

Šlikite, $\text{Zn}_2\text{Mg}(\text{CO}_3)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, a new Zn–Mg carbonate from Plavno, Jáchymov ore district, Czech Republic

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Abstract: Šlikite, $\text{Zn}_2\text{Mg}(\text{CO}_3)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ is a new supergene post-mining mineral from the Jáchymov (formerly St. Joachimsthal) ore district, Czech Republic, associated with brianzongite, hexahydrite, hydromagnesite, nesquehonite, serpierite, smithsonite and a ktenasite-like mineral. It forms snow-white radial aggregates, up to 2 mm across, in vugs or on surfaces of fragments of skarn rocks. Individual crystals are very thin blades, elongated along [110] and flattened on {001}, up to 200 μm in length. Šlikite has a white streak, a vitreous lustre, and does not fluoresce under either short- or long-wave ultraviolet light. Cleavage is perfect on {001}, the Mohs hardness is ~2, and the fracture is uneven. The mineral is brittle, although thin blades (fibres) are slightly flexible. The calculated density is 2.613 g/cm^3 . Šlikite is optically biaxial negative, the indices of refraction are $\alpha = 1.50(1)$, $\beta = 1.55(1)$, $\gamma = 1.59(1)$ and $2V_{\text{meas.}} = 80(1)^\circ$. The mineral is triclinic, space group $P\bar{1}$, $a = 6.335(4)$, $b = 6.340(1)$, $c = 13.923(4)$ Å, $\alpha = 99.985(7)^\circ$, $\beta = 92.74(1)^\circ$, $\gamma = 114.93(2)^\circ$, $V = 494.8(4)$ Å³, $Z = 2$. The six strongest lines in the X-ray powder diffraction pattern are [d (Å)]/ I (hkl): 13.575/100(001), 4.525/31(003), 3.573/2(113), 3.406/5(111), 2.996/3(113) and 2.773/3(112). The chemical analyses by electron microprobe yielded MgO 8.39, ZnO 46.28, CuO 0.05, MnO 0.68, CdO 0.04, $\text{CO}_{2\text{calc.}}$ 23.10, $\text{H}_2\text{O}_{\text{calc.}}$ 23.65, total 102.19 wt%. The empirical formula on the basis of 12 O atoms per formula unit is $\text{Zn}_{2.00}(\text{Mg}_{0.79}\text{Zn}_{0.17}\text{Mn}_{0.04})_{\Sigma 1.00}(\text{CO}_3)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. The crystal structure of šlikite was refined using synchrotron single-crystal data to $R_{\text{obs}} = 0.094$ for 1594 reflections with $I > 3\sigma(I)$. The structure of šlikite is based on heteropolyhedral layers of composition $[\text{Zn}_4\text{Mg}(\text{CO}_3)_4(\text{OH})_4]^{2-}$, parallel to {001}, with interlayer H-bonded $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and H_2O . Within the layers, [110] chains of corner-connected $\text{ZnO}_2(\text{OH})_2$ tetrahedra share corners with Mg-centred octahedra. The two types of polyhedra are connected via CO_3 groups. The Raman and infrared spectra of šlikite as well as tentative assignment of observed bands are given in this paper. The mineral is named in honour of the prominent Czech aristocrat Štěpán Šlik (1487–1526), founder of town St. Joachimsthal (now Jáchymov).

Key-words: šlikite; new mineral; Zn–Mg–carbonate; crystal structure; Raman spectroscopy; supergene post-mining; Jáchymov; Czech Republic.

1. Introduction

During our systematic mineralogical research focused chiefly on supergene minerals of the Jáchymov ore district in the Czech Republic, many rare and unusual minerals have been discovered (Hloušek *et al.*, 2014). One of these minerals is a new species with the ideal formula $\text{Zn}_2\text{Mg}(\text{CO}_3)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. In this paper, we report its description.

The new mineral is named šlikite in honour of the prominent Czech aristocrat Štěpán Šlik (1487–1526). In 1516, Štěpán Šlik founded the town “Thal”, later “St. Joachimsthal” (now Jáchymov) in the area of a rich deposit of silver in the Krušné hory Mountains. The newly founded town was declared a free mining town by Czech King Louis Jagellonský in 1520. During the ten years of Štěpán Šlik’s reign, Jáchymov became the second largest city in the Czech

Kingdom with about 18,000 inhabitants as a result of “silver fever”. In 1519, Štěpán Šlik also established a mint in Jáchymov, which produced silver coins known as “Joachimsthaler Gulden”, which was abbreviated “Thaler”. The name of the present American currency (“dollar”) derives from the word “Thaler”.

The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2018-120). The holotype specimen is deposited in the collections of the Department of Mineralogy and Petrology of the National Museum in Prague, Cirkusová 1740, Praha 9, Czech Republic, catalogue number P1P 46/2018. Crystals from the holotype used in this study are deposited in Natural History Museum of Los Angeles County under catalogue number 67057.

2. Occurrence

Šlikite was found on several samples originating from the Plavno mine, which is located in the south-eastern part of the Jáchymov ore district (formerly St. Joachimsthal), Krušné hory Mountains, approximately 20 km north of Karlovy Vary, northwestern Bohemia, Czech Republic.

The Jáchymov ore district is a classic example of Ag + As + Co + Ni + Bi and U vein-type hydrothermal mineralization. The ore veins cut a complex of medium-grade metasedimentary rocks of Cambrian to Ordovician age, in the envelope of a Variscan granite pluton. The majority of the ore minerals were deposited during Variscan mineralization from mesothermal fluids (Ondruš *et al.*, 2003a, b and d). Primary and supergene mineralization in this district resulted in extraordinarily varied associations; more than 440 mineral species have been reported from this ore district (Ondruš *et al.*, 1997a and b, 2003c and d; Hloušek *et al.*, 2014). The Jáchymov ore district is a type occurrence for more than 50 mineral species (www.mindat.org/loc-777.html). During recent years, mineralogical research on minerals from Jáchymov has been focused mainly on post-mining supergene minerals formed in abandoned mine adits (e.g., Plášil *et al.*, 2012, 2013a and b, 2014b, 2015a and b, 2017; Kampf *et al.*, 2017; Sejkora *et al.*, 2018) or in the oxidation zone *in situ* (e.g. Sejkora *et al.*, 2011a and b, 2012; Plášil *et al.*, 2014a).

The samples containing šlikite were discovered underground in the Vladimír shaft (2nd level) of the Plavno mine (Jáchymov ore district) by Bohuslav Bureš. The new mineral was found in association with brianyoungite, hexahydrite, hydromagnesite, nesquehonite, serpierite, smithsonite and a relatively abundant phase related to ktenasite on the surface of altered skarn (with sphalerite, magnetite, maghemite and chalcopyrite) in the vicinity of hydrothermal uranium vein No. 13. Šlikite is of post-mining supergene origin.

3. Morphology, physical properties and optical data

Šlikite occurs as bladed crystals in radial aggregates, up to 2 mm across (Figs. 1 and 2) in vugs or on surfaces of fragments of skarn rocks. Individual crystals are very thin blades, elongated on [110] and flattened on {001}, up to 200 µm in length (Figs. 2 and 3). Observed forms are {001} (dominant), with {110}, {100} and {010} likely, based upon scanning-electron-microscope images (Fig. 3). Šlikite is snow-white in colour; crystal aggregates are opaque to transparent; individual crystals or tiny fragments are translucent. The mineral has white streak and vitreous lustre. It does not fluoresce under either short- or long-wave ultraviolet light. Cleavage on {001} is perfect, the Mohs hardness is ~2 (similar to halite), and the mineral is brittle (aggregates) with an uneven fracture; thin blades (fibres) are slightly flexible. The density could not be measured because of the small size of crystals. The calculated density is 2.613 g/cm³ based on the empirical formula and unit-cell



Fig. 1. White radial groups of šlikite blade crystals in association with blue ktenasite, Plavno – Jáchymov, field of view 2.6 mm, photo J. Sejkora.

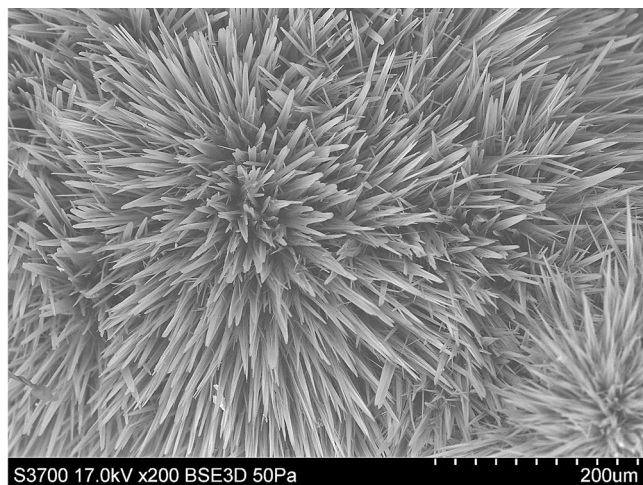


Fig. 2. Radial groups of very thin blades of šlikite, Plavno – Jáchymov; backscattered-electron (BSE) picture J. Sejkora.

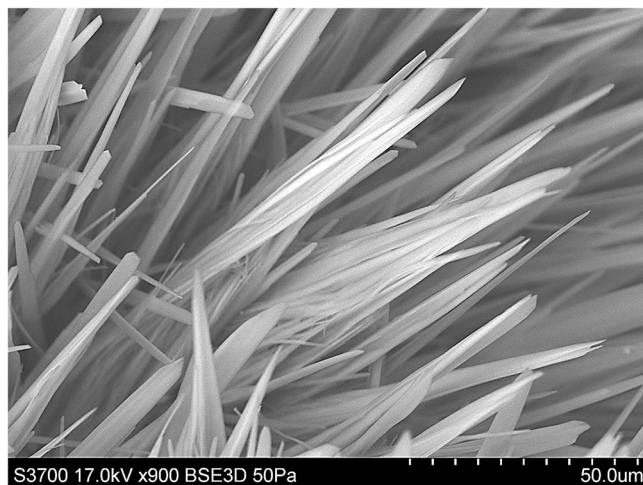


Fig. 3. Very thin, slightly flexible blades of šlikite, Plavno – Jáchymov; BSE picture J. Sejkora.

volume from single-crystal data; 2.558 g/cm³ for the ideal formula.

Šlikite is optically biaxial negative, with $\alpha = 1.50(1)$, $\beta = 1.55(1)$ and $\gamma = 1.59(1)$ (measured in white light), $2V_{\text{meas.}} = 80(1)^\circ$ based on extinction data using EXCALIBUR (Gunter *et al.*, 2004), $2V_{\text{calc.}} = 61.1^\circ$. The large uncertainties in the indices reflect the difficulty in observing the Becke lines for the small, thin blades. Dispersion could not be observed; pleochroism is *X* and *Y* colourless, *Z* very pale yellow; $X \approx Y < Z$. The partially determined optical orientation is $Y \approx c$, $Z \approx [110]$. Because the tiny šlikite blades are too small for conventional single-crystal diffraction and the results of the synchrotron data collection did not provide direct evidence for determining the directions of flattening and elongation, we have made morphological assumptions based upon the crystal structure. Specifically, we assume that the flattening of the blades is parallel to {001}, the plane of the heteropolyhedral layers, and that the elongation is along [110], the direction of the chains of corner-sharing Zn-centred tetrahedra and edge-sharing M3- and Mg5-centred octahedra. These assumptions have been employed above in specifying the optical orientation and the morphology.

The Gladstone–Dale compatibility index, $1 - (K_p/K_c)$, is 0.030 for the empirical formula and unit-cell parameters from single-crystal data, indicating excellent compatibility (Mandarino, 1981).

4. Chemical composition

Samples of šlikite were analyzed with a Cameca SX-100 electron microprobe (Laboratory of electron microscopy and microanalysis of the Masaryk University and Czech Geological Survey, Brno) operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 4 nA, and a beam diameter of 10 μm . The following lines and standards were used: $K\alpha$ for gahnite (Zn), Mg_2SiO_4 (Mg), spessartine (Mn); $L\alpha$ for lammerite (Cu) and Cd (Cd). Peak counting times were 20 s for main elements and 60 s for minor elements, half of this for each background. The raw intensities were converted to concentrations automatically using PAP (Pouchou & Pichoir, 1985) matrix-correction software. The elements Al, As, Bi, Ca, Cl, Co, F, Fe, K, Na, Ni, P, Pb, S, Si, Sb and V were sought, but found to be below the detection limit (about 0.01–0.03 wt%). Water and carbonate contents could not be analyzed directly because of the minute amount of material available. The CO_2 and H_2O contents were confirmed by Raman and infrared spectroscopy and calculated by stoichiometry (obtained from our crystal-structure study) on the basis of 12 O atoms per formula unit (*apfu*).

Table 1 gives the chemical composition of šlikite from Jáchymov (mean of thirteen determinations). Results of the chemical analyses correspond very well with the ideal formula $\text{Zn}_2\text{Mg}(\text{CO}_3)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, in which the *Mg* site is dominantly occupied by Mg atoms (0.72–0.85 *apfu*). The contents of Zn were found there to be in the range 0.12–0.23 *apfu*; minor contents of other elements (Mn, Cu, Cd) do not exceed 0.01–0.04 *apfu*. The empirical

Table 1. Chemical composition of šlikite from Jáchymov (wt%).

Constituent	Mean 13 analyses	Range	<i>SD</i>
MgO	8.39	7.72–8.88	0.35
ZnO	46.28	44.10–48.47	1.52
CuO	0.05	0.00–0.32	0.10
MnO	0.68	0.56–0.82	0.08
CdO	0.04	0.00–0.21	0.06
CO_2^*	23.10		
H_2O^*	23.65		
Total	102.19		

Note: contents of H_2O^* and CO_2^* were calculated on the basis of ideal composition derived from results of the crystal-structure study.

formula of šlikite based on 12 O atoms is $\text{Zn}_{2.17}\text{Mg}_{0.79}\text{Mn}_{0.04}\text{C}_2\text{O}_{12}\text{H}_{10}$ or in structural format $\text{Zn}_{2.00}(\text{Mg}_{0.79}\text{Zn}_{0.17}\text{Mn}_{0.04})_{\Sigma 1.00}(\text{CO}_3)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. The ideal formula is $\text{Zn}_2\text{Mg}(\text{CO}_3)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, which requires ZnO 42.70, MgO 10.57, CO_2 23.09, H_2O 23.64, total 100 wt%.

5. Raman and infrared spectroscopy

The Raman spectrum was collected in the range 4000–20 cm^{-1} using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on confocal Olympus microscope. The Raman signal was excited by a green 532 nm diode-pumped solid-state laser and detected by a CCD detector. The experimental parameters were: 50x objective, 30 s exposure time, 100 exposures, 400 lines/mm grating, 25 μm pinhole spectrograph aperture and 4 mW laser power level. The instrument was set up by a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration) and standardized white-light sources (intensity calibration). Spectral manipulations were performed using the Omnic 9 software (Thermo Scientific).

The Raman spectrum of šlikite in the full range is given in Fig. 4. Its interpretation is based on the paper by Čejka *et al.* (2013) and references therein. A very strong band observed at 3595 cm^{-1} was assigned to the ν OH stretching vibrations of free or very weakly hydrogen-bonded hydroxyls (approximately >3.2 Å). Weak bands at 3436, 3254 and 2949 cm^{-1} relate to the hydrogen-bonded water molecules and hydroxyls (approximately 2.83, 2.74 and 2.65 Å, respectively) (Libowitzky, 1999). Weak bands at 1553 and 1439 cm^{-1} are attributed to the doubly degenerate ν_3 CO_3^{2-} antisymmetric stretching vibrations, and a strong band at 1084 and a very weak band at 1012 cm^{-1} to the ν_1 CO_3^{2-} symmetric stretching vibrations. A very weak band connected with the δ M^{2+} –OH was observed at 983 cm^{-1} . Weak bands at 852, 826 and 802 cm^{-1} are attributed to the ν_2 (δ) CO_3^{2-} out-of-plane bending vibrations; however, some overlap or coincidence with the δ M^{2+} –OH or libration modes of water molecules may be expected. Very weak bands at 772, 747 and 712 cm^{-1} are attributed to the doubly degenerate ν_4 (δ) CO_3^{2-} in-plane bending vibrations. With regard to the $M^{2+}(\text{O},\text{OH},\text{H}_2\text{O})_x$ octahedra and tetrahedra ($x = 6, 4$), present in the structure of šlikite, very weak, weak and medium bands at 564, 548, 508, 485, 467, 443, 389 and 371 cm^{-1} ,

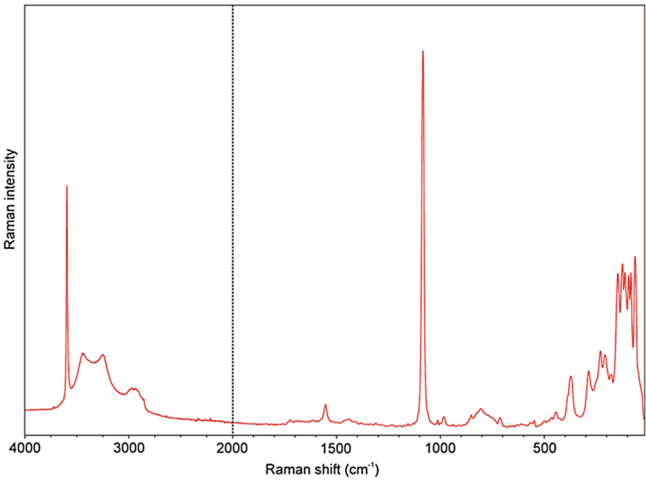


Fig. 4. Raman spectrum of šlikite (split at 2000 cm⁻¹).

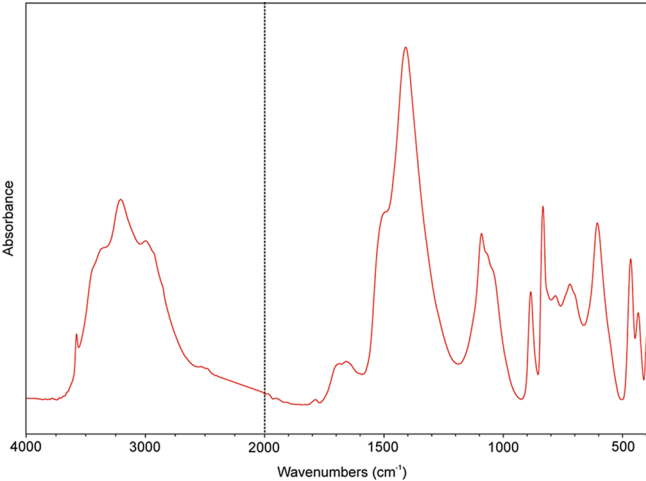


Fig. 5. Infrared spectrum of šlikite (split at 2000 cm⁻¹).

respectively, are assigned to the νM^{2+} -OH stretch; those at 286, 247, 229 cm⁻¹ and the medium strong band at 206 cm⁻¹ to the $\delta O-M^{2+}$ -OH bend, and strong and medium bands at 177, 145 125 and 109 cm⁻¹ are assigned to the $\delta HO-M^{2+}$ -OH bend. Lattice modes are observed at 93, 82, 61, 45 and 33 cm⁻¹.

The infrared vibrational spectrum of šlikite was recorded by the ATR method on a Nicolet iS5 spectrometer (range 4000–400 cm⁻¹, resolution 4 cm⁻¹, 64 scans). The infrared spectrum (Fig. 5) confirms the presence of molecular water, hydroxyls and carbonate ions. A weak band at 3577 cm⁻¹ is assigned to the ν OH stretching vibrations of free or only very weakly hydrogen-bonded hydroxyls. The very strong band at 3205 cm⁻¹, strong bands at 3367 and 2998 cm⁻¹ and shoulders at 3448 and 2931 cm⁻¹ may be attributed to the ν OH stretching vibrations of hydrogen-bonded water molecules and hydroxyls. According to Libowitzky (1999), inferred O-H...O hydrogen bond lengths vary in the range from approximately ~3.15–2.64 Å. The O-H...O hydrogen

Table 2. X-ray powder diffraction data (*d* in Å) for šlikite from Jáchymov.

<i>I</i> _{obs.}	<i>I</i> _{calc.}	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>h</i>	<i>k</i>	<i>l</i>
100.0	100.0	13.575	13.575	0	0	1
0.7	0.1	6.783	6.787	0	0	2
0.8	2.9	5.314	5.313	1	1	0
0.3	0.8	5.004	5.006	1	0	1
0.3	0.6	4.872	4.862	0	1	2
0.5	1.9	4.829	4.829	1	1	1
30.6	15.9	4.525	4.525	0	0	3
0.1	2.4	4.349	4.340	1	1	2
0.3	1.2	4.041	4.043	1	1	2
1.7	10.6	3.573	3.576	1	1	3
4.7	10.0	3.406	3.405	1	1	1
5.4	1.9	3.394	3.394	0	0	4
0.9	3.5	3.334	3.334	1	1	0
1.3	1.5	3.326	3.327	1	1	3
0.4	0.9	3.274	3.273	1	1	2
0.9	3.9	3.092	3.092	1	1	1
2.6	10.0	2.996	2.998	1	1	3
0.6	2.3	2.959	2.960	1	1	4
3.1	10.4	2.773	2.773	1	1	2
0.5	0.3	2.715	2.715	0	0	5
1.3	5.4	2.670	2.672	1	1	4
0.5	4.0	2.572	2.572	2	2	1
0.6	5.5	2.536	2.537	2	2	2
0.3	1.2	2.4529	2.4518	1	1	3
1.2	7.7	2.4144	2.4147	2	2	2
0.4	2.7	2.3670	2.3675	2	2	3
0.2	1.1	2.3565	2.3586	1	1	5
1.0	2.7	2.3487	2.3492	1	1	5
0.3	0.1	2.2635	2.2625	0	0	6
0.3	0.6	2.1368	2.1386	1	1	6
0.3	1.0	2.1170	2.1152	2	0	5
0.3	2.2	2.0476	2.0452	2	0	4
0.1	1.8	2.0456	2.0469	3	1	1
0.4	1.6	1.9722	1.9720	2	2	5
0.8	0.8	1.9392	1.9392	0	0	7
0.2	1.5	1.8405	1.8410	2	0	5
0.3	2.0	1.8331	1.8331	2	2	5
0.2	2.9	1.7880	1.7880	2	2	6
0.3	1.7	1.7828	1.7826	0	2	7
0.1	1.7	1.7734	1.7728	3	3	1
0.8	4.5	1.7029	1.7027	2	2	2
0.6	0.3	1.6979	1.6968	0	0	8
0.3	1.7	1.6336	1.6331	1	3	4
0.3	1.6	1.6005	1.6018	0	2	6

*I*_{calc.} calculated from the crystal-structure data.

bond lengths inferred from wavenumbers of related Raman and infrared bands are comparable. Weak bands at 1694 and 1653 cm⁻¹ are connected with ν_2 (δ) H₂O bending vibrations of hydrogen-bonded water molecules. The very strong band at 1408 cm⁻¹ with a shoulder at 1504 cm⁻¹ is assigned to the doubly degenerate ν_3 CO₃²⁻ antisymmetric stretching vibrations and the strong band at 1093 cm⁻¹ with a shoulder at 1065 cm⁻¹ to the CO₃²⁻ symmetric stretching vibrations. A strong band at 835 cm⁻¹ and a medium strong band at 887 cm⁻¹ are attributed to the ν_2 (δ) CO₃²⁻ out-of-plane bending vibrations and medium bands at 781 and 720 cm⁻¹ with a shoulder at 699 cm⁻¹ to the doubly degenerate ν_4 (δ) CO₃²⁻ in-plane bending vibrations. Some of

these bands and shoulders, however, may coincide with libration modes of water molecules or δM^{2+} –OH bending vibrations. Strong bands at 605 and 466 cm^{-1} and a medium strong band at 434 cm^{-1} may be connected with M^{2+} –OH stretch (Čejka *et al.*, 2013).

6. X-ray powder diffraction

Powder X-ray diffraction (XRD) data for šlikite were collected on a Bruker D8 Advance diffractometer (National Museum, Prague) with a solid-state 1D LynxEye detector using $\text{CuK}\alpha$ radiation and operating at 40 kV and 40 mA. In order to minimize the background, the powder samples were placed on the surface of a flat silicon wafer without any liquid. The powder pattern was collected using Bragg–Brentano geometry in the range 3–70° 2 θ , in 0.01° steps with a counting time of 20 s per step. Positions and intensities of reflections were found and refined using the PearsonVII profile-shape function with the ZDS program package (Ondruš, 1993) and the unit-cell parameters were refined by the least-squares algorithm implemented by Burnham (1962). The experimental powder pattern was indexed in line with the calculated values of intensities obtained from the crystal-structure refinement, based on the Lazy Pulverix program (Yvon *et al.*, 1977). The experimental powder data given in Table 2 agree well with the pattern calculated from the single-crystal data; experimental intensities are partly affected by preferred orientation (001). The refined unit-cell parameters of šlikite are: $a = 6.326(2)$, $b = 6.322(2)$, $c = 13.913(2)$ Å, $\alpha = 99.88(1)^\circ$, $\beta = 92.96(1)^\circ$, $\gamma = 114.78(1)^\circ$ and $V = 492.9(3)$ Å³.

7. Single-crystal X-ray diffraction

A thin blade of šlikite ($0.010 \times 0.003 \times 0.007$ mm) was used for a data collection on the macromolecular microfocus beamline MX2 of the Australian Synchrotron. Data were collected at 100 K with monochromatic wavelength, 0.7107 Å. The MX2 beamline is used predominantly for proteins and other organic compounds and is operated at 100 K. We confirmed that the low temperature used for the data collection did not bring about a phase change by comparing the pattern calculated from the single-crystal structural model to the room-temperature powder XRD pattern.

A structure solution in space group $P\bar{1}$ was obtained using SHELXT (Sheldrick, 2015). The model was found to have a layer structure, parallel to {001} with the layers including two independent CO_3 groups, two independent Zn-centred tetrahedral sites (Zn1 and Zn2) and two octahedral sites (M3 and Mg5); the M3 site was found to contain a mix of Zn and Mg and the Mg5 site was only fractionally occupied, by Mg. The interlayer region was found to be populated with octahedrally coordinated, hydrated cations $\text{Mg}_4(\text{H}_2\text{O})_6$ and H-bonded H_2O molecules. Application of TWINROT MAT showed twinning by 180° rotation about [001]. The structure was refined with anisotropic displacement parameters in JANA2006 (Petříček *et al.*, 2014),

Table 3. Summary of data-collection conditions, crystallographic details and structure refinement for šlikite.

Simplified formula	$\text{Zn}_2\text{Mg}(\text{CO}_3)_2(\text{OH})_2(\text{H}_2\text{O})_4$
Temperature	100 K
Wavelength	0.7107 Å
Space group	$P\bar{1}$
Unit-cell dimensions	$a = 6.335(4)$ Å, $\alpha = 99.985(7)^\circ$ $b = 6.340(1)$ Å, $\beta = 92.74(1)^\circ$ $c = 13.923(4)$ Å, $\gamma = 114.93(2)^\circ$
Volume	$494.8(4)$ Å ³
Z	2
Absorption coefficient	5.41 mm^{-1}
Crystal size	$0.010 \times 0.003 \times 0.007 \text{ mm}^3$
θ range for data collection	$1.5\text{--}31.9^\circ$
Index ranges	$-8 \leq h \leq 8$, $-9 \leq k \leq 8$, $0 \leq l \leq 18$
Reflections collected	7249
Independent reflections	2224 [$R_{\text{int}} = 0.058$]
Reflections with $I_o > 3\sigma(I)$	1594
Refinement method	Full-matrix least-squares on F
Constraints/restraints/parameters	6/0/164
Goodness-of-fit on F^2	1.99
Final R indices [$I > 3\sigma(I)$]	$R_{\text{obs}} = 0.094$, $wR_{\text{obs}} = 0.113$
R indices (all data)	$R_{\text{obs}} = 0.114$, $wR_{\text{obs}} = 0.122$
Largest diff. peak and hole	2.29 and -1.22 e. Å^{-3}

resulting in convergence at relatively high values of R (see Table 3). The high R factors reflect the relatively poor quality of the very weak diffraction data, from the ultra-thin blade. Details of the data collection and refinement are given in Table 3. The refined coordinates, equivalent isotropic displacement parameters, site occupancies and bond-valence sums (Gagné & Hawthorne, 2015) are given in Table 4. Anisotropic displacement parameters are given in Table 5. Polyhedral bond distances, as well as likely H-bonded anion pairs are reported in Table 6.

A view of the structure of šlikite is shown in projection along [110] in Fig. 6. Heteropolyhedral layers parallel to {001} are separated by interlayer hydrated cations, $\text{Mg}_4(\text{H}_2\text{O})_6$ and H-bonded H_2O . Within the layers, chains of corner-connected tetrahedra, centred on Zn1 and Zn2, are oriented along [110] (normal to the figure) and share corners with [110] chains of edge-shared octahedra, centred on M3 and Mg5. Two independent CO_3 groups, centred on C1 and C2, connect the two types of chains. Projections along [001] of the heteropolyhedral layers and the interlayer region are shown in Figs. 7 and 8. The latter shows that the $\text{Mg}_4(\text{H}_2\text{O})_6$ hydrated cations are surrounded by a pseudo-trigonal array of Ow4 water molecules, with H-bonds directed to the coordinated water molecules Ow2 and Ow3 (Table 6). The coordinated water molecules Ow1–Ow3 form H-bonds to the layer anions O2, O3, O5 and O6 (Table 6).

The bond distances in Table 6, as well as the BVS values in Table 4, show expected values for the two independent CO_3 groups, for the two Zn-centred tetrahedral sites and for the octahedrally coordinated M3 and Mg4 sites. The partially occupied Mg5 site is unusual in having much longer bonds than expected for Mg. This site is only one-third occupied, and it is likely that when it is occupied, the surrounding anions move inwards to meet the valence requirements

Table 4. Refined atomic coordinates, equivalent isotropic displacement parameters ($\text{\AA}^2$), site occupancies and bond valence sums (BVS).

	Occ.	x	y	z	U_{eq}	BVS
Zn1	1	0.38581(16)	0.48426(17)	0.85229(7)	0.0212(4)	1.93
Zn2	1	0.88988(16)	0.98993(17)	0.85488(7)	0.0215(4)	1.91
Mg3(M3)	0.60(1)	0	0.5	1	0.0154(8)	1.96
Zn3(M3)	0.40(1)	0	0.5	1	0.0154(8)	2.01
Mg4	1	0.5	0.5	0.5	0.0323(17)	2.02
Mg5	0.33(2)	0.487(4)	−0.028(3)	0.0009(18)	0.014(5)	1.33
C1	1	1.1065(16)	0.7081(15)	0.8195(9)	0.031(4)	4.00
C2	1	0.6381(15)	0.2353(14)	0.8165(8)	0.028(3)	4.04
O1	1	0.1474(10)	0.2941(9)	0.9278(4)	0.0170(18)	1.30
O2	1	1.1985(10)	0.5786(11)	0.7651(4)	0.021(2)	1.59
O3	1	0.5020(11)	0.2949(12)	0.7609(4)	0.022(2)	1.62
O4	1	0.6422(11)	0.7881(11)	0.9232(5)	0.023(2)	1.06
O5	1	1.0058(10)	0.8040(11)	0.7638(4)	0.023(2)	1.62
O6	1	0.7190(11)	0.0983(11)	0.7622(4)	0.023(2)	1.59
O7	1	0.6800(11)	0.2980(11)	0.9033(6)	0.029(2)	2.13
O8	1	1.1196(11)	0.7458(11)	0.9059(5)	0.030(2)	2.17
Ow1	1	0.3344(12)	0.2032(11)	0.5683(5)	0.035(2)	0.30
Ow2	1	0.8272(13)	0.5927(13)	0.5727(5)	0.038(3)	0.36
Ow3	1	0.5693(12)	0.2809(13)	0.3901(5)	0.035(3)	0.35
Ow4	1	0.1150(14)	−0.1834(14)	0.4186(5)	0.040(3)	–

Table 5. Anisotropic displacement parameters ($\text{\AA}^2$).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0171(5)	0.0194(5)	0.0259(5)	0.0051(4)	0.0044(4)	0.0089(4)
Zn2	0.0179(5)	0.0185(5)	0.0255(5)	0.0047(4)	0.0030(4)	0.0069(4)
M3	0.0104(10)	0.0122(10)	0.0196(11)	0.0000(7)	0.0031(7)	0.0066(7)
Mg4	0.034(2)	0.042(2)	0.022(2)	0.019(2)	0.0013(16)	0.0031(17)
C1	0.020(4)	0.018(4)	0.071(7)	0.013(3)	0.024(4)	0.029(4)
C2	0.018(4)	0.009(3)	0.062(6)	0.011(3)	0.008(4)	0.009(3)
O1	0.018(2)	0.010(2)	0.024(3)	0.007(2)	0.004(2)	0.0050(19)
O2	0.021(3)	0.023(3)	0.017(3)	0.008(2)	0.004(2)	0.006(2)
O3	0.022(3)	0.032(3)	0.015(2)	0.014(2)	0.006(2)	0.009(2)
O4	0.018(3)	0.020(3)	0.036(3)	0.008(2)	0.011(2)	0.016(2)
O5	0.018(3)	0.028(3)	0.023(3)	0.008(2)	0.000(2)	0.007(2)
O6	0.030(3)	0.025(3)	0.015(3)	0.014(3)	0.004(2)	0.004(2)
O7	0.020(3)	0.016(2)	0.055(4)	0.010(2)	0.008(3)	0.013(3)
O8	0.022(3)	0.027(3)	0.037(4)	0.007(3)	0.000(2)	0.006(3)
Ow1	0.031(3)	0.030(3)	0.028(3)	0.000(3)	−0.003(2)	0.003(2)
Ow2	0.038(4)	0.047(4)	0.031(3)	0.025(4)	−0.002(3)	0.003(3)
Ow3	0.032(3)	0.041(4)	0.027(3)	0.010(3)	0.013(3)	0.011(3)
Ow4	0.053(4)	0.046(4)	0.026(3)	0.023(4)	0.012(3)	0.010(3)

for the Mg. The carbon atoms C1 and C2, and the corresponding O8 and O7 anions that link the C atoms to Mg5 all have $U^{33} > U^{11}, U^{22}$, which most likely reflect displacements of these atoms in response to the Mg5 site being occupied or vacant. The formula from the crystal-structure refinement is $\text{Zn}_{2.2}\text{Mg}_{0.96}(\text{CO}_3)_2(\text{OH})_{1.68}\text{O}_{0.32}(\text{H}_2\text{O})_4$. Based on the BVS values in Table 4, the OH sites are O1 and O4.

8. Relationship to other species

Šlikite is a member of the group of carbonates with additional anions and H_2O , with medium-sized cations – Strunz

class 5.DA.05. It has a previously unreported structure type. It does not correspond to any unnamed mineral species or synthetic compound. We know many natural oxysalts, including silicates, with species-defining Mg and significant admixture of Zn, and *vice versa*, in which these crystallographically similar bivalent cations are disordered and commonly occur in the same crystallographic site. The newly described šlikite is an interesting counter-example where Mg and Zn are ordered in separate sites. Other known examples are rinmanite (Holtstam *et al.*, 2001), zemannite (Cametti *et al.*, 2017) and probably also reaphookhillite (Elliott, 2019), for which full data are not published yet.

Table 6. Polyhedral bond distances and likely H-bonded anions (Å).

Zn1–O1	1.970(6)	Zn2–O1	1.984(5)
Zn1–O2	1.992(7)	Zn2–O4	1.965(6)
Zn1–O3	1.975(7)	Zn2–O5	1.957(7)
Zn1–O4	1.972(5)	Zn2–O6	2.030(8)
Av.	1.977	Av.	1.984
M3–O1 ×2	2.059(7)		
M3–O7 ×2	2.131(6)	Mg5–O4	2.03(3)
M3–O8 ×2	2.125(8)	Mg5–O4	2.16(3)
Av.	2.105	Mg5–O7	2.57(2)
		Mg5–O7	2.28(2)
Mg4–Ow1 ×2	2.142(7)	Mg5–O8	2.34(2)
Mg4–Ow2 ×2	2.062(8)	Mg5–O8	2.50(2)
Mg4–Ow3 ×2	2.073(8)	Av.	2.313
Av.	2.092		
C1–O2	1.346(13)	C2–O3	1.343(14)
C1–O5	1.351(15)	C2–O6	1.330(13)
C1–O8	1.178(14)	C2–O7	1.186(13)
Av.	1.291	Av.	1.286
Ow1–O3	2.71	Ow4–Ow1	2.72
Ow2–O5	2.72	Ow4–Ow2	2.79
Ow3–O2	2.73		
Ow3–O6	2.79		

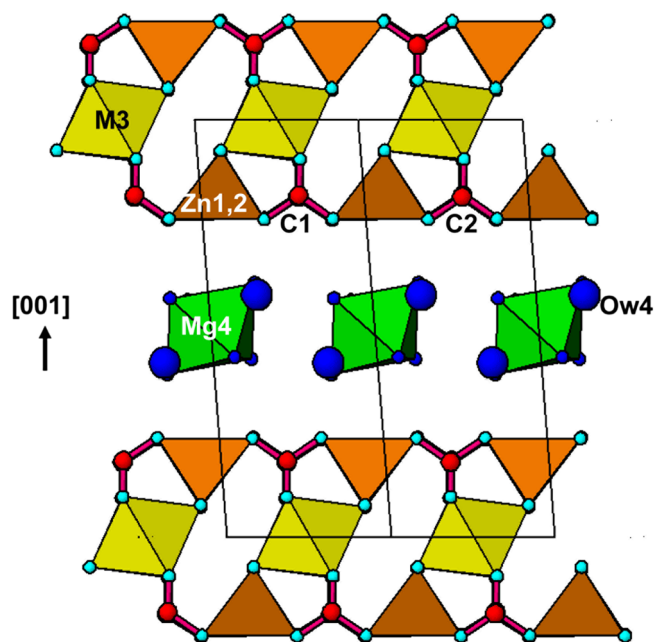


Fig. 6. [110] projection of the šlikite crystal structure.

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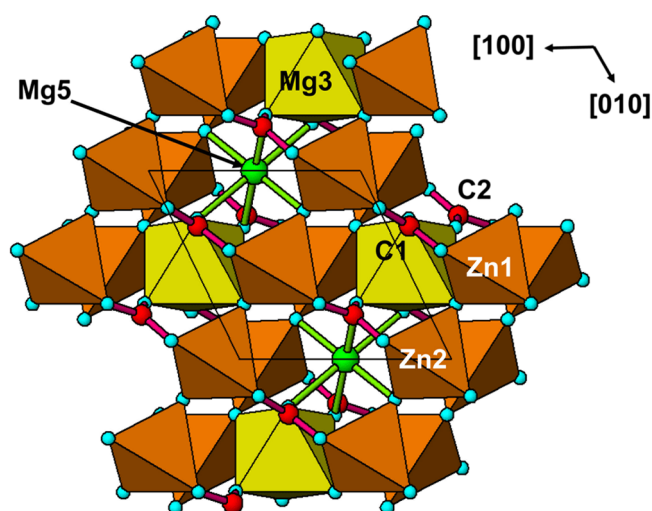


Fig. 7. The heteropolyhedral layer in šlikite, viewed along [001].

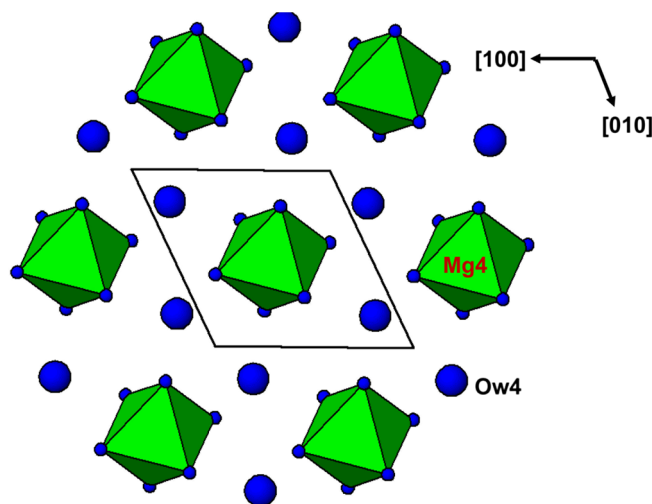


Fig. 8. The interlayer region in šlikite, viewed along [001].

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