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Orlymanite, $Ca_4Mn_3Si_8O_{20}(OH)_6 \cdot 2H_2O$, a new mineral from South Africa: A link between gyrolite-family and conventional phyllosilicate minerals?

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ABSTRACT

Orlymanite is a new mineral from the Wessels mine, Republic of South Africa, which is related to gyrolite-family minerals. It has space group $P\bar{3}$ or $P3$, with lattice parameters $a = 9.60(2)$ and $c = 35.92(10)$ Å. Microprobe analysis with H_2O by the Penfield method gave SiO_2 46.8, Al_2O_3 0.2, Fe_2O_3 0.8, MgO 1.6, CaO 21.6, MnO 19.7, Na_2O 0.6, H_2O 8.68, total = 100.0 wt%. The tentative formula is $Ca_4Mn_3Si_8O_{20}(OH)_6 \cdot 2H_2O$, with $Z = 5$. The strongest lines in the X-ray powder diffraction pattern are (d, I/I_o, hkl): 7.15, *70,* 005; 4.18, *70,* 200; 3.60, *100,* 109, 025, 00,10; 3.13, *80,* 210; 1.840, *90,* 10,19, 409, 235, 11,18, 21,16, 31,12.

Orlymanite occurs as dark brown radial spheres embedded in a massive layered mixture of orlymanite and other phases. It has perfect {001} cleavage, hardness approximately 4–5, density 2.7–2.8 (meas), 2.93 (calc) g/cm³. Optically, it is uniaxial, negative, with $\omega = 1.598$, O = pale brown, E' = dark brown.

Orlymanite serves as a link between gyrolite-family minerals that have the large, limiting cation Ca in brucite-like sheets and conventional phyllosilicates with small octahedrally coordinated cations such as Mg. Orlymanite and other minerals such as stilpnomelane have modulated structures and contain cations of intermediate radius.

INTRODUCTION

An uncommon mineral from South Africa was called to our attention by Joel Bartsch of Hilo, Hawaii. Our preliminary investigation suggested it was a new species, and this was borne out by subsequent detailed study. The new species is named *orlymanite* in recognition of the late Orlando Lyman, who founded the Lyman House Memorial Museum in Hilo, Hawaii; this new mineral was part of the collection held there. The new species and the name were approved by the Commission on New Minerals and Mineral Names, I.M.A. Holotype material is deposited in the Smithsonian Institution, under catalogue number NMNH 166368.

DESCRIPTION

Orlymanite occurs as layers of dark brown, radiating, tightly packed rosettes that form spheres 2–3 mm in diameter, or more irregular aggregates resembling a botryoidal texture in cross section. Such material forms a discontinuous core of a specimen that appears to be from a vein. In the aggregate, the orlymanite resembles radial fibrous johannsenite in texture, but on a smaller scale. The luster is vitreous, the streak is light brown, and there is no discernible response to ultraviolet radiation. The fibrils are elongate on *a,* an uncommon orientation for a hexagonal mineral; cleavage is perfect on {001} and easily produced; incipient cleavages are abundant. The density, measured using heavy-liquid techniques, is variable; measured values range from 2.7 to 2.8 g/cm³, compared with the calculated value of 2.93 g/cm³; the lower values may be the result of air trapped in the fibrous aggregates. The hardness (Mohs) is approximately 4–5.

Optically, orlymanite is uniaxial, negative, with $\omega = 1.598$; ϵ is undetermined owing to the extreme fibrous shape of fragments. Orlymanite is pleochroic, with O = pale brown, and E (observable only as E') = dark brown.

OCCURRENCE

Orlymanite has been found in only one specimen, labeled as being from the Wessels mine in the Republic of South Africa. There is no detailed information regarding its specific geologic occurrence.

Orlymanite occurs as part of an assemblage that resembles a vein; the specimen is flattened and the mineralization has a planar distribution. The assemblage is 1.5–2.0 cm thick, consisting of dark brown orlymanite spherules intermixed with a very light brown aggregate of micaceous grains of impure orlymanite that resembles bementite in physical appearance. Massive inesite and earthy hematite are sparsely distributed within this light brown material. Both surfaces of this assemblage consist of the light brown material, abundant spherules of inesite 1.0 cm in diameter, and minor calcite.

Back-scattered electron images and energy-dispersive

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TABLE 1. Powder X-ray diffraction data for orlymanite

Gandolfi pattern*				Diffractometer pattern**			
I/I_o	d_{obs}	d_{calc}	*hkl*	I/I_o	d_{obs}	d_{calc}	*hkl*
				4	12.01	11.97	003
				4	8.97	8.98	004
70	7.15	7.18	005†	56	7.19	7.18	005
10(D)	5.98	5.99	006†	19	6.00	5.99	006
				6	5.14	5.13	007
				4	4.45	4.45	008
70	4.18	4.16	200‡				
5	4.00	3.99	009†	24	4.00	3.99	009
		3.99	115				
100	3.60	3.60	109	100	3.60	3.59	00,10
		3.60	025				
		3.59	00,10†				
				9	3.28	3.27	00,11
80(D)	3.13	3.14	210‡				
		3.13	211				
5(D)	2.77	2.78	216				
		2.77	300‡				
		2.76	00,13				
		2.76	301				
40(D)	2.545	2.566	00,14				
		2.540	11,12				
40(D)	2.469	2.468	219				
		2.452	10,14				
10	2.210	2.227	226				
		2.195	315				
5(D)	2.123	2.143	11,15				
		2.116	228				
		2.113	00,17				
90	1.840	1.843	10,19				
		1.843	409				
		1.843	235				
		1.843	11,18				
		1.826	21,16				
		1.826	31,12				
20	1.619	1.620	12,19				
		1.619	505				
		1.619	30,18				
		1.619	41,10				
		1.615	40,14				
10	1.585	1.586	22,17				
		1.585	14,11				
		1.585	333				
		1.582	02,21				
		1.581	507				

Note: D = diffuse.

* Data obtained with a Gandolfi camera with a diameter of 114.6 mm, and Si standard, Fe$K\alpha$ (Mn-filtered) radiation. Intensities estimated visually.

** Data obtained with Philips diffractometer, Cu$K\alpha$, graphite monochromator, specimen spread as a slurry on a glass slide so that the preferred orientation gives rise only to 00*l* reflections.

† Indices preferred by comparison with intense 00*l* reflections of diffractometer pattern.

‡ Indices preferred by comparison with intense *hk*0 reflections of precession photographs.

X-ray analyses were obtained using a polished thin section. The dark brown orlymanite was found to be homogeneous in composition, but the light brown material was heterogeneous. Compositions varied between that of orlymanite and that of a Si-poor, Ca- and Mn-rich phase. The variation in composition suggested interlayering of two or more phases at the limits of resolution (~1 μm) of the methods. The boundary between the inesite and orlymanite had well-defined prismatic inesite crystals extending into the massive orlymanite, consistent with a vein assemblage in which inesite was an earlier phase. Small grains were also observed that gave rise to Mn, Cu + Fe, and Cu + Fe + Zn as the only elements detectable by EDS analysis.

EDS analyses were also obtained by STEM (see below), using an ion-milled sample. The sample consisted largely of layered, homogeneous orlymanite, but EDS analyses also showed the presence of a Ca- and Mn-rich phase poor in Si, and a phase having major Al, Si, Ca, and Mn. An X-ray diffraction pattern of the light brown phase is very similar to that of orlymanite, but with some additional weak reflections, the most prominent of which has $d = 3.4$ Å. The relations collectively show that the light brown phase consists principally of orlymanite, but mixed with other, unidentified minerals.

CRYSTALLOGRAPHY

Even very small cleavage fragments of orlymanite gave rise to single-crystal X-ray diffraction patterns with weak, diffuse, and ill-defined reflections. For example, reflections on Weissenberg photographs were spread up to 60° along ω. Nevertheless, oscillating crystal and Weissenberg photographs did show that the Laue symmetry is $6/m$ or $\bar{3}$, with $a = 9.3$ Å. Non-*hk*0 reflections were so imperfect, with severe streaking parallel to c^*, that it was not possible to determine a value of c with confidence, although the data implied that $c \sim 7$ Å or a multiple thereof. In addition, the lattice was shown to be type 6*P*, as opposed to 3*R*, the only other possibility given the Laue symmetry. A *c*-axis precession cone-axis photograph displayed no layer lines, but did give rise to diffuse streaks that clearly displayed threefold symmetry.

In order to obtain well-defined 00*l* reflections, a powder diffractometer pattern was obtained by spreading cleavage fragments on a glass plate, giving rise to a preferred orientation of (001). The resulting diffraction pattern displayed a rather striking and unique periodic series of 00*l* reflections consistent with $c = 35.99(5)$ Å (or 3 × 35.99 Å, if an extinction rule affects 00*l* reflections). The powder diffractometer data are listed in Table 1.

In order to further define the diffraction relations, specimens were prepared for study by transmission electron microscopy. Both ion-milled samples and those with cleavage fragments spread randomly on holey carbon films were used. The ion-milled sample was oriented so that c^* was normal to the electron beam, whereas holey carbon mounts preferentially gave rise to *hk*0 nets. The data were obtained using a Philips CM 12 scanning transmission electron microscope (STEM) fitted with a Kevex Quantum detector for energy-dispersive anlaysis (EDA). Small crystallites gave rise to diffraction patterns having sharp, well-defined reflections. Diffraction patterns obtained with the beam parallel to c^* were consistent with $\bar{3}$ symmetry and verified that $a = 9.6$ Å. General and 00*l* reflections verified that $c = 36$ Å, with no 00*l* extinctions. Lattice fringe images obtained with 00*l* reflections (Fig. 1) have 36 Å periodicity and are sometimes seen to be asymmetrically subdivided by weaker subfringes. Although no direct inferences regarding the structure can be

Fig. 1. Lattice fringe image obtained using 001 reflections. Fringes have $d = 36$ Å, with weak subfringes.

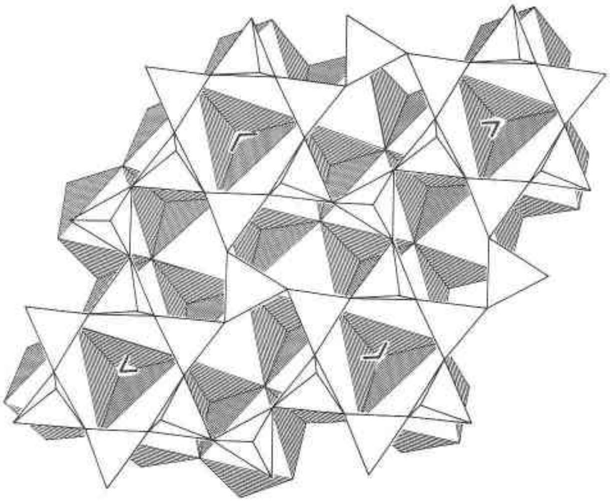

Fig. 2. Projection onto (001) of the portion of the reyerite structure from $Z = -0.25$ to $Z = 0.15$, including one of two kinds of tetrahedral sheets articulated to an octahedral sheet. After Merlino, 1988a.

drawn, the relations do imply that the *c*-axis period is divided into two dissimilar units.

A powder diffraction pattern free of preferred orientation effects was obtained by using a Gandolfi camera, a small number of crystallites, Fe$K\alpha$ (Mn-filtered) radiation, and Si as an internal standard. Data are in Table 1. Initial attempts at indexing were unsuccessful because of the large number of reflections resulting from the large unit cell. However, many reflections could be unambiguously indexed using indices of intense *hk*0 reflections from 0-level precession and electron diffraction patterns, and the intense 00*l* reflections of the diffractometer pattern. Least-squares refinement yields the lattice parameters $a = 9.60(2)$ and $c = 35.92(10)$ Å. The collective diffraction data are consistent with space groups $P\bar{3}$ and $P3$.

COMPOSITION

Orlymanite was analyzed using an ARL-SEMQ electron microprobe, utilizing an operating voltage of 15 kV, and a sample current of 0.025 μA, measured on brass. A wavelength-dispersive microprobe scan indicated the absence of other elements with an atomic number greater than 9, except those reported here. The standards used were hornblende (Si, Al, Fe, Mg, Ca, and Na), and manganite (Mn). Data were reduced using the Bence-Albee procedures (Bence and Albee, 1968).

The H_2O content was determined using 82.12 mg of material. Because of the possible occurrence of H_2O trapped between fibers, special precautions were taken. The sample was placed in a weighing bottle and dried at 100 °C for 2 h, after which it showed a weight loss of 1.16 wt%. After additional periods of drying and weighing, the final loss in weight at 100 °C was 1.60 wt%. The sample was next exposed to room air for 2 h and showed a gain in weight of 0.55 wt%. It was once more dried at 100 °C and lost the 0.55 wt% moisture absorbed during exposure to the atmosphere. This dried sample was mixed immediately with a flux of lead oxide and lead chromate. The H_2O content was determined by the Penfield method to be 8.68 wt%.

The combined analysis yields SiO_2 46.8, Al_2O_3 0.2, Fe_2O_3 0.8, MgO 1.6, CaO 21.6, MnO 19.7, Na_2O 0.6, H_2O 8.68, total = 100.0 wt%. The unit-cell contents, calculated using a density of 2.8 g/cm^3, are: $(Ca_{18.62}Mn_{13.43}Mg_{2.39}Na_{0.74}Fe^{3+}_{0.48})_{\Sigma 35.66}(Si_{37.66}Al_{0.19})_{\Sigma 37.85}O_{111.24} \cdot 23.29H_2O$. This is tentatively idealized as $Ca_4Mn_3Si_8O_{20}(OH)_6 \cdot 2H_2O$, with $Z = 5$ as described below.

DISCUSSION

The unit-cell parameters of orlymanite are similar to those of the gyrolite group, for which the structural relations were reviewed by Dunn et al. (1984) and more recently by Merlino (1988b). Gyrolite, reyerite, truscottite, fedorite, and minehillite, as well as the synthetic K- and Z-phases are either hexagonal, trigonal or pseudotrigonal in symmetry, with two lattice translations of approximately 9.7 Å related by an angle of approximately 120°, and a value of *c* ranging from 12 to 33 Å. The large values of *c* are caused by a layered structure in which tetrahedral and octahedral sheets are interlayered, as exemplified in Figure 2, where the scheme of articulation of a tetrahedral sheet and an octahedral sheet are illustrated. The octahedral sheets are brucite-like, but with Ca as the octahedral cation. Single tetrahedral sheets have composition Si_8O_{20}, the composition of a tetrahedral sheet in simple phyllosilicate structures. In gyrolite-family structures, however, not all tetrahedra articulate to a single octahedral sheet; as shown in Figure 2, the vertices of some tetrahedra are reversed, giving rise to linkage to octahedral sheets both above and below the tetrahedral sheet. Two sheets can also be cross-linked to give rise to a double tetrahedral layer of composition $Si_{16}O_{38}$. H_2O, or large cations such as K, can occupy voids within double tetrahedral sheets, or expandable layers consisting of H_2O coordinating Ca or Na may be inserted between double tetrahedral layers, as in gyrolite (Merlino, 1988b).

Calculation of unit-cell contents for orlymanite shows that there are 37.7 Si, 0.2 Al, and 35.7 large cations (Ca, Fe, Mg, Mn, and Na) per unit cell. A single trioctahedral layer of gyrolite-family minerals 9.7 × 9.7 Å contains seven cations. If it is assumed that the layered orlymanite structure contains similar units, the cell contents are consistent with five such units. Similarly, five tetrahedral layers would give rise to 40 tetrahedrally coordinated cations. This number exceeds the available Si + Al by 2.3 atoms, a difference that appears to exceed the probable error. Nevertheless, the predicted and observed numbers of tetrahedral cations are similar enough to conclude that the analogy is a sensible one. In part because other tetrahedral cell contents give rise to unacceptably complex formulae in combination with 35 octahedral cations, the tetrahedral cell contents are set to 40 atoms, with the admonition that the number is a tentative one.

The number of O atoms required of five tetrahedral sheets is 100, but if two sheets are polymerized to form a double tetrahedral layer, as in reyerite (Merlino, 1988a), the number of O atoms is decreased by two. Up to two such pairings are possible among five tetrahedral sheets. The number of tetrahedrally coordinating O atoms can therefore be 100, 98, or 96. Charge balance is achieved by OH ions in sheets that coordinate the large cations, principally Ca. Double tetrahedral sheets are very unlikely, however, as the cell contents clearly imply equal numbers of tetrahedral and octahedral sheets, and double tetrahedral sheets cause the loss of an octahedral sheet in the stacking sequence. Other structure relations are possible of course, and some are discussed below. However, for the purposes of deriving a simple, reasonable formula, the number of O atoms was tentatively set to 100. The H content was then divided between OH and H_2O, with the number of OH chosen to provide charge balance. Lastly, the numbers of Ca and Mn atoms correspond approximately to four and three per cell, respectively. The formula has been written to emphasize those numbers, based on a possibility of ordering, as is common among other (Ca,Mn) minerals, specifically in the associated inesite. The formula thus derived is $Ca_4Mn_3Si_8O_{20}(OH)_6 \cdot 2H_2O$. This must be judged only as a tentative formula, however, based as it is on a number of assumptions. Nevertheless, it must be close to the true formula; it distinguishes orlymanite from other minerals, and it defines a clear and simple composition.

The structure must be different in detail than the simple model discussed above, in which five tetrahedral sheets alternate with five octahedral sheets. Such a structure would be expected to display a subperiodicity of *c*/5 and no such relation is observed. Indeed, the diffractometer pattern implies a weak subperiodicity of *c*/2. In addition, the lattice-fringe images imply a lack of a simple tetrahedral + octahedral unit which would have a spacing of 36/5 = 7.2 Å and show the presence of two subunits having different spacings. The occurrence of H_2O as required by the formula is also problematical, in that H_2O occurs either in cavities within a double tetrahedral sheet or in an expandable sheet articulated with two tetrahedral sheets in gyrolite-type structures. The presence of the latter unit in orlymanite causes the value of *c* to be significantly in excess of 36 Å. All of the models hypothesized for the orlymanite structure that are based exclusively on gyrolite-structure relations also appear to be inadequate in detail.

A structure having the appropriate *c*-axis repeat (36 Å) and chemistry can be derived with a simple variant on gyrolite-family structure relations, however. A structure consisting of a double tetrahedral sheet, four octahedral sheets, and three single tetrahedral sheets would have a value of *c* of approximately 31.5 Å. Insertion of a single brucite-like layer with OH ions coordinating Mn or Ca would give rise to the observed relations. Such a structure is entirely hypothetical, but it does reflect the close relation existing between gyrolite-family structures and those of the phyllosilicates, as discussed in the next section.

GYROLITE/PHYLLOSILICATE RELATIONS

Mackay and Taylor (1953) originally showed that the structure of gyrolite is layered and that it is analogous to those of the phyllosilicates. Merlino (1988b) further emphasized the relation between gyrolite-family and phyllosilicate structures. Guggenheim and Eggleton (1987) subsequently summarized relations for layered structures in which the octahedral cations are so large as to give rise to a misfit that prevents articulation with a tetrahedral sheet as found in ordinary phyllosilicates. The misfit is accommodated through modulation of the tetrahedral sheets, which Guggenheim and Eggleton (1987, 1988) refer to as a "periodic perturbation" that may involve reversal in the direction of silica tetrahedra. Ca is generally excluded from both ordinary phyllosilicates and modulated 2:1-layer silicates, as its radius is even larger than those of octahedral cations found in the modulated structures, but Mn may be accommodated in some structures. Gyrolite-family phases all have only Ca as the cation in the brucite-like layer. The presence of the smaller Mn^{2+} cations in the gyrolite-related structure of orlymanite suggests a more general relation between phyllosilicates and the gyrolite family, based in part on the relation between cation radius and structure type described by Guggenheim and Eggleton (1987, 1988).

Ordinary 2:1 and 1:1 phyllosilicates such as micas and serpentine-family minerals have structures based on tetrahedral sheets that consist of linked six-membered rings. All apical vertices point in a single direction and are shared with octahedral sheets, giving rise to articulation of the octahedral and tetrahedral sheets. The linked six-membered rings form chains that are parallel to linked octahedra. In 1:1 trioctahedral phyllosilicates, the ratio of tetrahedral to octahedral cations is 4:6. In gyrolite-family structures, octahedrally coordinated Ca is so large that the kind of articulation found in common phyllosilicates cannot occur. Figure 2 shows, however, that the tetrahedral sheet maintains its basic topology. Articulation occurs, despite the misfit, through three mechanisms: (1) reversal of the apices of some tetrahedra (as in modulated structures) so that a given tetrahedral sheet is articulated to octahedral sheets both above and below, (2) rotation of individual tetrahedra about an axis normal to the layers, with resultant loss of ideal sixfold symmetry, as shown in Figure 2, and (3) relative rotation of the tetrahedral and octahedral sheets about the *c* axis, with rows of six-membered rings then not being parallel to linked octahedra, as shown in Figure 2. The ratio of tetrahedral to octahedral cations is 8:7, even though the trioctahedral and tetrahedral sheets each has the same topology as the corresponding units in ordinary phyllosilicates (except that apices of half the tetrahedra are reversed); that is, the number of octahedral cations decreases from 12, as in micas, to 7 per 8 tetrahedral cations.

Guggenheim and Eggleton (1987, 1988) showed that the modulated phyllosilicates are characterized by octahedral cations that are larger than those in nonmodulated phyllosilicates. The resulting misfit between octahedral and tetrahedral sheets is accommodated through reversal of apical directions of some tetrahedra, as in gyrolite-family minerals, but also by modulation of the normal linkage of the six-membered rings of the tetrahedral sheets. For example, in zussmanite six-membered rings of tetrahedra are interlinked by three-membered rings. The modulated tetrahedral sheet therefore has very different dimensions that permit articulation to the octahedral sheet. Guggenheim and Eggleton (1988) further noted the relation of gyrolite-group structures to those of modulated phyllosilicates; they noted that the analogy to phyllosilicates is limited because so few of the tetrahedra in a single sheet (only 50% of the sheet shown in Fig. 2) are linked to the adjacent octahedral sheet.

The relations described above imply that the extended family of layer silicates is limited by small octahedral cations such as Mg or Al, permitting articulation as found in micas or serpentine-family structures. Cations of intermediate size give rise to modulated structures in minerals with these general structure features, whereas Ca is the cation with the largest radius, giving rise to gyrolite-family structures. There is an analogous relation among the pyroxenes and pyroxenoids (Prewitt and Peacor, 1964). In those structures the small cations such as Mg permit simple articulation of single SiO_3 chains to rows of octahedra, giving rise to a chain with a repeat unit of two tetrahedra. In pyroxenoids where Ca is the dominant cation (e.g., wollastonite), the large cation causes articulation to be achieved only with a chain having a repeat of three tetrahedra. Cations with radii smaller than that of Ca give rise to articulated chains with repeats of 5 (3 + 2), 7 (3 + 2 + 2), . . . 2 (2 + 2 + 2 . . . as in pyroxene). Orlymanite may therefore be a link between conventional phyllosilicate and gyrolite-family minerals, with the relations between those two groups being analogous to those between pyroxenes and pyroxenoids and based on similar requirements of tetrahedral and octahedral articulation.

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