

Barysilite from Garpenberg Norra, Dalarna, Sweden: occurrence and crystal structure refinement

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ABSTRACT

A new occurrence of barysilite, $\text{Pb}_8\text{Mn}(\text{Si}_2\text{O}_7)_3$, at the polymetallic Garpenberg Norra Zn-Pb deposit, Hedemora, Dalarna, Sweden, is described. The mineral, which forms colourless, transparent grains, is characterized by X-ray diffraction and electron-microprobe analyses. The assemblage includes tephroite, zincian jacobsite, manganoan diopside and others. The crystal structure of a barysilite crystal from Garpenberg Norra was redetermined using single-crystal X-ray diffraction data (Mo-K α , CCD area detector) and has been refined in space group $R\bar{3}c$ with $a = 9.804(1)$, $c = 38.416(8)$ Å, $V = 3197.8(8)$ Å³, to $R1 = 2.32\%$ for 1025 'observed' reflections with $F_o > 4\sigma(F_o)$. A previous, low-precision structure determination (Lajzėrowicz, 1965; $R = 20\%$) is confirmed but improved considerably. The structure contains one distorted MnO_6 polyhedron with six equivalent Mn–O bonds (2.224 Å), one Si_2O_7 disilicate unit with an Si–O–Si angle of 120.9°, and two non-equivalent Pb sites. The Pb1 site has a highly irregular, one-sided coordination with six O ligands, indicating a stereoactive $6s^2$ lone-electron pair on the Pb^{2+} ion, whereas the [6+3]-coordinated Pb2 site is fairly regular, with Pb–O distances of 2.540 (3 ×), 2.674 (3 ×) and 3.098 (3 ×) Å. The Pb2 site contains ~10% of Ca (+Ba) replacing Pb, corresponding to the structural formula $\text{Pb}_{16}(\text{Pb,Ca})_2\text{Mn}(\text{Si}_2\text{O}_7)_3$. This is the first direct proof that not only the *M* site in barysilite-type $\text{Pb}_8M(\text{Si}_2\text{O}_7)_3$ compounds can be replaced by divalent cations.

KEYWORDS: barysilite, crystal structure, crystal chemistry, Garpenberg Norra, Sweden.

Introduction

BARYSILITE is a rare PbMn silicate first described by Sjögren and Lundström (1888) from the Harstigen mine, Filipstad, Värmland, Sweden. Later, it was also reported from the famous deposits Långban and Jakobsberg (both Filipstad, Sweden) and from Franklin, New Jersey, USA (Ito and Frondel, 1967; Dunn, 1985; Yeates, 1991, and references therein). Another occurrence of the mineral as minute tabular crystals, partly in association with cerussite, in a mining slag at the Glücksrad mine, Oberschulenberg, Harz mountains, Germany (Schellhorn, 1987; Wittern, 1994) is noteworthy.

The correct chemical formula of barysilite was the subject of some considerable debate. First thought to be a pure lead silicate, the formulae $(\text{Pb,Mn})\text{Si}_3\text{O}_{11}$ and $\text{Pb}_5\text{Mn}(\text{Si}_2\text{O}_7)_2$ were later suggested by Glasser (1964) and Ito and Frondel (1967), respectively. A low-precision single-crystal structure solution of barysilite from Långban, Sweden, yielded the formula $\text{Pb}_8\text{Mn}(\text{Si}_2\text{O}_7)_3$, and showed the presence of one Mn and two Pb sites in the structure (Lajzėrowicz, 1965; $a = 9.821(5)$, $c = 38.38(6)$ Å, $V = 3205.9$ Å³, space group $R\bar{3}c$, $R = 20\%$). The divalent character of Mn in barysilite was confirmed by electron paramagnetic resonance (Michoulier, 1967). The structure of synthetic barysilite-type $\text{Pb}_3\text{Si}_2\text{O}_7$ ($a = 10.126(3)$, $c = 38.678(2)$ Å, $V = 3434.8$ Å³) was reported by Petter *et al.* (1971) who referred to the compound as 'lead-barysilite' (see also Petter and Harnik,

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DOI: 10.1180/0026461026620034

1971). Their single-crystal study ($R = 4.2\%$) demonstrated that Pb substitutes for the Mn, and that $\text{Pb}_3\text{Si}_2\text{O}_7$ ($= \text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3$) represents the Pb analogue of barysilite, $\text{Pb}_8\text{Mn}(\text{Si}_2\text{O}_7)_3$. Several authors observed that the Mn can be replaced by a larger number of divalent cations without any apparent change of crystal symmetry or space group (Lajz rowicz, 1965; Ito and Frondel, 1967; Billhardt, 1969; Bordeaux and Lajz rowicz, 1969; Harnik, 1972; Schmidt *et al.*, 1982; Chen *et al.*, 2001). Also, both complete and partial solid solution series with isotopic germanates were reported (Lajz rowicz, 1965; Bordeaux and Lajz rowicz, 1969; Salnikow *et al.*, 1979; Schmidt *et al.*, 1982, 1983; Otto, 1983; Firsov *et al.*, 1984). Thus, the barysilite structure type apparently occurs for a large number of $\text{Pb}_8M^{2+}(\text{T}_2\text{O}_7)_3$ compounds with $M^{2+} = \text{Be}, \text{Mg}, \text{Ca}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Sr}, \text{Ba}, \text{Cd}$ or Pb, and $T = \text{Si}$ or Ge. Surprisingly, no crystal-structure refinements of any of these numerous compounds have been reported.

The very high R -value (20%) of the single previous structure determination of barysilite (Lajz rowicz, 1965), and incorrectly calculated metal–oxygen distances listed in that paper, suggested that a re-examination of the atomic structure of this mineral species was in order. A recent find of slightly calcian barysilite at Garpenberg Norra, Sweden, provided suitable material for this study. The present article reports and discusses a redetermination of the crystal structure of barysilite, and gives some details about the occurrence and paragenesis of the studied samples. We also performed studies on barysilite samples from both Harstigen and Långban by single-crystal methods, but none of them provided crystal fragments of suitable quality for structure determination.

Occurrence and paragenesis

The Garpenberg Norra mine in Hedemora, Dalarna, Sweden is part of the Garpenberg ore field which, along with the Zinkgruvan Pb–Zn deposit in Askersund,  rebro, are the only deposits currently mined for base metals in the old mining superdistrict of central Sweden known as ‘Bergslagen’. A good review of the metallogeny and volcanology of the Bergslagen district, including the Garpenberg ore field, is given in Allen *et al.* (1996). Garpenberg Norra is a Zn–Pb–(Fe–Mn–Cu–Sb–Ag) deposit associated with a marble unit, hosted by altered Svecofennian

metavolcanic rocks, and which is also intersected by the mines of Garpenbergs Odalf lt 3 km SW of Garpenberg Norra. The sulphide ores, dominated by sphalerite, galena and pyrite, form lenses and veinlets in close association with dolomite marble and silicate skarns (Sandecki, 1983). Over the last 5 years some 20 species new to the deposit, and two new to science (rambergite; Kalinowski, 1996, and rinmanite; Holtstam *et al.*, 2001), have been brought to light. Notable finds include alleghanyite, franklinite, harmotome, native Pb, magnussonite, manganosite, melanotekite, pyroxmangite, pyrargyrite, rom ite, samsonite, willemite, yeatmanite and zincite. To date, ~90 mineral species have been identified from the Garpenberg Norra deposit (Grensman *et al.*, 2001).

Occurrence

The samples originate from a dense skarn rock of unusual composition from the 900 m level of the Garpenberg Norra mine, and were supposedly taken from the contact zone between the ores and the marble wall rock. They are dominated by dark grey tephroite with associated coarse-grained brownish green richterite; barysilite is confined to aggregates several cm wide, in which the proportion of the mineral may reach >50%. The individual, anhedral mineral grains, ~2 mm in maximum dimension, are colourless and nearly transparent, with diamond lustre. The barysilite occurs in intimate association with tephroite, manganian diopside and zincian jacobsite (Fig. 1). Phlogopite and native copper are subordinate components of the assemblage, and native Pb and its alteration products are occasionally seen as superficial coatings.

Conditions of formation of barysilite

At Franklin, New Jersey, barysilite is accompanied by willemite, hardystonite, nasonite (often in intimate association), ganomalite, margarosanite, manganaxinite and andradite (Shannon and Berman, 1926; Ito and Frondel, 1967; Dunn, 1985; Yeates, 1991). At Långban, the mineral was observed in association with barylite, manganian diopside and garnet, but also in fissures and veins within cymrite-kentrolite and richterite-jacobsite skarns (Nysten *et al.*, 1999), while at Harstigen, barysilite occurs associated with calcite and hedyphane in fissures hosted by garnet-tephroite skarns (Sj gren and Lundstr m, 1888). Barysilite

BARYSILITE FROM GARPENBERG NORRA

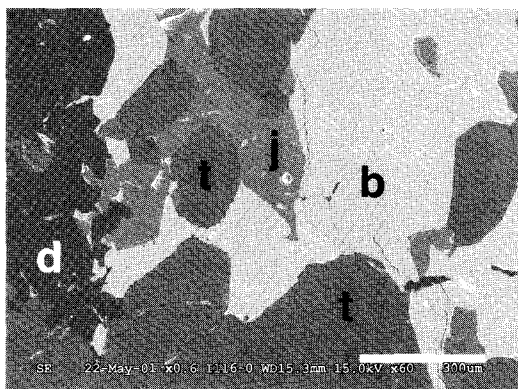


FIG. 1. Scanning electron micrograph of a polished rock section containing barysilite (sample from Garpenberg Norra; Swedish Museum of Natural History catalogue no. 00+156). b = barysilite, t = tephroite, j = (zincian) jacobosite, d = (manganian) diopside. Scale bar is 0.3 mm.

thus occurs in skarns formed at the climax of regional metamorphism, as well as in open late fractures and in slags. The conditions of peak metamorphism in the Garpenberg area have been determined as $T \geq 550^\circ\text{C}$ and $P \leq 3.5$ kbar (Vivallo, 1984). Fluid-inclusion studies of fracture-hosted minerals at Långban suggest formation at low T ($<200^\circ\text{C}$) and P close to atmospheric pressure (Jonsson and Bronman, 1998). A reasonable conclusion from these observations is that the T and P are not critical factors for the formation of barysilite in a geological environment. It is noteworthy that all barysilite-bearing rocks reported are silica-undersaturated and devoid of sulphide minerals.

Experimental

Chemical analysis

The sample studied belongs to the collection of the Swedish Museum of Natural History, Stockholm (catalogue no. 00+156). Quantitative wavelength-dispersive electron microprobe analyses (EMPA) of barysilite were carried out at 20 kV and 15 nA, using a Cameca SX50 instrument. Complete analytical results are given in Table 1; the average of five analyses (wt.%) is PbO 79.10, BaO 0.44, MnO 2.92, CaO 0.44, MgO 0.06, SiO₂ 16.16, Al₂O₃ 0.01, total 99.13. Na, K, Zn, Ti, Fe and Cl were below the limit of detection (≈ 0.05 wt.%). The material was found to be very homogeneous. An empirical formula based on 21 O atoms is $\text{Pb}_{7.88}\text{Ba}_{0.06}\text{Ca}_{0.18}\text{Mn}_{0.92}\text{Si}_{5.98}\text{O}_{21}$, corresponding to a slightly calcian (-barian) barysilite of idealized composition $(\text{Pb,Ca,Ba})_8\text{Mn}(\text{Si}_2\text{O}_7)_3$ (see also discussion below).

Single-crystal X-ray studies

Grain mounts of barysilite were studied using a polarized-light microscope. The grains are uniaxial negative but the studies also suggested that a very small deviation from optical uniaxiality could be present. No twinning was noted. Several optically homogeneous crystal fragments were mounted on a Nonius KappaCCD diffractometer equipped with a 300 μm diameter capillary-optics collimator to provide increased resolution. Preliminary investigations consistently gave unit-cell parameters similar to those reported previously, and sharp diffraction maxima. Intensity data of a suitable crystal fragment

TABLE 1. Chemical analyses (EMP) of barysilite from Garpenberg Norra.

Anal. no.	1	2	3	4	5	mean	σ
PbO	79.33	79.78	78.75	78.37	79.26	79.10	0.49
BaO	0.36	0.42	0.42	0.51	0.47	0.44	0.05
MnO	3.05	2.77	2.84	3.07	2.88	2.92	0.12
CaO	0.38	0.43	0.49	0.51	0.41	0.44	0.05
MgO	0.08	0.03	0.06	0.06	0.05	0.06	0.02
SiO ₂	15.88	16.18	16.26	16.11	16.38	16.16	0.17
Al ₂ O ₃	0.03	0.00	0.01	0.00	0.00	0.01	0.01
Sum	99.11	99.61	98.84	98.63	99.46	99.13	

EMP standards used: vanadinite (Pb- $L\alpha$), baryte (Ba- $L\alpha$), MnTiO₃ (Mn- $K\beta$), wollastonite (Ca- and Si- $K\alpha$), MgO (Mg- $K\alpha$), Al₂O₃ (Al- $K\alpha$)

were collected at room temperature using Mo- $K\alpha$ radiation (see Table 2 for details). The measured data were processed using the Nonius program suite DENZO-SMN and corrected for Lorentz, polarization, background and absorption effects. Systematic extinctions and normalized structure factor statistics indicated the centrosymmetric space group $R\bar{3}c$.

The crystal structure was solved by direct methods (SHELXS-97, Sheldrick, 1997a) and yielded a model close to that of Lajz rowicz (1965). Full-matrix least-squares refinement on F^2 (SHELXL-97, Sheldrick, 1997b) was carried out in space group $R\bar{3}c$. Conversion to anisotropic displacement parameters for the Pb and Mn atoms resulted in a preliminary $R1$ index of $\sim 2.4\%$. At this stage, occupancy refinements indicated that the Pb1, Mn and Si sites were fully occupied but that one or more lighter atoms were present on the Pb2 site (see further discussion below). Based on

the chemical analysis, Ca was assumed to substitute for Pb2. The occupancy was refined accordingly, resulting in a Pb2:Ca ratio of 0.909(3):0.091, in good agreement with the EMPA data. The final $R1$ index was 2.32% for 1025 'observed' reflections with $F_o > 4\sigma(F_o)$ and 35 refined parameters ($wR2 = 5.55\%$). Maximum peaks in the final difference-Fourier maps were 2.27 and $-2.30 \text{ e}/\text{Å}^3$, respectively. Because the optical properties of the sample suggested the possibility of a lower symmetry, the structure was also solved and refined in space group $C2/c$. A higher final $R1$ index, 3.6%, and problems with anisotropic refinement of some of the non-O atoms clearly indicated that the correct space group is $R\bar{3}c$. The final positional and displacement parameters are given in Table 3. Selected bond lengths and angles, and calculated bond-valence sums are listed in Table 4. Lists of observed and calculated structure factors have

TABLE 2. Crystal data, data collection information and refinement details for barysilite from Garpenberg Norra.

Crystal data	
Formula, space group	$\text{Pb}_8\text{Mn}(\text{Si}_2\text{O}_7)_3, R\bar{3}c$
a, c (Å)	9.804(1), 38.416(8)
V (Å ³), Z	3197.8(8), 6
$F(000)$, ρ_{calc} (g cm ⁻³)	5530, 6.812
μ (mm ⁻¹)	62.54
Absorption correction	multi-scan (Otwinowski and Minor, 1997)
Crystal dimensions (mm)	0.06 \times 0.08 \times 0.13
Data collection and refinement	
Diffractometer	Nonius KappaCCD system
λ (Mo- $K\alpha$) (Å), T (K)	0.71073, 293
Detector-crystal dist. (mm)	30
Rotation axis; rot. width (°)	ϕ, ω ; 1.0
Total no. of frames	522
Collection time per frame (s)	300
Collection mode, $2\theta_{\text{max}}$ (°)	sphere, 59.86
h, k, l ranges	$-13 \rightarrow 12, -11 \rightarrow 13, -53 \rightarrow 53$
Total reflections measured	9178
Unique reflections	1036
$R1(F)$, $wR2(F^2)$ *	2.32%, 5.55%
Observed reflections [$F_o > 4\sigma(F_o)$]	1025
Extinction coefficient	0.000145(8)
No. of refined parameters	35
GoF	1.255
$(\Delta/\sigma)_{\text{max}}$	0.0001
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (e/Å ³)	$-2.30, 2.27$

Unit-cell parameters were refined from nearly all recorded reflections

Scattering factors for neutral atoms were employed in the refinement

* $w = 1/[\sigma^2(F_o^2) + (0.0P)^2 + 130P]$; $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$

BARYSILITE FROM GARPENBERG NORRA

TABLE 3. Fractional atomic coordinates and displacement parameters (\AA^2) for barysilite from Garpenberg Norra.

Atom	x	y	z	U_{eq}/U_{iso}
Pb1	0.25627(3)	0.23661(3)	0.039503(6)	0.00562(12)
Pb2*	0.0	0.0	0.162640(10)	0.00605(17)
Mn	0.0	0.0	0.25	0.0027(4)
Si	0.59781(19)	0.60219(19)	0.04882(4)	0.0010(3)
O1	0.6129(6)	0.0	0.25	0.0034(11)
O2	0.6230(6)	0.7148(6)	0.01576(12)	0.0100(9)
O3	0.7069(5)	0.5215(5)	0.04550(11)	0.0040(8)
O4	0.4142(6)	0.4768(6)	0.05626(11)	0.0085(9)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	0.00412(16)	0.00347(16)	0.00719(16)	-0.00086(7)	-0.00097(8)	0.00033(10)
Pb2*	0.00610(19)	0.00610(19)	0.0059(2)	0.0	0.0	0.00305(10)
Mn	0.0020(6)	0.0020(6)	0.0040(9)	0.0	0.0	0.0010(3)

* Refined occupancy: $\text{Pb}_{0.909(3)}\text{Ca}_{0.091}$

been deposited with the Principal Editor of *Mineralogical Magazine* and are available upon request. They are also available in the electronic version of the paper (see www.minersoc.org).

TABLE 4. Selected bond distances (\AA), angles ($^\circ$) and calculated bond valences (v.u.) for the coordination polyhedra in barysilite from Garpenberg Norra.

Pb1–O4	2.170(5)	0.655	Mn–O3 \times 6	2.224(4)	$\frac{0.309}{2.85} \times 6$ v.u.
–O2	2.360(5)	0.445	<Mn–O>	2.22	
–O3	2.479(4)	0.349			
–O2	2.747(5)	0.202	Si–O4	1.618(5)	1.016
–O4	2.778(4)	0.190	–O2	1.619(5)	1.014
–O1	3.092(5)	0.10	–O3	1.622(5)	1.005
<Pb1–O>	[6]: 2.60	1.94 v.u.	–O1	1.666(3)	$\frac{0.893}{3.93}$ v.u.
			<Si–O>	1.63	
Pb2–O3 \times 3	2.540(4)	0.308 \times 3			
–O2 \times 3	2.674(5)	0.234 \times 3	Bond-valence sums for the O atoms are:		
–O4 \times 3	3.098(5)	$\frac{0.099}{1.92} \times 3$	O1,2,3,4 = 1.93, 1.90, 1.97, 1.87 v.u.		
<Pb2–O>	[6+3]: 2.61 + 3.10 [9]: 2.77	1.92 v.u.			
O2–Si–O4	112.9(3)		O3–Mn–O3 \times 3	119.5(2)	
O2–Si–O3	111.0(2)		O3–Mn–O3 \times 6	81.89(17)	
O4–Si–O3	113.4(2)		O3–Mn–O3 \times 3	84.4(2)	
O2–Si–O1	106.2(3)		O3–Mn–O3 \times 2	152.5(2)	
O4–Si–O1	107.34(18)				
O3–Si–O1	105.4(2)				
<O–Si–O>	109.4				

The bond-valence parameters used are from Brese and O'Keefe (1991), and from Krivovichev and Brown (2001) for the Pb–O bonds. The minor substitution of (Ca + Ba) for Pb2 has been ignored in these calculations

Results and discussion

Structure determination

The redetermination of the crystal structure of barysilite, $\text{Pb}_8\text{Mn}(\text{Si}_2\text{O}_7)_3$, confirms the basic atomic arrangement found in the previous low-precision study (Lajz rowicz, 1965; space group $R\bar{3}c$, $R = 20\%$). However, our results ($R1 = 2.32\%$) provide much more precise values for atomic coordinates, bond lengths and angles (see also below). The structure type is identical to that of synthetic $\text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3 (= \text{Pb}_3\text{Si}_2\text{O}_7)$ (Petter *et al.*, 1971; Petter and Harnik, 1971). [Note that the standardized coordinates for O(1) given in the original publication on synthetic $\text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3$ (Petter *et al.*, 1971) and also incorporated in the ICSD database are incorrect; the non-standard coordinates listed by Petter *et al.* (1971) are correct, however.]

Coordination polyhedra and cationic substitutions

The structure contains two non-equivalent Pb, one Mn, one Si and four O sites. The Si is tetrahedrally coordinated by O atoms at distances between 1.618(5) and 1.666(3)  . These distances are very similar to the corresponding ones in synthetic $\text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3$ (1.612 and 1.666  , Petter *et al.*, 1971). The range given in the previous structure determination by Lajz rowicz (1965), 1.56–1.63  , is considerably different (note that these values were recalculated; the originally given values are, as already mentioned, incorrect).

Two SiO_4 tetrahedra share the O1 atom to form isolated Si_2O_7 disilicate groups with a non-linear Si–O–Si axis. As is common for disilicate groups, the longest Si–O bond is that involving the bridging oxygen (O1). The refined Si–O–Si angle, $120.9(4)^\circ$, is considerably different from the value 144° calculated from the atomic coordinates given by Lajz rowicz (1965) (the originally given value, 133° , is incorrect), but close to the angle in synthetic $\text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3$, 125.2° (Petter *et al.*, 1971). As shown by Lajz rowicz (1965), this value is also influenced by cationic substitution for the Pb^{2+} and Mn^{2+} ions (see below). O–Si–O angles range between $105.4(2)$ and $113.4(2)^\circ$, with an average of 109.4° .

Mn^{2+} forms a MnO_6 polyhedron with six equivalent Mn–O bonds of length 2.224(4)  , but with a distorted geometry (range of O–Mn–O angles: $81.89(17)$ to $152.5(2)^\circ$) similar to that of a slightly twisted trigonal

'prism' (Fig. 2). The very minor Mg contents detected by EMPA (0.06 wt.%) suggest a very minor substitution of Mn by Mg; occupancy refinements of the Mn site provided no evidence of any non-negligible Mg substitution. Two adjacent corners of the MnO_6 are shared with the Si_2O_7 group (Fig. 2). In synthetic $\text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3$, the corresponding PbO_6 polyhedron exhibits six equivalent Pb–O bonds of length 2.50   (Petter *et al.*, 1971).

The first of the two non-equivalent Pb sites, Pb1, has a highly irregular, one-sided coordination with six O ligands (Pb–O range: 2.170(5)–3.092(5)  ), evidencing a very strong stereochemical influence of the $6s^2$ lone-electron pair on the Pb^{2+} ion (Fig. 3a). By comparison, the

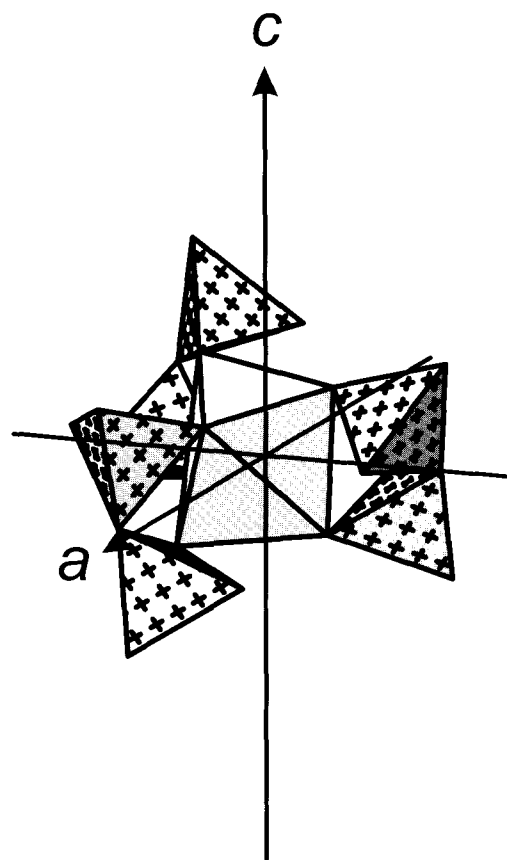


FIG. 2. The crystal structure of barysilite: view of the structural unit built of the distorted MnO_6 polyhedron (Mn at 0,0,0.25) corner-linked to the disilicate group. (Note: the c axis shown is halved). All drawings were done using ATOMS (Shape Software, 1999).

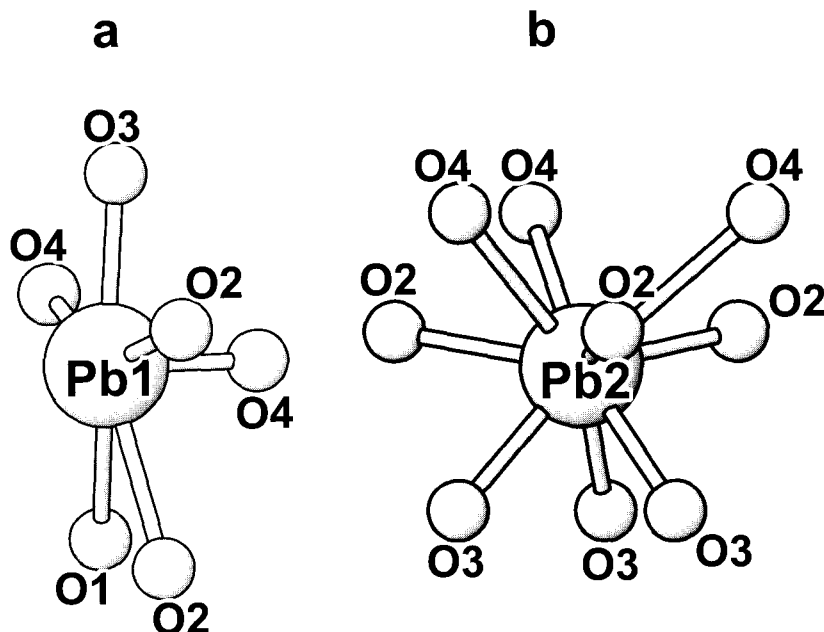


FIG. 3. The very different coordination polyhedra about Pb1 (a) and Pb2 (b) in the structure of barysilite from Garpenberg Norra.

[6+3]-coordinated Pb2 site is fairly regular, with Pb–O distances of 2.540(4) ($3 \times$), 2.674(5) ($3 \times$) and 3.098(5) ($3 \times$) Å (Fig. 3b). The earlier structure determination of Lajzéróvicz (1965) gives an incorrect description of the Pb2 coordination, because the coordinates of the O atoms were of low precision and because the Pb–O bond lengths were wrongly calculated; the reported coordinates of both Pb atoms, however, agree very well with those found in the present study.

The structural formula of barysilite-type compounds is $\text{Pb}_1\text{Pb}_2\text{M}^{2+}(\text{Si}_2\text{O}_7)_3$. Although previous authors concluded that cationic substitution is possible on the M site, but not on either the

Pb1 or Pb2 site, Schmidt *et al.* (1982, 1983) provided some evidence that certain divalent cations can also substitute to a certain degree for Pb2. According to the present refinement model for barysilite, the Pb2 site contains ~10% of Ca replacing Pb (refined occupancy: $\text{Pb}_{0.909(3)}\text{Ca}_{0.091}$). Our EMPA data indicate, however, that both Ca and Ba are probable minor substituents of Pb2. The preference of Ca for the Pb2 site, and not the Mn site, is indicated by a mean Pb2–O distance which is closer to that commonly observed for Ca–O bonds.

Schmidt *et al.* (1983) analysed the behaviour of refined unit-cell parameters of synthetic powder samples with compositions along the three solid-

TABLE 5. Crystal data reported for barysilite, $\text{Pb}_8\text{Mn}(\text{Si}_2\text{O}_7)_3$.

a (Å)	c (Å)	V (Å ³)	Reference
9.804(1)	38.416(8)	3197.8(8)	This work (single-crystal data)
9.806(1)	38.380(7)	3196.1	Schmidt <i>et al.</i> (1983)
9.80(1)	38.35(5)	3190.8	Billhardt (1969); ICDD 23-404
9.821	38.38	3205.9	Ito and Frondel (1967); ICDD 20-714
9.821(5)	38.38(6)	3205.9	Lajzéróvicz (1965); ICDD 71-2178, 74-2289

solution series $\text{Pb}_8\text{Cu}(\text{Si}_2\text{O}_7)_3$ – $\text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3$, $\text{Pb}_8\text{Cd}(\text{Si}_2\text{O}_7)_3$ – $\text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3$ and $(\text{Pb}, \text{Ca})_8\text{Ca}(\text{Si}_2\text{O}_7)_3$ – $\text{Pb}_8\text{Ca}(\text{Si}_2\text{O}_7)_3$ – $\text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3$. They concluded that Cu, Cd and Ca can all completely replace Pb at the *M* site, but that only Ca can partially replace Pb2 atoms. The most Ca-rich barysilite synthesized by Schmidt *et al.* (1983) has the approximate composition $\text{Pb}_{1.6}(\text{Pb}_{2.0,84}\text{Ca}_{1.16})_{\Sigma 2.00}\text{Ca}(\text{Si}_2\text{O}_7)_3$. The present single-crystal study confirms the conclusions of Schmidt *et al.* (1983), and is the first direct proof that not only the *M* site in barysilite-type $\text{Pb}_8\text{M}(\text{Si}_2\text{O}_7)_3$ compounds can be replaced by divalent cations. Any replacement of Pb at the very irregularly-coordinated Pb1 site (with a stereochemically-active lone pair) would appear unlikely. Single-crystal structure refinements of further Ca-, Sr- or Ba-rich barysilites are necessary to determine the exact solubility limits and their dependence on temperature of formation. The detection of a hypothetical natural Ca-rich barysilite with $\text{Ca} > \text{Pb}$ on the Pb2 site would obviously lead to nomenclature complications. As far as these substitutional limits are concerned, it is noteworthy that according to Billhardt (1969) intermediate members of the theoretical solid solution series $\text{Pb}_8\text{Mn}(\text{Si}_2\text{O}_7)_3$ – $\text{Pb}_8\text{Pb}(\text{Si}_2\text{O}_7)_3$ could not be prepared; he was only able to synthesize “two phases of different ‘barysilites’”.

The substitution of Pb by Cd, Ba and Sr in synthetic $\text{Pb}_3\text{Ge}_2\text{O}_7$ (‘lead germanate barysilite’) was investigated by Salnikow *et al.* (1979) using X-ray powder diffraction. They found that up to 25% of the Pb atoms can be substituted by Sr without change in structure. This indicates a Pb:Sr ratio as low as 3:1 by comparison with the ratio of 8:1 in the $\text{Pb}_8\text{Sr}(\text{Ge}_2\text{O}_7)_3$ end-member, and suggests a formula $\text{Pb}_{1.6}(\text{Pb}_{2.0,75}\text{Sr}_{1.25})_{\Sigma 2.00}\text{Sr}(\text{Ge}_2\text{O}_7)_3$. Because the germanate barysilites probably have a more open framework, a higher substitution level than in silicate barysilites appears possible.

The single-crystal unit-cell parameters refined here, $a = 9.804(1)$, $c = 38.416(8)$ Å, $V = 3197.8(8)$ Å³ (hexagonal setting), are fairly similar to those given previously for both natural and synthetic samples (see compilation of available crystal data in Table 5), although the *c* parameter appears slightly large by comparison. The minor Ca, Ba and Mg contents detected by EMPA certainly influence these parameters to some extent.

Calculated bond-valence sums for the atoms in barysilite are given in Table 4. These values were calculated using the parameters of Brese and O’Keeffe (1991) for Si–O and Mn–O bonds, and the revised parameters of Krivovichev and Brown (2001) for Pb^{2+} –O bonds which take into account the well-known high variability of Pb^{2+} environ-

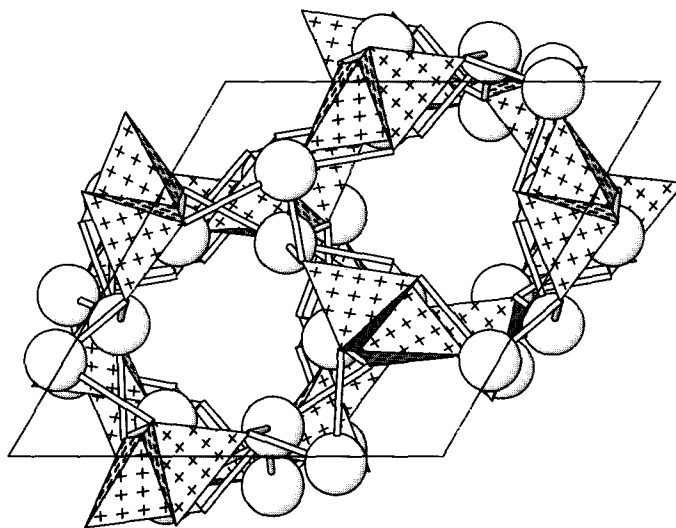


FIG. 4. View of the structure along [001], showing the framework with composition $[\text{Pb}_{1.2}\text{Si}_2\text{O}_7]^2$ and the infinite channels parallel to [001]. These channels are filled with Pb2 and Mn atoms (see text). The unit cell is also outlined.

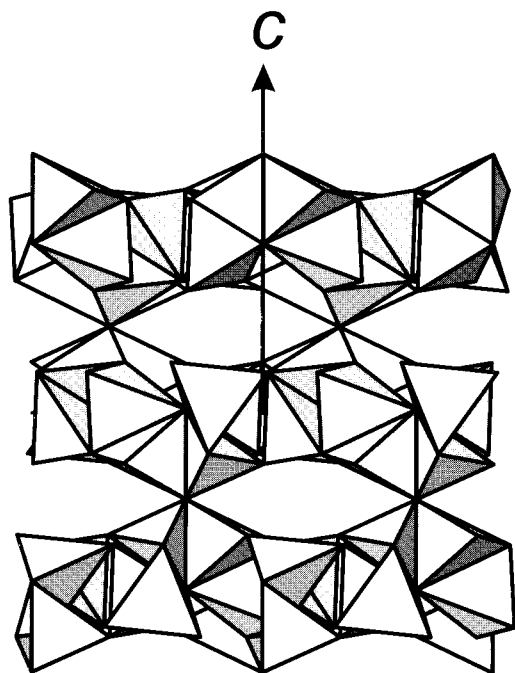


FIG. 5. An alternative description of the barysilite structure showing the connectivity between $O2M_4$ and $O3M_4$ tetrahedra which form an intricate framework hosting flattened voids (view along [010]; the direction of the c axis is indicated; O1 and O4 atoms have been omitted).

ments. The bond-valence sums for Si (3.93 v.u.), Mn (1.85 v.u.), Pb1 (1.94 v.u.) and Pb2 (1.92 v.u.) are in reasonable agreement with ideal values. When the parameters of Brese and O'Keeffe (1991) are used for the $Pb^{2+}-O$ bonds, the calculated sums for Pb1 and Pb2 (2.15 and 1.81 v.u., respectively), show less agreement with expected values. Bond-valence sums for the four O atoms, 1.93, 1.90, 1.97 and 1.87 v.u., are close to the ideal values.

Connectivity

The complicated connectivity of the barysilite structure is characterized by isolated Si_2O_7 disilicate groups which are linked by the irregularly coordinated Pb1 atoms to form a three-dimensional framework with the composition $[Pb_1Si_2O_7]^{2-}$. As shown in Fig. 4, this framework hosts infinite channels parallel to

[001] in which the more regularly coordinated Pb2 atoms, the Mn atoms and vacant positions are located in an alternating sequence ...-Pb2-Mn-Pb2-Vac-Vac-... . The mean channel diameter in barysilite is considerably smaller than in $Pb_8Pb(Si_2O_7)_3$ (cf. also Harnik, 1972).

An instructive alternative description of the atomic arrangement is possible when considering the linkage of more or less regular OM_4 ($M = Pb, Mn, Si$) tetrahedra (cf. Krivovichev *et al.*, 1998, and Krivovichev and Filatov, 1999*a,b*). Both O2 and O3 form such tetrahedra whereas O1 and O4, which are connected to 2 Si and 2 Pb (at $2 \times 3.09 \text{ \AA}$), and 1 Si and 3 Pb (at $2.17-3.08 \text{ \AA}$), respectively, would form very distorted OM_4 'tetrahedra'. Figure 5 shows $O2M_4$ and $O3M_4$ tetrahedra which are connected by both edges and corners to form an intricate, somewhat layered framework hosting flattened voids.

Acknowledgements

Prof. H. Effenberger provided valuable comments on the manuscript. This paper was partly written while the first author (UK) was supported financially by a Research Fellowship of the DFG (German Science Foundation).

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[Manuscript received 2 October 2001;
revised 22 February 2002]