THE PYROMALITE GROUP OF MINERALS
I. STRUCTURE REFINEMENT OF MANGANPYROMALITE

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ABSTRACT

Iron-rich manganpyromalite and manganpyromalite from the Kyurazawa mine, Japan, have space group \( P\overline{3}m1 \) 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 manganpyromalite (Takeuchi 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.

Key words: pyromalite, manganpyromalite, sheet silicate.

INTRODUCTION

Pyromalite 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 \( (\text{Mn}^{2+},\text{Fe}^{3+})_{16}(\text{Si},\text{As})\text{O}_{32}(\text{OH},\text{Cl})_{26} \) (Frondel & Bauer 1953). The names pyromalite 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 \( \text{As}^{3+} \) which, according to Berman (1937), substitutes for Si and forms a solid-solution series involving \( (\text{Fe}, \text{Mn})(\text{OH},\text{Cl}) \) and \( (\text{Si},\text{As}) \). However, Dunn et al. (1981) proposed a new formula for schallerite, \( (\text{Mn},\text{Fe})_{16}\text{Si}_{10}\text{O}_{32}(\text{OH})_{16}(\text{As}^{3+}3\text{O}_{8})(\text{OH})_{3} \), 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

<table>
<thead>
<tr>
<th>Mineral</th>
<th>a</th>
<th>c</th>
<th>Lattice type</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrosmalite</td>
<td>13.35 (\text{Å})</td>
<td>7.15 (\text{Å})</td>
<td>Hexagonal</td>
<td>2</td>
</tr>
<tr>
<td>Manganpyrosmalite</td>
<td>13.36 (\text{Å})</td>
<td>7.16 (\text{Å})</td>
<td>Hexagonal</td>
<td>4</td>
</tr>
<tr>
<td>Schallerite</td>
<td>13.43 (\text{Å})</td>
<td>7.16 x 2</td>
<td>Hexagonal</td>
<td>6</td>
</tr>
<tr>
<td>Friedelitea</td>
<td>13.40</td>
<td>7.15 x 3</td>
<td>Rhombohedral</td>
<td>6</td>
</tr>
</tbody>
</table>

\(a\) values are estimated from the cell contents recalculated to give structural formulae with the required multiplicities and charge balance.

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The essential configuration of the silicate sheet \([\text{Si}_{0.67}\text{O}_{4.86}]^-\) 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, \((\text{Mn}_{2.07\pm0.03}\text{Fe}^{2+}_{1.68}\text{Mg}^{2+}_{0.62}\text{Zn}_{0.06})\) \((\text{Si}_{11.05}\text{Fe}^{3+}_{1.18}\text{Al}_{0.05}\text{Ti}^{4+}_{0.03})\) \((\text{O}_{25.25}\text{OH}_{0.60}\text{Cl}_{2.35})\) and \((\text{Mn}_{12.90}\text{Fe}^{2+}_{2.89}\text{Mg}_{0.58}\text{Al}_{0.74}\square_{0.29})\) \((\text{Si}_{10.65}\text{OH}_{17.04}\text{Cl}_{2.91})\). The \(\text{Fe}^{2+}\) and \(\text{Ti}^{4+}\) 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 MoK\(\alpha\) radiation (\(\lambda = 0.71069 \text{Å}\) were used for intensity measurements. The values are: 1) for iron-rich manganpyrosmalite, \(a\) 13.391(4), \(c\) 7.139(2) \(\text{Å}\); 2) for manganpyrosmalite, \(a\) 13.422(5), \(c\) 7.165(2) \(\text{Å}\). The reported space group \(P3\overline{1}m\) was confirmed.

The intensities of reflections were measured with the \(\omega-2\theta\) scan mode up to \(2\theta = 60^\circ\). 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, \(\text{Mn}^{2+}_{2.3}\text{Si}_{1.18}\text{O}_{4.86}(\text{OH})_{16}\), 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 \(\text{OH}(1)\) was very small, 0.18 \(\text{Å}^2\) for iron-rich manganpyrosmalite and 0.06 \(\text{Å}^2\) for manganpyrosmalite, whereas the average \(B\) for the remaining three \(\text{OH}\) sites was 1.7 \(\text{Å}^2\) for iron-rich manganpyrosmalite and 0.78 \(\text{Å}^2\) for manganpyrosmalite.

The same relation had been observed in the previous structural study, based on photographic
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 6.0Vo for iron-rich manganpyrosmalite and 1A.5Vo for manganpyrosmalite, the weighted R value being 5.5Vo and 10.0Vo, respectively. The final R values (and weighted R values) for all reflections, including nonobserved reflections, were 11.5Vo (8.9Vo) for iron-rich manganpyrosmalite and 21.8Vo (14.8Vo) 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.

**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 SiO₄ 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
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 $P3m1$ 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.

ACKNOWLEDGEMENTS

We thank Dr. K. Sakurai for providing us with the specimens. We are indebted to Professor Gabrielle Donnay, McGill University, for critically reviewing the manuscript and for discussion. Computations were performed on the M-200 at the Computing Center of Kyushu University. The two referees and Associate Editor H.D. Grundy provided important and helpful comments.

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Received February 16, 1982, revised manuscript accepted June 1, 1982.