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Tvedalite, $(Ca,Mn)_4Be_3Si_6O_{17}(OH)_4 \cdot 3H_2O$, a new mineral from syenite pegmatite in the Oslo Region, Norway

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ABSTRACT

Tvedalite occurs as cream white to pale beige spherulites up to 3 mm in diameter in vugs in a nepheline syenite pegmatite of the Vevja quarry in Tvedalen, Brunlanes, Vestfold County, Norway. The tvedalite spherulites are always overgrown by a crust of chiavennite. Microprobe and wet chemical analyses as well as thermogravimetric data give the chemical formula $(Ca,Mn)_4Be_3Si_6O_{17}(OH)_4 \cdot 3H_2O$. The relative proportions of large divalent cations vary irregularly from rim to core. The two most extreme compositions are (in percent of the non-Be divalent atoms) $Ca_{50}Mn_{46}Fe_4$ and $Ca_{80}Mn_{18}Fe_2$. Crystallographic data were obtained by a combination of X-ray powder and electron diffraction methods. The mineral is orthorhombic, $a = 8.724(6)$, $b = 23.14(1)$, $c = 4.923(4)$ Å, $V = 993.8(9)$ Å^3, $Z = 2$. The strongest reflections [d in Å, (I/I_0), (hkl)] of the powder diffraction pattern are 11.6(93)(020), 5.80(68)(040,130), 3.87(75)(060), 3.16(74)(250,151), 2.889(75)(080,260,310), 2.837(100)(241), 2.494(58)(081,261). Cleavage is perfect {010}. $D_{meas} = 2.541(6)$ g/cm^3, $D_{calc} = 2.554$ g/cm^3. Mohs hardness is 4½. The average refractive index is $n = 1.604$.

INTRODUCTION

Be minerals are widespread in the syenite pegmatites of the Oslo Region, Norway. Hitherto, 16 Be minerals have been identified. These are bromellite (Larsen et al., 1987), chrysoberyl, behoite, berborite (Giuseppetti et al., 1990), hambergite, gadolinite-(Ce) (Segalstad and Larsen, 1978), barylite (Sæbø, 1966), bertrandite, meliphanite, leucophanite, eudidymite, epididymite (Flink, 1899), chiavennite (Raade et al., 1983), leifite, helvite, and genthelvite (Larsen, 1988). Meliphanite, leucophanite, eudidymite, and hambergite were thoroughly treated by Brøgger (1890) in his classic monograph on the minerals from the syenite pegmatites of the Oslo Region. An updated mineral list was published by Raade et al. (1980).

Since parallel descriptions of the new mineral chiavennite, $CaMnBe_2Si_5O_{13}(OH)_2 \cdot 2H_2O$, were published (Bondi et al., 1983; Raade et al., 1983), a dozen localities for this mineral have been found in the syenite pegmatites of the southern part of the Oslo Region, Norway. One of the most important findings was made in the Vevja quarry of the Tvedalen area, Brunlanes, Vestfold County. Shortly before the quarry was closed in 1984, several interesting pegmatite dikes were encountered, a couple of which contain abundant chiavennite. One of the minerals that occurred in close association with chiavennite was shown to have a chemical composition very similar to that of chiavennite, being a hydrated calcium manganese beryllium silicate, with an X-ray diffraction pattern that did not match any known substance. The mineral was named tvedalite after the Tvedalen area where quarrying for larvikite exposed numerous syenite pegmatite dikes containing considerable amounts of interesting minerals. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA. Cotype specimens are deposited at the Mineralogisk-Geologisk Museum, University of Oslo, Norway, under catalog number 14770.

OCCURRENCE AND PARAGENESIS

Most of the tvedalite-bearing material was recovered from blasted rock fragments on the floor of the Vevja quarry, and the actual pegmatite was never observed in situ. Tvedalite is found in close association with chiavennite, and therefore one can draw some general conclusions about this pegmatite from observations for other chiavennite-bearing pegmatites in the Tvedalen area. The major occurrences of chiavennite are in irregular pegmatite bodies that constitute swollen, heavily zeolitized, and hydrothermally altered parts of otherwise dikelike, flat-lying pegmatites. The following minerals are observed in the tvedalite-bearing pegmatite material from the Vevja quarry. First-stage (magmatic) minerals are grayish white microcline, aegirine, biotite, nepheline (completely altered to zeolites), magnetite (first generation), pyrochlore, and zircon. Minerals from the second, hydrothermal stage are sphalerite, arsenopyrite, pyrite,

Fig. 1. SEM photomicrograph showing details from a cross section of a tvedalite spherulite. Note the platy habit of the mineral and its well-developed {010} cleavage. Elongation of the SEM photomicrograph is in the direction from rim to core.

molybdenite, fluorite, magnetite (second generation), todorokite, calcite, parisite-(Ce), bastnäsite-(Ce), thorite, leucophanite, chlorite, epididymite, tvedalite, chiavennite, albite, analcime, and natrolite. Tvedalite, chiavennite, analcime, and natrolite were the last minerals to crystallize. Tvedalite spherulites are always overgrown with a crust of chiavennite microcrystals.

A few samples of tvedalite have been found in a second chiavennite-bearing pegmatite in the Vevja quarry (K. Eldjarn, personal communication, 1989). Here, tvedalite occurs as white, radially oriented, platy aggregates completely lining small cavities in analcime. A tvedalite lining 0.2 mm thick is overgrown with a thin chlorite crust. This material is not described in the present study.

Physical properties

Tvedalite occurs as spherulites up to 3 mm in diameter. A scanning electron microscope (SEM) photomicrograph (Fig. 1) shows that the spherulites are composed of densely packed, radially oriented platelets. Individual plates are a maximum of a few micrometers in length. Tvedalite has perfect {010} cleavage as observed from the SEM photomicrographs (Fig. 1).

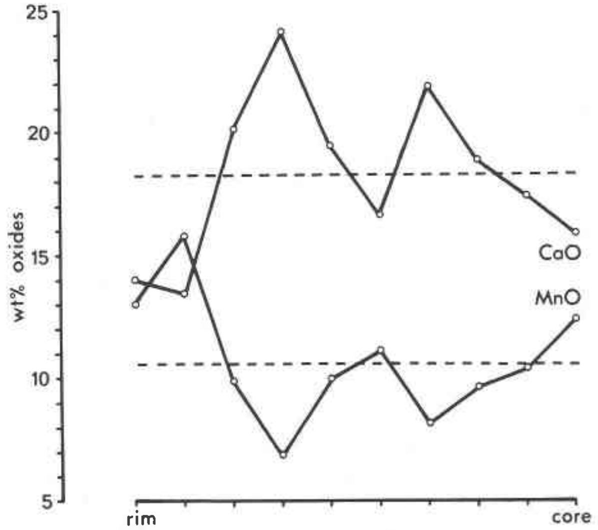

Fig. 2. CaO and MnO wt% from electron microprobe spot analyses across a traverse from rim to core of a tvedalite spherulite. Dashed lines indicate the average values for CaO and MnO.

Tvedalite spherulites show concentric zoning in white to pale gray and beige colors, probably because of the large variation in chemical composition (see Fig. 2). The powder and streak are white, and the luster is vitreous. Because of the extremely small size of the individual single crystals, it was not possible to make exact measurements of the optical properties. Attempts to measure the average refractive index gave an approximate value of $n = 1.604$. This is close to the values for chiavennite ($\alpha = 5.996$, $\beta = 1.600$, $\gamma = 1.618$) (Raade et al., 1983). Tvedalite is nonfluorescent in ultraviolet light.

The hardness was determined using splinters of tvedalite spherulites to scratch different standard minerals. Fluorite was scratched but not apatite. Thus the Mohs hardness of tvedalite is ~4½. Splinters of tvedalite spherulites were also used for density measurements. A density of 2.541(6) g/cm³ was determined using the sink-float method with diiodomethane diluted with acetone. The calculated density is 2.554 g/cm³ based on the empirical formula from the material analyzed wet chemically and the measured unit-cell dimensions, with $Z = 2$. Tvedalite is slightly soluble in hot, concentrated HCl.

Chemical composition

Tvedalite was analyzed at ten spots across a traverse from rim to core of a single spherulite. The analyses were performed with a Camebax electron microprobe with an operating voltage of 15 kV and a sample current of 10 nA, standardized on brass. The following standards were used: wollastonite (Ca and Si), fayalite (Fe), pyrophanite (Mn), and kyanite (Al). The results are shown in Table 1 (column A) and Figure 2. Material for wet chemical analysis and H_2O determination was hand picked under a binocular microscope. Si, Al, Fe, Mn, Ca, and Be were

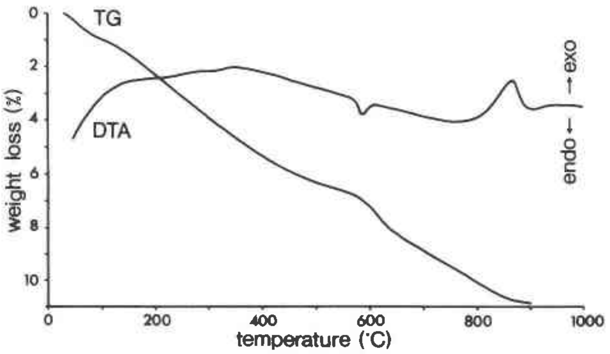

Fig. 3. DTA and TG curves for tvedalite.

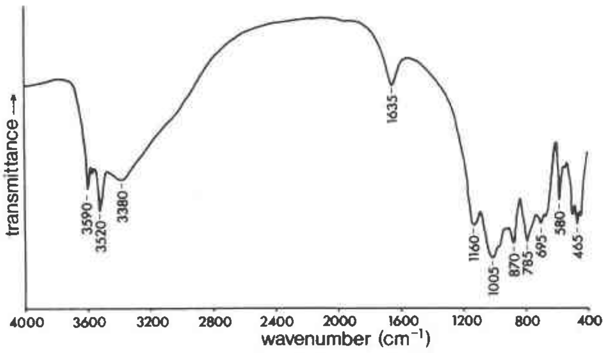

Fig. 4. Infrared spectrum of tvedalite. The principal absorption bands are indicated.

also analyzed using atomic absorption spectrometry after decomposition with HF and H_2SO_4 in a closed vessel. H_2O was analyzed using a Perkin-Elmer PE240 elemental analyzer. The results are shown in Table 1 (column B) and compared with two theoretical compositions with different Ca/Mn ratios.

As seen in Table 1 there is remarkable agreement between wet chemical analysis and the average of the spot analyses made using the electron microprobe. This indicates that the variations in the spot analyses are representative of the range in chemical composition for the Vevja tvedalite. The empirical formula from the wet chemical analysis, based on 13 cations per formula unit (excluding H), is $(Ca_{2.52}Mn_{1.25}Fe_{0.12})_{\Sigma 3.89}Be_{3.00}(Si_{5.74}Be_{0.27}Al_{0.10})_{\Sigma 6.11}O_{17}(OH)_4 \cdot 3.06H_2O$. The idealized formula is $(Ca,Mn)_4Be_3Si_6O_{17}(OH)_4 \cdot 3H_2O$. The spot analyses show that the variations in CaO and MnO are inversely proportional (Fig. 2), whereas the amounts of other elements are relatively invariant (Table 1). Based on the spot analyses and the idealized formula, the composition ranges from approximately $(Ca_{3.20}Mn_{0.72}Fe_{0.08})_{\Sigma 4.00}Be_3Si_6O_{17}(OH)_4 \cdot 3H_2O$ to $(Ca_{2.00}Mn_{1.86}Fe_{0.14})_{\Sigma 4.00}Be_3Si_6O_{17}(OH)_4 \cdot 3H_2O$, disregarding the minor substitution of Be and Al for Si.

TABLE 1. Chemical analyses (wt%) of tvedalite

	A	B	C	D
SiO_2	45.0 (44.2–45.8)	45.00	46.24	47.13
Al_2O_3	1.1 (0.6–1.4)	0.68		
FeO	1.4 (0.8–1.8)	1.11		
MnO	10.7 (6.9–15.8)	11.56	18.20	9.28
CaO	18.2 (13.4–24.1)	18.44	14.39	22.00
BeO	n.a.	10.69	9.62	9.81
H_2O	n.a.	11.8	11.55	11.78
Total	76.4	99.28	100.00	100.00
Number of atoms based on Σ cations = 13 (excluding H)				
Si	5.92	5.74	6.00	6.00
Al	0.17	0.10		
Fe	0.15	0.12		
Mn	1.19	1.25	2.00	1.00
Ca	2.57	2.52	2.00	3.00
Be		3.27	3.00	3.00
H		10.12	10.00	10.00

Note: A, average of ten microprobe analyses. Ranges are given in parentheses. B, wet chemical analysis. C, theoretical data for composition $Ca_2Mn_2Be_3Si_6O_{17}(OH)_4 \cdot 3H_2O$. D, theoretical data for composition $Ca_3MnBe_3Si_6O_{17}(OH)_4 \cdot 3H_2O$.

A thermogravimetric analysis on 7.482 mg of tvedalite at a heating rate of 10 °C per min in N_2 from room temperature to 900 °C gave weight losses in two distinct intervals (Fig. 3). The first interval occurred between room temperature and 590 °C (6.8% weight loss, corresponding to $3H_2O$). The second interval occurred between 590 and 900 °C [4.2% weight loss, corresponding to 4(OH)]. The total H_2O loss was 11%, which is 0.8% lower than the H_2O determination using the elemental analyzer. This is probably due to the fact that the decomposition temperature is higher in the latter instrument.

Tvedalite (18.4 mg) was analyzed in a Perkin-Elmer DTA 4/1700 at a heating rate of 20 °C per min in air from 50 to 1000 °C. The DTA curve is shown in Figure 3. An endothermal peak occurs at 590 °C, corresponding to the dehydroxylation and decomposition of the tvedalite crystal structure as shown on a high-temperature X-ray diffraction film. An exothermic recrystallization peak occurs at 870 °C.

A pellet of tvedalite mixed with anhydrous KBr was analyzed in a Nicolet 5SX FTIR spectrometer. The infrared spectrum (Fig. 4) shows the presence of both $(OH)^-$ and H_2O, indicated by the sharp absorption bands in the region 3380–3590 cm^{-1} superimposed on a broad absorption region at 3000–3700 cm^{-1}. The absorption band at 1635 cm^{-1} is also attributed to H_2O. The complex absorption bands in the region 400–1200 cm^{-1} are mainly due to Si-O and Be-O stretching and bending vibrations. Splitting of the OH stretching frequency shows that OH ions are present in two different structural sites, as was also indicated for chiavennite (Raade et al., 1983). The infrared spectrum has a strong resemblance to the chiavennite spectrum presented by Bondi et al. (1983) except for the lack of some minor absorption bands in the region 1400–3000 cm^{-1}.

X-RAY CRYSTALLOGRAPHIC DATA

X-ray powder diffraction

Tvedalite spherulites were carefully hand picked under a binocular microscope. Diffraction data were obtained

TABLE 2. X-ray powder diffraction data for tvedalite

hkl	d_{calc} (Å)	d_{obs} (Å)	I/I_0
020*	11.57	11.6	93
110*	8.16	8.18	14
040*	5.78	5.80	68
130*	5.78		
001*	4.92	4.93	10
111*	4.22	4.20	49
150*	4.09	4.08	21
220*	4.08		
060*	3.86	3.87	75
041*	3.75	3.76	13
131*	3.75		
201*	3.26	3.26	43
250	3.17	3.16	74
151	3.15		
170*	3.09	3.10	20
080*	2.892	2.889	75
260*	2.889		
310*	2.885		
241*	2.843	2.837	100
270*	2.635	2.633	14
081*	2.494	2.494	58
261*	2.492		
280*	2.411	2.411	17
331*	2.381	2.378	9
091*	2.279	2.275	7
290*	2.215	2.211	40
242	2.010	2.004	10
441*	1.885	1.886	27
192	1.742	1.742	15
480*	1.741		
352	1.741		
481*	1.642	1.642	10
023*	1.625	1.625	10
2,15,0	1.454	1.454	10

* Reflections used for refinement of cell parameters.

using a Philips APD 1700 diffractometer using graphite monochromated Cu*Kα* radiation (λ = 1.54059 Å) and Si (NBS 640a) as internal standard. The X-ray powder diffraction pattern is given in Table 2. The X-ray powder reflections show some broadening as a result of the considerable variation in chemical composition within each spherulite.

Because of the extremely small size and platy habit of the tvedalite crystals, no conventional single-crystal X-ray diffraction studies could be done. Approximate unit-cell dimensions were obtained using a trial-and-error method, taking into consideration the close relationship with chiavennite both in chemical composition and in X-ray powder pattern. It was found that the pattern could be indexed on an orthorhombic unit cell. The unit-cell dimensions found by least-squares refinement (Appleman and Evans, 1973) from 28 reflections are $a = 8.724(6)$, $b = 23.14(1)$, $c = 4.923(4)$ Å, and $V = 993.8(9)$ Å^3. X-ray powder reflections of the type *hkl* are restricted to $h + k = 2n$. This is consistent with a *C*-centered lattice.

A Guinier-Lenné high-temperature camera was used to obtain diffraction data from room temperature to 800 °C. The film shows that the H_2O loss induces a gradual contraction of the structure up to 580 °C, where a final collapse of the structure takes place.

Electron diffraction

Small amounts of tvedalite were ground in an agate mortar, and the fragments were dispersed on a holey carbon film suspended on a Cu grid. A JEOL 200 keV transmission electron microscope was used for the electron diffraction experiments. The contrast of bright-field images is uniform over large areas, consistent with even thickness caused by the perfect cleavage.

Using a goniometer, the crystallites could be tilted independently around two orthogonal axes. By tilting the specimen so that the shadow image of a platelet showed the maximum area, which means that the incident electron beam was normal to the face of the platelet, the diffraction pattern shown in Figure 5a ([010] zone) was observed, consistent with (010) being the cleavage plane. Based on the unit-cell dimensions determined from X-ray powder diffraction, the [110] zone image should be obtained by tilting from the [010] zone arc tan a/b = arc tan 8.724/23.14 = 20.7° around **c**. The [011] zone image should be obtained by tilting from the [010] zone arctan c/b = arctan 4.923/23.14 = 12.0° around **a**. These relations were, in fact, observed by tilting 21° ± 1° and 11.5° ± 1° around **c** and **a**, respectively (Figs. 5b, 5c). The electron diffraction patterns have been successfully indexed using the appropriate cell. The *d*-values and unit-cell dimensions determined from the electron diffraction observations deviate less than 1% from the X-ray powder diffraction results, which is within the experimental accuracy of the electron diffraction observations. This is in good agreement with the X-ray powder diffraction results with respect to unit-cell dimensions and choice of axes in relation to the cleavage plane.

GLADSTONE-DALE RELATIONSHIP

The Gladstone-Dale relationship gives $K_c = 0.2244$ (refractive energies based on data from wet chemical analysis, k values from Mandarino, 1981) and $K_p = 0.2365$ (refractive energy from calculated density 2.554 g/cm^3 and mean refractive index). This gives a compatibility index $1 - (K_p/K_c) = -0.0539$, which is good according to Mandarino (1979, 1981).

DISCUSSION

The similarity in composition and cell parameters of tvedalite and chiavennite as well as their close association suggests that the two minerals are structurally related. Chiavennite has composition $CaMnBe_2Si_5O_{13}(OH)_2 \cdot 2H_2O$, $Z = 4$, and material from Langangen, Norway, has $a = 8.666(7)$, $b = 31.34(2)$, and $c = 4.787(3)$ Å (Raade et al., 1983). The crystal structure of chiavennite was determined on material from Italy, with $R = 0.059$ for 4467 reflections (2084 independent) by Domeneghetti et al. (1981) and was briefly discussed by Merlino (1984) and Meier and Olson (1988). The structure is built of zigzag chains of SiO_4 tetrahedra that are interconnected by BeO_4 tetrahedra to form a three-dimensional framework. Ca and Mn occur in eight- and sixfold coordination, respec-

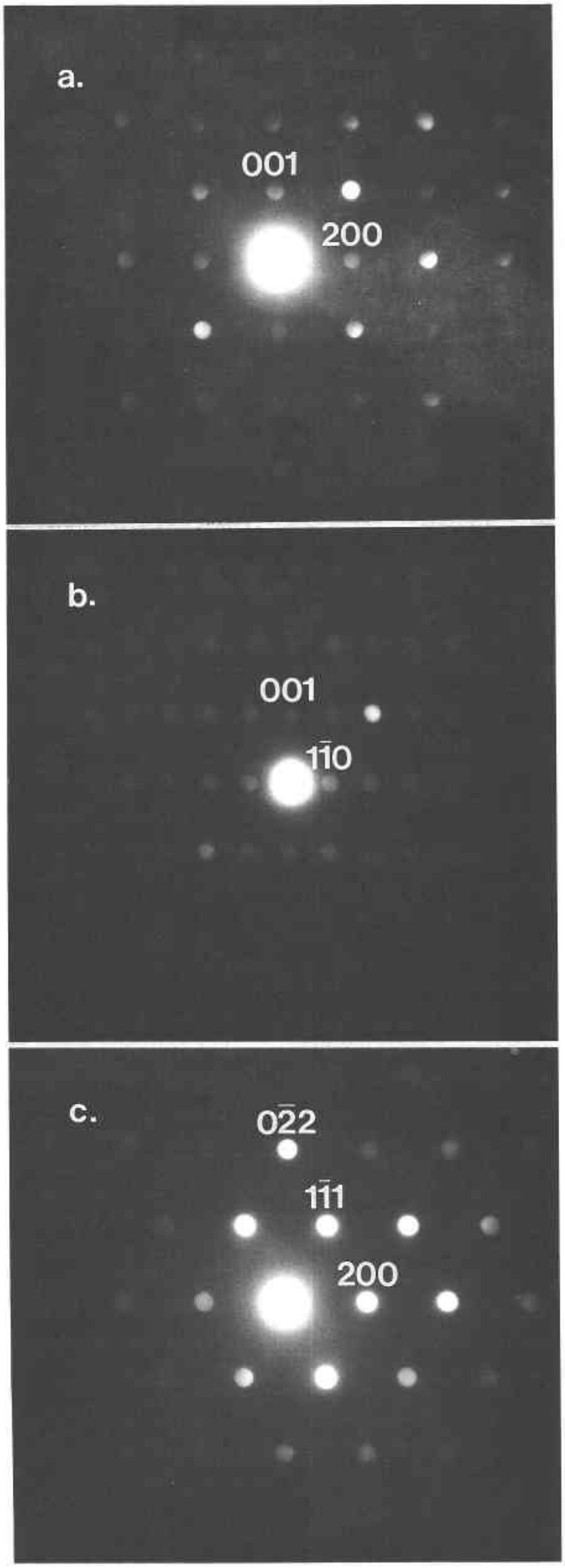

Fig. 5. Electron diffraction patterns from tvedalite: (**a**) [010] pattern, (**b**) [110] pattern, (**c**) [011] pattern.

tively. The framework contains channels along [001] formed by nine-membered rings of O atoms, with free channel diameters of 3.9 × 4.3 Å. It seems most likely that the tvedalite structure is composed of the same structural elements combined in a different way. Tvedalite has 8 (Ca + Mn + Fe) per unit cell. It ranges in composition (in percent of these atoms) from approximately $Ca_{50}Mn_{46}Fe_4$ to $Ca_{80}Mn_{18}Fe_2$. The fact that the lowest Ca content corresponds exactly to half the number of divalent atoms may indicate that, as in the chiavennite structure, there are two sites with multiplicity 4 for divalent cations, one occupied by Ca and the other capable of accepting the smaller ions Mn and Fe. In terms of formula units the variation would thus be from $Ca_{2.00}(Mn_{1.86}Fe_{0.14})_{\Sigma 2.00}$ to $Ca_{2.00}(Ca_{1.20}Mn_{0.72}Fe_{0.08})_{\Sigma 2.00}$, ($Z = 2$).

We are therefore faced with a possible problem of mineralogical nomenclature. In accordance with normal practice ("the 50% rule") we may be dealing with two different mineral species with either Mn or Ca as the dominant element in the second site. Practically speaking, it would be difficult to differentiate between two mineral species in one single-zoned spherulite. Another complication arises from the possibility that the second site may be split into two sites each with multiplicity 2 (which is possible in space groups *Cmm*2 and *Cmmm*). Until the structure of tvedalite is solved and more is known about its solid-solution relations, we propose that the mineral name should be used for the series within the compositional limits defined by the theoretical end-members $Ca_2Mn_2Be_3Si_6O_{17}(OH)_4 \cdot 3H_2O$ and $Ca_4Be_3Si_6O_{17}(OH)_4 \cdot 3H_2O$, i.e., with Ca ≥ Mn.

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