

Silvialite, a new sulfate-dominant member of the scapolite group with an Al-Si composition near the $I4/m-P4_2/n$ phase transition

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ABSTRACT

Silvialite, ideally $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$, is tetragonal, $I4/m$, $Z = 2$, with $a = 12.160(3)$, $c = 7.560(1)$ Å, $V = 1117.9(8)$ Å³, $c:a = 0.6217:1$, $\omega = 1.583$, $\varepsilon = 1.558$ (uniaxial negative), $D_m = 2.75$ g/cm³, $D_{\text{calc}} = 2.769$ g/cm³ and H (Mohs) = 5.5. It is transparent and slightly yellow, has a good {100} cleavage, chonchoidal fracture, white streak and a vitreous lustre. It occurs in upper-mantle garnet-granulite xenoliths hosted by olivine nephelinite, from McBride Province, North Queensland, Australia. The empirical formula, derived from electron-microprobe analysis, is $(\text{Na}_{1.06}\text{Ca}_{2.86})(\text{Al}_{4.87}\text{Si}_{7.13})\text{O}_{24}[(\text{SO}_4)_{0.57}(\text{CO}_3)_{0.41}]$. Crystal-structure refinement shows disordered carbonate and sulfate groups along the fourfold axis. Silvialite is a primary cumulate phase precipitated from alkali basalt at 900–1000°C and 8–12 kbar under high f_{SO_2} and f_{O_2} . The name silvialite, currently used in literature to describe the sulfate analogue of meionite, was suggested by Brauns (1914).

KEYWORDS: scapolite, meionite, silvialite, new mineral, sulfate, X-ray data, electron-microprobe data, Queensland, Australia.

Introduction

MINERALS of the scapolite group have the general formula $M_4T_{12}O_{24}A$, with $M = \text{Na, Ca, minor K}$; $T = \text{Al, Si}$ and $A = \text{Cl, CO}_3, \text{SO}_4$. Until now, the group consisted of two valid species: marialite (Ma) $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$, and meionite (Me) $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$. Early in this century, a significant SO_4 component was recognized in some samples of meionite, and Brauns (1914) suggested the name silvialite for the hypothetical SO_4 analogue of meionite. However, fifty years passed before SO_4 -dominant compositions were reported (Lovering and White, 1964). Since then, samples with $S > 0.5$ atoms per formula unit (a.p.f.u.) have been noted from a relatively large number of occurrences, but silvialite has not yet been accepted as a valid mineral name or defined as a distinct species. Here, we describe silvialite as a primary cumulate phase in mafic xenoliths from McBride Province, North Queensland. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Holotype material is housed in the

Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, Ontario, under catalogue number NMC 68080.

Silvialite in the Ma-Me series

Among the rock-forming minerals, the scapolite group has long been of interest for its unusual structural and stoichiometric features. Phase transitions from $I4/m$ to $P4_2/n$ and then again to $I4/m$ are very rare for silicate minerals, but occur with increasing Al across the series from marialite to meionite (Fig. 1A). In an earlier study, we presented arguments that the structural changes across the series are not caused by substitutions at the M - or A -sites, but are due to three distinct patterns of (Al,Si) order in each part of the series (Teertstra and Sherriff, 1996). The specific arrangements of Al in the framework must cause significant deviations from the plagioclase substitution, which maintain a nearly complete dominance of monovalent and divalent anions at the A -site of marialite and meionite (Fig. 1B; Teertstra and Sherriff, 1997). In low-symmetry

intermediate scapolite (calcian marialite to sodian meionite), Al is highly ordered mid-way across the series at $\text{Al}_{4.2}\text{Si}_{7.8}\text{O}_{24}$, approximately where compositional trends intersect the $(\text{CaAl})(\text{NaSi})_{-1}$ vector (at $\text{Al}_{4.0}\text{Si}_{8.0}\text{O}_{24}$).

Correlated with the phase transitions are two changes in the compositional trend across the solid-solution between the ideal anhydrous end-members (Ma) $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$ and (Me) $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$, dividing the series into marialite ($0 \leq \text{Me} < 15$), calcian marialite ($15 \leq \text{Me} < 50$), sodian meionite ($50 \leq \text{Me} < 65$) and meionite ($65 \leq \text{Me} \leq 100$). The changes in the compositional trend occur where stoichiometric deviation from the plagioclase substitution is greatest, i.e. at $[(\text{Na}_{3.4}\text{Ca}_{0.6})(\text{Al}_{3.6}\text{Si}_{8.4})\text{O}_{24}]^{-1}$ and $[(\text{Na}_{1.4}\text{Ca}_{2.6})(\text{Al}_{4.7}\text{Si}_{7.3})\text{O}_{24}]^{1.91}$ (Fig. 1B). Compositions of marialite are (Na,Si)-rich relative to the $(\text{CaAl})(\text{NaSi})_{-1}$ vector, the stoichiometric deviation serving to fully occupy the A-site with monovalent anions (dominantly Cl). Compositions in the meionite-silvialite solid-solution are (Ca,Al)-rich, and keep the A-site fully occupied by divalent oxyanions. In most intermediate compositions, H_2O plays an important role, supplying monovalent anions (OH, HCO_3 and HSO_4) as well as neutral groups (H_2O and possibly HCl), keeping the A-site fully occupied and satisfying local bond-valence requirements.

A review of scapolite compositions from the literature shows numerous occurrences of sodian meionite to meionite in which S occupies fifty to ninety per cent of the A-site; these have Si values ranging from 8.1 to 6.6 Si a.p.f.u. (Fig. 1C). The majority of these S-dominant scapolites have Si values of 7.0 to 7.5 a.p.f.u. on either side of the $P4_2/n$ - $I4/m$ phase transition at $\text{Si}_{7.3}$ (Fig. 1C). Thus, silvialite may occur in either space group, and structure refinement is one method which can determine this. Different S species (e.g. S_2^{2-} , SO_3^{2-} , SO_4^{2-}) can substitute for the triangular carbonate group; these species are not necessarily distinguished by spectroscopic measurement, but may be identified by refinement of the structure.

Occurrence and associated minerals

The typical occurrence of silvialite is in granulite-facies metamorphic rocks (Moecher and Essene, 1991; Devaraju and Coolen, 1983; Hoefs *et al.*, 1981; Coolen, 1980), and from mafic and ultramafic xenoliths from the lower crust or upper mantle (Stolz, 1987; Goff *et al.*, 1982;

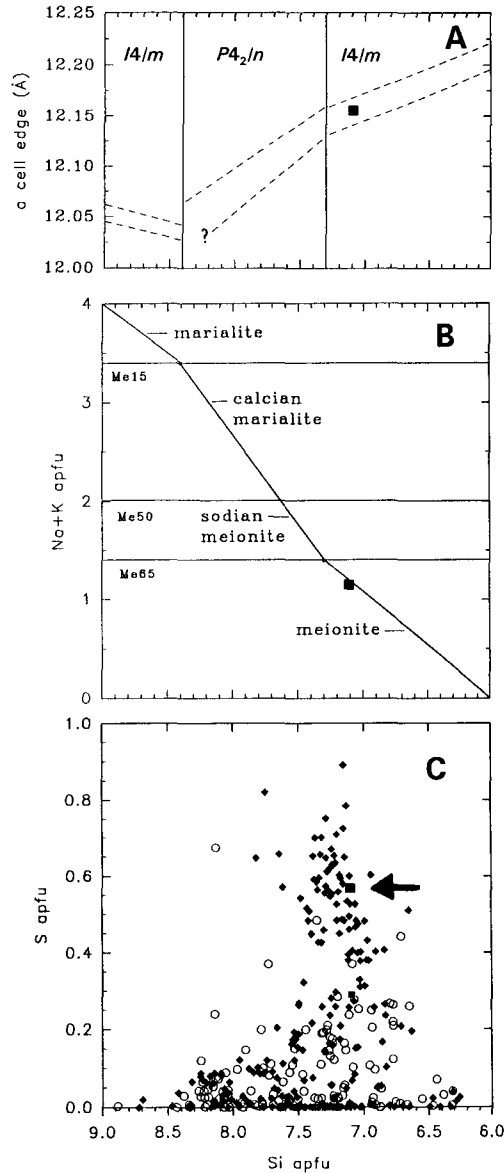


FIG. 1. (A) Variation in cell-edge a (Å) vs. Si a.p.f.u.; the range in a is indicated by dashed lines, and vertical lines at Si 8.4 and 7.4 denote change of space group. (B) (Na + K) vs. Si a.p.f.u., indicating scapolite-group nomenclature consistent with changes in compositional trend at Me_{15} and Me_{65} . (C) S vs. Si a.p.f.u. indicating data from wet-chemical (○) and electron-microprobe (◆) analysis. Additional information is available in Teertstra and Sherriff (1996, 1997). The datum for silvialite (this study) is marked with a square (■) and indicated by an arrow.

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Griffin *et al.*, 1979; Edwards *et al.*, 1979; Lovering and White, 1964). It also occurs in anorthosites at the Manicouagan meteorite-impact structure (Wolfe and Hörz, 1970). The silvialite examined here occurs in upper-mantle garnet-granulite xenoliths hosted by olivine nephelinite, McBride Province, North Queensland, Australia. Silvialite is a relatively abundant mineral in these rocks, forming up to 20 vol.% of the mafic xenoliths with grains up to 3 mm in length (Stolz, 1987; Rudnick and Taylor, 1987).

The silvialite grains have a symplectite corona of fine-grained plagioclase (An_{70}) and vermicular calcite (Fig. 2). Associated minerals are plagioclase (An_{45}), calcic amphibole, clinopyroxene, garnet and spinel (with exsolved ilmenite). All minerals in the assemblage have medium grain size (1–3 mm) and are compositionally homogeneous. Garnet is dominantly pyrope–almandine with a moderate grossular component: ($Pyr_{44.4}Alm_{39.6}Grs_{15.9}$). The spinel has a significant hercynite component: ($Mg_{0.558}Fe_{0.442}$) ($Al_{1.938}Fe_{0.043}Cr_{0.030}$) O_4 . The amphibole is ferroan pargasite: ($Na_{0.785}K_{0.215}$)($Ca_{1.812}Mg_{0.154}Na_{0.032}$)($Fe_{1.446}^{2+}Mg_{2.533}Ti_{0.351}Al_{0.655}Mn_{0.015}$) ($Al_{2.021}Si_{5.979}$) O_{22} ($O_{0.3}OH_{1.7}$); because OH^- values were calculated, minor Fe^{3+} may be present with increased O^{2-} values.

The clinopyroxene formula, calculated on the basis of six atoms of oxygen, is ($Ca_{0.837}Mg_{0.081}Na_{0.105}$)($Fe_{0.235}^{2+}Mg_{0.539}Ti_{0.044}Al_{0.182}$) ($Al_{0.215}Si_{1.785}$) O_6 . The cation sum of 4.023 departs from the ideal value of 4, indicating either a +0.6% net analytical error or minor

substitution of trivalent Fe; the latter interpretation is favoured: balanced end-member components could only be calculated by inclusion of 0.055 $NaFe^{3+}Si_2O_6$ (Ae) with 0.050 $NaAlSi_2O_6$ (Jd) p.f.u., and 0.044 $CaTiAl_2O_6$ and 0.132 $CaAlAlSiO_6$ Tschermak (Ts) end-members. Calculated in the sequence indicated, this gives $Jd_{2.9}Ae_{3.2}CaTi-Ts_{2.5}CaAl-Ts_{7.6}$ ($Wo_{37.9}En_{35.6}Fs_{10.3}$) $_{83.3}$. Values for $Q = (Ca + Mg + total Fe)$ of 1.692, $J = 2Na$ of 0.210 and $J/(Q + J)$ of 0.11 indicate a dominance of QUAD components (Morimoto, 1988); the clinopyroxene is properly named sodian aluminian diopside.

Origin of silvialite

Values for mg (100Mg/(Mg + total Fe)) for the clinopyroxene (73) and amphibole (65) are along trend lines established for equilibrium pairs (Stolz, 1987). Values for Na contents in plagioclase and clinopyroxene agree closely with those reported for scapolite-bearing mafic xenoliths (sample 85-106 of Rudnick and Taylor, 1987). Compositions of all minerals analysed here are similar to representative analyses previously reported for garnet granulite at this locality (Stolz, 1987; Rudnick and Taylor, 1987).

The plagioclase-calcite symplectite might be a feature of late reaction or primary in origin. The An_{70} content of this plagioclase is nearly identical to the Me_{72} content of silvialite, so that only a source of sulfate is needed to generate silvialite. Area measurement by image analysis indicated that 40(5)% of the symplectite is composed of calcite. If the symplectite were a breakdown product of meionite, its composition would be $3(Na_{0.30}Ca_{0.70}Al_{1.67}Si_{2.31}O_8)CaCO_3$ ($Me_{77.5}$) and 38% of the calcite would be in excess, and a S-rich phase is missing. If the symplectite is a growth feature of silvialite, the plagioclase An contents are high due to local equilibrium with calcite, the calcite is in excess of that required by silvialite. Abundances of silvialite are limited by the activity of sulfate, and compositions of coarse-grained plagioclase (An_{45}) are (Na,Si)-rich in equilibrium with (Ca,Al)-rich silvialite. It is significant to note that the McBride silvialite does not have bell-shaped compositional profiles with decreasing sulfate concentrations from core to rim, which are typical of samples from slowly-exhumed granulite terrains (e.g. Lovering and White, 1964; Coolen, 1980). The symplectite does not, therefore, appear to be a breakdown product of scapolite.

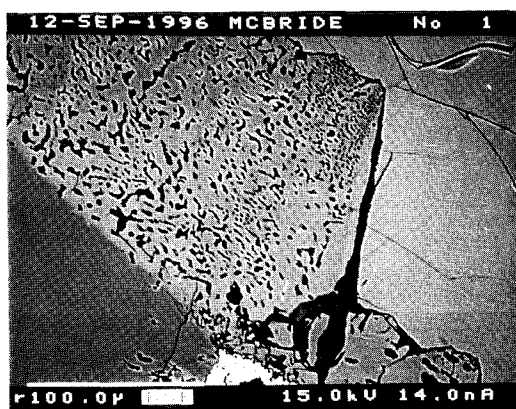


FIG. 2. Back-scattered electron image of silvialite (right), plagioclase (An_{70})-calcite symplectite corona, and plagioclase (An_{45} , left).

Stability relations indicate that silvialite is a true high-pressure as well as high-temperature phase. End-member silvialite requires a minimum temperature of 775°C to form at 17 kbar, and a minimum pressure of 10 kbar to form at 1200°C (Newton and Goldsmith, 1976). Somewhat less extreme conditions are required for Na-bearing meionite-silvialite solid-solutions (Goldsmith and Newton, 1977). The geothermometric and geobarometric calculations of Stolz (1987), indicating conditions of formation of the silvialite-bearing assemblage at 900–1000°C and 8–12 kbar, are in reasonable agreement with the experimental phase-stability data. Silvialite is probably a primary cumulate phase precipitated from hydrous alkali basalt under high f_{SO_2} and f_{O_2} .

Physical properties

Silvialite is transparent and slightly yellow. It is brittle, with conchoidal fracture, subvitreous lustre, one good cleavage parallel to {100} and a white streak. In thin section, silvialite has uniform extinction and is uniaxial negative. Subhedral grains are elongated along the *c*-axis. Indices of refraction, determined in immersion oil with white light, are $\omega = 1.585$ and $\varepsilon = 1.558$; the oils were calibrated by a Spencer refractometer. The Mohs hardness is estimated to be ~5.5. The measured density is 2.75 g/cm³ and the calculated density is 2.77 g/cm³. The density was measured using a Berman balance with toluene as the displacing medium. Silvialite does not fluoresce in ultraviolet light, but has faint deep-red cathodoluminescence.

Chemical composition

Mineral compositions were measured using a CAMECA SX-50 electron microprobe operating in wavelength-dispersion mode at 15 kV and 20 nA with a beam diameter of 10 µm. For silvialite, the principal standards used were albite (Na-*Kα*, Si-*Kα*), scapolite (Al-*Kα*), anorthite (Ca-*Kα*), baryte (Ba-*Lα*, S-*Kα*), SrTiO₃ (Sr-*Lα*), sanidine (K-*Kα*), fayalite (Fe-*Kα*) and tugtupite (Cl-*Kα*); F, Mn, Mg, Br, Ti, P and Ba were sought but not detected. Measured compositions are considered accurate to within 2%; details of the analytical method are given in Teertstra and Sherriff (1997).

The formula, normalized to (Si + Al) = 12 a.p.f.u., suggests that the minor Fe is divalent and occupies the *M*-site. The ΣM of 3.96 a.p.f.u. is

below the ideal value of 4.0, but near the average value of 3.95(7) a.p.f.u. recorded for 514 published compositions of scapolite (Teertstra and Sherriff, 1997). The Me contents of 72.2% were calculated according to the proportion of divalent cations occupying the *M*-site, using $\text{Me} = 100(\text{Ca} + \text{Fe} + \text{Sr})/4$. A carbonate content of 0.41 CO₃²⁻ p.f.u. was calculated by charge-balance using $\text{CO}_3^{2-} = [(\text{Na} + \text{K}) + 2(\text{Ca} + \text{Fe} + \text{Sr}) - \text{Al} - \text{Cl} - 2\text{S}]/2$. In this calculation, the S species is divalent and the negative charges of the *A*-site anions and framework are subtracted from the *M*-cation charge. The resulting ΣA value of 0.98 (Table 1) suggests good analytical accuracy and indicates nearly complete occupancy of the *A* site. The carbonate content of 0.43 CO₃²⁻ p.f.u., calculated using $\text{CO}_3^{2-}(\text{calc}) = (1 - \text{Cl} - 2\text{S})$ [i.e. assuming $\Sigma A = 1$], gives minor charge

TABLE 1. Composition of silvialite, McBride Province, Australia

	Average (N=11)	Range
SiO ₂ wt.%	45.26(36)	44.77–45.90
Al ₂ O ₃	26.25(28)	25.81–26.67
Fe ₂ O ₃	0.22(5)	0.17–0.31
Na ₂ O	3.49(14)	3.23–3.64
K ₂ O	0.06(1)	0.04–0.07
CaO	16.95(36)	16.20–17.66
SrO	0.08 (5)	0.00–0.18
Cl	0.02 (2)	0.00–0.06
SO ₃	4.82(22)	4.37–5.19
CO ₂ calc.	1.92	
Sum	99.08	
Si a.p.f.u.	7.13(4)	7.070–7.196
Al	4.87(4)	4.804–4.930
Fe	0.024(5)	0.020–0.035
Na	1.06(5)	0.983–1.116
K	0.011(2)	0.008–0.013
Ca	2.86(6)	2.743–2.968
Sr	0.001(1)	0.000–0.002
Cl	0.002 (2)	0.000–0.006
S	0.57(3)	0.515–0.620
ΣM	3.964	3.870–4.024
Me	72.2	69.2–75.2
CO ₂ (calc)	0.414	0.329–0.502
ΣA	0.984	0.844–1.122

Formula normalized to (Si+Al) = 12 a.p.f.u.

$\Sigma M = (\text{Na} + \text{K} + \text{Ca} + \text{Fe} + \text{Sr})$

$\text{Me} = 100(\text{Ca} + \text{Fe} + \text{Sr})/4$

$\text{CO}_2(\text{calc}) = [(\text{Na} + \text{K}) + 2(\text{Ca} + \text{Fe} + \text{Sr}) - \text{Al} - \text{Cl} - 2\text{S}]/2$

$\Sigma A = \text{Cl} + \text{S} + \text{CO}_2(\text{calc})$

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imbalance in the formula; neutrality would be attained if Ca values were higher by 0.04 a.p.f.u., or if there were 0.04 bicarbonate molecules p.f.u. at the A-site. The latter assumption is reasonable, as most samples of scapolite are hydrous and contain bicarbonate and bisulfate anions. However, we could not reliably measure such negligible quantities of H₂O in the limited amount of sample available, and we consider the 0.41 CO₃²⁻ value to be the most accurate for the essentially anhydrous silvialite. The estimated analytical accuracy of <2% is confirmed by the very close agreement of the calculated formula with the ideal stoichiometry indicated by refinement of the crystal structure.

X-ray crystallography

Powder diffraction

Insufficient material was available for powder X-ray diffraction using an automated diffractometer. Thus, selected crystals of the sample were mounted on a glass fibre and measured in a 114.6 mm Gandolfi camera using Cu-K α X-radiation and an internal quartz standard. The observed and calculated *d*-values, the estimated relative intensities (*I/I*₀) and the corresponding (*hkl*) indices of the powder pattern are listed in Table 2. The refined lattice constants from the powder pattern are *a* = 12.160(3), *c* = 7.560(1) Å.

Crystal-structure refinement

A single crystal of silvialite was ground to an approximate sphere with a diameter of 250 µm and was mounted on a Nicolet R3m automated four-circle diffractometer. The unit-cell dimensions (Table 3) were refined by least-squares from the setting angles of 15 automatically aligned reflections in the range 5° < 2θ < 30°. A total of 881

TABLE 2. X-ray powder-diffraction data for silvialite

<i>I/I</i> ₀	<i>d</i> (meas) [Å]	<i>d</i> (calc) [Å]	<i>hkl</i>
5	6.03(1)	6.08	020
20	3.82(1)	3.85	130
5	3.49(1)	3.43	031
100	3.45(1)	3.46	112
40	3.07(1)	3.08	231
15	3.04(1)	3.04	040
5	2.74(1)	2.75	141
15	2.69(1)	2.70	132
2	2.31(1)	2.32	341, 051
2	2.16(1)	2.16	251
2	2.14(1)	2.14	033
2	1.93(1)	1.93	161
2	1.92(1)	1.92	143
2	1.91(1)	1.89	004
1	1.74(1)	1.72	170, 550
1	1.57(1)	1.57	163
1	1.54(1)	1.52	453
1	1.44(1)	1.43	660
1	1.38(1)	1.38	235
4	1.37(1)	1.37	282
1	1.33(1)	1.33	563

symmetry-independent reflections were measured (3° ≤ 2θ ≤ 60°), with index ranges of 0 ≤ *h* ≤ 17, 0 ≤ *k* ≤ 14, 0 ≤ *l* ≤ 10. The experimental setup method followed the procedure of Burns *et al.* (1994). The structure was refined using SHELXTS PC PLUS system of programs (Sheldrick, 1990). The bond-lengths and angles were calculated with SADIAN90 (Baur and Kassner, 1991). The structural data of Peterson *et al.* (1979) were used to initiate the refinement.

The carbonate group was refined as a planar triangle disordered around the A-site with *z* = 0 for the corresponding oxygen atom O(6C). The

TABLE 3. Experimental data of silvialite

Crystal system Space group	Tetragonal <i>I4/m</i>	Crystal size wavelength	Sphere with <i>d</i> = 250 µm Mo-K α (0.71073 Å)
<i>a</i> Å	12.134(2)	No. of <i>l</i>	955
<i>c</i> Å	7.576(2)	No. of unique <i> F </i>	881
<i>V</i> Å ³	1115.4(8)	No. of <i> F_{obsj} </i> > 5σ	753
<i>Z</i>	2		
<i>R</i> %	2.6	$R = \sum(F_o - F_c) / \sum F_o$	
<i>R_w</i> %	2.6	$R_w = \sum w(F_o - F_c)^2 / \sum F_o^2)^{1/2}$, <i>w</i> = 1	

TABLE 4. Positional coordinates and equivalent displacement factors, the occupancy factors, the site symmetry (*Sym.*) and Wyckoff positions (*Wy.*) for silvialite

Site	<i>Sym.</i>	<i>Wy.</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	<i>Occupancy</i>
<i>T</i> (1)	m..	8h	0.16079(4)	0.09174(6)	0	0.0085(2)	1
<i>T</i> (2)	1	16i	0.16030(4)	0.41297(4)	0.20683(8)	0.0096(2)	1
<i>M</i> (Ca)	m..	8h	0.35868(6)	0.28328(7)	0	0.0218(3)	0.613(6)
<i>M</i> (Na)	m..	8h	0.35868(6)	0.28328(7)	0	0.0218(3)	0.387(6)
<i>A</i> (S)	2/m..	4c	1/2	1/2	0	0.0165(5)	0.522(3)
<i>A</i> (C)	2/m..	4c	1/2	1/2	0	0.0165(5)	0.478(3)
O(1)	m..	8h	0.04213(2)	0.1518(2)	0	0.0187(6)	1
O(2)	m..	8h	0.1870(2)	0.3730(8)	0	0.0174(6)	1
O(3)	1	16i	0.4495(1)	0.1505(1)	0.2068(2)	0.0212(4)	1
O(4)	1	16i	0.2666(1)	0.3655(1)	0.6724(3)	0.0272(5)	1
O(5)	1	16i	0.4008(6)	0.4815(6)	0.107(1)	0.031(2)	0.261(3)
O(6)	m..	8h	0.605(1)	0.511(1)	0	0.079(5)	0.359(3)

occupancy factors for the *M*(Ca,Na) and *A*(S,C) sites were fixed at unity. The oxygen positions O(5S) sulfate and O(6C) carbonate groups were located using difference-Fourier maps. Initially, their occupancy factors were refined independently, but they were subsequently constrained by the corresponding refined values of S and C at the *A*(S,C) site. After refinement of the anisotropic-displacement factors, the structure converged to an R-index of 2.6%. The experimental data are listed in Table 3, the final atomic positions and displacement factors in Table 4 and selected interatomic distances and angles in Table 5.

Crystal structure

The silvialite structure was refined in the space group *I4/m* which has two *T*-sites, both with (Al,Si) disorder (Fig. 3). The average $\langle T(1)\text{-O} \rangle$ bond length of 1.640 Å is larger than the value of 1.605 in end-member marialite for a *T*(1) site occupied by Si, indicating that the *T*(1) site in silvialite contains minor Al. The average $\langle T(2)\text{-O} \rangle$ bond length of 1.675 Å is considerably shorter than the maximum value of 1.750 Å in highly ordered *P4_{2/n}* scapolite for a *T*(2) site completely occupied by Al, indicating (Al,Si)-disorder at *T*(2) and enrichment in Al in silvialite. The above bond lengths agree well with those previously reported for scapolite (cf. summary by Teertstra and Sherriff, 1996).

The *M* cations are coordinated by seven atoms of framework oxygen (O2, O3 ($\times 2$) and O4 ($\times 4$)); the remaining bond-valence is satisfied by oxygen atoms of the *A*-site complex anions. The ranges of the $\langle M\text{-O} \rangle$ bond lengths, from 2.29 Å

to 2.899 Å, are typical for Na-O and Ca-O bonds, respectively.

In agreement with a previous refinement of a sulfate-rich meionite in space-group *I4/m* (0.29 S, 7.1 Si a.p.f.u.; Peterson *et al.*, 1979), the sulfate group in the silvialite structure is disordered around position 4c with site-symmetry *4/m*. The $\langle \text{S-O} \rangle$ distance of 1.468(7) Å is in the normal range for SO₄ groups. The refined site-scattering for the S-atom gives an SO₄ content of 0.522 a.p.f.u.. This value is in the range of the microprobe-determined SO₄ contents of 0.515 to 0.620 a.p.f.u., but somewhat lower than the mean content of 0.570 a.p.f.u.. Assuming 98% site occupancy, the CO₃²⁻ contents of 0.458 p.f.u.

TABLE 5. Interatomic distances [Å] and angles [°] in silvialite

<i>T</i> (1)-O(1)	1.614(3)	<i>T</i> (2)-O(2)	1.672(1)
<i>T</i> (1)-O(1')	1.628(3)	<i>T</i> (2)-O(3)	1.672(3)
<i>T</i> (1)-O(4)	1.659(2)	<i>T</i> (2)-O(3)'	1.673(1)
<i>T</i> (1)-O(4)'	1.659(2)	<i>T</i> (2)-O(4)	1.683(2)
$\langle T(1)\text{-O} \rangle$	1.640(2)	$\langle T(2)\text{-O} \rangle$	1.675(2)
<i>M</i> -O(6)	2.29(1)	C(1)-O(6C) $\times 4$	1.28(1)
<i>M</i> -O(2)	2.350(5)	S(1)-O(5S) $\times 8$	1.468(8)
<i>MO</i> (3) $\times 2$	2.503(2)		
<i>M</i> -O(6)'	2.53(1)	<i>T</i> (1)-O(1)- <i>T</i> (1)	157.0(2)
<i>MO</i> (5) $\times 2$	2.540(7)	<i>T</i> (2)-O(2)- <i>T</i> (2)	139.2(5)
<i>MO</i> (5)' $\times 2$	2.591(8)	<i>T</i> (2)-O(3)- <i>T</i> (2)	145.8(1)
<i>MO</i> (4) $\times 2$	2.697(2)	<i>T</i> (1)-O(4)- <i>T</i> (2)	136.7(1)
<i>MO</i> (4)' $\times 2$	2.899(2)		

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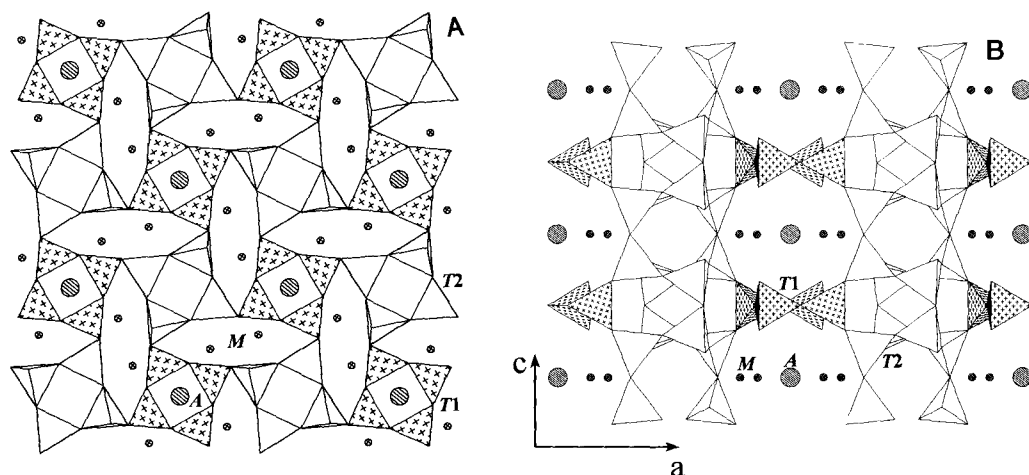


FIG. 3. The crystal structure of silvialite. (A) View along channels perpendicular to the c -axis. (B) View perpendicular to the a -axis. The large circles (A) indicate the positions of the A -site (SO_4 , CO_3) groups, the smaller circles (M) represent the M -site (Na,Ca) atoms.

measured from the total refined scattering power (e.p.f.u.) at the A -site are somewhat higher than the calculated values of 0.41 to 0.43 CO_3^{2-} p.f.u. Nevertheless, the compositional measurements determined *via* structure refinement indicate dominance of S at the A -site and atomic proportions of $\text{S} > \text{C}$.

In order that long-range tetragonal symmetry be maintained, the planar triangular CO_3 group must exhibit positional disorder (e.g. Lin and Burley, 1973*a,b*, 1975; Levien and Papike, 1976; Peterson *et al.*, 1979). However, Aitken *et al.* (1984) refined the structure of synthetic $I4/m$ meionite in which the oxygen positions of the carbonate group could be split into eight different positions. In silvialite, attempts to split the carbon or the O(6C) oxygen sites during the refinement were unsuccessful. The oxygen atom lies at Wyckoff position 8h and C is at position 4c (Table 4), and the carbonate group displays an average square-planar configuration. Nevertheless, the equivalent isotropic displacement factor for O(6) is higher than that of any other oxygen atom in the silvialite structure.

Discussion

Silvialite is a new member of the scapolite group and forms a solid-solution series with meionite. In silvialite, more than 50% of the A -site is occupied by the sulfate anion. The mineral name was proposed by Brauns (1914) for the hypothetical

sulfate-scapolite end-member, but fifty years passed before sulfate-dominant compositions were reported (Lovering and White, 1964). This is not a modern definition of an old species; the mineral name is old, but until now, sulfate-dominant scapolite has never been characterized sufficiently for definition as a mineral species. The name has been used (and misused) intermittently in the literature (as has 'sulfate-scapolite'); we chose to keep close to the original German spelling rather than adopt 'sylvialite'. The mineral is named after Silvia Hillebrand, daughter of Tschermak, and Brauns placed an 'l' in the name instead of the convention of adding 'ite' to denote a mineral name, hence silvialite instead of 'silviaite'.

The end-member formula of silvialite is $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$. A simplified formula may also be written: $\text{NaCa}_3\text{Al}_5\text{Si}_7\text{O}_{24}\text{SO}_4$ is closer in composition to the empirical formula of silvialite than is the end-member formula, but is incorrect. The Na content shows a link to marialite, but silvialite is the sulfate analogue of meionite, $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$. The simplified formula is analogous to Cl-free 'mizzonite', $\text{NaCa}_3\text{Al}_5\text{Si}_7\text{O}_{24}\text{CO}_3$, which is not a species, variety or end-member, but an integral-stoichiometry composition near the change of substitution mechanism at $[(\text{Na}_{1.4}\text{Ca}_{2.6})(\text{Al}_{4.7}\text{Si}_{7.3})\text{O}_{24}]^{1.9-}$ which marks the $P4_2/n-I4/m$ phase-transition. The NaCa_3 stoichiometry might mistakenly imply the presence of NaCa_3SO_4 'clusters', the exist-

tence of which has no structural basis. The Al_5Si_7 stoichiometry might imply a particular (Al,Si)-ordered arrangement, beyond which Al-O-Al bonds cannot be avoided in Al-rich scapolite; however, a distinct change in the pattern of (Al,Si) order occurs instead at the non-integral $\text{Al}_{4.7}\text{Si}_{7.3}$ stoichiometry.

According to the close correlation established between structure and composition, we anticipate that sodian silvialite ($\text{Me} < 65$, $\text{Si} > 7.3$ a.p.f.u.) has the space group $P4_2/n$, and that silvialite (our sample and others with $\text{Me} \geq 65$, $\text{Si} \leq 7.3$ a.p.f.u.) occurs in the space group $I4/m$. In samples with lower symmetry and a higher degree of (Al,Si) order, ordering of the sulfate and carbonate groups is also possible, and additional study might observe such ordering on a scale of several unit cells.

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