Crystal structure refinement of sahlinite, $Pb_{14}(AsO_4)_2O_9Cl_4$

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ABSTRACT

The crystal structure of sahlinite [$Pb_{14}(AsO_4)_2O_9Cl_4$] from Långban (Sweden) has been refined up to $R = 0.071$ using single-crystal diffraction data collected at the Elettra synchrotron facility. Sahlinite is monoclinic, space group $C2/c$, with $a = 12.704(4)$, $b = 22.576(5)$, $c = 11.287(4)$ Å, $\beta = 118.37(3)°$. Sahlinite is isostructural with kombatite, its vanadium counterpart. Both are derivatives of the litharge form of PbO. In the structure of sahlinite there are seven independent Pb atoms, which are linked to Cl and/or O atoms, with coordination number ranging from V to VIII. The coordination polyhedra are irregularly shaped, due to the $6s^2$ lone-pair effect displayed by Pb^{2+}.

Introduction

SAHLINITE is a rare lead arsenate chloride with formula $Pb_{14}(AsO_4)_2O_9Cl_4$. The first occurrence of the mineral was found at Långban, Värmland, Sweden (Aminoff, 1934). The mineralogy of that famous site, which is the type locality for more than 20 arsenate minerals, including sahlinite, is carefully outlined by Moore (1970) and by Holtstam and Langhof (1999). More recently, sahlinite was also described from Kombat mine, Namibia (Dunn, 1991).

Aminoff (1934) did not carry out a complete X-ray characterization of sahlinite, and did not give either the space group symmetry or the unit-cell parameters. Welin (1968) presented an unindexed X-ray powder pattern for the mineral. More recently the crystallography of sahlinite was re-examined by Rouse and Dunn (1985), who, on the basis of precession and Gandolfi patterns, determined the monoclinic symmetry of the mineral, already suggested by Aminoff (1934), indicated Cc or $C2/c$ as possible space groups, and refined the following unit-cell parameters: $a = 12.710(13)$, $b = 22.498(8)$, $c = 11.360(9)$ Å, $\beta = 118.99(3)°$. A pronounced pseudo-tetragonal sub-cell with dimensions $\sim 4 \times 4 \times 22.5$ Å was observed.

Rouse and Dunn (1985) also provided electron microprobe data, which were in agreement with the original chemical formula.

A mineral closely related to sahlinite from both the chemical and structural point of view is kombatite, $Pb_{14}(VO_4)_2O_9Cl_4$, which was discovered some 50 years later, and was described by Rouse *et al.* (1986) as a new mineral species from the Kombat mine, Tsumeb, Namibia. Kombatite is the vanadium analogue of sahlinite.

Experimental

A small fragment of sahlinite (dimensions $0.2 \times 0.2 \times 0.1$ mm) was first mounted on a conventional Siemens four-circle diffractometer. The search and centering of a set of reflections from a Polaroid photograph for the determination of the orientation matrix led to the pseudo-tetragonal sub-cell already reported by Rouse and Dunn (1985). A structural study of the related mineral kombatite (Cooper and Hawthorne, 1994) confirmed the correctness of the above-mentioned monoclinic cell and the $C2/c$ space group. Therefore the pseudo-tetragonal sub-cell was converted into the monoclinic cell, and a set of intensity measurements was collected.

However, the refinement of the structure failed due to the low ratio between observed reflections [only 249 with $F_{obs} > 4\sigma(F_{obs})$] and structural variables.

TABLE 1. Final atomic positions and displacement parameters for sahlinite.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	0.11429(5)	0.08398(2)	0.18224(5)	0.0211(3)	0.0072(3)	0.0191(3)	−0.0007(1)	0.0136(2)	−0.0005(1)
Pb2	0.36895(5)	0.08654(3)	0.07549(6)	0.0213(3)	0.0108(3)	0.0213(3)	−0.0018(1)	0.0139(2)	−0.0001(1)
Pb3	0.12639(5)	0.42056(2)	0.45084(6)	0.0228(3)	0.0114(3)	0.0193(3)	0.0022(2)	0.0133(2)	0.0021(2)
Pb4	0.37823(5)	0.41754(3)	0.30760(5)	0.0239(3)	0.0121(3)	0.0184(3)	0.0014(1)	0.0142(2)	0.0039(2)
Pb5	0.35314(6)	0.19520(2)	0.29905(6)	0.0253(3)	0.0084(3)	0.0217(3)	−0.0023(2)	0.0157(2)	−0.0033(2)
Pb6	0.12256(5)	0.19867(3)	0.42339(5)	0.0235(3)	0.0098(3)	0.0217(3)	−0.0041(1)	0.0157(2)	−0.0042(1)
Pb7	0.39927(6)	0.30312(2)	0.06056(5)	0.0214(3)	0.0082(3)	0.0194(3)	0.0021(1)	0.0130(2)	0.0006(2)
As	0.1364(1)	0.32136(8)	0.1776(1)	0.0241(7)	0.0151(7)	0.0206(6)	−0.0012(5)	0.0142(5)	0.0011(5)
Cl1	0.3739(3)	0.5000(2)	0.0623(3)	0.028(2)	0.025(2)	0.023(2)	−0.003(1)	0.017(2)	−0.007(1)
Cl2	0.3798(3)	0.0144(3)	0.3088(3)	0.022(2)	0.026(2)	0.025(2)	0.000(1)	0.015(1)	0.002(1)
O1	0.236(1)	0.1435(4)	0.111(1)	0.023(5)	0.008(4)	0.015(4)	0.002(3)	0.010(4)	0.001(3)
O2	0.255(1)	0.1373(5)	0.381(1)	0.033(6)	0.013(5)	0.014(4)	−0.004(3)	0.014(4)	−0.006(4)
O3	0.473(1)	0.3575(5)	0.486(1)	0.021(5)	0.020(5)	0.014(4)	0.000(4)	0.016(4)	0.003(4)
O4	0.013(1)	0.3531(5)	0.047(1)	0.028(5)	0.023(5)	0.033(6)	0.002(5)	0.009(4)	0.002(4)
O5	0.252(1)	0.3396(6)	0.145(1)	0.023(7)	0.029(6)	0.032(5)	−0.004(5)	0.026(5)	−0.005(5)
O6	0	0.1456(6)	1/4	0.023(7)	0.005(5)	0.015(6)	0	0.011(5)	0
O7	1/2	0.1429(7)	1/4	0.020(7)	0.014(7)	0.020(7)	0	0.011(5)	0
O8	1/2	0.3674(6)	1/4	0.028(7)	0.014(6)	0.020(6)	0	0.020(6)	0
O9	0.174(1)	0.3515(6)	0.329(1)	0.046(8)	0.030(6)	0.029(6)	−0.012(5)	0.023(6)	0.002(5)
O10	0.122(1)	0.2490(6)	0.181(1)	0.054(9)	0.010(5)	0.031(6)	−0.002(4)	0.029(6)	−0.004(4)

Therefore the same crystal was mounted on the beamline 5.2 R (X-ray diffraction), at the Elettra synchrotron facility (Basovizza, Trieste, Italy). The wavelength of the radiation was set to ~0.7 Å and calibrated as 0.6992 Å using a powder pattern of standard silicon (a = 5.43095 Å). A 165 mm MarCCD detector was placed at 35 mm from the crystal. In this configuration, the resolution is ~0.7 Å ($2\theta_{max}$ = 60º). A total of 65 frames with $\Delta\varphi$ = 3º were collected.

The frames were processed with the HKL package of programs (XDISP, DENZO and SCALEPACK; Otwinowsky and Minor, 1992). A total of 15535 intensities ($-19 \leqslant h \leqslant 19$, $-34 \leqslant k \leqslant 33$, $-17 \leqslant l \leqslant 17$) was extracted from the 65 frames and corrected for background, Lorentz and polarization factors. Initially, no absorption correction was performed, assuming that the scaling procedure of SCALEPACK could take into account the absorption effects. However, the linear absorption coefficient of sahlinite is very high (85.27 mm^{-1}), and the scaling did not adequately account for the absorption effects. As a consequence, severe oddities in the displacement parameters were observed (most atoms were non-positive definite). To overcome this, the data were not scaled at all (i.e. the instructions "scale restrains 0.00001" and "fix B" were set in SCALEPACK), and were processed with the program MULTISCAN included in the WinGX package (Farrugia, 1999), which performs an absorption correction based upon the Blessing algorithm (Blessing, 1995). The extracted intensities were finally reduced to a set of 4342 independent squared amplitudes, with an internal consistency R_{int} (from merging equivalents) of 0.0857. The following unit-cell parameters were obtained: a = 12.704(4), b = 22.576(5), c = 11.287(4) Å, β = 118.37(3)º. These parameters match well those given by Rouse and Dunn (1985), except for the β angle which is significantly smaller in our case. The reported esd values are those obtained through least-square fits of 2θ values of a set of reflections of the same crystal centred on the Siemens diffractometer, given the limited precision of the values obtainable with DENZO.

The refinement of the structure (SHELXL-93 package; Sheldrick, 1993) was initiated using the atomic coordinates of kombatite (Cooper and Hawthorne, 1994) as a starting set, and was completed with anisotropic displacement parameters for all atoms. The refinement converged to the following indices: R1 (conventional R factor) = 0.0710 for 3785 reflections with $F_{obs} > 4\sigma(F_{obs})$ and 0.0750 for all 4342 reflections, R2 (weighted R on squared F values) = 0.1903, S (goodness of fit) = 0.998. The number of refined parameters was 170, the maximum Δ/σ in the last least squares cycle was 0.002, and the maximum peak and hole in the final difference Fourier synthesis were +9.34 and -8.39 e/Å^3, respectively. The latter values are apparently high, but this result is quite a common feature for Pb halides. All positive maxima are close to Pb atoms, indicating minor inaccuracies in the treatment of absorption effects, and resulting in somewhat elongated

TABLE 2. Selected interatomic distances (Å) and angles (º) for sahlinite.

Pb1–O6	2.384(8)	Pb5–O1	2.257(10)
Pb1–O2	2.420(10)	Pb5–O2	2.277(10)
Pb1–O1	2.453(11)	Pb5–O7	2.482(7)
Pb1–O3[a]	2.470(12)	Pb5–O4[k]	2.781(12)
Pb1–Cl1[b]	3.308(4)	Pb5–O10	2.851(14)
Pb1–Cl2	3.365(4)		
Pb1–Cl1[c]	3.394(3)	Pb6–O6	2.190(7)
Pb1–Cl1[d]	3.410(3)	Pb6–O3[f]	2.311(12)
		Pb6–O2	2.403(11)
Pb2–O7	2.270(8)	Pb6–O10	2.966(11)
Pb2–O1	2.307(11)	Pb6–O10[g]	2.980(13)
Pb2–O5[d]	2.777(13)	Pb6–O9[f]	2.989(14)
Pb2–O4[d]	2.828(14)		
Pb2–Cl2	3.044(4)	Pb7–O1[d]	2.231(10)
Pb2–Cl2[e]	3.255(4)	Pb7–O3[e]	2.279(12)
Pb2–Cl1[d]	3.346(4)	Pb7–O8	2.390(9)
		Pb7–O5	2.603(11)
Pb3–O2[f]	2.206(11)	Pb7–O10[d]	2.856(11)
Pb3–O9	2.341(12)		
Pb3–O4[g]	2.342(13)		
Pb3–Cl2[f]	3.121(4)	As–O10	1.646(13)
Pb3–Cl1[h]	3.306(4)	As–O9	1.681(12)
Pb3–Cl2[i]	3.476(4)	As–O4	1.720(12)
Pb3–Cl2[j]	3.584(4)	As–O5	1.727(11)
		<As–O>	1.694
Pb4–O3	2.241(11)		
Pb4–O8	2.248(7)	O4–As–O5	104.0(6)
Pb4–O5	2.495(12)	O4–As–O9	113.8(7)
Pb4–O9	3.100(15)	O4–As–O10	111.6(6)
Pb4–Cl1	3.315(4)	O5–As–O9	105.0(6)
Pb4–Cl1[e]	3.338(4)	O5–As–O10	110.6(6)
Pb4–Cl1[h]	3.447(3)	O9–As–O10	111.3(6)
Pb4–Cl2[j]	3.626(4)	<O–As–O>	109.4

Symmetry codes for equivalent positions: a: $x-\frac{1}{2}$, $-y+\frac{1}{2}$, $z-\frac{1}{2}$; b: $x-\frac{1}{2}$, $y-\frac{1}{2}$, z; c: $-x+\frac{1}{2}$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$; d: $-x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z$; e: $-x+1$, y, $-z+\frac{1}{2}$; f: $-x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z+1$; g: $-x$, y, $-z+\frac{1}{2}$; h: x, $-y+1$, $z+\frac{1}{2}$; i: $x-\frac{1}{2}$, $y+\frac{1}{2}$, z; j: $-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$; k: $x+\frac{1}{2}$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$

thermal ellipsoids (the greatest r_{max}/r_{min} ratio is 3.6 among Pb atoms, and 5.6 among O atoms).

Description of the structure

Final atom positions and displacement factors for sahlinite are given in Table 1. Selected bond distances and angles are given in Table 2.

The crystal structure of sahlinite is depicted in Fig. 1 as projected down (001). The structure is constructed by alternation along [010] of two distinct structural units: a complex unit with formal composition $[Pb_{14}(AsO_4)_2O_9]^{4+}$ alternates with an almost planar layer formed by chlorine anions only. Bisecting each $[Pb_{14}(AsO_4)_2O_9]^{4+}$ is an *n* glide (at $y = ¼$ and $¾$). As already pointed out by Cooper and Hawthorne (1994) in their study of kombatite, the former unit can be viewed as a derivative of the structure of the litharge (tetragonal) modification of Pb oxide (Leciejewicz, 1961; Adams *et al.*, 1992). The pseudo-tetragonal sub-cell of sahlinite clearly displays its structural relationship with litharge. In fact the tetragonal cell of litharge has $a = b = 3.98$ Å, $c = 5.02$ Å, and the *a* and *c* parameters of sahlinite are related as follows: $\mathbf{a}_s = 3\mathbf{a}_l + \mathbf{b}_l$; $\mathbf{c}_s = 2\mathbf{b}_l - 2\mathbf{a}_l$.

In the structure of sahlinite some Pb and O atoms are replaced by (AsO$_4$) tetrahedra.

The substitution relationship from the litharge to the sahlinite structure is quite interesting. The basic litharge sheet can be described as $\phi - Pb - O_2 - Pb - \phi$ quintuple layer (ϕ = lone pair). The sahlinite layer can then be generated if: (1) some $Pb^{2+}-\phi$ dipoles are replaced by $As^{5+}-O$ in an ordered fashion. This is similar to the replacement of $Pb^{2+}-\phi$ by $Ti^{4+}-O$ in the Ti-doped litharge (Garnier *et al.*, 1990). (2) Since As is tetrahedrally coordinated, it only requires bonds to three O atoms in the central layer of the sheet, not four. Therefore some O atoms are missing, but the number of O vacancies is reduced by clustering the As in pairs (Fig. 2).

The compound layer of the compound sheet in sahlinite that corresponds to a litharge sheet are thus $\phi_8 - Pb_8 - O_{15}\square - Pb_6As_2 - \phi_6O_2$ ($\square$ = vacancy). Two such layers sit back-to-back with As$-$O tetrahedral apices pointing at each other to make up the full module, and are linked by longer Pb$-$O bonds involving O10 atoms.

With respect to kombatite, the atomic parameters have been refined with better esd values and therefore we have a more accurate insight into the geometrical features of sahlinite, mainly as concerns the coordination polyhedra.

There are seven independent Pb atoms in the structure of sahlinite (Fig. 3), which can be roughly divided in two groups. Pb1 to Pb4 are
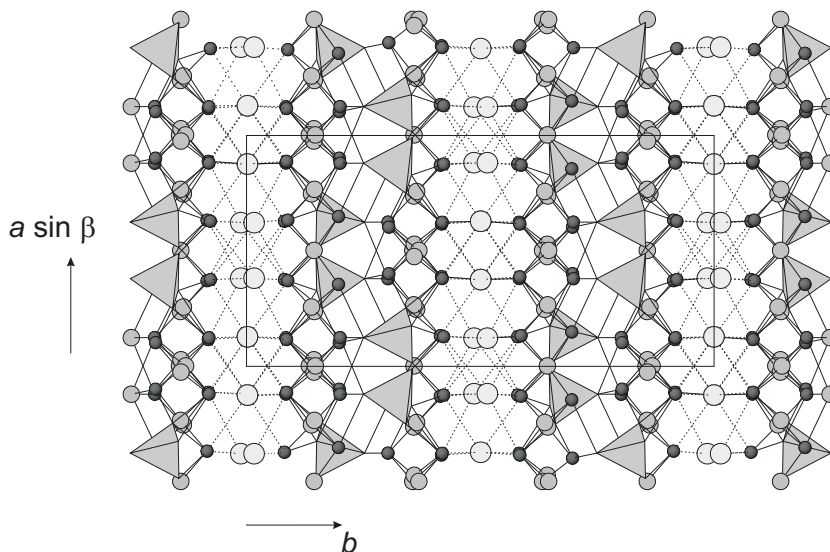

FIG. 1. The crystal structure of sahlinite, as seen along [001]. The unit cell is outlined. The chlorine layers (light grey circles) at $y = 0$ and $y = ½$ alternate with structural slabs of composition $[Pb_{14}(AsO_4)_2O_9]^{4+}$. In the latter, besides (AsO$_4$) tetrahedra, black and mid-grey circles indicate Pb and O, respectively. Pb$-$O and Pb$-$Cl bonds are denoted with single and dotted lines, respectively.
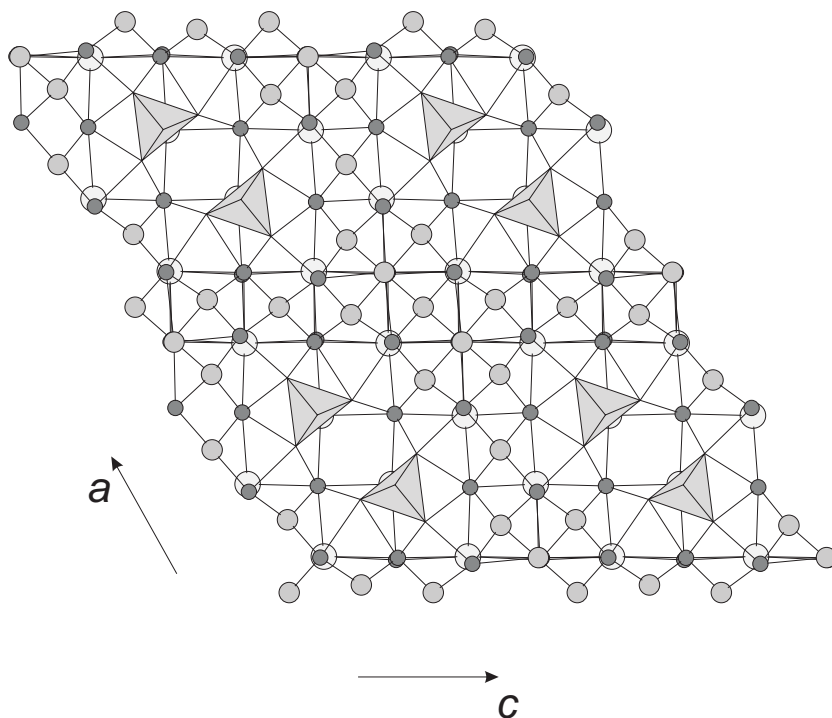
FIG. 2. The crystal structure of sahlinite, as seen along [010]. Same shadings as in Fig. 1. The pseudo-tetragonal arrangement of Pb and O – as in the litharge structure – is evident, as well as the substitution of some Pb and O atoms by pairs of (AsO$_4$) tetrahedra.

linked to both O and Cl atoms, with a coordination number ranging from VII to VIII. The O and Cl atoms lie approximately in two planes on the opposite sides of the cation, respectively; the ratio between O and Cl atoms is 4/4 (for Pb1 and Pb4), 4/3 (for Pb2) and 3/4 (for Pb3). The polyhedra can be considered as square antiprisms or diminished square antiprisms, depending on the total number of anions. Pb5 to Pb7 are linked to O only, with coordination

number ranging from V to VI. The anions define open, irregular-shaped polyhedra.

Pb–anion distances are spread over a wide range. On average, Pb−O distances (<Pb−O> = 2.507 Å) are shorter than the theoretical value (2.61 Å) obtained with the effective ionic radii given by Shannon (1976), whereas the Cl−O distances are markedly longer than expected (<Pb−Cl> = 3.336 Å against a theoretical value of 3.04 Å). This fact and the geometry of the
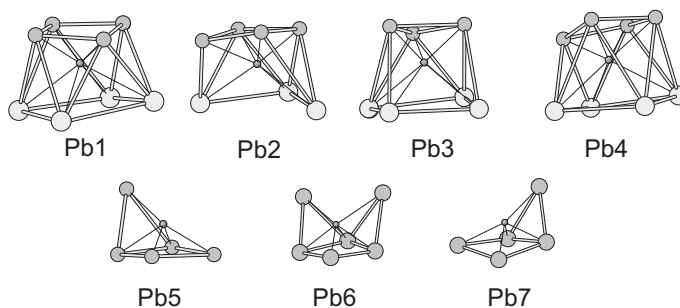

FIG. 3. The seven independent Pb-centred polyhedra in the structure of sahlinite. Atom shadings as in Fig. 1.

TABLE 3. Bond valence balance (v.u.) for sahlinite. Parameters were taken from Brese and O'Keeffe (1991) or (for $Pb^{2+}-O$ interaction only) from Krivovichev and Brown (2001).

	Pb1	Pb2	Pb3	Pb4	Pb5	Pb6	Pb7	As	$\Sigma_a v$
O1	0.368	0.496			0.549		0.579		1.992
O2	0.394		0.609		0.527	0.407			1.937
O3	0.356			0.567		0.492	0.525		1.940
O4		0.173	0.461		0.188			1.135	1.957
O5		0.190		0.338			0.271	1.114	1.913
O6	0.424*					0.629*			2.106
O7		0.534*			0.347*				1.762
O8				0.559*			0.418*		1.954
O9			0.462	0.098		0.123		1.262	1.945
O10					0.163	0.129 0.126	0.162	1.387	1.967
	0.128			0.120					
Cl1	0.097	0.110	0.123	0.113					0.868
	0.093			0.084					
			0.202						
Cl2	0.105	0.249	0.078	0.052					0.885
		0.141	0.058						
$\Sigma_c v$	1.965	1.893	1.993	1.931	1.774	1.906	1.955	4.898	

* Two equivalent bonds for the given anion

polyhedra indicate the presence of a stereoactive lone-pair of $6s^2$ electrons in Pb^{2+} cations. Indeed, as can be seen from Table 2, some Pb–Cl distances are definitely long (up to 3.626 Å for $Pb4-Cl2^j$), but we preferred to consider those anions, too, as belonging to the coordination polyhedra since they were in expected positions to complete the bases of Pb-centred square antiprisms.

Also, the (AsO_4) tetrahedron is slightly distorted, the As–O distances ranging from 1.646 to 1.727 Å, but this is a common feature for (AsO_4) tetrahedra.

A bond-valence analysis of sahlinite is presented in Table 3. Calculations made using the parameters given by Brese and O'Keeffe (1991) resulted in marked deviations from ideal values, with bond valence sums on average higher for O (up to 2.578 v.u. for O6) and lower for Cl. This reflects the lone-pair effect upon coordinations by Pb, but could also depend on the inaccuracy of the bond-valence parameter for the $Pb^{2+}-O$ interaction given by Brese and O'Keeffe (1991), as suggested by Krivovichev and Brown (2001) in the case of O^{2-} encapsulated in a tetrahedral $[OPb_4]$ cluster. In the case of sahlinite, six O atoms are surrounded by 4 Pb, three by 3 Pb + 1 As, and one by 4 Pb + 1 As.

Therefore the new parameters r_0 and b given by Krivovichev and Brown (2001) were adopted for $Pb^{2+}-O$ interactions, resulting in a much better balance.

Besides sahlinite (and kombatite), another lead oxychloride mineral which can be viewed as a structural derivative of PbO is thorikosite, $Pb_3(Sb,As)O_3(OH)Cl_2$ (Dunn and Rouse, 1985). Apart from that, no evident structural relationships exist between sahlinite and other minerals. The closest chemical similarities are with gebhardite, $Pb_8(As_2O_5)_2OCl_6$ (Medenbach et al., 1983) and georgiadesite, $Pb_4(AsO_3)Cl_4(OH)$ (Pasero and Vacchiano, 2000). In both these minerals, however, arsenic occurs as As^{3+}.

Acknowledgements

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