Crystal structure of undersubstituted Sb-rich vikingite Vik$_{40}$

$\text{Ag}_{2.85} \text{Pb}_{1.23} (\text{Bi}_{0.92} \text{Sb}_{0.27})_7 \Sigma = 10.80 \text{S}_{30}$: site population and comparison with structure of vikingite Vik$_{50}$ $\text{Ag}_{3.5} \text{Pb}_{11.0} \text{Bi}_{11.5} \text{S}_{30}$

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Crystal structure of Sb-rich vikingite with lillianite substitution percentage L% below 50% from Kutná Hora ore district, Czech Republic, was solved and refined from single-crystal diffraction data to determine the site populations of metal sites concerning a) the decreasing “lillianite” substitution 2 Pb$^{2+}$ = Ag$^{+}$ + Bi$^{3+}$ b) Sb content not known in vikingite from other localities throughout the world. Vikingite is monoclinic, $\text{C}_{2}$/m, with $a = 13.5394(10)$, $b = 4.0992(3)$, $c = 25.506(3)$, $\alpha = 95.597(8)^\circ$, $V = 1408.9(2)$ Å$^3$, $Z = 1$, $D_{\text{z}} = 7.0412$ g/cm$^3$. The structural formula derived from the refinement is $\text{Ag}_{2.85} \text{Pb}_{1.23} (\text{Bi}_{0.92} \text{Sb}_{0.27})_7 \Sigma = 10.80 \text{S}_{30}$, corresponding to Vik$_{out}$. The structure of vikingite is composed of thinner slabs ($L$ slab) of four octahedra Me$_2$–Me$_1$–Me$_1$–Me$_2$ and thicker slabs ($L$ slab) of seven octahedra Me$_4$–Me$_5$–Me$_6$–Me$_7$–Me$_6$–Me$_5$–Me$_4$ separated by Pb atoms Me$_3$ in trigonal prismatic coordination. The refinement showed differences between the structures of Vik$_{out}$ and the previously published structure of Vik$_{in}$. The drop of L% below 50% shows most profoundly in the marginal octahedral site Me$_2$ of the thinner $L$ slabs, which becomes a Bi–Pb–Ag site with 28.6% of silver next to 50% of Bi and 21.4% of Pb. The central Me$_1$ site from $L$ slabs which is almost a pure Bi site in Vik$_{in}$ (0.97 Bi + 0.3 Ag) becomes a Bi-Pb site with minor Sb (0.54 Bi + 0.06 Sb + 0.40 Pb) in Vik$_{out}$. The Sb for Bi substitution was found to take place in the semimarginal site Me$_5$ (0.74 Bi + 0.26 Sb) in the thicker $L$ slabs, which is a pure Bi site in Sb-free Vik$_{50}$. Another important change against Vik$_{out}$ is verified and the occupancies of mixed sites were fine-tuned employing charge distribution calculations in program ECoN21. In Vik$_{out}$ the weighted average bond lengths $R_{\text{w}}$ of the marginal sites Me$_2$ and Me$_4$ and of the central site Me$_1$ are significantly larger than in Vik$_{in}$, reflecting the lower Ag content and the presence of Pb, while the Bi site Me$_5$, which is partly substituted by Sb and the site Me$_6$ with minor Bi at the expense of Pb exhibit adequately shortened $R_{\text{w}}$ values.

Keywords: vikingite, structure, site populations, charge distribution, ECoN, Kutná Hora

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1. Introduction

The mineral vikingite was discovered among lillianite homologues from Ivigtut, Greenland, and described by Makovicky and Karup-Moller (1977b). Vikingite is a lillianite homologue with a homologue order number equal to 5.5, which is the average of the number of octahedra in two neighboring slabs separated by Pb atoms in trigonal prismatic coordination. In vikingite, there are 4 and 7 octahedra in two adjacent slabs. The value of the average N can be established without a structural analysis solely from the results of electron microprobe chemical analyses on the basis of equations given by Makovicky and Karup-Moller (1977a). In nature, vikingite can have various degrees of the lillianite substitution 2 Pb = Bi + Ag, usually from L% = 45 to 75%. The formula $\text{Ag}_{2.85} \text{Pb}_{1.23} \text{Bi}_{13} \text{S}_{30}$ for vikingite from the type locality Ivigtut, given by Makovicky and Karup-Moller (1977b), corresponds to Vik$_{71.5}$. The structure of vikingite was solved by Makovicky et al. (1992) on a sample from La Roche Balue, France, with the composition corresponding to Vik$_{50}$. However, it was unknown how the structure behaves with decreasing lillianite substitution under 50%, i.e., with increasing Pb content accompanied by decreasing Ag and Bi contents. Also, the structure of Vik$_{50}$ displayed some discrepancies, reflected in the differences between the ideal chemical formula for Vik$_{in}$ and the formula established from the refinement (chemical formula $\text{Ag}_{2.85} \text{Pb}_{1.23} \text{Bi}_{13} \text{S}_{30}$ versus structural formula $\text{Ag}_{2.85} \text{Pb}_{1.23} \text{Bi}_{13} \text{S}_{30}$).

In the Kutná Hora ore district, lillianite homologues were described by Pažout (2017) and the entire Bi-mineralization by Pažout et al. (2017). Typical for Kutná Hora and unique on a world scale is the presence of antimony in otherwise pure Ag–Pb–Bi sulfosalts. For lillianite homologues with N = 4, the Sb for Bi substitution was found to be nearly complete from almost pure
Sb members through transition members with ca. 50 : 50 ratio of Bi : Sb, such as staročeskéite (Pažout and Dušek 2010; Pažout and Sejkora 2018) to Sb-rich gustavite (Pažout and Dušek 2009), later described from Julcani, Peru, as a new mineral terrywallaceite (Yang et al. 2013) and to pure Bi members (gustavite with no Sb). Lillianite homologues with N > 4 from Kutná Hora (vikingite – 5L, treasurite – 6L, eskimoite – 7L, heyrovskýite – 7L, erzwiesite – 8L) also exhibit some contents of antimony which are unique and not known from other localities throughout the world. The Sb for Bi substitution is less pronounced than in N = 4 members with a general trend of decreasing Sb content with higher N. Thus, vikingite with N = 5.5 was found to have the Bi/(Bi + Sb) ratio as much as 0.75 (7.21 wt. % of Sb), while erzwiesite with N = 8 has a maximum Sb content equal to 0.89 (2.96 wt. % of Sb). The compositions of vikingite from the Staročeské pásmo Lode of Kutná Hora ore district varies: N = 5.17–5.75, Bi/(Bi + Sb) = 0.75–0.95. The sample for single-crystal analysis used in this study has this ratio equal to 0.89. The substitution percentage L % for vikingite from Kutná Hora ranges from 37% (corresponding to Ag, Pb, Bi, Sb) to 85% (corresponding to Ag, Pb, Sb). For the crystal structure study, the compositions close to end members are the most interesting. Therefore the vikingite grain used in this study was a good example of the low-end of the lillianite substitution, another reason being the Sb content.

The aim of this study was to determine the site populations of metal sites with regard to the two substitutions which take place in lillianite homologues in Kutná Hora ore district: 1) “lillianite” substitution 2 Pb²⁺ = Ag⁺ + Bi³⁺ and 2) Sb³⁺ = Bi³⁺. The study aims to establish which sites are filled and with what atoms with decreasing content of Ag and Bi and increasing Pb and whether antimony substitutes only for bismuth or also for lead.

2. Sample

The fragment of vikingite investigated by single-crystal X-ray diffraction was recovered from a specimen found by the first author on medieval mine dumps of Staročeské pásmo Lode of the Kutná Hora ore district, Czech Republic. The sample was extracted from a specimen of quartz gangue (ST 187) with fairly rich accumulations of silver grey metallic grains and crystal aggregates of several millimeters in size, consisting of Ag–Pb–Bi–Sb sulfosalts of lillianite homologous series, accompanied by Bi-rich jamesonite (Pažout 2020). Vikingite forms grey metallic grains associated with gustavite Gus₅₄S₁₈ with Bi/(Bi + Sb) = 0.80 and izoklakeite with Bi/(Bi + Sb) = 0.63–0.70 (Fig. 1). Patches of parallel lamellation in Fig. 1 are formed by darker and brighter lamellae of Sb-rich gustavite (Bi/(Bi + Sb) > 0.75) which differ in L % (brighter lamellae have lower L % resulting in higher Pb and lower Ag + Bi). When the Sb content rises even more and the ratio Bi/(Bi + Sb) drops below ≤ 0.75, the lamellae-forming mineral becomes terrywallaceite (Yang et al. 2013) and again, the darker and brighter lamellae differ only in L %.

Microprobe data are in Tab. 1. The entire composition range of the vikingite grain, out of which the fragment for single-crystal analysis was extracted (Fig. 1), is Vik₃₇.₅₄₋₅₅.₉ N is between 5.17 and 5.71 and Bi/(Bi + Sb) is 0.88–0.89, corresponding to 2.22–2.84 wt. % of Sb.

3. Single-crystal X-ray crystallography

A tiny fragment of vikingite with dimensions of 0.184 × 0.066 × 0.039 mm was extracted from a polished sec-

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**Tab. 1** Chemical compositions of the Sb-rich vikingite grain (Fig. 1), from which the fragment for single-crystal X-ray analysis was extracted (wt. % and empirical formula coefficients, apfu).

|     | 1     | 2     | 3     | 4     | 5     | mean |
|-----|-------|-------|-------|-------|-------|------|
| Ag  | 5.02  | 4.80  | 5.54  | 5.23  | 5.62  | 5.24 |
| Cu  | 0.00  | 0.01  | 0.01  | 0.03  | 0.03  | 0.02 |
| Pb  | 43.14 | 43.94 | 39.70 | 40.06 | 40.22 | 41.41|
| Fe  | 0.02  | 0.04  | 0.03  | 0.02  | 0.03  | 0.03 |
| Bi  | 32.64 | 32.33 | 35.47 | 34.71 | 34.85 | 34.00|
| Sb  | 2.31  | 2.22  | 2.84  | 2.74  | 2.61  | 2.54 |
| S   | 16.15 | 16.00 | 16.20 | 16.30 | 16.09 | 16.15|
| Total | 99.26 | 99.32 | 99.78 | 99.08 | 99.45 | 99.38|
| CH  | –2.0  | –1.0  | 0.5   | –1.6  | 0.3   |      |
| apfu| 56    | 56    | 56    | 56    | 56    |      |

**Apfu**

CH – charge balance; N – order of lillianite homolog (Makovicky and Karup-Møller 1977); L % – percentage of the lillianite substitution 2 Pb²⁺ = Ag⁺ + (Bi, Sb)³⁺; x – substitution coefficient.
tion of sample ST 187 and separated under the optical stereomicroscope. The intensity data were collected using an Oxford Diffraction SuperNova single-crystal diffractometer equipped with an Atlas S2 CCD detector and monochromated MoKα radiation (55 kV, 30 mA) focused by the mirrors. The unit-cell parameters were refined by a least-squares algorithm using the CrysAlis Pro Package (Rigaku 2019) from 2140 reflections and gave \(a = 13.5394(10), b = 4.0992(3), c = 25.506(3)\) Å, \(\beta = 95.597(8)^\circ\) with \(V = 1408.9(2)\) Å³ and \(Z = 1\), space group \(C2/m\). From the total of 10503 measured reflections, 7441 were classified as observed \([I_{obs} > 3\sigma(I)]\). After averaging, 2049 reflections were independent and 1627 were classified as observed. Data were corrected for background, Lorentz and polarization effects, and an absorption correction based on the crystal shape (gaussian approach), followed by a multi-scan correction based on spherical harmonic functions, resulting in \(R_{int}\) of the merged data equal to 0.0692.

The crystal structure was solved from X-ray diffraction data by the charge-flipping algorithm (Palatinus and Chapuis 2007), independently from the previous structure solution (Makovicky et al. 1992). The obtained model was refined by the full-matrix least-squares of the Jana2006 program (Petřiček et al. 2014). All atomic positions were found from the structure solution. Atom numbering scheme used in this study is the same as in Makovicky et al. (1992). Because the dominant metal atoms in the structure are lead and bismuth, undistinguishable by X-ray diffraction (but distinguishable by bond lengths, bond valences and charge density distribution), it was helpful first to establish an estimate of the electron content (number of electrons) of each metal site concerning heavy atoms content (Pb\(^{2+}\), Bi\(^{3+}\)) versus lighter metal atoms content (Ag\(^+\), Sb\(^{3+}\)). To this end, all metal atoms were assumed to be bismuth and their occupancies refined with isotropic displacement parameters. The refinement showed that the electron content of the marginal site \(Me4\) of thicker \(L\) slabs is lower than that of marginal site \(Me2\) of \(4L\) slabs (i.e., \(Me4\) contains more Ag than \(Me2\), unlike the structure of Vik\(_{87-46}\) where \(Me4\) has less Ag than \(Me2\). However, X-ray data were not very sensitive to changes in the chemical composition of individual sites. As a result, the chemical changes in different structural models were not efficiently reflected in a change of \(R\) factors or residual electron density. Eventually, the program ECoN21 (Ilinca, pers. comm.) for calculation of charge distributions (CD) elaborated in papers of Hoppe et al. (1989) and Nespolo (2016), proved to be the most effective tool to check the correctness of each refined structural model, with emphasis on the comparison and match between oxidation numbers of cations \(q_x\) (corrected for site occupancy factors – sof) and anions \(q_y\) with charges received by cations \(Q_x\) and anions \(Q_y\) of each site in each structural model. The program calculates various parameters, including weighted average bond lengths, effective coordination numbers of each polyhedron, charges received by cations versus oxidation numbers of cations and bond valence sums. Similar to the approach of first estimating the electron content of each metal site from X-ray data by refining occupancies of all atoms set to Bi, a method of “bracketing” can be applied for the calculations in ECoN21. This meant that the charge distributions of all atoms in an initial refined structural model were calculated in ECoN21 and in the next step, a completely reversed configuration was applied, i.e., Bi atoms were replaced by Pb atoms, Pb atoms by Bi atoms and Ag–Bi sites by Ag–Pb sites. The new model was refined and subsequently calculated in ECoN21 and the charge distribution of all sites was compared to the reversed model. The calculations in ECoN21 showed several things that would be difficult to reveal from X-ray data only: 1. the mixed sites \(Me2\) and \(Me4\) are not composed of just Bi and Ag, but also contain Pb; 2. the central site \(Me1\) in \(L\) slabs is not Bi (or Bi with minor Ag), but a Bi–Pb mixed site; 3. the site \(Me6\) is not a pure Pb site but contains some Bi.

In the Ag–Bi–Pb sites \(Me2\) and \(Me4\), the Pb content could be refined against Ag with the Bi occupancy fixed at 0.50 (as estimated from ECoN21), the sum of the site occupancies of all three atoms kept at unity and the coordinates and atomic displacement parameters (ADPs) of all three atoms kept identical. Finally, the anisotropic displacement parameters of all metal atoms were refined. An inspection of the refinement listing revealed a possible problem with nonmatching reflections. Because X-ray data from fragments of sulfosalts extracted from polished sections are rarely perfect (and especially those
containing significant Pb and Bi or other metals with high absorption), it was necessary to exclude the outliers in groups of symmetrically equivalent reflections, and these not on the basis of their deviation from the average measured intensity, but on how they deviate from individual calculated structure factors. Therefore, unaveraged reflection data were used for the final cycles of refinement. A criterion of skipping non-matching reflections with \( |F_{\text{obs}} - F_{\text{calc}}| > 5\sigma(F_{\text{obs}}) \) was used. The final correct structural model was obtained using averaged intensity data (i.e., in a standard manner) where the influence of nonmatching reflections is not so strong but shows in higher residual electron density. The correct composition obtained using averaged reflections indicates that the structural model is correct and can be used to identify bad (nonmatching) reflections in unaveraged intensity data. After removing these bad reflections, i.e., by using the \( |F_{\text{obs}} - F_{\text{calc}}| > 5\sigma(F_{\text{obs}}) \) cutoff, we have returned to the correct final structural model. Nevertheless, this time it was with a better residual electron density and better \( R \) factors.

Similar to the structure of vikingite \( \text{Vik}_{30} \) by Makovicky et al. (1992), anisotropic displacement parameters (ADP) were refined for metal sites, isotropic displacement parameters were used for sulfur. The rather large displacement parameters of \( Me3 \) and \( S1 \) point to the possibility that the two positions are slightly disordered. The final refinement converged to an \( R = 0.0860, wR = 0.0783 \) with a GOF of 2.09 for 8500 measured reflections. Details of the data collection and the crystallographic and structure

### Tab. 2 Crystallographic data and refinement details for Sb-rich vikingite from Kutná Hora, Czech Republic.

| Crystal data | |
| --- | --- |
| Structure formula | \( \text{Ag}_{2.8}\text{Pb}_{12.6}\text{Bi}_{3.2}\text{Sb}_{0.2}\text{S}_{3.2} \) |
| Crystal system | monoclinic |
| Space group | \( C2/m \) |
| Unit-cell parameters: \( a, b, c \) [Å] | 15.394(10), 4.0992(3), 25.506(3) |
| \( \beta [^\circ] \) | 95.597(8) |
| Unit-cell volume [Å³] | 1408.9(2) |
| \( Z \) | 1 |
| Calculated density [g/cm³] | 7.0412 |
| Crystal size [mm] | 0.184 \( \times 0.066 \times 0.039 \) |
| \( F_{\text{calc}} \) | 2482 |

### Data collection

| Diffractometer | Oxford Diffraction SuperNova, Atlas detector |
| --- | --- |
| Temperature [K] | 284 |
| Radiation. wavelength [Å] | MoKα, 0.71073 (50 kV, 30 mA) |
| \( \theta \) range for data collection [°] | 3.02–29.57 |
| Limiting Miller indices | \( h = –18 \rightarrow 18, k = –5 \rightarrow 5, l = –35 \rightarrow 33 \) |
| Axis, frame width (°), time per frame (s) | \( \omega, 1, 65 \) |
| Total reflections collected | 10503 |
| Observed reflections, criterion | 7441, \( |I > 3\sigma(I)| \) |
| Absorption coefficient \([\text{mm}^{–1}]\); type | 69.04; gaussian |
| \( T_{\text{min}}/T_{\text{max}} \) | 0.019/0.139 |
| \( R_{\text{int}} \) | 0.0692 |

### Structure refinement by Jana2006

| R, \( wR \) (obs) | 66, 0, 48 |
| \( R, \ wR \) (all) | 8.60, 7.83 |
| GOF obs/all | 2.34, 2.09 |
| Weighting scheme, weights | \( \sigma, w = 1/(\sigma^2(I)+0.0001 F) \) |
| Largest diffraction peak and hole (e Å⁻³) | 7.67, –8.94 |

### Tab. 3 Atom coordinates and displacement parameters for the crystal structure of Bi-rich vikingite from Kutná Hora, Czech Republic.

| Atom | Occupancy | \( x/a \) | \( y/b \) | \( z/c \) | \( U_{	ext{eq}} \) |
| --- | --- | --- | --- | --- | --- |
| Me1 | Bi 0.54 | 0.12910(5) | 0.5 | 0.96118(3) | 0.0148(2) |
| Sb 0.06 | 0.12910(5) | 0.5 | 0.96118(3) | 0.0148(2) |
| Pb 0.40 | 0.12910(5) | 0.5 | 0.96118(3) | 0.0148(2) |
| Me2 | Bi 0.50 | 0.39275(6) | 0.5 | 0.89496(4) | 0.0233(3) |
| Pb 0.214(7) | 0.39275(6) | 0.5 | 0.89496(4) | 0.0233(3) |
| Ag 0.286(7) | 0.39275(6) | 0.5 | 0.89496(4) | 0.0233(3) |
| Me3 | Pb 1.0 | 0.14505(6) | 0 | 0.80680(5) | 0.0403(4) |
| Me4 | Bi 0.50 | 0.36003(7) | 0.5 | 0.71343(4) | 0.0267(4) |
| Pb 0.074(8) | 0.36003(7) | 0.5 | 0.71343(4) | 0.0267(4) |
| Ag 0.426(8) | 0.36003(7) | 0.5 | 0.71343(4) | 0.0267(4) |
| Me5 | Bi 0.741(9) | 0.57168(6) | 0 | 0.64576(4) | 0.0237(3) |
| Sb 0.259(9) | 0.57168(6) | 0 | 0.64576(4) | 0.0237(3) |
| Me6 | Pb 0.90 | 0.28533(6) | 0 | 0.57122(4) | 0.0371(3) |
| Bi 0.10 | 0.28533(6) | 0 | 0.57122(4) | 0.0371(3) |
| Me7 | Pb 1.0 | 0.5 | 0.5 | 0.5 | 0.0389(5) |
| S1 | 0.5 | 0.5 | 0 | 0.128(6) |
| S2 | 0.248(3) | 0 | 0.92198(19) | 0.0179(10) |
| S3 | 0.0202(3) | 0.5 | 0.86723(17) | 0.0100(9) |
| S4 | 0.286(2) | 0.5 | 0.8035(2) | 0.0267(12) |
| S5 | 0.4958(4) | 0 | 0.7342(2) | 0.0248(12) |
| S6 | 0.6996(6) | 0.5 | 0.6860(3) | 0.065(2) |
| S7 | 0.4305(4) | 0.5 | 0.6053(2) | 0.0280(12) |
| S8 | 0.3501(4) | 0 | 0.4696(2) | 0.0297(13) |
refinement parameters are listed in Tab. 2. The final atom coordinates, occupancies and isotropic displacement parameters are given in Tab. 3 and the anisotropic displacement parameters are given in Tab. 4. The interatomic distances in Sb-rich vikingite Vik\textsubscript{40} and comparison with equivalent distances in vikingite Vik\textsubscript{50} are in Tab. 5. The detailed results of charge distribution calculations of metal and sulfur sites in the structure of Sb-rich vikingite Vik\textsubscript{40} by program ECoN21 are in Tab. 6. The comparison of refinement results on using different cutoffs of nonmatching reflections is in Tab. 7. The table shows potential problems may include high residual electron density, negative values of occupancies, negative atomic displacement parameters, or structural formula deviating too much from the chemical analysis. The CIF file, also containing a block with the reflections, is provided as a Supplementary file at the Journal’s web page www.jgeosci.org.

4. Results

The crystal structure of vikingite contains fifteen independent sites, eight of them occupied by S and seven metal sites (Fig. 2). Of these, two are pure Pb sites (Me\textsubscript{3} and Me\textsubscript{7}), two are Ag-Bi-Pb sites (Me\textsubscript{2} and Me\textsubscript{4}), two are Pb-Bi sites (Me\textsubscript{6} and Me\textsubscript{1} with minor Sb) and one is Bi-Sb site (Me\textsubscript{5}). All sites except for Me\textsubscript{3} are in distorted octahedral coordination.

The structure of vikingite is composed of thinner slabs (\textsuperscript{4}L) of four octahedra Me\textsubscript{2}–Me\textsubscript{1}–Me\textsubscript{1}–Me\textsubscript{2} and thicker slabs (\textsuperscript{7}L) of seven octahedra Me\textsubscript{4}–Me\textsubscript{5}–Me\textsubscript{6}–Me\textsubscript{7}–Me\textsubscript{6}–Me\textsubscript{5}–Me\textsubscript{4} separated by Pb atoms Me\textsubscript{3} in trigonal prismatic coordination.

The arrangement of \textsuperscript{4}L and \textsuperscript{7}L slabs in the crystal structure of vikingite is in Fig. 3.

The bicapped trigonal prism Me\textsubscript{3}, separating the \textsuperscript{4}L and \textsuperscript{7}L slabs and surrounded by Me\textsubscript{2} and Me\textsubscript{4} octahedra, is one of the least distorted polyhedra in the structure (together with Me\textsubscript{7}), with an effective coordination number ECoN = 6.91, a value close to ideal 7, and is thus even less distorted than the same prism in Vik\textsubscript{50} (ECoN = 6.87). The site is occupied solely by Pb, as in all lillianite homologues with L\% \leq 100. The weighted average bond length \( \bar{R} \) is similar in both structures, 3.037 Å in Vik\textsubscript{40}, 3.045 Å in Vik\textsubscript{50}. The influence of Ag + Bi for Pb substitution on the position of S atoms which cap the vertical faces of the prism (S2 and S6), has not been confirmed in the current study. This influence, reported by Makovicky et al. (1992) in the structure of Vik\textsubscript{50}, showed a shortening of these distances with more pronounced Ag–Bi substitution (higher Ag content). In Vik\textsubscript{40}, the Me\textsubscript{3}–S2 distance of 3.13 Å and Me\textsubscript{3}–S6 distance of 3.29 Å are in agreement with the more pronounced Ag–Bi substitution in the Me\textsubscript{2} site (0.48 Ag + 0.52 Bi) adjacent to S2 in the \textsuperscript{4}L slabs and with the less pronounced substitution in Me\textsubscript{4} (0.38 Ag + 0.62 Bi) adjacent to S6 in the \textsuperscript{7}L slabs (Makovicky et al. 1992). However, in vikingite Vik\textsubscript{40}, the distances are very similar (Me\textsubscript{3}–S2 distance of 3.13 Å and Me\textsubscript{3}–S6 distance of 3.24 Å) although the

### Table 4

| Atom | \( U_{11} \) (Å\(^2\)) | \( U_{22} \) (Å\(^2\)) | \( U_{33} \) (Å\(^2\)) | \( U_{12} \) (Å\(^2\)) | \( U_{13} \) (Å\(^2\)) | \( U_{23} \) (Å\(^2\)) |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Me1  | 0.0032(3)       | 0.0029(4)       | 0.0383(5)       | 0               | 0.0019(3)       | 0               |
| Me2  | 0.0193(5)       | 0.0129(6)       | 0.0380(7)       | 0               | 0.0044(4)       | 0               |
| Me3  | 0.0205(4)       | 0.0081(5)       | 0.0909(8)       | 0               | –0.0019(5)      | 0               |
| Me4  | 0.0231(6)       | 0.0131(6)       | 0.0444(8)       | 0               | 0.0050(5)       | 0               |
| Me5  | 0.0221(5)       | 0.0136(5)       | 0.0354(6)       | 0               | 0.0029(4)       | 0               |
| Me6  | 0.0307(5)       | 0.0275(6)       | 0.0534(7)       | 0               | 0.0052(4)       | 0               |
| Me7  | 0.0438(8)       | 0.0291(8)       | 0.0428(8)       | 0               | –0.0019(7)      | 0               |

Fig. 2 Atom labelling in the crystal structure of vikingite. The atom numbering scheme is the same as in the structure of vikingite by Makovicky et al. (1992).
Ag–Bi substitution exhibits the opposite, as $Me2$ has only 28.6 % Ag and $Me4$ has 42.6 % Ag. This may be caused by the presence of lead in these sites, more pronounced in the $Me2$ position (see below). The bond lengths are typical of lead atoms in trigonal prismatic coordination in lillianite homologs.

All detectable Ag substitution occurs in the marginal octahedral sites $Me2$ and $Me4$ with typical short and long opposing distances, 2.62 and 2.92 Å for $Me2$ and 2.594 and 3.005 Å for $Me4$, more contrasting for the latter in line with a more pronounced Ag substitution in $Me4$. At the same time, the bond length ratio of the opposing short and long bonds of these sites is considerably less pronounced than in the case of Vik$_{50}$ (2.525 and 3.100 Å) and (Ag,Bi)-bearing heyrovskýite Hey$_{50}$ (2.479 and 3.043 Å, Makovicky et al. 1991), in agreement with the hybrid character of the triply substituted mixed sites in Vik$_{50}$.

$Me4$ is an octahedral site at the margin of the thicker $L$ slabs with the composition 0.426(8) Ag + 0.574 (Bi + Pb), very similar to the Bi3Ag3 site in synthetic orthorhombic N = 8 member ($^{56}$L) of the lillianite homologous series (Topa et al. 2010). Slightly larger values reflect the Pb content in this site in Vik$_{50}$. Charge distribution results from ECoN21 suggested a small amount of lead, eventually refined as 0.074(8) Pb. With the effective coordination number $ECoN = 5.309$, this octahedron is less distorted than $Me4$ in Vik$_{50}$ which has 0.38 Ag + 0.62 (Bi + Pb) and $ECoN = 5.053$. The weighted average bond length $R_w$ of 2.801 Å is larger than that of Vik$_{50}$ (2.771 Å, Tab. 5), reflecting both the lower Ag content and the presence of lead in this site in Vik$_{50}$.

$Me2$ represents a marginal octahedral site in the thinner $L$ slabs. In contrast to Vik$_{50}$, the occupancy of Ag is lower, refined as 0.286(7) Ag + 0.214(7) Pb + 0.50 Bi. So the depletion of Ag and Bi, which is related to the decrease of L%, shows most profoundly in this marginal site of thinner $L$ slabs. This is the biggest difference compared to Vik$_{50}$ where this site is basically 0.5 Ag + 0.5 Bi. This is also reflected in the $R_w$ value of 2.816 Å in Vik$_{50}$ which is significantly larger than 2.758 for Vik$_{50}$. With the effective coordination number $ECoN = 5.632$, this octahedron is much less distorted than $Me2$ in Vik$_{50}$ which has 0.48 Ag + 0.52 Bi and $ECoN = 4.902$. The positional disorder of $Me2$ and $Me4$ is smaller (and similar to Vik$_{50}$), but the coordinated sulfur atom S1 displays high atomic displacement parameters.

With decreasing substitution and growing Pb content, the central site $Me1$ in the thinner $L$ slabs, a practically pure Bi site in Vik$_{50}$ (0.97 Bi + 0.03 Ag), becomes a Bi–Pb site with minor Sb (0.54 Bi + 0.06 Sb + 0.40 Pb). The weighted average bond length $R_w$ of 2.816 Å is significantly larger than 2.758 Å in Vik$_{50}$; the average of the three shortest bonds is 2.80 Å compared to 2.71 Å in Vik$_{50}$, evidencing a significant presence of lead in this

| Tab. 5 | Interatomic distances in Sb-rich vikingite Vik$_{50}$ (this paper, left column) and in the structure of vikingite Vik$_{50}$ (Makovicky et al. 1992, right column). |
|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|        | **Sb-rich vikingite Vik$_{50}$** | **vikingite Vik$_{50}$ (1992)** |
| $Me1$  | S1  | 2.6884(3) | S1  | 2.5818 |
|        | S2  | 2.8503(2) | S2  | 2.7775 |
|        | S2  | 2.8505(2) | S2  | 2.7777 |
|        | S1  | 2.9280(2) | S1  | 2.9440 |
|        | S1  | 2.9281(2) | S1  | 2.9441 |
|        | S2  | 3.2655(4) | S2  | 3.2238 |
|        | $R_w$ | 2.857 | $R_w$ | 2.788 |
| $Me2$  | S4  | 2.6205(3) | S4  | 2.5253 |
|        | S3  | 2.8128(2) | S3  | 2.7556 |
|        | S3  | 2.8130(2) | S3  | 2.7558 |
|        | S1  | 2.9200(3) | S1  | 2.9231 |
|        | S1  | 2.9595(2) | S1  | 3.1001 |
|        | S2  | 2.9597(2) | S2  | 3.1003 |
|        | $R_w$ | 2.816 | $R_w$ | 2.758 |
| $Me3$  | S4  | 2.8086(1) | S4  | 2.8064 |
|        | S4  | 2.8087(1) | S4  | 2.8065 |
|        | S2  | 3.1296(4) | S2  | 3.1260 |
|        | S3  | 3.1540(2) | S3  | 3.2278 |
|        | S3  | 3.1542(2) | S3  | 3.2280 |
|        | S6  | 3.2379(4) | S5  | 3.2582 |
|        | S5  | 3.3132(2) | S5  | 3.2583 |
|        | S5  | 3.3134(2) | S6  | 3.2883 |
|        | $R_w$ | 3.037 | $R_w$ | 3.045 |
| $Me4$  | S4  | 2.5941(3) | S4  | 2.5343 |
|        | S5  | 2.7697(1) | S5  | 2.7562 |
|        | S5  | 2.7698(1) | S5  | 2.7563 |
|        | S7  | 3.0055(3) | S7  | 2.9543 |
|        | S6  | 3.0185(2) | S6  | 3.0656 |
|        | S6  | 3.0187(2) | S6  | 3.0657 |
|        | $R_w$ | 2.801 | $R_w$ | 2.771 |
| $Me5$  | S5  | 2.5677(3) | S5  | 2.6067 |
|        | S6  | 2.8122(2) | S6  | 2.8075 |
|        | S6  | 2.8124(2) | S6  | 2.8077 |
|        | S7  | 2.9215(2) | S7  | 2.9418 |
|        | S7  | 2.9216(2) | S7  | 2.9419 |
|        | S8  | 3.2216(4) | S8  | 3.1525 |
|        | $R_w$ | 2.793 | $R_w$ | 2.814 |
| $Me6$  | S8  | 2.8771(3) | S8  | 2.9221 |
|        | S8  | 2.8763(2) | S8  | 2.9222 |
|        | S8  | 2.8765(2) | S8  | 2.9435 |
|        | S7  | 2.9126(2) | S7  | 2.9351 |
|        | S7  | 2.9127(2) | S7  | 2.9352 |
|        | S6  | 3.2517(4) | S6  | 3.0598 |
|        | $R_w$ | 2.902 | $R_w$ | 2.948 |
| $Me7$  | S7  | 2.9308(3) | S7  | 2.9840 |
|        | S7  | 2.9311(3) | S7  | 2.9849 |
|        | S8  | 2.9351(2) | S8  | 2.9053 |
|        | S8  | 2.9353(2) | S8  | 2.9055 |
|        | S8  | 2.9353(2) | S8  | 2.9060 |
|        | S8  | 2.9355(2) | S8  | 2.9062 |
|        | $R_w$ | 2.934 | $R_w$ | 2.929 |

$R_w$ - weighted average bond length calculated by ECoN 21 (Ilinca 2021, pers.comm.)
site in Vik₄₀. Charge distribution calculations also indicated that a small part of bismuth is substituted by antimony. The effective coordination number $ECoN = 5.379$. Thus this octahedron is less distorted than Me1 in Vik₄₀, which has $ECoN = 5.101$. The two opposing short and long distances perpendicular to the 4 Å c axis are 2.688 and 3.266 Å, suggesting a hybrid character caused by the mixing of lead and bismuth combined with antimony in this site.

The thicker 7L slabs are formed, apart from the marginal octahedron Me4, by a semimarginal octahedral site Me5 and two central octahedra Me6 and Me7. The most central site Me7 is a pure Pb site in Vik₄₀ and Vik₄₀, with a similar weighted average bond lengths and effective coordination numbers. $R_w$ = 2.934 Å in Vik₄₀ and 2.929 Å in Vik₄₀ and $ECoN$ = 6.000 and 5.968, respectively, which shows that this polyhedron is very symmetric and close to an ideal octahedron in both structures.

A different situation is in the other central site Me6 (second from the center, third from the margin), which is a pure Pb site in Vik₄₀, but in Vik₄₀, with lower L %, higher Pb and lower Bi, this site becomes a Pb–Bi site with 10 % of Bi, by paradox, as shown by charge-density calculations in ECoN21. Coordination-wise, this site is the least characteristic site as it has a long bond of 3.252 Å with the opposing too-long “short” bond of 2.818 Å, suggesting a positional/occupational disorder. The weighted average bond length $R_w$ of 2.902 Å is significantly shorter than 2.948 Å in Vik₄₀. The average of the three shortest bonds is 2.857 Å compared to 2.929 Å in Vik₄₀, showing this site is not a pure Pb site in Vik₄₀. This is also supported and reflected by the distortion of the polyhedron. The pure Pb site in Vik₄₀ is much less distorted with $ECoN = 5.949$ while in Vik₄₀ $ECoN$ = 5.609. Pure octahedral Pb sites in sulfosalts usually show a very good match with the ideal coordination number 6.00 for the polyhedron.

The semimarginal site Me5, a pure Bi site in Vik50 with no Sb, was found to be the site where the Sb for Bi substitution occurs. It contains 0.741(9) Bi + 0.259(9) Sb. It is the most distorted site in the structure, probably due to the pronounced electron pair micelle, with $ECoN$ = 5.131. The weighted average bond length $R_w$ of 2.793 Å is slightly shorter than 2.814 Å in Vik₃₀ with no antimony content. The shortest bond Me5–S5 of 2.568 Å is considerably shorter than the equivalent shortest bond in Vik₃₀ of 2.607 Å.

**Tab. 6** Detailed results of charge distribution calculations of metal and sulfur sites in the structure of Sb-rich vikingite Vik₄₀ in the cation-centered description by program ECoN 21 (Ilinca, pers. comm.).

| Cation | sof | $R_w$ | ECoN | $q_A$ | $Q_A$ | $q/Q_A$ | BVS |
|--------|-----|-------|------|-------|-------|----------|-----|
| Me1    | 0.540 Bi, 0.060 Sb, 0.400 Pb | 2.857 | 5.379 | 2.600 | 2.590 | 1.004 | 2.458 |
| Me2    | 0.500 Bi, 0.214 Pb, 0.286 Ag | 2.816 | 5.632 | 2.214 | 2.255 | 0.982 | 2.078 |
| Me3    | Pb | 3.037 | 6.908 | 2.000 | 2.062 | 0.970 | 1.955 |
| Me4    | 0.074 Pb, 0.500 Bi, 0.426 Ag | 2.801 | 5.309 | 2.074 | 2.096 | 0.989 | 1.780 |
| Me5    | 0.741 Bi, 0.259 Sb | 2.793 | 5.131 | 3.000 | 3.006 | 0.998 | 2.795 |
| Me6    | 0.900 Pb, 0.100 Bi | 2.902 | 5.609 | 2.100 | 2.029 | 1.035 | 2.177 |
| Me7    | Pb | 2.934 | 6.000 | 2.000 | 1.923 | 1.040 | 2.076 |

MAPD(Qₐ): 1.97 % MAPD(BVS): 6.05 %

**Tab. 7** The comparison of refinement results on using different cutoffs of nonmatching reflections.

| X-ray data | All reflections | Excluded reflections | $R_w$ | w$R_w$ | GOF(all) | residual density (e Å⁻³) | structure formula coefficients |
|------------|----------------|----------------------|-------|--------|----------|--------------------------|-------------------------------|
| averaged   | 2049           | 16.33                | 19.12 | 7.76   | 18.91    | 23.05                    | S2 negative                   |
| unaveraged | 10503          | none                 | 15.05 | 16.49  | 4.83     | 18.73                   | 21.88                        | 2.88  12.32  9.49  1.31         |
| unaveraged cutoff 15 | 10315 | 188                  | 13.75 | 13.95  | 4.01     | 15.69                   | 21.33                        | Pb4 0.032 3.18 12.02 8.81 1.99 |
| unaveraged cutoff 10 | 9933  | 570                  | 12.12 | 11.73  | 3.35     | 13.70                   | 16.81                       | Pb4 0.16 3.63 11.57 8.02 2.78  |
| unaveraged cutoff 5  | 8500 | 2003                 | 8.60  | 7.83   | 2.09     | 7.67                    | 8.94                        | ok 2.85 12.36 9.52 1.28        |
The average of the three shortest bonds does not differ that much: 2.731 Å in Vik$_{50}$ and 2.741 in Vik$_{40}$. It is a mixed cation site with hybrid distances characteristic of mixed Bi–Sb positions with opposing distances of 2.568 and 3.222 Å and similar to Bi$_2$B$_4$ site in Sb-rich gustavite with almost the same Bi:Sb ratio (Pažout and Dušek 2009).

Generally speaking, sites in Vik$_{50}$ (Makovicky et al. 1992) are more distorted than in Vik$_{40}$ (this paper). The most distorted site in Vik$_{50}$ is Me2 with $ECoN = 4.902$, followed by Me4 ($ECoN = 5.053$) and Me1 ($ECoN = 5.101$). In Vik$_{40}$, the most distorted sites are Me5, followed by Me4 and Me1. Me2, where the biggest change against Vik$_{50}$ occurs in the form of considerably lower Ag content, is much less distorted, with $ECoN$ similar to Me6 (Tab. 6).

The final structural formula is Ag$_{2.35}$Pb$_{12.35}$ (Bi$_{9.52}$Sb$_{1.272}$)$_{50}$, corresponding to Vik$_{40}$, ideally Ag$_{2.572}$Pb$_{12.228}$ (Bi$_{9.5}$Sb$_{0.5}$)$_{50}$, which is a very good fit between structure and chemistry. From the results of structure determination, the composition of the thinner \(^7\)L slabs, together with its share of trigonal prismatic Pb and S4 sites, is Ag$_{0.572}$Pb$_{2.228}$ (Bi$_{2.682}$Sb$_{0.518}$)$_{50}$, which does not correspond to any composition on the gustavite–lillianite join. Nevertheless, the Pb content corresponds to Gus$_{50}$ which would, however, requires 0.38 apfu Ag and 2.38 apfu Bi, while we have 0.57 apfu Ag (0.20 more) and 2.20 apfu Bi (0.18 less). This composition is not electrically neutral like in Vik$_{50}$, the charge of cations is +11.628 and the charge of anions is –12. The composition of \(^7\)L slabs is Ag$_{0.832}$Pb$_{3.548}$ (Bi$_{2.682}$Sb$_{0.518}$)$_{50}$, which would require 1.025 apfu Ag and 3.025 apfu Bi while we have 0.852 apfu Ag (0.17 less) and 3.20 apfu Bi (0.175 more). The charge of cations in ‘L slabs is +18.348, the charge of anions is –18. Because the structure as a whole is neutral (overall charge balance is +59.952 against –60.000), the charge compensation is materialized within both kinds of slabs, i.e., within the unit cell.

The last issue to discuss is the periodicity of vikingite. Very weak 8 Å levels in diffraction data of vikingite from Ivigtut, Greenland, were reported by Makovicky and Karup-Møller (1977b) and even weaker 8 Å levels in the material from La Roche Balue, France (Makovicky et al. 1992), on which the crystal structure of Vik$_{50}$ was solved. They concluded that the ordering of Ag and Bi in marginal octahedral sites Me2 and Me4 causes twinning with the unit cell parameters for the true cell of the ordered vikingite structure calculated from the subcell dimensions as $a = 7.07$, $b = 8.20$, $c = 25.12$, $\beta = 84.72^\circ$, the space group $P\bar{1}$.

However, in the material from Kutná Hora, Czech Republic, there were no signs or traces of 8 Å levels. This is apparently caused by formation conditions not favorable for the origin of an ordered structure. To sum up the experience from diffraction experiments on vikingite material from various localities, it is obvious that vikingite can have weak (or very weak) 8 Å levels on the one hand or no traces of this on the other hand. If we accept the fact that some of vikingites in nature are (more or less) ordered and have an 8 Å periodicity with triclinic $P\bar{1}$ symmetry and others have 4 Å periodicity with monoclinic $C2/m$ symmetry, then we can consider the 4 Å cell of the latter to be their true cell.

Then it is a matter of discussion if both cases are still the mineral vikingite or we deal with two different minerals. However, there is an IMA rule saying that ordered and disordered varieties have the same mineral name.

**Fig. 3** General arrangement of \(^7\)L and \(^7\)L slabs in the crystal structure of vikingite. Chemical compositions of octahedral metal sites are differentiated by color: green (marginal octahedra Me2 and Me4): mixed Bi–Pb–Ag site; dark red (Me1 in the middle of \(^7\)L slab): Pb–Bi mixed site with minor Sb; red (Me5): Bi–Sb site; blue (Me6): Pb–Bi mixed site; violet (Me7 in the center of \(^7\)L slabs): pure Pb site and trigonal prismatic site Me3 that separates \(^7\)L and \(^7\)L slabs.
5. Conclusions

The comparison of the structures of vikingite Vik$_{50}$ and Vik$_{90}$ indicated how the decrease of the “lillianite” substitution $2 \text{Pb}^{2+} = \text{Ag}^{+} + \text{Bi}^{3+}$ shows in site populations of metal sites. It was observed that up to 50% of this substitution, the composition of marginal sites Me2 and Me4 is approximately 50% Ag and 50% Bi. When the L% decreases below 50% (i.e., Ag and Bi drop and Pb rises), the content of Ag begins to drop in one of the marginal sites below 50% and simultaneously, this site is filled with lead. The content of Bi remains approximately 50% even at this decrease. At the same time, the Ag content in the other marginal site decreases as well, but much more moderately. The site with the more substantial decrease in Ag content was identified to be Me2 of the thinner ‘L slabs.

Major changes against the previously published structure of Vik$_{50}$ include:

1) Marginal octahedral sites Me2 and Me4, where the Ag–Bi substitution occurs, become Ag–Pb–Bi sites. The decrease of the $2 \text{Pb} = \text{Ag} + \text{Bi}$ substitution below 50% shows first in lowering of the Ag content of the marginal octahedral site Me2 in thinner ‘L slabs – which for vikingite with L% $\geq$ 50 is an app. fifty-fifty Ag–Bi site. The missing Ag is simultaneously replenished by Pb. At the same time, the occupancy of Ag in the marginal site Me4 in thicker ‘L slabs does not depart from 50% so profoundly, 0.426 Ag + 0.574 (Bi + Pb).

2) The central Me1 site from ‘L slabs has no or minimal content of Ag. The central octahedron Me1 in thinner ‘L slabs, which is almost a pure Bi site in Vik$_{50}$ (0.97 Bi + 0.3 Ag) becomes in Vik$_{90}$ a Bi–Pb site with minor Sb (0.54 Bi + 0.06 Sb + 0.40 Pb).

3) Sb substitutes for bismuth. The Sb for Bi substitution takes place in semimarginal site Me5, refined as 0.741(9) Bi + 0.259(9) Sb. A small amount of antimony was detected in the Bi–Pb site Me1. The substitution of Sb for lead could not be confirmed.

4) The central octahedron Me6, a pure Pb site in Vik$_{50}$, becomes a Pb–Bi site with (0.9 Pb + 0.1 Bi).

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