sum = 100%)	13.10
Total	100.00

play an intense band with maxima at  $510$  and  $470 \text{ cm}^{-1}$  (the valence oscillations of the Mn–O bonds). The boundary maxima are not well resolved; their intensities are comparable, but the high-frequency maximum at  $510 \text{ cm}^{-1}$  is somewhat more intense than the low-frequency one at  $470 \text{ cm}^{-1}$ .

The shape and intensity of the IR bands of birnessite and vernadite are similar, suggesting a similarity in filling of the octahedral layers of the two minerals. The main birnessite band is narrower than that of vernadite. One of its maxima ( $510 \text{ cm}^{-1}$ ) essentially coincides with a high-frequency maximum of vernadite ( $510 \text{ cm}^{-1}$ ), indicating that one of the Mn–O distances is similar in both minerals. Since the degree of occupation of the  $\text{MnO}_6$  octahedra of birnessite is greater than that of vernadite, its structure is more compact and more ordered.

The data reported here show that birnessite and vernadite ( $\delta\text{-MnO}_2$ ) are two independent mineral species and cannot be dealt with under the same name. Each belongs to the hexagonal system; the unit-cell parameters are almost identical along the  $a$  axis, but they are conspicuously different along the  $c$  axis. Birnessite has  $a_0 = 2.87$ ,  $c_0 = 7.05 \text{ \AA}$  (in vacuum); vernadite has  $a_0 = 2.86$ ,  $c_0 = 4.7 \text{ \AA}$ . Single crystal particles of both minerals can be identified only under an electron microscope. Birnessite is less common than vernadite.

#### RANCIEITE

For no substantial reasons rancieite has been assigned to the psilomelane group. Most rancieite aggregates are cryptocrystalline, and under the electron microscope, they look like irregularly shaped platelets (Figure 4).

At the Rancié deposit in France, rancieite occurs in lenticular ferromanganese ore bodies enclosed in lime-stones. Perceil (1967) concluded that the mineral from Rancié can be given the formula  $\text{RO} \cdot 4\text{MnO}_2 \cdot 4\text{H}_2\text{O}$ . Fleisher and Richmond (1943) stated that the inclusion of rancieite in the psilomelane group was not justified.

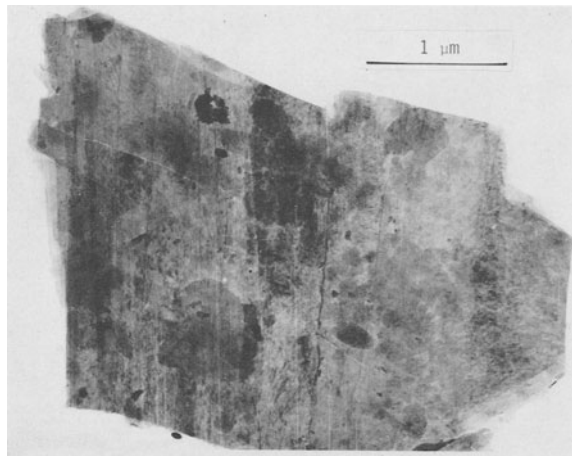


Figure 4. Transmission electron micrograph of rancieite from the Urals.

Rancieite from Cuba was given a formula of  $(\text{Ca}, \text{Mn}^{2+})\text{Mn}^{4+}_4\text{O}_9 \cdot 3\text{H}_2\text{O}$ , which later became common in the literature. In a later publication, Richmond *et al.* (1969) presented the formula as  $(\text{Ca}, \text{Mn})\text{O} \cdot 4\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ . A number of specimens examined by them and labeled as rancieite turned out to be impure todorokites. Judging by XRD patterns, rancieite from Rancié studied by Perseil, contains calcite and todorokite.

Recently, Bardossy and Brindley (1978) studied rancieite from a Greek occurrence at the contact of karst bauxites and underlying limestones. The empirical formula of this rancieite is  $(\text{Ca}_{0.55}\text{Mn}^{2+}_{0.22}\text{Mg}_{0.04})\text{O} \cdot 4\text{MnO}_2 \cdot 3.66\text{H}_2\text{O}$ . Chemically this rancieite appears similar to the species from Cuba whose formula can be written as  $(\text{Ca}_{0.73}\text{Mn}^{2+}_{0.21})\text{O} \cdot 4\text{MnO}_2 \cdot 3.25\text{H}_2\text{O}$ . Takanelite from Japan (Nambu and Tanida, 1971) is closely related to rancieite and contains  $\text{Mn}^{2+}_{0.89}\text{Ca}_{0.23}\text{Mg}_{0.03}$  per  $4\text{MnO}_2$  in the formula unit.

The parameters of the hexagonal unit cell of takanelite ( $a_0 = 3.68$ ,  $c_0 = 9.00$  Å) are believed to be incorrect. The powder pattern of this mineral can be indexed on the basis of a hexagonal cell analogous to that of rancieite with parameters  $a_0 = 2.843$ ,  $c_0 = 7.53$  Å.

Water from rancieite from Greece is considered as molecular (dehydration takes place between 25° and 300°C). At 300°C the  $d(001)$ -spacing characteristic of the mineral drops from 7.55 Å to 5.3 Å. Bardossy and Brindley (1978) concluded that rancieite belongs to a group of layered manganese hydroxides which contain various cations and water molecules between sheets of Mn-O or Mn-OH octahedra. The parameters of the hexagonal unit cell of rancieite are  $a_0 = 2.83(4)$  Å and  $c_0 = 7.55$  Å.

XRD patterns of different rancieites have identical reflections. Some display the lines indicative of admixtures, such as todorokite, which can be seen by elec-



Figure 5. Infrared spectra of rancieite from the Urals (1 = sample 1, 2 = sample 2) and the birnessite from the Pacific Ocean (3 = sample 3). Abscissa in  $\text{cm}^{-1}$ .

tron microscopy. The particles of rancieite in the specimens prepared from the suspensions occur in electron microscope as irregularly shaped platelets similar to those of birnessite. Rancieite specimens from the Urals are characterized by a hexagonal cell with  $a_0 = 2.86$  Å and  $c_0 = 7.5$  Å.

From the electron diffraction data the authors have shown the hexagonal unit cell parameters of rancieite to be  $a_0 = 2.85$  and  $c_0 \approx 7$  Å (7.0–7.05). This  $c_0$  value is less than that for natural rancieite which may be due to a partial dehydration of the mineral in the vacuum of the electron microscope.

The parameters of the unit cell and the character of the diffraction patterns generally points to a similarity between the rancieite and birnessite structures, which was noted by Bardossy and Brindley (1978). The IR

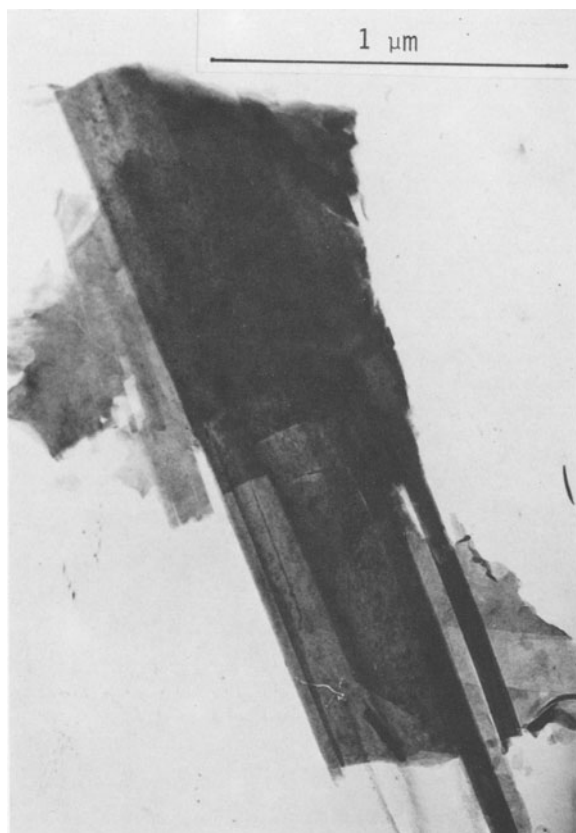


Figure 6. Transmission electron micrograph of 14-Å, Ca-bearing birnessite.

spectra of rancieite and birnessite also are similar (Figure 5).

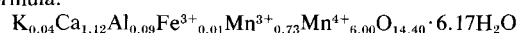
The present authors have confirmed the similarity of the unit-cell parameters of rancieite ( $a_0 = 2.85 \text{ \AA}$ ,  $c_0 = 7.50 \text{ \AA}$ ) and birnessite ( $a_0 = 2.84$ ,  $c_0 = 7.31\text{--}7.08 \text{ \AA}$ ). The difference between the two minerals lies in dissimilar interlayer cations. In rancieite, where the interlayer cation is Ca (in addition to  $\text{Mn}^{2+}$ ),  $d(001) \sim 7.5 \text{ \AA}$ . If the  $\text{Mn}^{2+}$  and  $\text{Ca}^{2+}$  are replaced by other cations (Na, K, Mg, etc.),  $d(001)$  diminishes to  $7.08 \text{ \AA}$ . The formula of an ideal calcium rancieite is  $\text{Ca}_2\text{Mn}_6\text{O}_{14} \cdot n\text{H}_2\text{O}$ , but no such species has been found in nature.

The variation of the calcium percentage in the rancieite-birnessite series may be determined from the ratio of Ca atoms in a formula unit calculated on the basis of  $\text{Ca}_2\text{Mn}_6\text{O}_{14} \cdot n\text{H}_2\text{O}$ , to the total number of the interlayer cations in it (Na, K, Mg, Ca,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ , etc.) which is usually equal to two. In typical rancieite this ratio varies from 0.4 to 0.8, whereas in birnessite it is between 0.2 and 0.3. Table 4 lists electron microprobe data for rancieite from the Sheliya deposit in the Urals. The excess of manganese over  $\text{Mn}_{6.00}$  in the formula is treated as  $\text{Mn}^{3+}$ . In the vacuum of the electron micro-

Table 4. X-ray microprobe analysis of rancieite from the Sheliya deposit in the Urals.

Components	wt. %
$\text{SiO}_2$	0.09
$\text{MnO}_2$	76.22
$\text{Al}_2\text{O}_3$	0.61
$\text{Fe}_2\text{O}_3$	0.15
CaO	8.20
$\text{K}_2\text{O}$	0.25
$\text{H}_2\text{O}$ (from difference to sum = 100%)	14.48
Total	100.00

Formula:



scope, all rancieites (like birnessites) have  $d(001)$  values of about  $7 \text{ \AA}$ .

The fact that many rancieites include admixed todorokite can be explained by the genesis of rancieite which replaces todorokite. It has to be noted that a newly formed rancieite, replacing todorokite, as in the case with vernadite, inherits the morphological features of todorokite, which are recognizable macroscopically. Oxygen-bearing solutions (those rich in calcium in particular) should be regarded as the main cause of the conversion of todorokite into rancieite.

#### BIRNESSITE-LIKE MINERALS

A coccolith mud specimen collected in 1977 by the members of the 24th Expedition aboard "Academician Kurchatov" from the Atlantis fracture zone in the Atlantic Ocean at a depth of 5520 m (270–280 cm beneath the ocean floor) was found to contain dark, brown-black micronodules about 0.5 mm in diameter (Chukhrov *et al.*, 1979). Microprobe analysis with a Kevex energy dispersive spectrometer revealed two minerals: a 14-Å, Ca-bearing birnessite and a 7-Å, Ca-bearing birnessite.

The 14-Å mineral occurs as elongated platelets (Figure 6) from fractions of a micrometer to a few micrometers in length. The platelets vary greatly in width after dispersion since they split into laths not larger than a few micrometers across.

The electron diffraction patterns of individual platelets taken with the basal plane normal to the beam show a dense hexagonal net of reflections. However, the hexagonal arrangement is somewhat distorted from particle to particle. The diffraction pattern has been interpreted in terms of an orthorhombic unit cell with  $a_0 = 8.53 \text{ \AA}$ ,  $b_0 = 15.1 \text{ \AA}$ , and  $c_0 = 14.1 \text{ \AA}$ . The phase having these parameters represents 14-Å, Ca-bearing birnessite. The parameters of this mineral are practically the same as those of synthetic Na-birnessite having  $a_0 = 8.52 \text{ \AA}$ ,  $b_0 = 15.33 \text{ \AA}$ , and  $c_0 = 14.39 \text{ \AA}$  (Giovanoli *et al.*, 1975). The small difference of the  $b_0$  and  $c_0$  param-

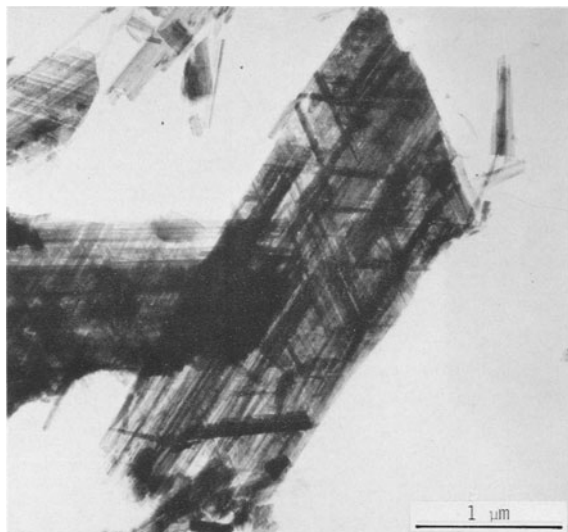


Figure 7. Transmission electron micrograph of todorokite particles from Charko Redondo, Cuba.

eters is probably due to variations in the degree of vacancy in the octahedral layers and to the presence of dehydrated birnessite in the vacuum of the electron microscope. Electron microprobe analysis of the platy microcrystallites shows that Mn and Ca are the principal cations in the natural 14-Å birnessite from these micronodules.

A second mineral in the nodules forms characteristic laths varying in diameter from fractions of a micrometer to several micrometers. The electron diffraction patterns display a hexagonal net of widely dispersed  $hk$  reflections. Many diffraction patterns from laths with coiled edges contain, apart from  $hk$  and  $001$  reflections, three-dimensional  $hkl$  reflections. The electron diffraction data show that the second mineral is characterized by a hexagonal unit cell with  $a_0 = 2.34$  Å and  $c_0 = 7.07$  Å. Electron microprobe measurements showed that the second mineral contains manganese and calcium and must be regarded as 7-Å, Ca-bearing birnessite.

### TODOROKITE

Todorokite has been found in weathering products in sedimentary manganese ores in deep-sea iron-manganese nodules, and in crusts. According to Straczek *et al.* (1960), the approximate formula of todorokite is  $(\text{Na}, \text{Ca}, \text{K}, \text{Mn}^{2+})(\text{Mn}^{4+}, \text{Mn}^{2+}, \text{Mg})_6\text{O}_{12} \cdot 3\text{H}_2\text{O}$ . The variation of  $\text{Mn}^{4+}$ ,  $\text{Mn}^{2+}$ , or  $\text{Mn}^{3+}$  contents in todorokites is not known. The mineral is orthorhombic (or monoclinic, with beta near  $90^\circ$ ) with  $a_0 = 9.75$  Å,  $b_0 = 2.84$  Å, and  $c_0 = 9.59$  Å. Under the electron microscope it appears as thin laths parallel to  $(001)$  usually elongated along the  $b$  axis.

Burns and Burns (1977) postulated that todorokite

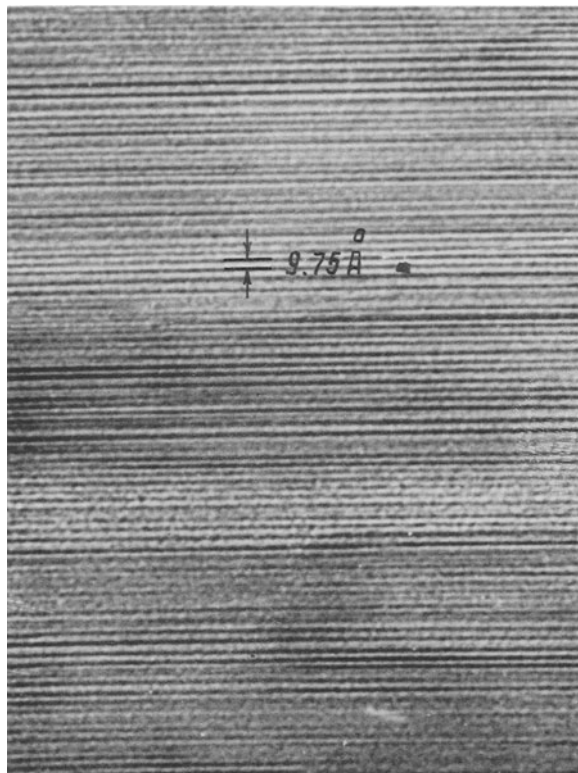


Figure 8. Direct electron microscope image of the planes  $(100)$  of the todorokite with  $a_0 = 9.75$  Å.

has a structure related to that of hollandite which has features similar to the structure of rutile as demonstrated by the tendency of todorokite to form as flat, netted trillings of elongated particles discernible under the electron microscope. These intergrowths are characteristic of todorokite, and form hexagonal, trigonal, and rhombic nets (Figure 7). The electron diffraction patterns of the three kinds of intergrowths are superpositions of three diffraction patterns with relative rotations of  $120^\circ$ . According to SAD data, the basal plane of a todorokite lath is  $(001)$ .

Electron diffraction patterns of todorokites examined by the authors show that, apart from todorokite with parameters  $a_0 = 9.75$ ,  $b_0 = 2.84$ , and  $c_0 = 9.59$  Å found in many deposits throughout the world, species having  $a_0 = 14.6$  Å and  $24.40$  Å also occur in nature, as proved by a study of specimens collected from the Pacific Ocean, Bakal, and Sterling Hill, New Jersey (the  $b_0$  and  $c_0$  values are the same). Macroscopically, as well as under the electron microscope, these todorokites appear indistinguishable from todorokites with  $a_0 = 9.75$  Å. A difference between the  $a_0$  parameter can be seen in the direct electron microscope images showing the  $(100)$  spacings (Figures 8, 9). Individual laths with different  $a_0$  parameters, as shown by electron mi-

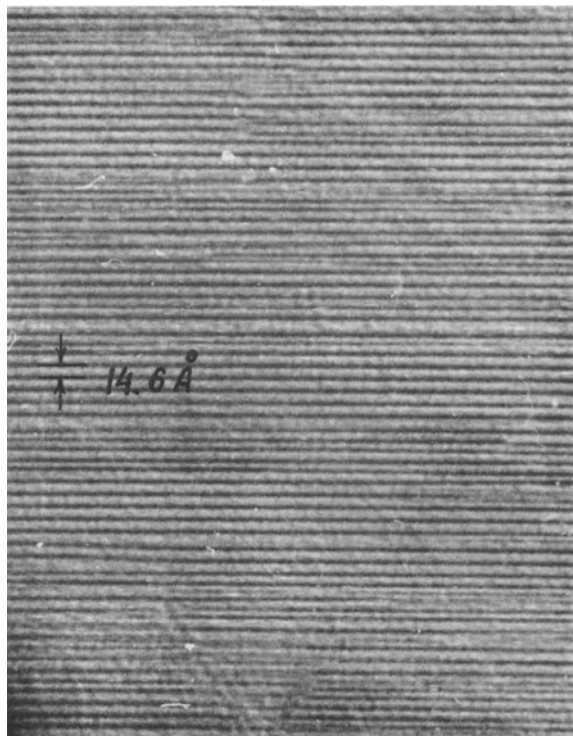


Figure 9. Direct electron microscope image of the planes (100) of the todorokite with  $a_0 = 14.6 \text{ \AA}$ .

croprobe have no appreciable chemical difference. The only dissimilarity displayed by the three species of todorokites is a variation of interplanar spacings characterized by spatial hkl reflections which give a clue to the true value of the  $a_0$  parameter. The strong hkl and (001) reflection of these structural varieties have approximately the same d-spacing (Chukhrov *et al.*, 1978c).

The  $a_0$  parameters of todorokites (9.75, 14.6, and 24.38 Å) are multiples of 4.88 Å. The different values are clearly indicated by the alternating frequency of reflections along the  $a^*$  axis. Thus in the electron diffraction pattern with (001) normal to the electron beam, todorokite with  $a_0 = 9.75 \text{ \AA}$  shows between strong reflections 400 forming a pseudo-hexagonal net, 3 additional reflections of lesser intensity along  $a^*$ . When  $a_0 = 14.6 \text{ \AA}$ , five weak reflections are present between these strong ones. In this case the reflection at  $d = 2.44 \text{ \AA}$  towards the  $a^*$  axis has indices 600. Where todorokite has  $a_0 = 24.40 \text{ \AA}$ , the strong reflections along the  $a^*$  axis are accompanied by four weak reflections on each side, which, if other reflections are absent, would determine a unit cell and the extinction law  $h + k = 2n$  for the plane (001)\*. However, a fifth, weak reflection is present which violates the condition and proves the unit cell to be primitive. In this case the above-men-

tioned strong reflections at  $d_0 = 2.44 \text{ \AA}$  has indices 10·0·0.

Under the electron microscope, todorokite with the parameter  $a_0 = 14.6 \text{ \AA}$  has been observed in the nucleus of an iron-manganese nodule, collected from the floor of the Pacific Ocean. As seen by naked eye, the flaky todorokite from the Bakal deposit consists of three member intergrowths of two todorokite species having parameters  $a_0 = 14.6$  and  $24.4 \text{ \AA}$ . Todorokite with  $a_0 = 24.40 \text{ \AA}$  has been found in specimens from Sterling Hill, New Jersey and from the Takhta-Karacha deposit in Middle Asia.

Thus, todorokite may exist with a diversity of unit cells which have different  $a_0$  parameters, all multiples of 4.88 Å. It seems natural to assume that todorokites having  $a_0$  parameters with other multiples of 4.88 Å also may exist in nature, for example, with  $a_0 = 4.88 \times 1$ ,  $a_0 = 4.88 \times 4 = 19.5 \text{ \AA}$ . Some differences in chemical composition and local environment of crystallization may be responsible for the variations of  $a_0$  parameters, thereby producing the todorokite superstructures.

Unaltered todorokite contains more  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  than does vernadite. This fact is consistent with supposedly lower Eh values in the medium where todorokite originates (Glasby, 1972). If  $\text{Mn}^{2+}$  oxidizes into  $\text{Mn}^{4+}$ , todorokite commonly converts to vernadite ( $\delta\text{-MnO}_2$ ). Even when the replacement of todorokite by vernadite is complete, the fibrous or flaky structure of the former is preserved. In the absence of comprehensive electron microscopy data the products of partial or complete replacement of todorokite by vernadite can be mistaken for todorokite. Among these products are commonly partially vernadite-replaced todorokite and pseudomorphs of vernadite after todorokite. A consequence of vernaditization is an essential percentage of  $\text{Mn}^{4+}$  as compared with  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  in todorokite.

Since in the future, new members of the todorokite family may be found in nature or be produced experimentally, it appears reasonable to use the following symbols for todorokite species: todorokite I with  $a_0 = 4.88 \text{ \AA}$ , todorokite II with  $a_0 = 4.88 \text{ \AA} \times 2$ , todorokite III with  $a_0 = 4.88 \text{ \AA} \times 3$ , todorokite IV with  $a_0 = 4.88 \text{ \AA} \times 4$ , todorokite V with  $a_0 = 4.88 \text{ \AA} \times 5$ , etc. Todorokites II, III, and V are currently known in nature.

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**Резюме**—Вернадит (MnO<sub>2</sub> · nH<sub>2</sub>O) представляет минерал с плохо упорядоченной структурой, его синтетический аналог описывается под названием  $\delta$ -MnO<sub>2</sub>. Бёрнессит и вернадит представляют различные минеральные виды и не могут описываться под одним и тем же названием. Их гексагональные элементарные ячейки характеризуются одинаковым параметром  $a_0$  при разных значениях параметра  $c_0$ . Рансёит структурно подобен бёрнесситу. Впервые авторами описан природный 14 Å кальцийсодержащий бёрнессит. Помимо обычного тодорокита ( $a_0 = 9,75$ ,  $b_0 = 2,84$ ,  $c_0 = 9,59$  Å) в природе установлены другие тодорокиты с параметром  $a_0$ , кратным 4,88 Å (14,6 и 24,40 Å). Параметры  $b_0$  и  $c_0$  у всех тодорокитов одинаковы.

**Resümee**—Vernadit (MnO<sub>2</sub> · nH<sub>2</sub>O) ist ein Mineral mit einer schlecht geordneten Struktur. Sein synthetisches Analogon wird  $\delta$ -MnO<sub>2</sub> genannt. Birnessit und Vernadit sind zwei verschiedene Minerale und können nicht länger mit demselben Namen bezeichnet werden. Sie haben ähnlich hexagonale Parameter der Elementarzelle,  $a_0$ , aber verschiedene  $c_0$ -Parameter. Ranciéite hat eine dem Birnessit ähnliche Struktur. Das natürliche Vorkommen Calcium-führenden 14-Å Birnessits wurde zum ersten Mal von den Autoren beschrieben. Außer dem Todorokit mit den Parametern  $a_0 = 9,75$  Å,  $b_0 = 2,84$  Å, und  $c_0 = 9,59$  Å sind andere Arten von natürlichem Todorokit bekannt. Sie haben  $a_0$ -Parameter, die ein Vielfaches von 4,88 Å sind, wie 14,6 und 24,40 Å. Die  $b_0$ - und  $c_0$ -Parameter sind dieselben. [U.W.]

**Résumé**—La vernadite (MnO<sub>2</sub> · nH<sub>2</sub>O) est un minéral ayant une structure pauvrement ordonnée. Son analogue synthétique est désigné  $\delta$ -MnO<sub>2</sub>. La birnessite et la vernadite sont des espèces minérales indépendantes et ne peuvent plus être décrites par la même appellation. Elles ont des paramètres de maille hexagonale pareils,  $a_0$ , mais des paramètres  $c_0$  différents. La ranciéite a une structure semblable à celle de la birnessite. La birnessite 14 Å contenant du calcium, trouvée dans la nature, a été décrite pour la première fois par les auteurs. En plus de la todorokite ayant les paramètres  $a_0 = 9,75$  Å,  $b_0 = 2,84$  Å, et  $c_0 = 9,59$  Å, on sait que d'autres espèces de todorokite ont des paramètres  $a_0$  qui sont des multiples de 4,88 Å égal à 14,6 et 24,40 Å, les paramètres  $b_0$  et  $c_0$  étant les mêmes. [D.J.]