

Scheuchzerite, Na(Mn,Mg)₉[VSi₉O₂₈(OH)](OH)₃, a new single-chain silicate

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ABSTRACT

Scheuchzerite, Na(Mn,Mg)₉[VSi₉O₂₈(OH)](OH)₃, is a new mineral from the metamorphosed syn-sedimentary exhalative Mn deposit of Fianel, Val Ferrera, Central Alps, Switzerland. It is dedicated to the Swiss naturalist Johann Jakob Scheuchzer (1672–1733). Scheuchzerite is associated with saneroite and tiragalloite in veins resulting from the remobilization of ore components during retrograde Tertiary Alpine metamorphism. Scheuchzerite forms yellow-orange, transparent acicular crystals up to 0.5 mm in length with yellow-orange streak and vitreous luster, Mohs' hardness ~2.5, d_{calc} 3.47 (electron microprobe) to 3.52 g/cm³ (structure refinement); d_{meas} 3.50(2) g/cm³, good cleavage parallel to fiber elongation. Scheuchzerite is biaxial positive, $n_{\text{min}} = 1.74$ and $n_{\text{max}} = 1.75$; n_{mean} (Gladstone-Dale) 1.74; weakly pleochroic, X = brown yellow, Y = pale yellow. The empirical chemical formula is Na_{0.97}(Mn_{7.79}Mg_{0.95}Zn_{0.16}Ni_{0.04}Ca_{0.03}Al_{0.01})_{Σ=8.98}(V_{0.95}As_{0.02}Si_{9.08})_{Σ=10.05}O_{32.05}H₄. Scheuchzerite is triclinic, $P\bar{1}$, $a = 9.831(5)$ Å, $b = 10.107(5)$ Å, $c = 13.855(7)$ Å, $\alpha = 86.222(10)^\circ$, $\beta = 73.383(9)^\circ$, $\gamma = 71.987(9)^\circ$; $V = 1254.2(10)$ Å³; $Z = 2$. The crystal structure was solved with direct methods on the basis of 1616 unique reflections with $I > 4\sigma F$ and refined to $R_1 = 9.4\%$. The crystal structure consists of tetrahedral layers separated by layers containing chains of edge-sharing [Mn(O,OH)₆] octahedra as well as [NaO₈] polyhedra. The tetrahedral layers consist of [Si₉O₂₅(OH)] loop-branched chains of corner-sharing silicate tetrahedra extending along [011]. The loops contain 6 tetrahedra and are separated by 3 tetrahedra in a broken 4-loop arrangement. A hydrogen atom is probably shared by two O atoms (symmetrical hydrogen bond), replacing the missing silicon atom. A vanadate (VO₄)³⁻ tetrahedron branches off the 6-tetrahedra loop, and hence the overall formula of the tetrahedral chains is [VSi₉O₂₈(OH)]. In the notation of Liebau (1985), scheuchzerite is a single chain silicate (monopolysilicate) {olB,1¹_z}[VSi₉O₂₈(OH)]. The topology of the scheuchzerite structure is reminiscent of that of the double-chain silicates of the amphibole group, but scheuchzerite contains a new type of silica chain.

Keywords: Scheuchzerite, new mineral, Fianel mine, Val Ferrera, Central Alps, Switzerland, crystal structure, single chain silicate

INTRODUCTION

Metamorphosed Mn-rich deposits, such as those at Långban in Sweden; the Kombat mine in Namibia; and at Franklin, New Jersey, U.S.A., are among the richest mineralogical “rainforests” on Earth (Pring 1995), and are still contributing a steady stream of new minerals. Many of these minerals contain arsenic or vanadium as a major component. In this paper, we describe the occurrence and mineralogy of a new sodium-manganese silicate-vanadate, occurring in the small metamorphosed Mn-Fe deposit of Fianel, canton Graubünden, Switzerland.

The new mineral is dedicated to the Swiss naturalist Johann Jakob Scheuchzer (1672–1733). Scheuchzer was junior physician of the city of Zürich, curator of the Kunstkammer—a cabinet of natural history and curiosities—and he held the chair of physics and mathematics at the University of Zürich. Scheuchzer's work

on Swiss geology and mineralogy was essential for his time; for example, he studied Alpine quartz, measuring the angles of many crystals (Scheuchzer 1708) and describing fluid inclusions and gas bubbles in the crystals (Scheuchzer 1718). The latter observation was fundamental in invalidating Plinius' popular theory that quartz crystals consist of water irreversibly frozen by the great cold in the mountains (Plinius the Old, 23–79 BC).

The new mineral and its name have been approved by the International Mineralogical Association (proposal number 2004-044), and the type material is deposited at the Musée Géologique Cantonal, Lausanne, Switzerland (Holotype specimen, MGL 79355).

OCCURRENCE

Scheuchzerite occurs sparingly at the Fianel Fe-Mn mine near Ausserferrera, Ferrera valley, Graubünden, Switzerland (Brugger and Gieré 1999, 2000). Fianel is a small Fe-Mn deposit of syn-sedimentary to diagenetic origin, embedded in the Trias-

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sic carbonates of the Suretta nappe. It underwent a polyphase Tertiary metamorphism, climaxing under blueschist- to greenschist-facies conditions (Nussbaum et al. 1998). The following three stages of vanadate crystallization have been recognized at Fianel (Brugger and Gieré 2000): (1) crystallization of medaite $(\text{Mn,Ca})_6(\text{V,As})\text{Si}_5\text{O}_{18}(\text{OH})$ along the main greenschist-facies Alpine schistosity; (2) formation of palenzonaite $\text{NaCa}_2\text{Mn}_2(\text{VO}_4)_3$, saneroite $\text{Na}_2\text{Mn}_{10}\text{VSi}_{11}\text{O}_{34}(\text{OH})_4$, minor quantities of pyrobelonite $\text{PbMnVO}_4(\text{OH})$, tiragalloite $\text{Mn}_4\text{AsSi}_3\text{O}_{12}(\text{OH})$, and scheuchzerite in veinlets filled with massive quartz, aegirine, and rhodonite that cross-cut the main schistosity; and (3) crystallization of fianelite $\text{Mn}_2\text{V}(\text{V,As})\text{O}_7 \cdot 2\text{H}_2\text{O}$ (type locality; Brugger and Berlepsch 1996), ansermetite $\text{MnV}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ (type locality; Brugger et al. 2003), and Fe oxyhydroxides in thin fractures near or across the palenzonaite-bearing veinlets.

Appearance, physical, and optical properties

Scheuchzerite occurs as acicular crystals up to 0.5 mm in length and as smaller prismatic crystals filling veinlets up to 1 mm in width (Fig. 1). Scheuchzerite is yellow-orange in color with a streak of similar color. The new species is intimately associated with orange-red massive to prismatic saneroite, and intergrowths of both minerals are common (e.g., Fig. 1). Scheuchzerite is transparent with a vitreous luster. It does not fluoresce under the UV lamp. Optically, scheuchzerite is biaxial positive, with $n_{\text{min}} = 1.74$ and $n_{\text{max}} = 1.75$. The refractive indices were measured at 24 °C by the immersion method (Na_D light). The refractive index of the liquid (Cargille Labs) was checked using a Leitz-Jelley micro-refractometer. The average refractive index is 1.74, calculated using the Gladstone-Dale relationship with the constants of Mandarino (1976), the average chemical analysis of Table 1 normalized to a sum of 100%, and a density of 2.50 g/cm^3 . Scheuchzerite is weakly pleochroic, with X = brown yellow and Y = pale yellow. The Mohs' hardness was estimated by depositing scheuchzerite fragments on fresh cleavages of gypsum, calcite, and fluorite and rubbing them with a Teflon needle. Scheuchzerite scratches only gypsum and therefore has a Mohs' hardness be-

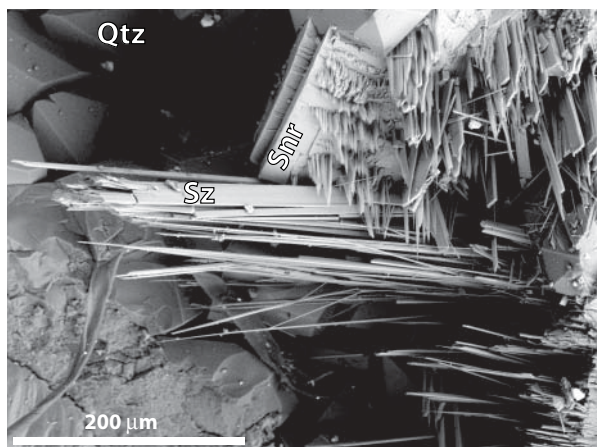


FIGURE 1. Scanning electron microscope image (Back Scattered Electron mode) of acicular scheuchzerite crystals (Sz) partially intergrown with platy saneroite (Snr) in a vug lined with minute quartz (Qtz) crystals. Part of holotype specimen MGL 79355.

tween 2 and 3. Scheuchzerite is brittle and has a good cleavage parallel to $[1\bar{1}1]$, i.e., parallel to fiber elongation. The measured density of 3.50(2) g/cm^3 represents the average on three different grains and was obtained by immersion in a thallium malonate/formate (Clerici liquor)—water gradient tube. The solution at the level of the crystals was sampled using a chromatography syringe, and its density was deduced from its refractive index. The density calculated from the electron microprobe analyses (Table 1) and the cell volume from the single crystal refinement (see below) is 3.47(1) g/cm^3 ; calculated density based on the crystal structure refinement is 3.52 g/cm^3 .

Chemical composition

Chemical analyses were carried out with a Cameca SX51 electron microprobe (Table 1), using the following standards: V, pure metal; As, synthetic GaAs; Si and Al, almandine; Mg, forsterite; Mn, rhodonite; Ca, wollastonite; Na, albite; Ni, cobaltite; Zn, sphalerite. The microprobe was operated at 15 kV, 20 nA, peak counting times of 10 and 5 s on each side of the peak for background. The beam was tightly focused. The empirical chemical formula obtained for scheuchzerite, based upon normalization on 20 cations per formula unit (pfu) and a fixed content of 4 H atoms pfu is: $\text{Na}_{0.97}(\text{Mn}_{7.79}\text{Mg}_{0.95}\text{Zn}_{0.16}\text{Ni}_{0.04}\text{Ca}_{0.03}\text{Al}_{0.01})_{\Sigma=8.98}(\text{V}_{0.95}\text{As}_{0.02}\text{Si}_{9.08})_{\Sigma=10.05}\text{O}_{32.05}\text{H}_4$ (Table 1), in good agreement with the chemical formula from the crystal structure refinement $\text{Na}_{0.80}(\text{Mg,Na})_{0.20}(\text{Mn}_{8.57}\text{Mg}_{0.43})[\text{VSi}_9\text{O}_{28}(\text{OH})](\text{OH})_3$ (see below), and with the simplified chemical formula $\text{Na}(\text{Mn,Mg})_9[\text{VSi}_9\text{O}_{28}(\text{OH})](\text{OH})_3$.

The presence of water in the form of hydroxyl group was

TABLE 1. Electron microprobe analysis of scheuchzerite

	Average	Min	Max
V ₂ O ₅	6.46	5.91	6.84
As ₂ O ₅	0.14	0.00	0.31
SiO ₂	41.02	39.20	44.10
Al ₂ O ₃	0.04	0.02	0.07
MgO	2.86	2.56	3.15
MnO	41.54	39.58	42.35
CaO	0.13	0.07	0.17
Na ₂ O	2.25	1.93	2.38
NiO	0.22	0.11	0.37
ZnO	0.96	0.60	1.27
H ₂ O	2.71	2.65	2.71
Sum	98.33	96.69	98.55
Si	9.08	8.85	9.87
V	0.95	0.87	1.00
As	0.02	0.00	0.04
Sum	10.05	9.86	10.76
Mn ²⁺	7.79	7.50	8.03
Mg	0.95	0.85	1.05
Zn	0.16	0.00	0.21
Ni	0.04	0.00	0.07
Ca	0.03	0.02	0.04
Al	0.01	0.00	0.02
Sum	8.98	8.41	9.16
Na	0.97	0.84	1.03
H	4.00		
O	32.05	31.87	32.78

Notes: Average of 20 analyses. PbO ≤ 0.13 wt%; CuO ≤ 0.06; Cr₂O₃ < 0.05; FeO < 0.05. No additional element with atomic number ≥ 9 was detected (<0.1 wt%). Water content calculated on the basis of 4 H atoms pfu.

Empirical chemical formula: $\text{Na}_{0.97}(\text{Mn}_{7.79}\text{Mg}_{0.95}\text{Zn}_{0.16}\text{Ni}_{0.04}\text{Ca}_{0.03}\text{Al}_{0.01})(\text{V}_{0.95}\text{As}_{0.02}\text{Si}_{9.08})\text{O}_{32.05}\text{H}_4$.

confirmed using an FT-IR spectrum (650 to 4000 cm^{-1}) collected on ground material with a Perkin Elmer Paragon 1000 FT-IR equipped with a Graseby Specac ATR accessory (diamond top-plate). A strong band at 1466 cm^{-1} is attributed to the stretching mode of a H atom involved in a strong hydrogen bond, whereas a small band at around 3496 cm^{-1} is attributed to a H atom involved in a weak hydrogen bond (Libowitzky 1999). No absorption band was observed around 1600–1650 cm^{-1} (bending mode of H_2O) indicating the absence of molecular water in scheuchzerite (Fig. 2).

Powder X-ray diffraction study

The X-ray powder diffraction pattern of scheuchzerite was collected using a 114.6 mm diameter Gandolfi camera and $\text{CuK}\alpha/\text{Ni}$ -filtered X-ray radiation. The powder pattern is in good agreement with the results of the crystal-structure analysis in terms of the comparison between calculated and observed d -spacings and intensities (Table 2). The unit-cell parameters calculated using the least-squares method on the basis of 18 unambiguously indexed reflections (program UnitCell, Holland and Redfern 1997) are: $a = 9.83(1)$ Å, $b = 10.12(2)$ Å, $c = 13.89(2)$ Å, $\alpha = 86.4(1)^\circ$, $\beta = 73.25(10)^\circ$, $\gamma = 71.9(1)^\circ$, $V = 1258(2)$ Å³, in good agreement with those obtained by single crystal diffraction (Table 3).

SINGLE-CRYSTAL X-RAY DIFFRACTION STUDY

Experimental methods

A prismatic crystal fragment of scheuchzerite, about $80 \times 30 \times 6$ μm^3 in size, was mounted on a Bruker AXS three-circle diffractometer equipped with a CCD 1 K area detector and a flat graphite monochromator. More than a hemisphere of data was collected with an exposure time of 300 s and frame widths of 0.3° in ω using $\text{MoK}\alpha$ -radiation from a fine focus sealed tube. The unit-cell dimensions (Table 3) were determined from least-squares refinement of 1014 reflections. The data were reduced and filtered for statistical outliers using the Bruker program SAINT, and were corrected for Lorentz, polarization, and background effects. An empirical absorption correction based on 195 reflections was applied assuming an ellipsoidal crystal shape. This correction lowered R_{int} from 9.4 to 7.7%. Additional information pertinent to the data collection is given in Table 3.

The Bruker SHELXTL Version 5 package was used for the determination and refinement of the structure. The structure was solved initially in the non-centrosymmetric triclinic group $P1$ and later transformed into the centrosymmetric group $P1$ using the PLATON program (Spek 2005). The structure was refined on the basis of F^2 for all unique data. The final refinement included positional parameters of

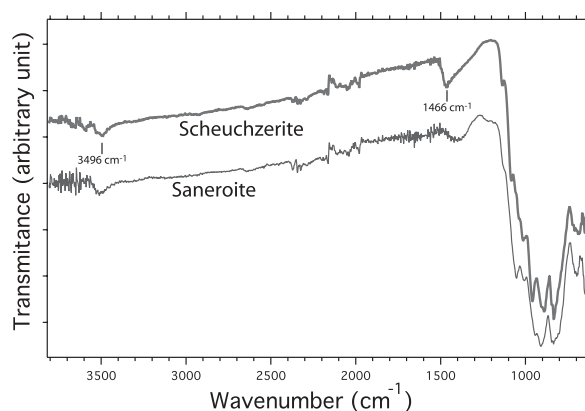


FIGURE 2. Infrared spectra of scheuchzerite and saneroite from Fianel, Val Ferrera, Switzerland.

all atoms, with an allowance for anisotropic displacement of Mn sites only, and a weighting scheme for the structure factors. The occupancies of the cation sites were first refined and then fixed at the refined values with slight corrections to satisfy the electroneutrality condition. The refinement of the structure converged to an agreement index ($R1$) of 9.4%, which was calculated for the 1616 unique observed reflections ($F_o \geq 4\sigma F_o$). The relatively high $R1$ value is the consequence of the relatively large mosaic spread, which suggests that the crystal under study is an aggregate of semi-parallel crystals, or consists of domains with slightly different orientations. Final positional and displacement parameters of atoms, bond-valence sums, and selected interatomic distances are listed in Tables 4, 5, and 6.

TABLE 2. Measured and calculated powder diffraction data for scheuchzerite

h	k	l	d_{calc}	I_{calc}	d_{meas}	I_{meas}
1	0	1	8.64	53	8.68	50
1	1	0	7.86	70	7.91	70
2	1	1	4.82	21	4.83	30
0	2	0	4.80	9		
2	0	2	4.32	12	4.32	20
0	1	3	4.06	5	4.08	10
0	2	2	3.94	4		
2	0	1	3.93	6	3.94	30
2	2	0	3.93	10		
1	2	1	3.78	7	3.79	30
2	2	2	3.77	5		
2	1	1	3.77	8		
1	2	2	3.72	8	3.74	10
1	3	0	3.36	5		
2	2	3	3.33	10	3.35	10
3	1	1	3.27	9	3.26	10
3	1	2	3.22	27	3.22	40
2	3	1	3.13	14	3.13	20
2	0	4	3.12	4		
1	2	3	3.09	6		
2	2	2	3.09	20	3.09	80
2	3	0	3.09	7		
3	2	1	3.08	51		
3	0	2	3.07	10	3.02	10
1	3	2	2.905	35	2.92	40
1	1	5	2.706	100	2.71	100
2	2	1	2.702	85		
3	1	2	2.698	9		
0	0	5	2.654	14	2.66	30
1	3	1	2.649	17		
0	3	3	2.625	35	2.63	30
3	1	4	2.380	16	2.38	10
3	1	3	2.273	19	2.27	10
2	4	3	2.270	16		
2	1	6	2.255	17	2.26	30
3	2	0	2.251	21		
2	4	2	2.209	37	2.22	30
1	4	3	2.141	6	2.15	10
3	4	1	2.138	7		
3	2	6	2.053	21	2.06	30
4	1	0	2.052	18		
4	2	7	1.721	7		
5	1	1	1.720	10	1.72	10
4	5	1	1.688	18	1.69	20
5	2	2	1.687	8		
4	5	4	1.686	6		
1	3	6	1.643	30	1.64	30
6	3	3	1.606	8		
1	2	8	1.603	16	1.61	40
2	5	0	1.600	15		
1	3	7	1.598	8		
0	6	1	1.595	8	1.58	10
5	3	7	1.536	8	1.53	10
6	3	5	1.535	6		
0	3	8	1.488	9	1.49	20
1	6	2	1.485	10		

Notes: Gandolfi camera, 114.6 mm, $\text{CuK}\alpha/\text{Ni}$ -filtered, 40 kV, 30 mA, 99 h exposure time. Intensities were visually estimated. The calculated intensities are from the crystal structure analysis.

TABLE 3. Crystallographic data and refinement parameters for scheuchzerite

<i>a</i> (Å)	9.831(5)
<i>b</i> (Å)	10.107(5)
<i>c</i> (Å)	13.855(7)
α (°)	86.222(10)
β (°)	73.383(9)
γ (°)	71.987(9)
<i>V</i> (Å ³)	1254.2(10)
Space group	<i>P</i> $\bar{1}$
μ (mm ⁻¹)	5.20
<i>Z</i>	2
Cell content	Na _{0.80} (Mn _{8.57} Mg _{0.63})[VSi ₉ O ₂₈ (OH)](OH) ₃
<i>D</i> _{calc} (g/cm ³)	3.52
Crystal size (mm ³)	0.08 × 0.03 × 0.006
Diffractometer	Bruker SMART 1K
Radiation	MoK α
Total Ref.	7467
Unique Ref.	5441
Unique $ F_o \geq 4\sigma F$	1616
<i>R</i> _{int}	0.077
<i>R</i> ₁	0.094
<i>wR</i> ₂	0.166
<i>S</i>	0.781

Notes: $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $S = [\sum w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$.

Crystal structure

The structure of scheuchzerite contains nine symmetrically independent Mn sites each octahedrally coordinated by six anions (O and OH). The average <Mn-O> bond lengths are in the range of 2.15–2.26 Å, whereas individual bond lengths vary from 2.067 to 2.530 Å (Table 6). During refinement, it was noticed that the Mn4, Mn7, and Mn8 sites are under-occupied if refined using the Mn scattering factor. Taking into account the considerable amount of Mg in the structure, the occupancies of these sites were refined by means of mixed Mn-Mg scattering curves (Table 4).

There is one independent Na site in the structure that is surrounded by 8 O atoms with distances between 2.39 and 3.07 Å. This Na site has an occupancy of 80% calculated on the basis of Na. This is seemingly in disagreement with the results of chemical analysis that gives 0.97 Na per formula unit. The possible explanations for this disagreement are: (1) the crystal studied had slightly different chemical composition; and (2) some Na is incorporated into Mn sites or the disordered Mg site. The disordered Mg site has a very low occupancy of 20% and may, in fact, represent a highly disordered site that accommodates excessive amounts of both Na and Mg that do not fit into the Mn sites (Table 4).

The V site in the structure of scheuchzerite is split into two sites, V1 and V1A, that have occupancies of 89% and 11%, respectively. The overall coordination of these sites is tetrahedral; however, bond lengths are definitely in error, especially for the V1A site, because of the disorder. This leads to a low bond valence sum for the V1A site (Tables 4 and 6).

The bond-valence sums for the cation and anion sites are given in Table 4. Bond-valence sums for all sites with occupancies exceeding 50% are in good agreement with their expected values. The bond-valence sums for O26 and O29 sites are 1.48 and 1.53 v.u., respectively. The O26–O29 distance is 2.35 Å. Note that these atoms are not part of the same coordination polyhedron, which may indicate a symmetrical O–H–O hydrogen bond between the O26 and O29 sites. Another possible configuration is a disordered hydrogen bond with the O26 and O29 sites occupied by O and OH in equal proportion.

TABLE 4. Atomic coordinates, displacement parameters (Å²), and bond-valence sums (BVS, v.u. = valence units) for scheuchzerite

Atom	Occupancy	BVS	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mn1	Mn _{1.00}	2.00	0.0757(3)	0.8310(3)	0.0136(2)	0.0085(10)
Mn2	Mn _{1.00}	2.05	0.5671(3)	0.6937(3)	0.1599(2)	0.0114(7)
Mn3	Mn _{1.00}	1.89	0.1538(3)	0.0823(3)	0.5619(2)	0.0146(10)
Mn4	Mn _{0.93} Mg _{0.07}	2.14	0.7129(3)	0.3634(3)	0.1903(2)	0.0096(10)
Mn5	Mn _{1.00}	1.86	0.7499(3)	0.4835(3)	0.9689(2)	0.0107(7)
Mn6	Mn _{1.00}	2.21	0.3262(3)	0.7645(3)	0.5880(2)	0.0085(10)
Mn7	Mn _{0.84} Mg _{0.16}	2.29	0.4794(3)	0.4353(3)	0.6140(3)	0.0127(12)
Mn8	Mn _{0.80} Mg _{0.20}	2.04	0.6306(3)	0.1039(3)	0.6374(2)	0.0111(7)
Mn9	Mn _{1.00}	1.97	0.1425(3)	0.9711(3)	0.7869(2)	0.0126(10)
Na	Na _{0.80}	0.93	0.131(1)	0.4358(9)	0.2935(7)	0.026(3)
Mg	Mg _{0.20}	1.73	0.109(5)	0.557(5)	0.649(4)	0.050(18)
V1	V _{0.89}	4.77	0.8167(4)	0.2386(3)	0.7693(3)	0.010*
V1A	V _{0.11}	2.85	0.951(3)	0.297(3)	0.770(2)	0.010*
Si1	Si	4.20	0.4550(5)	0.7412(5)	0.9501(4)	0.0058(11)
Si2	Si	4.05	0.2825(5)	0.0474(5)	0.9656(4)	0.0097(12)
Si3	Si	4.21	0.0371(5)	0.1425(5)	0.3656(4)	0.0058(11)
Si4	Si	4.11	-0.5200(5)	0.1836(5)	0.2658(4)	0.0102(12)
Si5	Si	4.28	0.6926(5)	0.6304(5)	0.5435(4)	0.0080(11)
Si6	Si	4.10	0.9340(6)	0.5555(5)	0.1366(4)	0.0113(12)
Si7	Si	4.30	0.0804(5)	0.2371(5)	0.1490(4)	0.0092(12)
Si8	Si	4.34	0.7539(6)	0.7385(5)	0.3257(4)	0.0130(12)
Si9	Si	4.06	0.8450(5)	0.3251(5)	0.5500(4)	0.0097(12)
O1	O	2.02	0.3109(12)	0.6926(11)	0.9527(8)	0.007(3)
OH2	OH	1.15	0.4944(12)	0.4802(11)	0.7588(8)	0.010(3)
O3	O	2.17	0.5457(12)	0.6038(11)	0.5341(9)	0.010(3)
O4	O	2.03	-0.0682(12)	0.2056(11)	0.1429(8)	0.007(3)
O5	O	2.03	-0.0988(12)	0.0925(11)	0.3562(9)	0.011(3)
O6	O	1.95	0.1432(12)	0.0098(11)	0.9403(9)	0.011(3)
O7	O	2.11	0.6968(12)	0.2872(11)	0.5556(9)	0.012(3)
OH8	OH	1.17†	0.2692(12)	0.5927(11)	0.6638(9)	0.010(3)
O9	O	1.91‡	0.9164(13)	0.1186(12)	0.8378(9)	0.016(3)
O10	O	2.06	-0.3615(13)	0.1939(12)	0.2723(9)	0.015(3)
O11	O	2.02	0.7892(12)	0.5351(11)	0.1161(9)	0.010(3)
OH12	OH	1.10	0.3811(12)	0.9364(11)	0.5120(9)	0.010(3)
O13	O	1.94	0.1507(12)	0.0328(11)	0.4170(9)	0.010(3)
O14	O	2.01	0.5975(12)	0.7299(11)	0.3174(9)	0.011(3)
O15	O	1.96	0.6667(13)	0.1889(12)	0.7688(9)	0.016(3)
O16	O	1.98	0.5537(12)	0.6440(11)	0.0175(9)	0.013(3)
O17	O	2.17‡	0.7899(12)	0.8761(11)	0.3067(8)	0.009(3)
O18	O	2.05‡	0.9266(12)	0.2407(11)	0.6354(9)	0.013(3)
O19	O	1.82‡	0.7603(13)	0.4006(12)	0.8198(9)	0.019(3)
O20	O	1.97‡	0.0202(12)	0.6468(11)	0.0628(9)	0.013(3)
O21	O	2.34†	0.8117(12)	0.4896(11)	0.5668(9)	0.013(3)
O22	O	2.21†	0.0649(12)	0.4020(11)	0.1387(9)	0.012(3)
O23	O	2.06†	0.7716(13)	0.7015(12)	0.4420(9)	0.018(3)
O24	O	2.26†	0.1109(12)	0.1989(11)	0.2573(9)	0.016(3)
O25	O	2.09	0.3949(13)	0.9012(12)	0.9902(9)	0.019(3)
O,OH26	O _{0.5} (OH) _{0.5}	1.48	0.3661(12)	0.1245(11)	0.8720(9)	0.011(3)
O27	O	2.13	0.2245(12)	0.1509(11)	0.0643(9)	0.016(3)
O28	O	1.98†‡	0.8894(13)	0.6113(12)	0.2559(9)	0.019(3)
O,OH29	O _{0.5} (OH) _{0.5}	1.53	-0.5246(13)	0.0258(12)	0.2672(9)	0.020(3)
O30	O	1.93†	-0.0300(12)	0.2863(11)	0.4368(9)	0.017(3)
O31	O	2.16	0.6573(13)	0.7324(11)	0.6382(9)	0.017(3)
O32	O	2.01	0.5579(12)	0.7320(11)	0.8333(8)	0.009(3)

* Fixed during refinement.

† Assuming neighboring Mg site is vacant.

‡ Assuming V1 is occupied (V1A vacant).

The symmetrical hydrogen bond configuration is supported by bond valence considerations and by the IR data. The bond-valence sums on the O atoms of symmetrically bonded (OH)– groups are typically ~1.5 v.u., excluding the H-atom contribution (Burns and Hawthorne 1994a, 1994b; Cahill et al. 2001), in agreement with those observed for the O26 and O29 sites in scheuchzerite. Furthermore, the IR band at 1466 cm⁻¹ (Fig. 2) indicates a hydrogen bond between O atoms less than ~2.5 Å apart, in agreement with the O26–O29 distance of 2.35 Å (Libowitzky 1999). The IR band at 3496 cm⁻¹ is related to a hydrogen bond between O atoms separated by 2.8 to 3.0 Å (Libowitzky 1999), suggesting weak hydrogen bonding between OH12 and OH12 (2.95 Å) or between OH2 and OH19 (2.87 Å).

The crystal structure of scheuchzerite consists of tetrahedral layers separated by layers containing chains of edge-sharing $[\text{Mn}(\text{O},\text{OH})_6]$ octahedra as well as $[\text{NaO}_8]$ polyhedra (Fig. 3a). The layers are parallel to (211). The tetrahedral layers consist of $[\text{Si}_6\text{O}_{25}(\text{OH})]$ loop-branched chains of corner-sharing silicate tetrahedra extending along [011] (Fig. 4a). The loops contain 6 tetrahedra and are separated by 3 tetrahedra in a broken 4-loop arrangement. A hydrogen atom is probably shared by two O atoms, replacing the missing silicate tetrahedron (Fig. 4a). A vanadate $(\text{VO}_4)^{3-}$ tetrahedron branches off the 6-tetrahedra loop, and hence the overall formula of the tetrahedral chains is $[\text{VSi}_6\text{O}_{28}(\text{OH})]$. There is only one type of chain (multiplicity = 1) and the periodicity is 7. In the notation of Liebau (1985), scheuchzerite is a single chain silicate (monopolysilicate) $\{\text{oIb}, 1^1_\infty\}[\text{VSi}_6\text{O}_{28}(\text{OH})]$.

TABLE 5. Anisotropic-displacement parameters (\AA^2) for the Mn sites in the structure of scheuchzerite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	0.0069(16)	0.0062(16)	0.0068(17)	-0.0010(12)	0.0003(12)	0.0041(12)
Mn2	0.0094(15)	0.0117(16)	0.0097(17)	-0.0052(12)	-0.0017(13)	0.0018(13)
Mn3	0.0151(18)	0.0133(17)	0.0107(18)	-0.0037(13)	-0.0021(13)	0.0019(13)
Mn4	0.0104(18)	0.0072(17)	0.0079(19)	-0.0017(13)	-0.0014(14)	0.0012(13)
Mn5	0.0104(15)	0.0099(15)	0.0060(16)	0.0005(12)	-0.0007(12)	0.0037(12)
Mn6	0.0084(18)	0.0105(18)	0.0042(18)	-0.0009(13)	-0.0009(13)	0.0000(14)
Mn7	0.012(2)	0.011(2)	0.012(2)	-0.0016(15)	-0.0003(16)	-0.0022(15)
Mn8	0.0110(16)	0.0117(15)	0.0061(16)	-0.0017(12)	-0.0010(13)	0.0021(13)
Mn9	0.0141(19)	0.0124(17)	0.0048(17)	-0.0036(12)	0.0017(13)	0.0019(13)

TABLE 6. Selected distances (\AA) in the structure of scheuchzerite

Mn1-O20	2.116(11)	Mg-OH8	1.78(5)
Mn1-O9	2.182(12)	Mg-O30	2.01(5)
Mn1-O6	2.199(12)	Mg-O28	2.08(5)
Mn1-O6	2.202(11)	Mg-O23	2.74(5)
Mn1-O1	2.248(11)	Mg-O24	2.82(5)
Mn1-O4	2.250(11)	Mg-O21	2.90(5)
<Mn1-O>	2.20	Mg-O22	2.93(5)
		<Mg-O>	2.47
Mn2-O,OH26	2.116(11)		
Mn2-O16	2.118(12)	V1-O19	1.686(12)
Mn2-OH2	2.174(11)	V1-O15	1.701(11)
Mn2-O15	2.199(12)	V1-O9	1.725(12)
Mn2-O11	2.217(11)	V1-O18	1.863(12)
Mn2-O14	2.352(12)	<V1-O>	1.74
<Mn2-O>	2.20		
		V1A-O19	1.80(3)
Mn3-O13	2.112(12)	V1A-O28	2.00(3)
Mn3-O17	2.148(11)	V1A-O9	2.05(3)
Mn3-O5	2.162(11)	V1A-O18	2.07(3)
Mn3-OH12	2.204(11)	<V1-O>	1.98
Mn3-O18	2.300(12)		
Mn3-O23	2.504(11)	Si1-O16	1.608(12)
<Mn3-O>	2.26	Si1-O25	1.617(12)
		Si1-O1	1.628(11)
Mn4-OH2	2.118(11)	Si1-O32	1.636(12)
Mn4-OH8	2.164(12)	<Si1-O>	1.62
Mn4-O11	2.181(11)		
Mn4-O1	2.189(11)	Si2-O,OH26	1.619(12)
Mn4-O10	2.192(11)	Si2-O25	1.630(12)
Mn4-O4	2.193(11)	Si2-O27	1.632(13)
<Mn4-O>	2.17	Si2-O6	1.661(11)
		<Si2-O>	1.64
Mn5-O16	2.067(12)		
Mn5-O20	2.169(12)	Si3-O13	1.603(11)
Mn5-O1	2.176(11)	Si3-O5	1.607(11)
Mn5-O19	2.245(13)	Si3-O24	1.619(12)
Mn5-O11	2.301(12)	Si3-O30	1.657(12)
Mn5-O22	2.530(11)	<Si3-O>	1.62
<Mn5-O>	2.25		
		Si4-O,OH29	1.608(12)
Mn6-OH12	2.106(11)	Si4-O10	1.622(12)

According to the Chemical Structural Mineral Classification System of Strunz and Nickel (2001), scheuchzerite can be classified as insilicate with 7-periodic chain (9.DO.).

RELATION TO OTHER SPECIES

Scheuchzerite is related to saneroite $\text{Na}_2\text{Mn}_{10}\text{VSi}_{11}\text{O}_{34}(\text{OH})_4$ (Lucchetti et al. 1981), a mineral with which it is intimately associated. Both minerals are chain silicates, but saneroite contains simple chains (Basso and Della Giusta 1980) with periodicity of 5 (Fig. 4b). A tetrahedron labeled Si6 branches off the chain, and consists of 50% Si and 50% V (Fig. 4b). The saneroite chain can be seen as a distorted fragment of the scheuchzerite chain (numbered tetrahedra in Figs. 4a and 4b). The scheuchzerite chain is obtained by completing the saneroite chain with 3 additional silicate tetrahedra, corresponding to 6a, 6b, and 7 in Figure 4a. It is therefore possible that the intergrowth commonly observed among scheuchzerite and saneroite represents epitaxial growth along the extension of the silicate chains (Fig. 1).

Similarly to the structure of scheuchzerite, saneroite contains $[\text{Mn}(\text{O},\text{OH})_6]$ octahedra that form chains; however, the chains have different topology (2-2-3-3 in saneroite; 3-3-4-4-4 in scheuchzerite; Figs. 5a and 5b). The disordered V1A site (11% occupancy) is located in the space left by the missing octahedron

TABLE 6.—Continued

Mn6-OH8	2.110(11)	Si4-O32	1.642(11)
Mn6-O10	2.150(12)	Si4-O31	1.651(13)
Mn6-O7	2.179(12)	<Si4-O>	1.63
Mn6-O5	2.201(12)		
Mn6-O3	2.219(12)	Si5-O3	1.590(11)
<Mn6-O>	2.16	Si5-O31	1.613(13)
		Si5-O21	1.621(12)
Mn7-O14	2.103(11)	Si5-O23	1.638(12)
Mn7-O3	2.139(11)	<Si5-O>	1.61
Mn7-OH8	2.139(12)		
Mn7-OH2	2.141(12)	Si6-O20	1.575(12)
Mn7-O7	2.157(12)	Si6-O11	1.603(11)
Mn7-O3	2.209(12)	Si6-O28	1.672(13)
<Mn7-O>	2.15	Si6-O22	1.687(12)
		<Si6-O>	1.63
Mn8-O,OH29	2.092(12)		
Mn8-O13	2.115(11)	Si7-O27	1.601(13)
Mn8-OH12	2.178(12)	Si7-O24	1.611(12)
Mn8-O15	2.223(12)	Si7-O4	1.614(11)
Mn8-O7	2.278(11)	Si7-O22	1.626(11)
Mn8-O14	2.291(12)	<Si7-O>	1.61
<Mn8-O>	2.20		
		Si8-O17	1.527(11)
Mn9-O17	2.095(11)	Si8-O14	1.603(11)
Mn9-O6	2.190(12)	Si8-O28	1.652(13)
Mn9-O4	2.200(11)	Si8-O23	1.676(13)
Mn9-O9	2.203(12)	<Si8-O>	1.61
Mn9-O10	2.245(12)		
Mn9-O5	2.314(12)	Si9-O7	1.598(11)
<Mn9-O>	2.21	Si9-O21	1.611(12)
		Si9-O18	1.661(12)
Na-O21	2.390(15)	Si9-O30	1.675(12)
Na-O19	2.476(14)	<Si9-O>	1.64
Na-O22	2.484(15)		
Na-O24	2.556(15)		
Na-O31	2.616(14)		
Na-O28	2.653(15)		
Na-O30	2.831(14)		
Na-O32	3.071(14)		
<Na-O>	2.63		

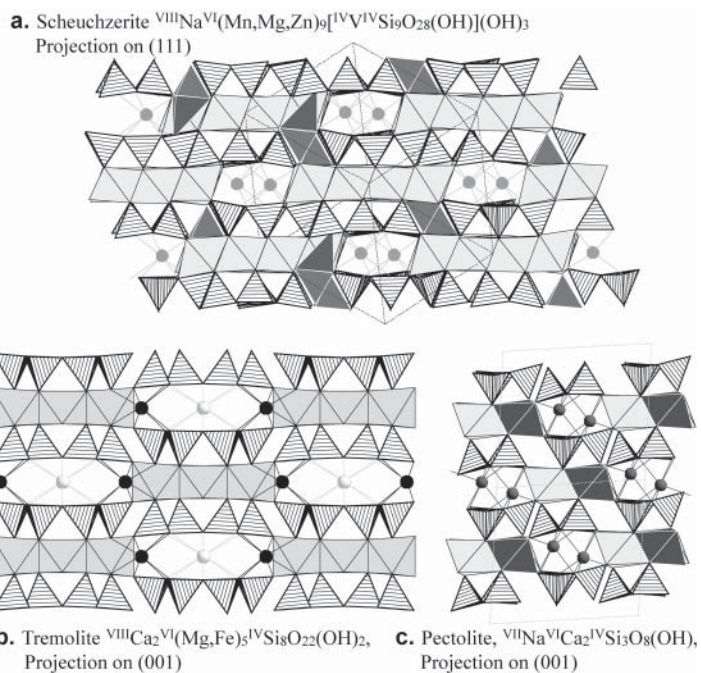


FIGURE 3. Stacking of octahedral and tetrahedral layers in (a) scheuchzerite; (b) tremolite (Hawthorne and Grundy 1976), and (c) pectolite (Ohashi and Finger 1978). Octahedral sites represented as gray octahedrons; tetrahedral sites as striped tetrahedrons; and seven- and eight-coordinated sites are drawn as atoms and bonds. The gray tetrahedron located in the octahedral layer of scheuchzerite corresponds of the highly disordered VIA site, and the gray tetrahedron in the tetrahedral layer corresponds to VI.

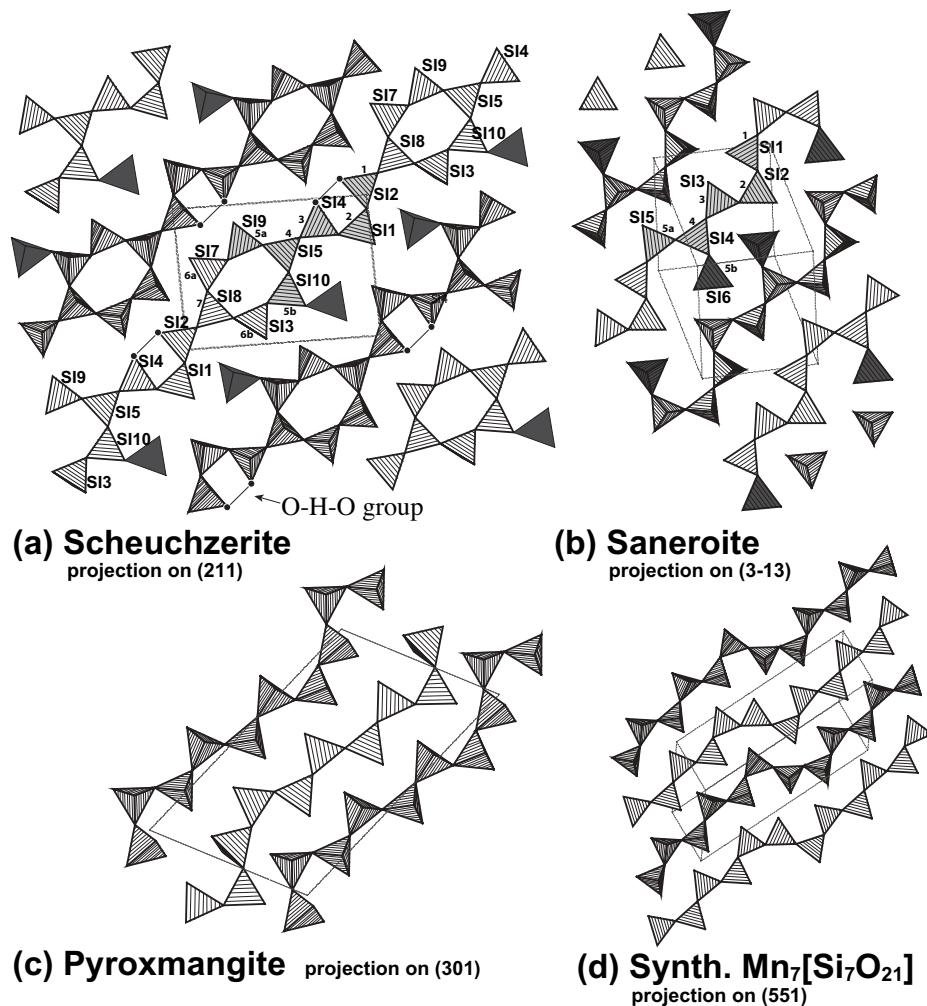


FIGURE 4. Tetrahedral chains in the structures of (a) scheuchzerite; (b) saneroite (Basso and Della Giusta 1980), (c) pyroxmangite (Ohashi and Finger 1975) and (d) synthetic $Mn_7[Si_7O_{21}]$ (Ohashi and Finger 1978). The silicon sites and chain periodicities are labeled in the structures of scheuchzerite and saneroite. The grayed tetrahedra contain vanadium in scheuchzerite and 50% silicon and vanadium in saneroite.

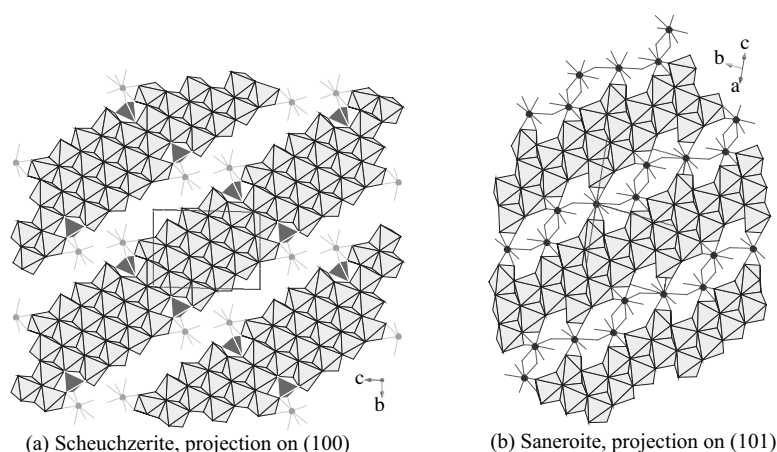


FIGURE 5. Topology of the octahedral layers in the structures of (a) scheuchzerite and (b) saneroite. The dark gray tetrahedral site corresponds to the highly disordered VIA site (11% occupancy).

in the 3-octahedral units of scheuchzerite (Fig. 5a). The $[\text{NaO}_8]$ polyhedra link two octahedral chains in saneroite, but are connected to only one in scheuchzerite.

Generally, the topology of the scheuchzerite structure is reminiscent of that of the double-chain silicates of the amphibole group (Fig. 3b) or of pyroxenoids such as pectolite (Fig. 3c). The only known silicates with a periodicity of 7 are pyroxmangite (Fig. 4c), pyroxferroite (Burnham 1971) and synthetic $\text{Mn}_7[\text{Si}_7\text{O}_{21}]$ described by Narita et al. (1977; Fig. 4d); none of these contain loops.

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