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# THE PYROSMALITE GROUP OF MINERALS
# I. STRUCTURE REFINEMENT OF MANGANPYROSMALITE

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## ABSTRACT

Iron-rich manganpyrosmalite and manganpyrosmalite from the Kyurazawa mine, Japan, have space group $P\bar{3}m1$ and cell dimensions *a* 13.391(4), *c* 7.139(2) Å, and *a* 13.422(5), *c* 7.165(2) Å, respectively. Refinements using X-ray data and isotropic temperature parameters confirm the structure proposed for manganpyrosmalite (Takéuchi *et al.* 1969). Newly discovered features include: (1) the elongation of silicate tetrahedra: pyramidal edges are longer than basal edges by about 5%; (2) the tilting of tetrahedra with respect to the octahedral layer, which contributes to the ditrigonal symmetry of the six-membered rings, and (3) the preferential substitution of Cl ions at the OH(1) site, causing the *M*(1)–OH(1) distance in each mineral to be about 13% larger than the average *M*–OH value for the other three octahedra.

*Keywords:* pyrosmalite, manganpyrosmalite, sheet silicate.

## SOMMAIRE

Deux spécimens de manganpyrosmalite provenant de la mine de Kyurazawa (Japon), le premier à haute teneur en fer, cristallisent en $P\bar{3}m1$ avec des mailles suivantes: *a* 13.391(4), *c* 7.139(2) Å, et *a* 13.422(5), *c* 7.165(2) Å, respectivement. L'affinement, à partir des données de diffraction X et de paramètres de température isotropes, confirme dans chaque cas la structure proposée par Takéuchi *et al.* (1969). Parmi les caractéristiques récemment reconnues, signalons: (1) l'allongement des tétraèdres $SiO_4$: la longueur des arêtes pyramidales excède celle des arêtes basiques de 5%; (2) l'inclinaison des tétraèdres sur la couche octaédrique d'où résulte la symétrie ditrigonale des anneaux à six tétraèdres; (3) la substitution de tout le Cl à OH uniquement au site OH(1), ce qui explique pourquoi la distance *M*(1)–OH(1), dans chacun de nos deux spécimens, est d'environ 13% plus grande que la valeur moyenne *M*–OH pour les trois autres octaèdres.

(Traduit par la Rédaction)

*Mots-clés:* pyrosmalite, manganpyrosmalite, silicate en feuillets.

## INTRODUCTION

Pyrosmalite and friedelite, which have been recognized since the early nineteenth century (Zambonini 1901), together with schallerite (Gage *et al.* 1925), comprise a group of sheet silicates whose basic cell content may be simplified by the formula $(Mn^{2+},Fe^{2+})_{16}(Si_{12}O_{30})(OH,Cl)_{20}$ (Frondel & Bauer 1953). The names *pyrosmalite* and *friedelite* refer to the Fe and Mn end-members, respectively, of the solid-solution series (Winchell 1951); *schallerite* is a variant of this group containing $As^{3+}$ which, according to Berman (1937), substitutes for Si and forms a solid-solution series involving (Fe, Mn)(OH,Cl) and (Si,As). However, Dunn *et al.* (1981) proposed a new formula for schallerite, $(Mn,Fe)_{16}Si_{12}O_{30}(OH)_{14}[(As^{3+}{}_3O_6)(OH)_3]$, based on the results of five detailed chemical analyses.

On the basis of X-ray studies of more than 20 specimens from various localities, Frondel & Bauer (1953) revealed the existence of "poly-

TABLE 1. UNIT-CELL DIMENSIONS OF PYROSMALITE AND RELATED MINERALS[†]

| Mineral | a | c | Lattice type | Z |
|---|---|---|---|---|
| Pyrosmalite | 13.35 Å | 7.15 Å | Hexagonal | 2 |
| Manganpyrosmalite | 13.36 | 7.16 | Hexagonal | 2 |
| Schallerite | 13.43 | 7.16 x 2 | Hexagonal | 4 |
| Friedelite* | 13.40 | 7.15 x 3 | Rhombohedral | 6 |

[†] Taken from Frondel & Bauer (1953). * Revised cell is monoclinic, $a$ 23.33, $b$ 13.396, $c$ 7.447 Å, β 105.17° and $Z = 2$ (Ozawa *et al.*, in prep.).

morphic relations" between the minerals of this group. In Table 1, which is a modified version of the table provided by Frondel & Bauer, the value of $a$ of the unit cell in hexagonal axes is shown to be virtually identical for these minerals, whereas the values of $c$ are almost exact multiples. The minerals schallerite and friedelite may then be regarded as two-layer hexagonal and three-layer rhombohedral variants of the basic one-layer hexagonal structure-type of pyrosmalite. The existence of manganpyrosmalite (Frondel & Bauer 1953), which is a Mn-rich variant of the pyrosmalite structure-type, suggests the existence in this group of minerals of a polytypic series that could be similar to that among the micas.

The essential configuration of the silicate sheet $[Si_6O_{15}]^{6-}$ was unraveled by Takéuchi *et al.* (1969) when they determined the structure of manganpyrosmalite from the Kyurazawa mine, Japan. They also suggested possible structures or stacking sequences for schallerite and friedelite, assuming the two-layer hexagonal and three-layer rhombohedral structures reported by Frondel & Bauer (1953). Further discussions along this line were made by Kashaev (1968) and Kashaev & Drits (1970). The present paper describes the results of our structure refinements of two crystals of manganpyrosmalite using X-ray-diffraction data.

## EXPERIMENTAL

Two specimens of manganpyrosmalite used for the present study came from the Kyurazawa mine, Tochigi Prefecture, Japan. The reported cell contents of these specimens (Watanabe & Kato 1957, Watanabe *et al.* 1961), recalculated to give structural formulae with the required multiplicities and charge balance, are, respectively, $(Mn^{2+}{}_{8.13}Fe^{2+}{}_{7.00}Mg^{2+}{}_{0.86}Zn_{0.01})$ $(Si_{11.65}Fe^{3+}{}_{0.28}Al_{0.05}Ti^{4+}{}_{0.02})$ $(O_{29.67}OH_{16.99}Cl_{3.34})$ and $(Mn_{12.00}Fe^{2+}{}_{2.72}Mg_{0.58}Al_{0.21}\square_{0.29})$ $Si_{12}(O_{29.63}OH_{17.46}Cl_{2.91})$. The $Fe^{3+}$ and $Ti^{4+}$ ions were assumed to substitute for Si atoms. The specimen having the former composition may be called an iron-rich manganpyrosmalite. Crystal fragments having approximate dimensions of 0.24 x 0.20 x 0.12 mm (iron-rich manganpyrosmalite) and 0.18 x 0.15 x 0.09 mm (manganpyrosmalite) were selected and used for X-ray study. Cell dimensions of these specimens were obtained by least squares applied to $2\theta$ values of 25 reflections. A four-circle diffractometer and graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å were used for intensity measurements. The values are: 1) for iron-rich manganpyrosmalite, $a$ 13.391(4), $c$ 7.139(2) Å; 2) for manganpyrosmalite, $a$ 13.422(5), $c$ 7.165(2) Å. The reported space group $P3m1$ was confirmed.

The intensities of reflections were measured with the $\omega$–$2\theta$ scan mode up to $2\theta = 60°$. Of the 688 reflections for iron-rich manganpyrosmalite, those with intensities smaller than $3\sigma(I)$ were excluded, and remaining 475 reflections were used for refinement; the corresponding numbers for manganpyrosmalite were 693 and 423, respectively. Most of the diffuse reflections observed in X-ray photographs, particularly of manganpyrosmalite, were found to give intensities smaller than $3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects and for absorption, the latter being calculated using the program ACACA based on a procedure provided by Wuensch & Prewitt (1965). The structure-factor tables are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

## REFINEMENT

The crystal structure reported by Takéuchi *et al.* (1969) provided an initial set of atomic co-ordinates. At first, structure-factor calculations were based on the idealized formula, $Mn^{2+}{}_8Si_6O_{15}(OH)_{10}$, and atomic scattering factors for these atoms were taken from the *International Tables for X-ray Crystallography* (Vol. IV). Repeated cycles of isotropic least-squares refinement, using the program FLS4 in the UNICS system (Sakurai 1967) and adopting the unit-weight scheme for significant reflections, converged to give $R = 6.8\%$ (weighted $R = 6.0\%$) for iron-rich manganpyrosmalite and 10.8% (10.3%) for manganpyrosmalite. At this stage we noted that the isotropic temperature-factor of OH(1) was very small, 0.18 Å$^2$ for iron-rich manganpyrosmalite and 0.06 Å$^2$ for manganpyrosmalite, whereas the average $B$ for the remaining three OH sites was 1.7 Å$^2$ for iron-rich manganpyrosmalite and 0.78 Å$^2$ for manganpyrosmalite.

The same relation had been observed in the previous structural study, based on photographic

TABLE 2. ATOMIC COORDINATES AND TEMPERATURE FACTORS

| Atom | Equipoint | Site Symmetry | x | y | z | B Å$^2$ | x | y | z | B Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Iron-rich manganpyrosmalite | | | | Manganpyrosmalite | | | |
| M(1) | 1a | $\bar{3}m$ | 0 | 0 | 0 | 1.17 | 0 | 0 | 0 | 1.29 |
| M(2) | 6g | 2 | 0.2549(1) | 0 | 0 | 0.84 | 0.2542(2) | 0 | 0 | 0.76 |
| M(3) | 3e | 2/m | 1/2 | 0 | 0 | 0.73 | 1/2 | 0 | 0 | 0.51 |
| M(4) | 6i | m | 0.5026(1) | 0.2513 | 0.0222(2) | 0.64 | 0.5024(2) | 0.2512 | 0.0288(3) | 0.52 |
| Si | 12j | 1 | 0.4375(2) | 0.1046(2) | 0.6245(2) | 0.54 | 0.4369(3) | 0.1036(3) | 0.6241(3) | 0.52 |
| O(1) | 6h | 2 | 0.3413(6) | 0 | 1/2 | 1.11 | 0.3405(8) | 0 | 1/2 | 1.40 |
| O(2) | 6i | m | 0.5640(5) | 0.1280 | 0.5582(10) | 0.98 | 0.5644(9) | 0.1288 | 0.5574(12) | 1.20 |
| O(3) | 6i | m | 0.4316(5) | 0.2158 | 0.5551(10) | 0.87 | 0.4302(9) | 0.2151 | 0.5553(12) | 1.05 |
| O(4) | 12j | 1 | 0.4199(4) | 0.0841(4) | 0.8491(9) | 0.68 | 0.4200(8) | 0.0839(8) | 0.8486(15) | 0.48 |
| OH(1) | 6i | m | 0.1680(3) | 0.0840 | 0.7756(6) | 2.09 | 0.1684(7) | 0.0842 | 0.7733(15) | 2.21 |
| OH(2) | 6i | m | 0.3366(5) | 0.1683 | 0.1330(11) | 0.91 | 0.3350(9) | 0.1675 | 0.1407(18) | 0.46 |
| OH(3) | 6i | m | 0.5809(5) | 0.1618 | 0.1450(11) | 0.89 | 0.5815(9) | 0.1630 | 0.1495(18) | 0.40 |
| OH(4) | 2d | 3m | 1/3 | 2/3 | 0.1218(22) | 0.40 | 1/3 | 2/3 | 0.1233(32) | 0.52 |

intensity-data (Takéuchi *et al.* 1969). This relation is more evident in the present case and suggests that the Cl is preferentially located at this position, as proposed by Takéuchi *et al.* (1969). Noting that both iron-rich manganpyrosmalite and manganpyrosmalite contain approximately three Cl ions per cell and that the OH(1) positions have rank 6, we used for this position a modified scattering-factor consisting of the average value for O and Cl, and continued least-squares refinement. The resulting *R* values were only slightly reduced to 6.0% for iron-rich manganpyrosmalite and 10.5% for manganpyrosmalite, the weighted *R* value being 5.8% and 10.0%, respectively. The final *R* values (and weighted *R* values) for all reflections, including nonobserved reflections, were 11.5% (8.9%) for iron-rich manganpyrosmalite and 21.8% (14.8%) for manganpyrosmalite. The final difference-Fourier map did not show any anomalies at the octahedral positions; therefore, no attempt was made to locate Mg and Zn atoms. Table 2 gives the final atomic parameters of both mineral species, and Table 3 lists representative values of bound lengths and bond angles.

TABLE 3. INTERATOMIC DISTANCES AND BOND ANGLES

Iron-rich manganpyrosmalite

Si tetrahedron

| Bond | Bond length | Edge | Edge length | Bond angle |
|---|---|---|---|---|
| Si - O(1) | 1.615(5) Å | O(1) - O(2) | 2.626(10) Å | 108.0(4)° |
| - O(2) | 1.631(10) | O(2) - O(3) | 2.571(16) | 105.0(5) |
| - O(3) | 1.609(10) | O(3) - O(1) | 2.544(11) | 104.2(4) |
| - O(4) | 1.624(5) | O(1) - O(4) | 2.721(5) | 114.3(2) |
| Average | 1.620 | O(2) - O(4) | 2.693(9) | 111.6(4) |
| | | O(3) - O(4) | 2.696(10) | 113.0(4) |
| | | Average | 2.642 | 109.4 |

Octahedra

| Bond | Bond length | Bond | Bond length |
|---|---|---|---|
| M(1) - OH(1) x6 | 2.523(7) Å | M(3) - O(4) x4 | 2.189(6) Å |
| | | - OH(3) x2 | 2.144(8) |
| | | Average | 2.174 |
| M(2) - OH(1) x2 | 2.549(7) | M(4) - O(4) x2 | 2.300(4) |
| - OH(2) x2 | 2.170(8) | - OH(2) | 2.082(11) |
| - O(4) x2 | 2.195(5) | - OH(3) x2 | 2.135(8) |
| Average | 2.305 | - OH(4) | 2.162(8) |
| | | Average | 2.186 |

Manganpyrosmalite

Si tetrahedron

| Bond | Bond length | Edge | Edge length | Bond angle |
|---|---|---|---|---|
| Si - O(1) | 1.612(5) Å | O(1) - O(2) | 2.645(13) Å | 108.7(5)° |
| - O(2) | 1.641(13) | O(2) - O(3) | 2.583(12) | 104.8(6) |
| - O(3) | 1.620(14) | O(3) - O(1) | 2.543(11) | 103.8(4) |
| - O(4) | 1.628(11) | O(1) - O(4) | 2.728(10) | 114.7(3) |
| Average | 1.625 | O(2) - O(4) | 2.703(14) | 111.5(5) |
| | | O(3) - O(4) | 2.701(15) | 112.6(5) |
| | | Average | 2.651 | 109.4 |

Octahedra

| Bond | Bond length | Bond | Bond length |
|---|---|---|---|
| M(1) - OH(1) x6 | 2.543(8) Å | M(3) - O(4) x4 | 2.193(10) Å |
| | | - OH(3) x2 | 2.177(11) |
| | | Average | 2.188 |
| M(2) - OH(1) x2 | 2.558(10) | M(4) - O(4) x2 | 2.311(9) |
| - OH(2) x2 | 2.192(11) | - OH(2) | 2.123(11) |
| - O(4) x2 | 2.212(8) | - OH(3) x2 | 2.147(15) |
| Average | 2.321 | - OH(4) | 2.177(11) |
| | | Average | 2.203 |

## DISCUSSION

The refined structures of iron-rich manganpyrosmalite and manganpyrosmalite are essentially the same as that of manganpyrosmalite first reported by Takéuchi *et al.* (1969), and isotypic with pyrosmalite (Kashaev 1968). The structure consists of brucite-type octahedral layers alternating with $Si_6O_{15}$ tetrahedral sheets. The tetrahedral sheet consists of six-membered rings of tetrahedra having two different orientations; the apical oxygen atoms of the tetrahedral rings in one orientation are bonded to Mn atoms in the lower octahedral layer, whereas those of the ring in the other orientation are bonded to Mn atoms in the upper octahedral layer (Fig. 1). The six-membered rings are

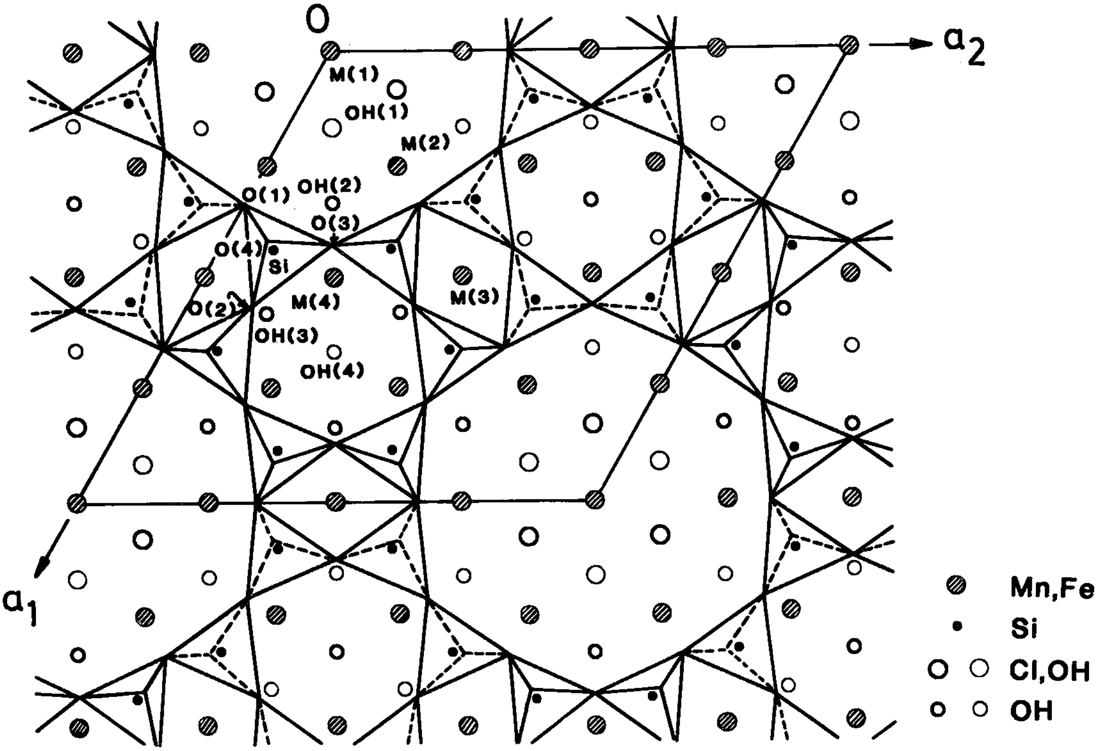

FIG. 1. The crystal structure of iron-rich manganpyrosmalite viewed along the *z* axis, showing the tetrahedral sheet and the octahedral sheet below the silicate sheet.

linked together to form twelve-membered rings and four-membered rings to complete the continuity of the sheet (Fig. 1).

As will be described in detail in Part II (Ozawa *et al.*, in prep.), the minerals of the pyrosmalite group are characterized by stacking disorder, which is most pronounced in the Mn-rich members of the group. The high *R*-factor (10.5%) of the structure of manganpyrosmalite can be rationalized in terms of stacking disorder. We find, nonetheless, that the bond lengths and angles of manganpyrosmalite (Table 3) are close to those of iron-rich manganpyrosmalite. In both structures, the silicate tetrahedra are elongated toward their apical oxygen atom O(4); the average length of the pyramidal edges exceeds that of the basal edges by 4.8% in iron-rich manganpyrosmalite and 4.6% in manganpyrosmalite. It follows that, in both structures, the mean of the tetrahedral angles subtended at the central cation by the pyramidal edges is about 6.6% larger than that of the angles subtended by the basal edges (Table 3). The tilt of the tetrahedra (Fig. 1) enhances the ditrigonal character of the six-membered rings, a feature well illustrated by the differences in bond length between Si–O(2) and Si–O(3) (Table 3) and in bond angles between Si–O(2)–Si and Si–O(3)–Si; in iron-rich manganpyrosmalite, for example, the former angle has a value of 141.0° and the latter, 143.6°.

When all Cl is assigned to the OH(1) position, the ratio Cl:OH for that site is about 1:1. The isotropic temperature-factor, which, as we pointed out above, was abnormally small before Cl was introduced, is now relatively large. This is to be expected since the OH and Cl differ in radius. The long bond-lengths *M*(1)–OH(1) and *M*(2)–OH(1) confirm the presence of all Cl atoms in the OH(1) site (Table 3); they are responsible for the larger edge-lengths of the octahedron about *M*(1) as compared with those of the other octahedra (Fig. 2).

In both structures, the octahedra about *M*(3) have the smallest mean *M*–O distances (Table 3), indicating the presence of the smaller cations, such as Mg and Zn, and vacant sites. However, since neither the isotropic temperature-factor for *M*(3) (Table 2) nor the difference-Fourier map, as mentioned above, shows any anomaly when all four octahedral cation

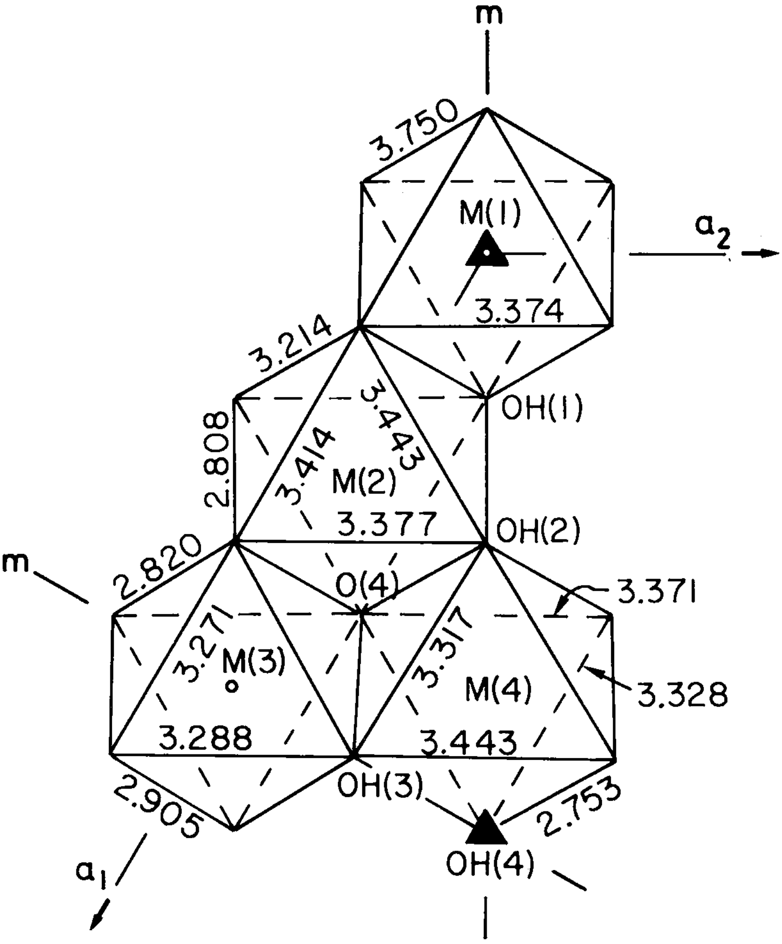

FIG. 2. Four nonequivalent edge-sharing octahedra in the iron-rich manganpyrosmalite structure, showing their edge lengths. Some of the symmetry elements of $P\bar{3}m1$ are indicated as an aid in identifying symmetrically equivalent edges.

positions are given equal chemical character, the preferential location of Mg at the *M*(3) site is not conclusive.

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