

Crystal structure of $\text{SrMn}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$, a new mineral of the lawsonite type

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Abstract : Crystals with the composition $\text{SrMn}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$ were found in a sugilite, serandite-pectolite rich sample from the Wessels Mine, Kalahari, South Africa. The crystal structure of the new compound with space group *Cmcm*, $a = 6.255(1)$, $b = 9.034(2)$, $c = 13.397(2)$ Å, $Z = 4$ was determined from X-ray single-crystal data ($R = 0.048$). The structure is of the lawsonite type where Al is completely replaced by Mn^{3+} and Ca by Sr. $[\text{Mn}^{3+}\text{O}_6]$ octahedra forming edge-sharing chains parallel to a exhibit a Jahn-Teller distortion with four short and two long Mn^{3+} -O distances. Sr is in eight-fold coordination and H_2O is disordered on a split position. Together with orientite, macfallite, ruizite, and okhotskite the new compound belongs to a family of structures which have the fundamental building block $[\text{Mn}^{3+}_2(\text{OH})_2(\text{SiO}_4)_2]$ and 6×9 Å cell dimensions in common.

Key-words : lawsonite, soro-silicate, crystal structure, Mn^{3+} Jahn-Teller distortion.

Introduction and sample description

During a study of sugilite from the Wessels Mine of the Kalahari manganese fields in South Africa (Armbruster & Oberhänsli, 1988b), a petrographic thin section of a $7 \times 7 \times 7$ cm hand specimen (NMBE-B5564), composed of idiomorphic sugilite up to 0.5 mm in size embedded in fibrous serandite-pectolite, was investigated. This fairly homogeneous assemblage is crosscut by small veins (*ca.* 2-5 mm in width), which are filled with serandite-pectolite and minor concentrations of unknown minerals. One of these minerals appears yellow-brown under the polarizing microscope and has significantly higher refractive indices than the surrounding serandite-pectolite. Irregular aggregations up to 1 mm in diame-

ter of this mineral are markedly intergrown with serandite-pectolite and less so with sugilite. The mineral also occurs less commonly in the form of a felty matrix in sugilite-rich parts of the sample. Routine electron-microprobe energy dispersive spectra (EDS) reveal only Mn and Si as cations but the analytical sums are extremely low (<70 wt. %) assuming only SiO_2 and Mn_2O_3 . To elucidate the chemical and structural nature of this striking mineral, a strongly intergrown crystal fragment was separated from the thin section and used to determine the space group *Cmcm* with $a = 6.2$, $b = 9.0$, $c = 13.4$ Å. In spite of the low crystal quality (inclusions of serandite-pectolite), a single-crystal X-ray data set collected at 130 K enabled the structure to be solved by direct methods. Results indicate that the structure

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is of the lawsonite type. Test refinements also show that the cations in the structural interstices (X site), which are occupied by Ca in lawsonite, display longer X-O distances than are known for Ca-O and that the electron density on X is higher than would be expected for Ca. Subsequent test refinements were performed for Sr and Ba on X. Best agreement ($R = 13\%$) was found for Sr. We speculated from this evidence that the new mineral has the composition $\text{SrMn}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$. Sr is not routinely detected in electron microprobe EDS spectra because Sr_L lines are hidden by Si_K lines.

Although the authors have never visited the Wessels Mine (the sample was obtained from a mineral collector), we believe that the small veins in which the new mineral occurs must be of hydrothermal origin. De Villiers (1971) describes a five-period sequence of mineral formation at the Kalahari field: (1) sedimentary stage, (2) minerals formed by lithification, (3) metamorphic stage, (4) supergene mineralization, (5) hydrothermal mineralization (*e.g.* acgirine, cymrite, piemontite). In the Falotta manganese depo-

sits (Oberhalbstein, Grison, Switzerland) Sr-enriched piemontite (up to 15 wt. % SrO) has also been related to late hydrothermal fluid circulation (Perseil, 1990).

The present paper describes the chemical and structural analysis of this new compound from the Wessels Mine.

Chemical composition

A polished thin section mount, one inch in diameter, was used for electron and ion-microprobe analyses. The elements Si, Al, Ti, Fe, Mg, Mn, Sr, Ba, Ca, Na and K were analyzed with the SEMQ-TN2000 electron microprobe at the University of Bern. A detailed description of analytical procedures is given in Armbruster & Oberhänsli (1988a). Mn and Fe were assumed to be in the three-valent state because of stoichiometric and structural reasons. Lithium on the same grains was later analyzed on an IMS-4F ion microprobe at the Cameca Corporation laboratory in Paris. Measuring conditions were chosen according to

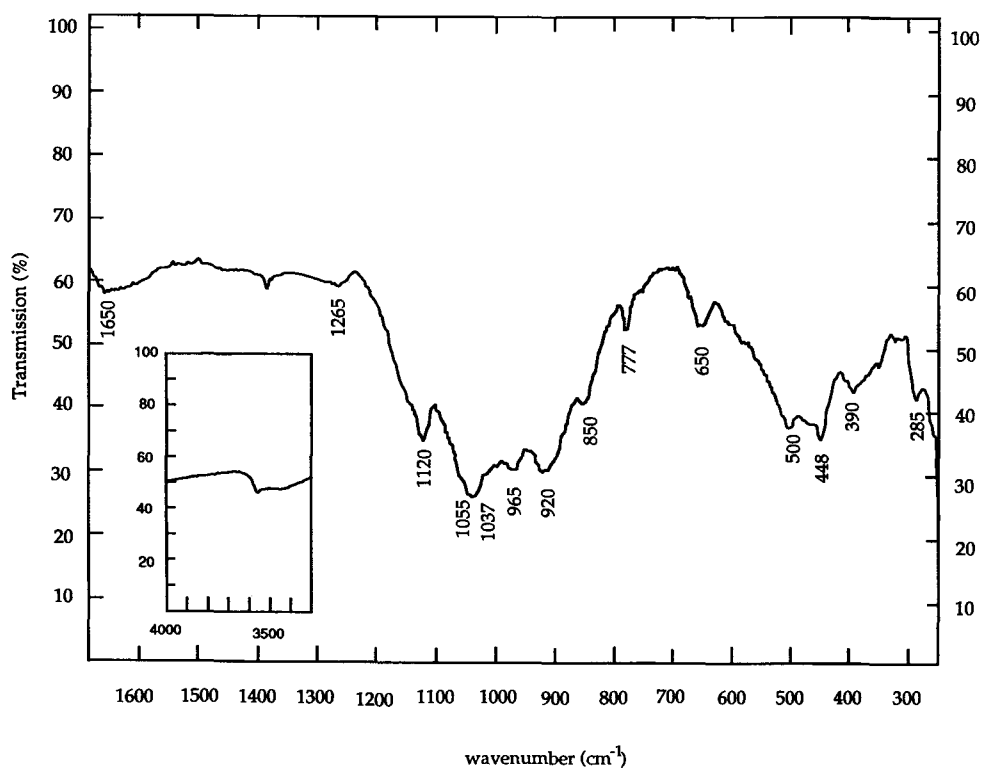


Fig. 1. IR powder spectrum of $\text{SrMn}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$ in KBr.

Table 1. Average of 13 electron microprobe analyses and formula normalized on 5 cations.

oxide	wt. % ideal	wt. % obs.	range obs.	atoms p.f.u
SiO_2	28.77	28.22	28.06 - 28.66	1.97
Mn_2O_3	37.80	37.82	37.27 - 38.57	2.01
Fe_2O_3		0.53	0.46 - 0.62	0.03
SrO	24.81	24.32	23.9 - 25.2	0.98
BaO		0.46	0.1 - 0.9	0.01
CaO		0.02	0.0 - 0.03	0.00
H_2O	8.62	n.d.		
Σ	100.00	91.37		5.00

The elements Al, Ti, Mg, Na, and K were below the detection limit. Qualitative tests with the ion probe indicated that concentrations of Li and F are not significant.

Steele *et al.* (1981) and analytical methods applied are as described by Dutrow *et al.* (1986). These ion microprobe analyses confirm that the new mineral does not contain significant Li concentrations, despite coherent intergrowth with sugilite and Li-bearing serandite-pectolite. Qualitative tests with the ion-probe also indicate that fluorine is not a significant component in the mineral under investigation. Results given in Table 1 show that the mineral exhibits almost end-member composition $\text{SrMn}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$.

A KBr-pellet IR powder spectrum was collected (sample/KBr ratio = 1/100) between 4000 and

250 cm^{-1} (Fig. 1). The spectrum between 1000 and 1200 cm^{-1} is similar to that for lawsonite (Moenke, 1962). Strong absorptions between 800 and 1000 cm^{-1} are similar to those for ilvaite (Moenke, 1962). IR bands in this frequency range are due to vibrations of $[\text{Si}_2\text{O}_7]$ units as discussed by Lazarev (1974). An absorption at 3555 cm^{-1} accompanied with a diffuse shoulder towards lower frequencies and one diffuse band at *ca.* 1650 cm^{-1} are characteristic of OH and H_2O (Labotka & Rossman, 1974).

X-ray data collection and structure refinement

Space group *Cmcm* ($Z = 4$) and approximate cell dimensions were obtained from several crystals studied on precession and Weissenberg X-ray cameras with $\text{MoK}\alpha$ and $\text{FeK}\alpha$ radiation. The crystal selected for structural investigation at room temperature was $0.05 \times 0.15 \times 0.15$ mm in dimension. 623 unique reflections up to $\theta = 30^\circ$ were measured in the 2.5° omega-scan mode using graphite monochromated $\text{MoK}\alpha$ radiation and a CAD4 Enraf Nonius diffractometer. Reflections with $26^\circ > \theta > 20^\circ$ were used for cell-dimension refinement yielding $a = 6.255(1)$, $b = 9.034(2)$, $c = 13.397(2)$ Å. A 130 K test data set collected on a larger crystal yielded $a = 6.2372(6)$, $b = 9.015(2)$, $c = 13.386(5)$ Å.

An empirical absorption correction was applied using the psi-scan technique. Data reduction, including background and Lorentz-polarisation correction, was carried out with the SDP program system (Enraf Nonius, 1983). The structure was solved by direct methods, and sub-

Table 2. Atomic coordinates, B_{eq} values and anisotropic displacement parameters ($U_{ij} \times 10^2$).

Atom	x/a	y/b	z/c	B_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	0	0.3114(2)	1/4	1.29(3)	2.67(9)	1.42(8)	0.82(7)	0	0	0
Mn	1/4	1/4	0	0.97(2)	1.44(7)	1.26(7)	1.00(7)	-0.29(8)	0.43(8)	-0.30(6)
Si	0	-0.0306(4)	0.1322(2)	0.93(5)	1.7(2)	1.1(2)	0.7(1)	0	0	0
O1	0	0.022(2)	1/4	1.3(2)	2.4(7)	1.8(7)	0.9(5)	0	0	0
O2	0.285(1)	0.3707(7)	0.1160(4)	1.5(1)	2.4(4)	1.5(3)	1.6(3)	-0.5(3)	0.5(3)	-0.5(2)
O3	0	0.1259(9)	0.0747(6)	1.0(1)	1.7(4)	0.8(3)	1.2(4)	0	0	-0.2(3)
O4	0	0.368(1)	0.5413(7)	1.5(1)	2.2(5)	1.7(4)	1.6(4)	0	0	-0.7(4)
O5	0.043(3)	0.607(2)	1/4	1.7(3)						

Table 3. $\text{SrMn}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$, interatomic distances [Å] and angles [°] compared to lawsonite (Baur, 1978).

		$\text{SrMn}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$		$\text{CaAl}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$	
	Si - O3	1.614(9)		1.647(1)	
2	Si - O2	1.627(7)		1.616(2)	
	Si - O1	1.646(5)		1.654(1)	
	<Si - O>	1.629		1.633	
1	O3 - O1	2.53(1)	102.1(6)	2.552(1)	101.3(1)
2	O2 - O1	2.62(1)	106.5(3)	2.661(1)	109.0(1)
1	O2 - O2	2.68(1)	111.3(4)	2.659(1)	110.7(1)
2	O2 - O3	2.73(1)	114.7(3)	2.724(1)	113.2(1)
	Si-O1-Si		146.6(9)		136.9(1)
X = Ca, Sr					
4	X - O2	2.587(6)		2.400(1)	
1	X - O1	2.62(1)		2.494(2)	
1	X - O5	2.69(2)		2.433(2)	
2	X - O3	2.892(6)		2.976(1)	
	<X - O>	2.680		2.560	
Y = Al, Mn					
2	Y - O2	1.909(6)		1.913(1)	
2	Y - O4	1.972(6)		1.867(1)	
2	Y - O3	2.170(6)		1.960(1)	
	<Y - O>	2.017		1.913	
2	O4 - O3*	2.63(1)	80.9(3)	2.460(2)	80.0(1)
2	O2 - O3	2.73(1)	89.9(3)	2.738(1)	90.0(1)
2	O4 - O2	2.76(1)	90.7(3)	2.694(1)	90.9(1)
2	O2 - O3	2.89(1)	90.1(3)	2.740(1)	90.0(1)
2	O4 - O2	3.13(1)	89.3(3)	2.652(1)	89.1(1)
2	O4 - O3	3.16(2)	99.2(3)	2.932(1)	100.0(1)

Note: shared octahedral edge is starred

sequently by Fourier analyses using the program SHELXS-86 (Sheldrick, 1986). The program SHELX76 (Sheldrick, 1976) was used for structure refinement. Neutral-atom scattering factors and both real and imaginary anomalous dispersion corrections were applied. 448 structure factors with a cutoff $F_{\text{obs}} > 6 \sigma (F_{\text{obs}})$ and unit weights were used. Refinements converged to $R = 4.8 \%$ ($R = (\sum |F_{\text{obs}} - F_{\text{calc}}|) / (\sum F_{\text{obs}})$) with 44 parameters.

Results

Final atomic coordinates and displacement parameters are given in Table 2.

Interatomic distances and angles are summarized in Table 3. The structure is essentially that of lawsonite (Baur, 1978) where octahedral Al is replaced by Mn^{3+} and Ca by Sr (Fig. 2). The H_2O molecule at O5 displayed a high displacement amplitude along a and was subsequently displaced from the mirror plane and refined as split position with an isotropic displacement parame-

ter. This disorder was also observed in the 130 K test data set. Hydrogens of OH and H_2O groups could not be localized due to the low crystal quality, the small crystal size, heavy atoms in the structure, and disorder of H_2O .

Discussion

It is well-established that Mn^{3+} (d^4 high-spin electron configuration) in octahedral coordination displays a Jahn-Teller effect with a characteristic distortion of four short and two long Mn-O distances (Table 3). This is also observed for $\text{SrMn}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$ where $d(\text{Mn}-\text{O}3) = 2.170$ is significantly longer than $d(\text{Mn}-\text{O}2) = 1.972$ and $d(\text{Mn}-\text{O}4) = 1.909$ Å. Moore *et al.* (1985), studying the Mn^{3+} minerals ruizite, macfallite, orientite and bermanite, noticed that in all examples a similar distortion was observed. These authors also report that three kinds of ligand arrangements occur in such structures: (a) O with 2 Mn^{3+} and 1 Si, (b) O with 1 Mn^{3+} and

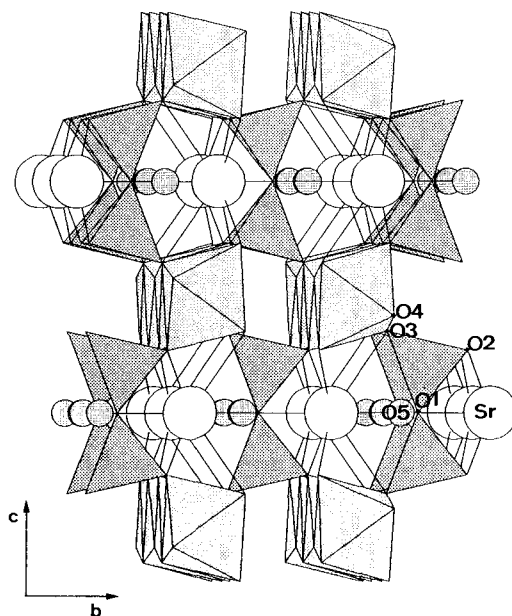


Fig. 2. Coordination polyhedra model of $\text{SrMn}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$. Edge-sharing Mn^{3+}O_6 octahedra form endless chains parallel to a . The chains are cross-linked by $(\text{Si}_2\text{O}_7)^{6-}$ units along c . Sr and H_2O (on O5) are situated in structural channels. O4 represents an oxygen of the OH group.

1 Si, and (c) OH with 2 Mn^{3+} . In each structure, the extended Mn^{3+} -O bonds correspond to ligand type (a). This is also true in case of the new compound. In lawsonite (Baur, 1978) Ca possesses a 6+2 coordination with six Ca-O distances between 2.4 and 2.5 Å; two additional oxygens have Ca-O distances of 2.98 Å. In the Sr-Mn analogue, the 6 short Sr-O distances are significantly longer than the corresponding Ca-O distances. The two long Sr-O3 distances are significantly shorter than the corresponding distances for Ca-O3 where O3 is also the oxygen which contributes to the elongated Mn-O distances. In other words, the 6+2 coordination for Ca in lawsonite approaches an eight-fold Sr coordination in the new compound, an arrangement which is favoured by the $[\text{MnO}_6]$ Jahn-Teller distortion. The structural channels running parallel to the a axis are widened along c by stretching of the Si-O1-Si angle from 136.9° in lawsonite to 146.6° for the Sr-Mn analogue. Following the outline of Gibbs (1982), this expansion should lead to a slight decrease of the bridging Si-O1

distance; this is observable but is only 2 e.s.d.'s below the value for lawsonite.

Wilson & Dunn (1978) described orientite and ruizite from the Kalahari manganese field. These minerals, among others, all have the same fundamental building blocks of the type $[\text{Mn}^{3+}_2(\text{OH})_2(\text{TO}_4)_2]$ which are also present in the lawsonite structure type (Moore *et al.*, 1985). These structures have 6×9 Å cell dimensions in common. Moore *et al.* (1985) remark that in case of ruizite ($\text{Ca}_2\text{Mn}^{3+}_2(\text{OH})_2[\text{Si}_4\text{O}_{11}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$), macfallite ($\text{Ca}_2\text{Mn}^{3+}_3[\text{SiO}_4][\text{Si}_2\text{O}_7](\text{OH})_3$), and orientite (formula according to Mellini *et al.* (1986): $\text{Ca}_8\text{Mn}^{3+}_{10}[\text{SiO}_4]_3[\text{Si}_3\text{O}_{10}]_3(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$) the refinement does not yield the R-values anticipated for compounds of such an intermediate atomic number and they suspect that some degree of twinning or disorder must be involved, especially in the interlayer units. This hypothesis was confirmed by a combined X-ray and HRTEM structure analysis of orientite (Mellini *et al.*, 1986). These authors proposed an improved structural model for orientite and demonstrated faulted sequences characterized by the extensive occurrence of microvoids and domains of a new polytypic variant. Application of single crystal X-ray methods and HRTEM technique on sursassite ($\text{Mn}_2\text{Al}_3[\text{SiO}_4][\text{Si}_2\text{O}_7](\text{OH})_3$), a 6×9 Å mineral isostructural with macfallite, yielded extensive pumpellyite-like lamellae and less frequent domains similar to lawsonite intergrown with sursassite. A pumpellyite-related 6×9 Å mineral with the building block $[\text{Mn}^{3+}_2(\text{OH})_2(\text{SiO}_4)_2]$ was recognized by Togari & Akasaka (1987) and named okhotskite. Independent of Moore *et al.* (1985), Hawthorne (1984) solved the structure of ruizite from X-ray single-crystal data; he decreased the space-group from $A2/m$ to $A2$ and obtained improved R-values with reasonably low displacement parameters for all atoms.

Before we collected the test data set at 130 K, we noticed in reflection scans that some peaks were composed of several maxima within an omega range of 5°. However, we were not able to determine whether this was due to disorder, twinning or intergrowth with other phases such as serandite-pectolite or sugilite. In collecting the room-temperature data, we tried to circumvent this problem by working with a small crystal and a wide omega scan. Displacement parameters of all atoms within the fundamental building blocks are higher along a than parallel to any other direction. Strong anisotropy is observed for H_2O on

O5 (refined as isotropic split position) and for Sr. In addition, B_{eq} and U_{ij} values seem rather high for a dense sheet. Thus we cannot exclude the possibility that the refined structure represents an average of several domains, as already speculated by Moore *et al.* (1985) for ruizite, macfallite, and orientite and demonstrated by Mellini *et al.* (1984, 1986) for sursassite and orientite.

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