Pb-Si ordering in sheet-oxychloride minerals: the super-structure of asisite, nominally $Pb_7SiO_8Cl_2$

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ABSTRACT

The original structure determination of asisite, nominally $Pb_7SiO_8Cl_2$, has been re-evaluated in the light of electron-diffraction data (TEM) on the original sample material. Electron diffraction patterns indicate a super-structure based upon a metrically tetragonal 26-cation-site super-sheet motif ($14 \times 14 \times 23$ Å). Given the strong ordering of elements substituting for Pb in closely-related litharge-based oxychlorides (parkinsonite, symesite, kombatite, schwartzembergite), the asisite super-structure is inferred to be due to strong ordering of Si within the PbO sheet. The original chemical analyses of asisite given by Rouse *et al.* (1988) are shown to be consistent with such a super-structure, which has a 12Pb:1Si cation ratio. A new formula for asisite is proposed that is based upon this super-structure: $Pb_{12}(SiO_4)O_8Cl_4$ ($Z = 8$). The structure of asisite determined by Rouse *et al.* (1988) is that of the average Pb/Si-disordered tetragonal sub-cell (*I4/mmm*: $4 \times 4 \times 23$ Å) and belies the highly ordered real state. The structure of the tetragonal sub-cell has been re-determined here: $R = 5.6\%$ for 178 unique $F_o > 4\sigma F_o$ and an anisotropic model. A significantly reduced 72% occupancy of the Pb(2) site was found that implies the nominal formula $Pb_7SiO_8Cl_2$, thus confirming the findings of Rouse *et al.* (1988). Comparisons with kombatite and symesite support the assignment of Si to Pb(2) and imply that Si in asisite is also likely to be in tetrahedral coordination, with the apical oxygen cross-linking PbO sheets. However, because most of the key information relating to the location of Si is provided by the super-lattice reflections, the inability of X-ray diffraction to register these reflections introduces a significant ambiguity into the interpretation of Pb/Si ordering behaviour in this mineral.

KEYWORDS: asisite, lead oxychloride, electron diffraction, X-ray diffraction, cation ordering, super-structure.

Introduction

THE sheet-oxychloride minerals of the nadorite group have structures that are derivatives of litharge and massicot, the tetragonal and orthorhombic polymorphs of PbO, respectively. Sheets of PbO structure alternate with sheets of Cl atoms which serve to charge-balance the structure when cations substitute for Pb^{2+}. The PbO structure is remarkable in the diversity of substituent cations that it can accommodate. So far, the observed substituent cations have valences of 3+ (As, I, Sb, Bi), 4+ (Si), 5+ (As, Sb, V) and 6+ (Mo, S, W). In some cases (parkinsonite and schwartzembergite), X-ray structure determinations have seen only the tetragonal/pseudo-tetragonal sub-structure. Electron-diffraction (TEM) reveals that these minerals have well developed super-structures arising from cation ordering within the PbO sheets (Pb^{2+}/Mo^{6+} in parkinsonite and Pb^{2+}/I^{3+} in schwartzembergite). In other cases (e.g. kombatite, symesite) the super-structure is clearly visible by single-crystal X-ray diffraction (XRD). In those cases where there is a cryptic super-structure, the minerals have well defined and reproducible stoichiometries that do not conform to the X-ray sub-cell which is based upon eight cations. In such cases the sub-cell represents an average structure and implies a disordered cation distribution. Hence, XRD can seriously misrepresent the cation-ordering behaviour of these minerals.

Here, a re-evaluation of the ordering of Pb and Si in asisite, nominally $Pb_7SiO_8Cl_2$ (Rouse *et al.*, 1988), is presented that is based upon electron-diffraction patterns collected on the type material upon which the original X-ray structure determination was made by Rouse *et al.* (1988). The tetragonal sub-cell of asisite (*I4/mmm*, $a = 3.897$, $c = 22.81$ Å) is shown in Fig. 1 and consists of alternating sheets of [Pb,Si],O and Cl atoms and empty anion layers as in parkinsonite, nominally $Pb_7MoO_9Cl_2$ (Symes *et al.*, 1994). Rouse *et al.* (1988) did not locate the Si atoms, but recognized a reduced 75% occupancy of Pb(2) that they attributed to Si, thus acknowledging that Si is an essential component of the asisite structure and leading to a probable formula $Pb_7SiO_8Cl_2$ based upon their XRD study. The difficulty of directly locating Si in asisite arises from it being a much weaker X-ray scatterer than Pb and it is also present in small amounts in asisite. Rouse *et al.* (1988) report that Pb contributes ~80% of the X-ray scattering from asisite. However, in principle, the substitution of Si for Pb can be inferred from reduced Pb site occupancies. Two distinct sets of electron-microprobe analyses of different grains of asisite in the same probe mount were given by Rouse *et al.* (1988) that lead to the formulae (normalized to 7 Pb): $Pb_7Si_{0.77}O_{7.62}Cl_{1.80}$ and $Pb_7Si_{0.55}O_{7.07}Cl_{2.07}$. Are these minor Si variations incidental or might they correspond to distinct super-structures arising from Pb-Si ordering? This question is addressed in this paper.

Experimental procedures

Transmission electron microscopy

Hand-picked crystals of greenish-yellow asisite were taken from an aliquot of the type specimen GSC #64565. This specimen was kindly provided by Richard Herd of the Canadian Geological Survey (Ottawa). The crystals were crushed gently by hand with an agate pestle and mortar under high-purity ethanol. A suspension in ethanol was prepared and crystals were deposited by pipette onto a holey-carbon copper grid (Agar Products). Observations were made using a JEOL CX200 transmission electron microscope fitted with a LaB_6 filament and operated at 200 kV. A 120 μm condenser aperture and a 40 μm selected-area aperture were used. These conditions optimized brightness while minimizing beam damage to the sample (melting). Exposure times of 32–90 s were used. Although much weaker than the sub-lattice reflections, the super-lattice
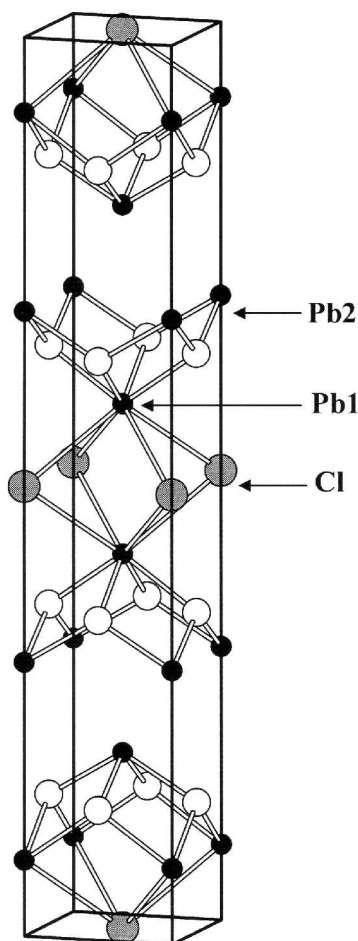

FIG. 1. The *I4/mmm* sub-cell of asisite, $a = 3.893$ Å and $c = 22.803$ Å. This type of sub-cell is shared with parkinsonite. Structure refinement indicates that ~75% of the Pb(2) sites are occupied. Pb(1) forms a $Pb[O_4Cl_4]$ square antiprism; Pb(2) forms a PbO_4 array and is not bonded to Cl.

reflections are visible in 32 s exposures. This exposure time is much shorter than was used for parkinsonite and schwartzembergite (Welch *et al.*, 1996, 2001), where exposures of 1–2 min were needed to register superlattice reflections.

X-ray diffraction

In order to reduce the effects of absorption on diffracted intensities, a small {001} crystal plate of asisite showing uniform extinction and good optical quality was mounted in Crystalbond® and

polished down to a thickness of 45 μm, giving final dimensions of $110 \times 90 \times 45$ μm. An initial study of this crystal by precession photography was performed in order to search for weak superlattice reflections observed by electron diffraction. Exposure times of more than two days were required to register the very weak super-lattice reflections in $hk0$ diffraction patterns.

The crystal was then mounted on an Enraf-Nonius CAD4 diffractometer operated at 55 kV, 32 mA with graphite-monochromated Mo-$K\alpha$ radiation. Unit-cell parameters and the orientation matrix were obtained from the setting angles of 25 centred reflections of the $I4/mmm$ sub-cell based upon four-position centering ($\pm\theta, \pm\chi$) in the range $10-32°2\theta$: $a = 3.8932(6)$ Å, $c = 22.803(4)$ Å, $V = 345.63(10)$ Å^3. These values are very close to those determined by Rouse $et\ al.$ (1988): $a = 3.897(2)$ Å, $c = 22.81(2)$ Å, $V = 346.3(3)$ Å^3. After obtaining the sub-cell dimensions, an attempt was made to search for weak super-lattice reflections using a transformed cell based upon the super-cell observed by electron diffraction. However, no diffracted intensities at the expected positions of super-lattice reflections were registered in scans of 6 min duration. This observation is in keeping with the long exposure times required to observe these very weak reflections by precession photography. Reflections in a hemisphere of reciprocal space were collected from $-5 \leqslant h \leqslant 5, 0 \leqslant k \leqslant 5,$ $-32 \leqslant l \leqslant 32$, giving a total of 1149 intensities covering $10-60°2\theta$ Reflections were scanned in $\omega-2\theta$ mode. Three standard reflections were monitored every 100 reflections. Raw peak intensities were corrected for Lp and background effects. An absorption correction was applied based upon ψ scans (North $et\ al.$, 1968) on nine reflections covering a wide 2θ range using a ϕ rotation interval about the diffraction vector of 10°, which resulted in $R_{azimuthal} = 6.1\%$. Symmetry-equivalent reflections were averaged ($R_{merge} = 10.8\%$) and then reduced to structure factors. The structure was solved and refined using the SHELX97 suite of programs (Sheldrick, 1997) within the WinGX package (Farrugia, 1999). Neutral scattering factors were used. An attempt was also made to observe the super-lattice reflections using a CCD area detector (M.A. Cooper, pers. comm.), but even here they were not registered.

Results and discussion

Electron diffraction

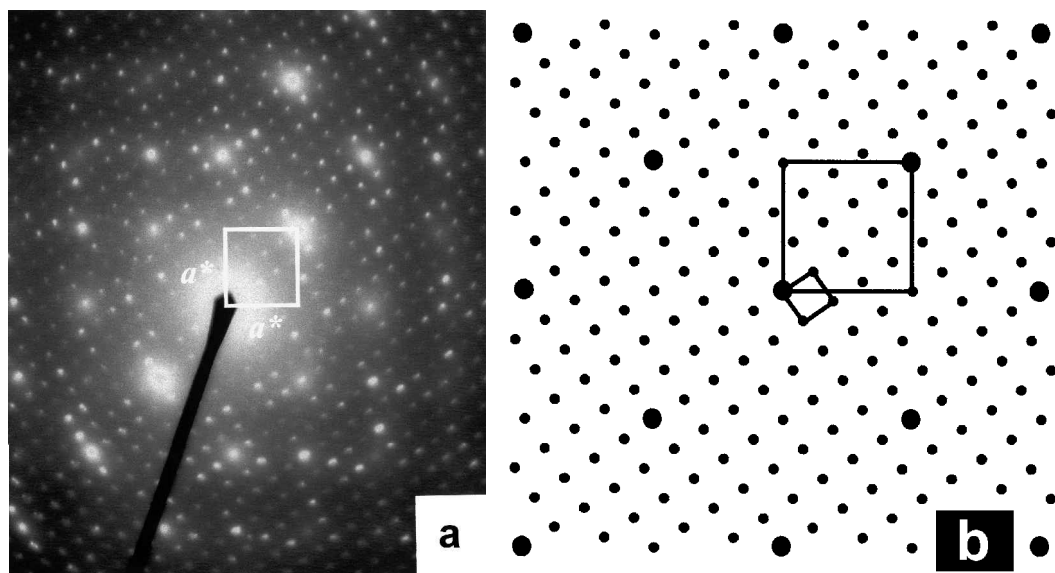A typical $hk0$ electron diffraction pattern of asisite is shown in Fig. 2a with an ideal schematic

FIG. 2. (a) A typical $hk0$ electron diffraction pattern of asisite with the reciprocal sub-cell shown. (b) A schematic of the geometrical relationship between the reciprocal sub- and super-cells of asisite superimposed upon the $hk0$ electron diffraction pattern.

version in Fig. 2*b*. Strong sub-lattice reflections are evident which arise from the *I4/mmm* sub-cell. In addition, there are many much weaker super-lattice reflections in a square array. From the orientation and dimensions of the reciprocal sub-lattice it is possible to deduce the metric topology of the super-structure (super-sheet) motif as shown in Fig. 3. This motif is based upon twenty-six cation sites. How does such a super-lattice compare with the chemical analyses of asisite given above? Interestingly, one of the formulae given by Rouse *et al.* (1988: Table 2, grains 1−3), $Pb_7Si_{0.55}O_{7.07}Cl_{2.07}$, recalculates (Pb = 12) to $Pb_{12}Si_{0.94}O_{12.12}Cl_{3.55}$, which is close to a 12Pb:1Si ratio. Clearly, this formula is consistent with the observed 26-site super-structure, i.e. the super-structure has a $Pb_{12}Si$ cation stoichiometry. Note that a 13-cation-site motif is not possible for the PbO sheet topology.

On the basis of the super-structure inferred from the electron-diffraction patterns and the chemical analyses of asisite (Rouse *et al.*, 1988), a revised ideal formula is proposed that reflects the fact that Pb and Si are very likely to be highly

ordered: $Pb_{12}SiO_{12}Cl_4$. The other chemical formula of asisite reported by Rouse *et al.* (1988), $Pb_7Si_{0.77}O_{7.62}Cl_{1.80}$, recalculates (Pb = 9) to $Pb_9Si_{0.99}O_{9.80}Cl_{2.31}$, suggesting that a second super-structure with an ideal formula of $Pb_9SiO_{10}Cl_2$ may also exist. A 9:1 cation stoichiometry defines the super-structure of synthetic $Pb_9MoO_{11}Cl_2$, which has a parkinso-nite-like structure (Welch *et al.*, 1996).

X-ray crystal structure determination

In the absence of observable super-lattice reflections (see above), it was only possible to determine the structure of the asisite sub-cell by XRD. The Pb and Cl atoms were located by direct methods and the oxygen atom appeared in the first difference-Fourier synthesis. At this point it was noticed that Pb(2) had a U_{iso} twice that of Pb(1) (0.016 and 0.033 $Å^2$), suggesting the possibility of partial occupancy of the Pb(2) site, or mixed-occupancy involving a light element, in this case probably Si. The scattering from asisite is dominated by Pb, with minor contributions from
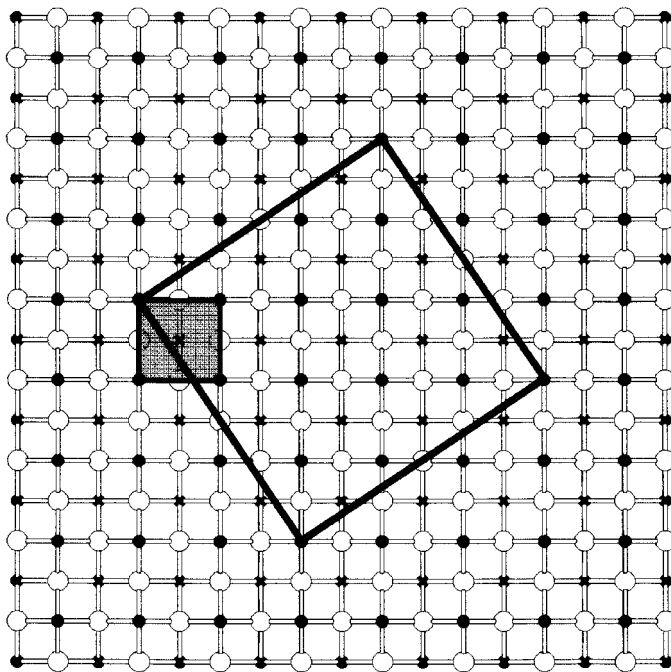

FIG. 3. A schematic of the relationship between super-cell and sub-cell (shaded) superimposed upon a PbO sheet. Solid circles are Pb sites that lie above and below the sheet of oxygen atoms (open circles). Asisite has a 26-cation-site motif [13 Pb(1) + 13 Pb(2)] within the sheet and there are two Si atoms (not shown explicitly) per super-sheet. The super-sheet repeat is 14.06 Å.

Cl and O. Only the sub-lattice reflections were measurable by XRD, and the contribution of Si to these reflections is likely to be very minor compared with Pb. The key information that might allow Si to be located directly is contained in the super-lattice reflections, which were not registered. However, some estimate of the Si occupancy of Pb(2) can be gained by refining the site occupancy. In order to reduce correlations between occupancy and U_{iso}, a partially-constrained iterative model was adopted in which the Pb(2) occupancy was refined while refining U_{iso} for Pb(1) and Pb(2) as equal. The refined Pb(2) occupancy was 72(1)% and the U_{iso} value for Pb(1,2) was 0.018(2) $\mathring{A}^2$. The occupancy of Pb(2) was then fixed at 72% and the U_{iso} parameters of Pb(1) and Pb(2) uncoupled and refined isotropically in the next four refinement cycles to give values of 0.017(1) and 0.018(1) $\mathring{A}^2$, respectively, thus removing the big discrepancy between the initial Pb U_{iso} values and stabilizing at a more reasonable value for the U_{iso} of Pb(2). This occupancy refinement strategy is similar to that used by Armbruster and Gnos (2000) in their study of the hydrogarnet substitution in vesuvianite. All atoms were then refined anisotropically and finally a reflection weighting scheme and an overall extinction coefficient were refined that led to final values of R_1 = 5.6% and wR_2 = 13.3%. Fourteen parameters were refined by least-squares. The Δ/σ of the last refinement cycle was 0.001 and the final maximum and minimum residual electron densities were +8.6 and -2.9 e/$\mathring{A}^3$, located close to the Pb atoms, and could not be meaningfully assigned. Information

relating to the structure determination is summarized in Table 1; atom parameters are listed in Table 2 along with those given by Rouse *et al.* (1988). A table of structure factors is deposited with the Principal Editor, and is available from the Mineralogical Society website at www.minersoc.org/pages/e_journals/dep_mat.htm

It was possible to achieve lower R factors (e.g. R_1 = 4.4% and wR_2 = 10.8%) by freely, but illegitimately, refining Pb(2) occupancy and displacement parameters simultaneously, but this led to predictably high correlations, marked and persistent differences between Pb(1) and Pb(2) displacement parameters (e.g. U_{iso} values of 0.017 and 0.027 $\mathring{A}^2$, respectively), and also a relatively large and unrealistic Cl displacement along z (e.g. U_{33} = 0.091 $\mathring{A}^2$).

The data in Table 2 show that the sub-structure determined here is almost identical to that of Rouse *et al.* (1988). Atom coordinates of the two studies are the same within the small standard errors, and Pb displacement parameters in the two studies are very similar. Bond lengths obtained here are: Pb(1)–O = 2.37(2) $\mathring{A}$, Pb(1)–Cl = 3.351(1) $\mathring{A}$ and Pb(2)–O = 2.28(2) $\mathring{A}$. These values are identical within error to those obtained by Rouse *et al.* (1988). The relatively large U_{eq} and U_{ij} values of the oxygen atom probably reflect the spread of oxygen positions in the super-structure rather than any dynamic positional disorder.

As indicated above, it proved possible to refine site occupancies successfully and to show that there is a significantly reduced occupancy of the Pb(2) site (72±1%), whereas Pb(1) is full. The

TABLE 1. Miscellaneous information relating to the structure determination of asisite.

Space group	*I4/mmm*	Crystal size (mm)	Plate $0.11 \times 0.09 \times 0.045$
a ($\mathring{A}$)	3.8932(6)	radiation/monochromator	Mo-$K\alpha$/graphite
c ($\mathring{A}$)	22.803(4)	Total no. of intensities	1149
V ($\mathring{A}^3$)	345.63(10)	No. of unique intensities	191
		No. of "observed" F_o ($F_o > 4\sigma(F_o)$)	178
Model unit-cell content: $Pb_7O_8Cl_2$		μ_{calc} (mm^{-1})	85.3
		Absorption correction	psi scans
D_{calc} (g/cm^3) = 7.92		R_{merge} (%)	10.8
		R_1 (%) for $F_o > 4\sigma(F_o)$	5.6
$R_1 = \Sigma(\|F_o\|-\|F_c\|)/\Sigma\|F_o\|$		R_1 (%) for all unique F_o	5.8
$wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$		wR_2(%) "observed" data	13.0
$w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$*		wR_2 (%) all	13.3
		GooF	1.24
Ext. coeff.	0.0006	$\Delta\rho_{max}, \Delta\rho_{min}$ (e/$\mathring{A}^3$)	+8.6, -2.9

* *a* and *b* refined

TABLE 2. Atom coordinates and thermal parameters ($\mathring{A}^2 \times 10^3$) for asisite (*I4/mmm*). The upper entries are from this study and the lower entries are from Rouse *et al.* (1988).

	x	*y*	*z*	s.o.f.	U_{11}	U_{22}	U_{33}	U_{eq}
Pb(1)	0	0	0.0838(1)	0.125	22(1)	22(1)	7(1)	17(1)
			0.0838(2)	0.125	20(1)	20(1)	7(1)	16
Pb(2)	0	0	0.3049(1)	0.090(1)	31(1)	31(1)	14(1)	18(1)
			0.3047(2)	0.094	20(1)	20(1)	10(2)	17
Cl	0	0	½	0.0625	34(6)	34(6)	60(16)	43(5)
				0.0625	60(18)	60(18)	30(22)	50
O	0	½	0.143(2)	0.25	62(22)	58(21)	56(24)	59(10)
			0.144(3)	0.25	–	–	–	74(17)

refined Pb(2) occupancy implies a model formula $Pb_7\square_1O_8Cl_2$, ($\square$ = Pb[2] 'vacancy'), which is also the model formula proposed by Rouse *et al.* (1988) who found 75% occupancy of Pb(2). Speculation that the vacancy may be due to the missing Si led to the nominal formula for asisite $Pb_7SiO_8Cl_2$. Comparisons with kombatite (Cooper and Hawthorne, 1994) and symesite (Welch *et al.*, 2000) also imply that Si substitutes at Pb(2), as this site offers the possibility of forming additional $Si-O$ bonds across the vacant (Cl-free) interlayer, providing cross-sheet connectivity.

While the full super-structure of asisite proposed here may elude determination by XRD, the electron-diffraction data presented here, taken with a re-evaluation of the chemical analyses of asisite, clearly indicate that a well-defined super-structure exists and that it is due to a high degree of ordering of Si within the PbO sheets. X-ray structure determinations based upon just sub-lattice reflections appear to seriously misrepresent the role of Si in this mineral and its chemical formula. However, these studies have provided important information regarding the preferential ordering of Si in the sheet of Pb(2)-type sites. Note that ordering of Si in one of the two different Pb layers (Pb1 and Pb2) of the PbO sheet is consistent with a 26- (not 13-) cation-site super-sheet.

Comparison with kombatite and symesite

The sheet-oxychloride minerals kombatite, $Pb_{14}(VO_4)_2O_9Cl_4$ (Cooper and Hawthorne,

TABLE 3. Compilation of subsituted Pb-sheet-oxychloride minerals.

Pb:*X*	Mineral	*X*	Given ideal formula	Reference
1	nadorite	Sb^{3+}	$PbSbO_2Cl$	1
	perite	Bi^{3+}	$PbBiO_2Cl$	2
3	thorikosite	Sb^{3+}, As^{3+}	$Pb_3(Sb_{0.6}As_{0.4})O_{3.5}(OH)Cl_2$	3
	pinalite	W^{6+}	$Pb_3WO_5Cl_2$	4
5	schwartzembergite	I^{3+}	$Pb_5IO_6H_2Cl_3$	5
7	kombatite	V^{5+}	$Pb_{14}(VO_4)_2O_9Cl_4$	6
	sahlinite	As^{5+}	$Pb_{14}(AsO_4)_2O_9Cl_4$	7
	asisite	Si	$Pb_7SiO_8Cl_2$	8
	parkinsonite	Mo^{6+}	$Pb_7MoO_9Cl_2$	9,10
9	parkinsonite	Mo^{6+}	$Pb_9MoO_{11}Cl_2$	10
10	symesite	S^{6+}	$Pb_{10}(SO_4)O_7Cl_4.H_2O$	11
12	asisite	Si	$Pb_{12}(SiO_4)O_8Cl_4$	this study

1. Guiseppetti and Tadini (1973); 2. Ketterer and Krämer (1985); 3. Rouse and Dunn (1985); 4. Grice and Dunn (2000); 5. Welch *et al.* (2001); 6. Cooper and Hawthorne (1994); 7. Bonaccorsi and Pasero (2003); 8. Rouse *et al.* (1988); 9. Symes *et al.* (1994); 10. Welch *et al.* (1996); 11. Welch *et al.* (2000)

1994), and symesite, $Pb_{10}(SO_4)O_7Cl_4.H_2O$ (Welch *et al*, 2000), have their substituent cations (V^{5+} and S^{6+}, respectively) in tetrahedral coordination. These minerals have 16- and 22-site super-sheet motifs, respectively. Given the low-pressure coordination chemistry of Si, it also is very likely to be in tetrahedral coordination in asisite. The full structural formula of asisite, recognizing that Si is in tetrahedral coordination, is then $Pb_{12}(SiO_4)O_8Cl_4$. Table 3 is a compilation of all known substituted Pb-sheet-oxychloride minerals, most of which have an odd Pb:X ratio (1, 3, 5, 7, 9). Asisite is the second member, after symesite, to have an even ratio. Almost nothing is understood about the crystal-chemical controls determining which super-structure forms for which substituent.

The bonding configurations of SO_4 and VO_4 tetrahedra in symesite and kombatite, respectively, are shown schematically in Fig. 4. In symesite, the apical oxygen of the SO_4 group accepts two hydrogen bonds from different interlayer H_2O groups to give a nearly ideal bond-valence sum of 1.9 v.u. (valence units) for the apical oxygen. In kombatite, the apical oxygen of the VO_4 group is bonded to four Pb^{2+} cations of the overlying PbO sheet, giving an ideal bond-valence sum for this oxygen of 2.00 v.u. (Cooper and Hawthorne, 1994). It is proposed that the SiO_4 group in asisite (Fig. 4) has a bonding arrangement analogous to that of kombatite. A deficiency of 1 v.u. at the apical oxygen must be made good by four Pb–O bonds from the overlying PbO sheet, averaging 0.25 v.u. per bond, with a corresponding average Pb–O(apical) bond length of ~2.6 Å (Brown and Altermatt, 1985). The additional Pb–O bond implies some relaxation of the four other Pb–O bonds in the overlying PbO sheet to give bond valences of 0.35–0.4 v.u. The structure of kombatite suggests that such an arrangement is realistic.

The occurrence of the two different super-structures in the same probe mount of asisite can be explained in terms of their precipitation from a Pb-loaded saline fluid having a Pb:Si ratio between 12:1 and 9:1. As pointed out by Welch *et al.* (1996), the Pb-sheet-oxychloride minerals do not appear to form solid solutions, but instead they have distinct compositions defined by super-structures that arise from strong ordering of Pb^{2+} and the substituent cation.

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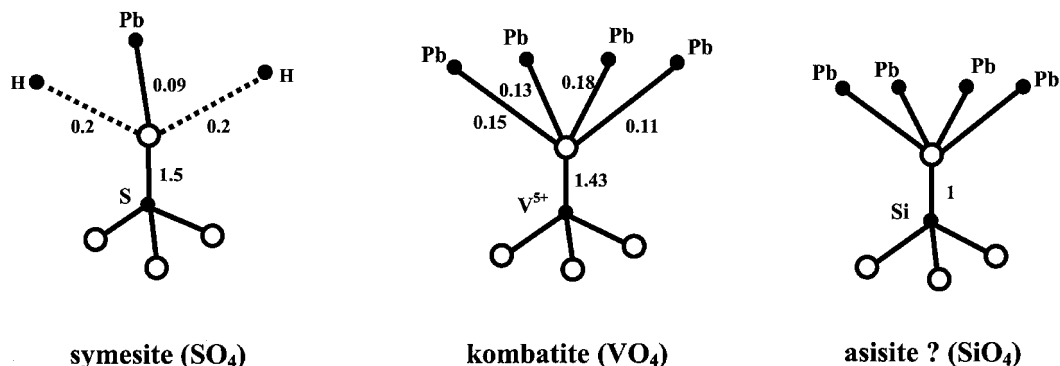

Fɪɢ. 4. Comparison of the local environments of the tetrahedral cations in symesite (SO_4), kombatite (VO_4) and that proposed for asisite (SiO_4). Numbers refer to bond valences.

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