

Erikjonssonite, $(\text{Pb}_{32}\text{O}_{21})[(\text{V},\text{Si},\text{Mo},\text{As})\text{O}_4]_4\text{Cl}_9$, a new mineral from the Kombat mine and structural classification of layered lead oxychlorides related to litharge

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Abstract: The new lead oxychloride vanadate mineral erikjonssonite was discovered at the abandoned Kombat copper mine, Grootfontein district, Namibia, in association with hausmannite, calcite, glaucocochoite, baryte, cerussite, and an insufficiently studied mineral chemically related to kombatite. Erikjonssonite forms thick tabular orange-red grains up to $0.3 \times 0.5 \times 0.5 \text{ mm}^3$. The new mineral is brittle, has Mohs' hardness of $2\frac{1}{2}$ and an uneven fracture. Distinct cleavage on (010) is observed. $D_{\text{calc}} = 7.967 \text{ g/cm}^3$. The reflectance values [R_{max} , %/ R_{min} , % (λ , nm)] are: 20.4/18.9 (470), 19.0/17.6 (540), 18.5/17.1 (589), 18.0/16.6 (650). The infrared spectrum shows the absence of H-, C- and B-bearing groups. The chemical composition is (wavelength-dispersive mode electron microprobe, wt%): SiO_2 0.86, V_2O_5 1.73, As_2O_5 0.96, MoO_3 1.70, PbO 92.54, Cl 4.15, $-\text{O}=\text{Cl}$ -0.94 , total 101.00. The empirical formula based on 46 O + Cl atoms per formula unit (apfu) is $\text{Pb}_{31.50}(\text{V}_{1.45}^{5+}\text{Si}_{1.09}\text{Mo}_{0.90}^{6+}\text{As}_{0.63}^{5+})_{\Sigma 4.07}\text{Cl}_{8.89}\text{O}_{37.11}$. The simplified formula is $(\text{Pb}_{32}\text{O}_{21})[(\text{V},\text{Si},\text{Mo},\text{As})\text{O}_4]_4\text{Cl}_9$. The crystal structure has been refined to $R = 4.3\%$ based on 7730 independent reflections with $I > 2\sigma(I)$. Erikjonssonite is monoclinic, $C2/c$, $a = 23.200(5)$, $b = 22.708(5)$, $c = 12.418(3) \text{ \AA}$, $\beta = 102.167(4)^\circ$, $V = 6395(2) \text{ \AA}^3$, and $Z = 4$. The structure of erikjonssonite is very similar to that of hereroite: in both minerals two $[\text{Pb}_{32}\text{O}_{21}]^{22+}$ oxocentred blocks formed by OPb_4 tetrahedra with inserted TO_4 tetrahedral groups alternate with one chloride sheet. Average $\langle \text{T}-\text{O} \rangle$ bond lengths in the tetrahedral groups demonstrate very similar values which is interpreted as both T1 and T2 sites having mixed occupancies of V^{5+} , Si^{4+} , Mo^{6+} and As^{5+} , unlike hereroite where $\langle \text{T}-\text{O} \rangle$ bond lengths are different and one site is exclusively occupied by As^{5+} . The strongest lines of the powder X-ray diffraction pattern [d , Å (I , %) (hkl)] are: 3.501 (24) (531, $\bar{2}61$), 2.980 (100) (551, $\bar{2}24$), 2.794 (45) ($\bar{8}02$, $\bar{5}14$), 1.990 (24) ($\bar{8}82$), 1.977 (21) ($\bar{6}06$), 1.762 (20) (715, $\bar{8}10.2$, 10.6.2), 1.648 (33) ($\bar{1}1.5.5$). The mineral is named in honour of the Swedish mineralogist Erik Jonsson (b. 1967). The holotype material is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia. The concept of a "defect number (DN)" which is the number of O^{2-} ions removed from the ideal $[\text{PbO}]$ block per cavity area is suggested in order to classify the layered Pb oxychloride minerals structurally related to litharge.

Key-words: erikjonssonite; new mineral; lead oxychloride vanadate; crystal structure; litharge; layered structures; Kombat mine; Namibia.

1. Introduction

This paper describes a new lead oxychloride vanadate mineral from the abandoned Kombat copper mine situated in the Grootfontein district, Otjozondjupa region, Northern Namibia ($19^\circ 46' 59'' \text{ S}$, $18^\circ 1' 0'' \text{ E}$). Kombat

is the type locality for 16 mineral species including several lead oxychloride minerals: kombatite $\text{Pb}_{14}(\text{VO}_4)_2\text{O}_9\text{Cl}_4$ (Rouse *et al.*, 1986), asisite $(\text{Pb}_7\text{SiO}_8)\text{Cl}_2$ (Rouse *et al.*, 1988; Welch, 2004), damaraite $\text{Pb}_3\text{O}_2(\text{OH})\text{Cl}$ (Criddle *et al.*, 1990), vladkrivovichevite $[\text{Pb}_{32}\text{O}_{18}\text{Mn}_2(\text{BO}_3)_8]\text{Pb}_4\text{OCl}_{14} \cdot 2\text{H}_2\text{O}$ (Turner *et al.*, 2012a), hereroite

{(Pb₃₂O₂₀(O,□))(AsO₄)₂((Si,As,V,Mo)O₄)₂}Cl₉ (Turner *et al.*, 2012a; Siidra *et al.*, 2013a), janchevite Pb₇V⁵⁺(O_{8.5}□_{0.5})Cl₂ (Chukanov *et al.*, 2018a), and erikjonssonite {(Pb₃₂O₂₁)[(V,Si,Mo,As)O₄]₄}Cl₉ (this work). Most of these minerals were discovered in late-stage zoned veins which are crosscutting the primary hausmannite ores (Criddle *et al.*, 1990).

The new mineral described in the present paper is named erikjonssonite in honour of the Swedish mineralogist Dr. Erik Jonsson (b. 1967), Senior Geologist of the Geological Survey of Sweden, Department of Mineral Resources, and Adjunct Professor of the Dept. of Earth Sciences, Uppsala University. Erik Jonsson has extensive experience of field work in both the Fennoscandian shield and Africa. Non-sulfide lead mineralization of the Långban deposit in Sweden and the Kombat mine in Namibia is an area of particular specialist interest to him.

Erikjonssonite and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2018-058). The holotype specimen is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 5226/1.

2. General appearance and physical properties

Erikjonssonite is known only in a single specimen of hausmannite rock. The new mineral occurs as thick tabular, flattened on (010) anhedral to subhedral orange-red grains up to $0.3 \times 0.5 \times 0.5$ mm³ (Figs. 1 and 2) in a polymineral granular aggregate composed of hausmannite, calcite, glaucocroite, as well as accessory baryte, cerussite and an insufficiently studied lead oxychloride.

The last-mentioned mineral forms yellow-orange anhedral grains up to 0.2 mm across. According to semiquantitative EDS analysis, it is chemically close to the kombatite end-member. This mineral distinctly differs from erikjonssonite in low contents of Si, Mo and As, as well as in lighter yellow-orange colour. No other lead oxychlorides were found in this association.

Erikjonssonite is brittle, has Mohs' hardness of 2½ and an uneven fracture. Hardness was measured by the micro-indentation method (load 20 g, six measurements) and is in the range 69.5–89.3 kg/mm² (mean 79.8 kg/mm²). A distinct cleavage on (010) is observed.

Density could not be measured because of the lack of heavy liquids with densities more than 5 g cm⁻³ and the small size of the mineral grains, insufficient for a volumetric method. Density calculated using the empirical formula is equal to 7.967 g cm⁻³.

Reflectance values (R_{\max}/R_{\min}) for erikjonssonite (Table 1) were measured on a polished microprobe section in air using a MSF-21 microspectrophotometer (LOMO JSC, St. Petersburg, Russia). SiC (Reflection standard 474251, No. 545, Germany) was used as a standard. Erikjonssonite is weakly anisotropic, with $\Delta R_{589} = 1.4\%$. The colour in reflected light is pale grey, with deep red to brown-red internal reflections.



Fig. 1. Erikjonssonite grains (orange-red) with hausmannite (black), calcite (colourless), and an unidentified lead oxychloride mineral

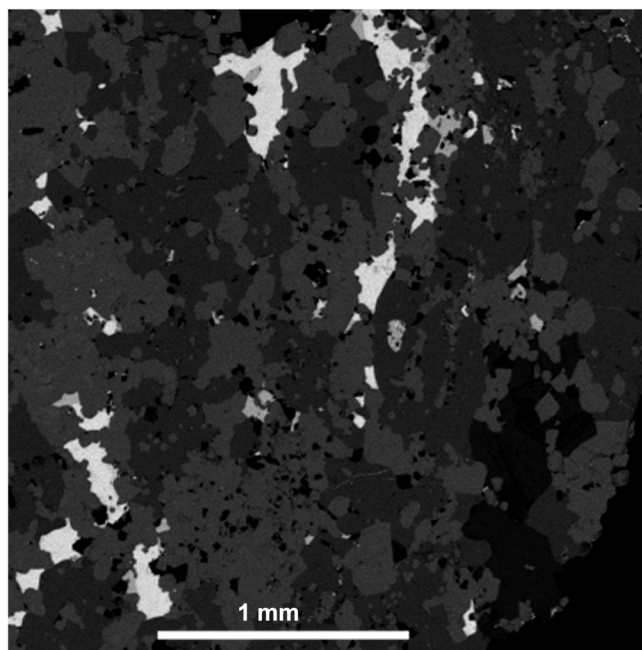


Fig. 2. Erikjonssonite (white) with hausmannite (light grey), glaucocroite (dark grey), and calcite (black). Polished section; back-scattered electron image.

3. Infrared spectroscopy

In order to obtain the infrared (IR) absorption spectrum of erikjonssonite, a powdered monomineral fraction was mixed with dried KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) with a resolution of 4 cm⁻¹ and 16 scans. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The IR spectrum of erikjonssonite (Fig. 3) contains bands of Mo⁶⁺-O-stretching vibrations (at 594 cm⁻¹), V⁵⁺-O and As⁵⁺-O stretching vibrations (at 740–796 cm⁻¹), Si-O

Table 1. Reflectance values (R_{\max}/R_{\min}) for erikjonssonite.

λ (nm)	R_{\max}	R_{\min}	λ (nm)	R_{\max}	R_{\min}
400	22.3	20.7	560	18.8	17.4
420	21.6	20.15	580	18.58	17.2
440	21.1	19.6	589	18.5	17.1
460	20.6	19.1	600	18.48	17.0
470	20.4	18.9	620	18.2	16.8
480	20.2	18.7	640	18.1	16.7
500	19.7	18.2	650	18.0	16.6
520	19.35	17.9	660	17.9	16.5
540	19.06	17.6	680	17.7	16.35
546	19.0	17.6	700	17.5	16.2

In bold: reference wavelengths of the Commission on Ore Mineralogy (COM).

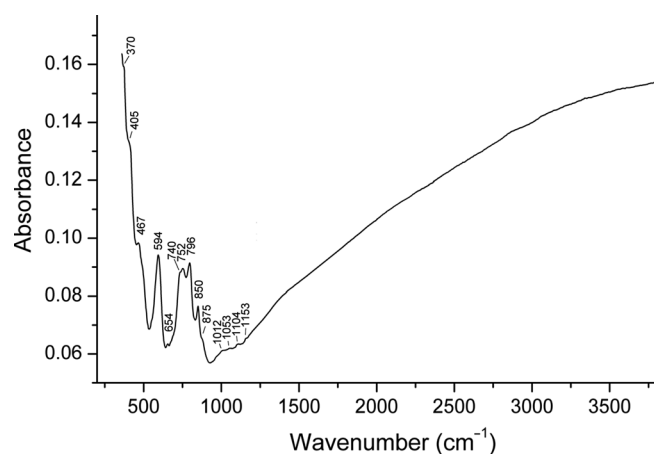


Fig. 3. Powder infrared absorption spectrum of erikjonssonite.

stretching vibrations (at 860–875 cm^{-1}), O–T–O bending vibrations (at 405–467 cm^{-1} , T = Mo, V, As, Si), and Pb–O stretching vibrations (strong absorption below 400 cm^{-1}). Very weak bands in the range from 1000 to 1200 cm^{-1} correspond to overtones and combination modes. A strong IR radiation scattering is observed above 1500 cm^{-1} .

The absence of IR bands in the range 890–990 cm^{-1} indicates the absence of vanadyl VO^{2+} and molybdenyl MoO^{3+} cations in the structure of erikjonssonite (Larson & Moore, 1963; Kalinnikov *et al.*, 1967; Stranford & Condrate, 1984; Said *et al.*, 1992). No bands of CO_3^{2-} anions and H-bearing groups are observed in the range 1200–3800 cm^{-1} .

4. Chemical data

Seven chemical analyses were carried out on three orange-red grains using an SEM Tescan XMU equipped Oxford INCA Wave 700 detector (WDS mode, 20 kV, 20 nA, 1 μm beam diameter) housed at the Institute of Experimental Mineralogy RAS, Chernogolovka. Analytical data are given in Table 2. The measurement of other elements with atomic number >8 revealed them to be below detection limits. H_2O and CO_2 were not measured because no bands of CO_3^{2-}

Table 2. Mean chemical composition of erikjonssonite (in wt%, SD = standard deviation on last digit given).

Constituent	Mean (SD)	Range	Standard
SiO_2	0.86(9)	0.65–1.02	SiO_2
V_2O_5	1.73(11)	1.55–1.96	V
As_2O_5	0.96(5)	0.89–1.04	InAs
MoO_3	1.70(9)	1.55–1.79	Mo
PbO	92.54(25)	92.01–92.83	PbTe
Cl	4.15(11)	3.92–4.49	NaCl
–O = Cl	–0.94		
Total	101.00		

Table 3. Powder X-ray diffraction data (d in \AA) of erikjonssonite.

I_{obs} (%)	d_{obs}	I_{calc} * (%)	d_{calc} **	hkl
2	11.32	4	11.354	020
6	5.67	11	5.677, 5.669	040
15	3.892	16	3.923	511
3	3.779	5	3.785	060
24	3.501	20, 2	3.524, 3.507	531, $\bar{2}$ 61
100	2.980	100, 2	2.994, 2.990	551, 224
13	2.835	18	2.838	080
45	2.794	43, 1	2.805, 2.790	802, $\bar{5}$ 14
6	2.507	4	2.515	571
8	2.269	10	2.271	0.10.0
6	2.248	5	2.254	862
24	1.990	14	1.995	882
21	1.977	17	1.964	606
2	1.891	2	1.892	0.12.0
1	1.829	0.5, 0.5	1.832, 1.827	$\bar{2}$.10.4, $\bar{3}$.11.3
20	1.762	2, 11, 2	1.766, 1.765, 1.762	715, $\bar{8}$.10.2, 10.6.2
5	1.722	2, 0.5	1.725, 1.725	735, 12.4.1
33	1.648	13	1.646	$\bar{1}$ 1.5.5
8	1.622	5, 1	1.630, 1.622	10.8.2, 0.14.0
18	1.598	11	1.600	5.13.1
4	1.567	2	1.569	$\bar{8}$.12.2
3	1.553	1	1.555	775
5	1.491	4	1.497	10.10.2
7	1.398	4, 0.5	1.403, 1.395	$\bar{1}$ 6.0.4, $\bar{1}$ 5.7.2

*For the calculated pattern, only reflections with intensities ≥ 0.5 are given.

**For the unit-cell parameters calculated from single-crystal data.

anions and H-bearing groups are observed in the IR spectrum.

The empirical formula based on 46 O + Cl *apfu* (in accordance with structural data, see below) is $\text{Pb}_{31.50}(\text{V}_{1.45}^{5+}\text{Si}_{1.09}\text{Mo}_{0.90}^{6+}\text{As}_{0.63}^{5+})_{\Sigma 4.07}\text{Cl}_{8.89}\text{O}_{37.11}$. In accordance with the IR spectrum (see above), valences of V and Mo are 5+ and 6+, respectively. The simplified formula is $(\text{Pb}_{32}\text{O}_{21})[(\text{V},\text{Si},\text{Mo},\text{As})\text{O}_4]_4\text{Cl}_9$.

5. X-ray diffraction data and crystal structure

Powder X-ray diffraction data were collected at Saint-Petersburg State University with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image-plate detector using Debye-Scherrer geometry ($d = 127.4$ mm). Data (for $\text{CoK}\alpha$) are given in Table 3.

Table 4. Crystallographic data and structure refinement details for erikjonssonite.

<i>Crystal data</i>	
Crystal system	Monoclinic
Space group	<i>C2/c</i>
Unit-cell dimensions	
<i>a</i> (Å)	23.200(5)
<i>b</i> (Å)	22.708(5)
<i>c</i> (Å)	12.418(3)
β (°)	102.167(4)
Unit-cell volume (Å ³)	6395(2)
<i>Z</i>	4
Calculated density (g·cm ⁻³)	8.081
Absorption coefficient (mm ⁻¹)	84.967
Crystal size (mm)	0.1 × 0.1 × 0.005
<i>Data collection</i>	
Temperature (K)	296(2)
Radiation, wavelength (Å)	MoK α , 0.71073
<i>F</i> (000)	12 723
θ range (°)	1.269–28.000
<i>h</i> , <i>k</i> , <i>l</i> ranges	$\bar{3}0 \rightarrow 30$, $29 \rightarrow 29$, $\bar{1}6 \rightarrow 16$
Total reflections collected	36 872
Unique reflections (<i>R</i> _{int})	7730 (0.0654)
Unique reflections <i>F</i> > 4 σ (<i>F</i>)	4636
<i>Structure refinement</i>	
Refinement method (on <i>F</i> ²)	Full-matrix least-squares
Weighting coefficients <i>a</i> , <i>b</i>	0.0300, 0.0000
Data/restraints/parameters	7730/0/376
<i>R</i> ₁ [<i>F</i> > 4 σ (<i>F</i>)], <i>wR</i> ₂ [<i>F</i> > 4 σ (<i>F</i>)]	0.0429, 0.0993
<i>R</i> ₂ all, <i>wR</i> ₂ all	0.0823, 0.1194
GoF on <i>F</i> ²	1.007
Largest diff. peak and hole (<i>e</i> Å ⁻³)	4.950 (0.76 Å from Pb15), -3.375 (0.58 Å from Pb14)

Monoclinic unit-cell parameters refined from the powder data are *a* = 23.06(1), *b* = 22.69(1), *c* = 12.50(1) Å, β = 102.49(5)°, *V* = 6383(10) Å³.

The crystal of erikjonssonite selected for single-crystal data collection was mounted on a thin glass fibre for an X-ray diffraction analysis. More than a hemisphere of X-ray diffraction data with the frame widths of 0.5° (ω and φ scans), and with 20 s spent counting for each frame were collected at room temperature using a Bruker three-circle Smart APEX II X-ray diffractometer operated at 50 kV and 40 mA with MoK α radiation and housed at Saint-Petersburg State University. The data were integrated and corrected for absorption using an empirical ellipsoidal model by means of the Bruker programs *APEX* and *XPREP*. The observed systematic absences were consistent with the space group *C2/c*. The atom coordinates for hereroite published by Siidra *et al.* (2013a) were used as a starting model, and the structure was successfully refined using the SHELX software package (Sheldrick, 2015). The structure of erikjonssonite was refined to *R*₁ = 0.043 based on 7730 independent reflections with *I* > 2 σ (*I*). Experimental and structure refinement details are given in Table 4. Final atom coordinates and selected interatomic distances are listed in Tables 5 and 6. Bond-valence sums (BVS) were calculated using the parameters of Krivovichev (2012) for the Pb²⁺–O bonds and Brese & O’Keeffe (1991) for the Pb–Cl and V⁵⁺–O bonds.

Anisotropic displacement parameters are given in Table S1 in Supplementary Material linked to this article and freely available from <https://pubs.geoscienceworld.org/eurjmin>.

The structural topology of erikjonssonite {(Pb₃₂O₂₁)[(V,Si,Mo,As)O₄]₄}Cl₉ is very similar to that of hereroite {(Pb₃₂O₂₀(O,□))(AsO₄)₂((Si,As,V,Mo)O₄)₂}Cl₉ (Turner *et al.*, 2012a; Siidra *et al.* 2013a). It is to be noted that there is a typo in the published formula of hereroite with 10 Cl atoms per formula unit (Turner *et al.*, 2012a). Actually, it should contain nine Cl atoms. The Cl1 atom is located at the 4*d* site, whereas Cl2, Cl3, Cl4 and Cl5 are at the 8*f* site (Table 5). Thus the total number of chlorine atoms in hereroite and erikjonssonite cannot exceed nine atoms per formula.

Erikjonssonite belongs to the 2:1 type of layered lead oxychlorides (Fig. 4) (Krivovichev *et al.*, 2009; Siidra *et al.*, 2013b). Two [Pb₃₂O₂₁]²²⁺ oxocentred blocks formed by OPb₄ tetrahedra with inserted tetrahedral groups alternate with one chloride sheet (Fig. 4a). The [Pb₃₂O₂₁]²²⁺ layer (Fig. 4b) can be described as a modified, or defect [PbO]_n-type layer (Boher & Garnier, 1984) in which some PbO_n groups of the Pb–O block are substituted by TO₄ tetrahedral groups (T = V, Si, Mo, As). Resulting cavities in the Pb–O block have the form of a square (*i.e.*, symesite-type: Welch *et al.*, 2000) and a double square (*i.e.*, komatite-type: Cooper & Hawthorne, 1994; Bonaccorsi & Pasero, 2003). Cavities (Fig. 4b) are organized into alternating diagonal stripes of a similar structure. It is noteworthy that all O atom sites in the [Pb₃₂O₂₁]²²⁺ block are completely occupied, in contrast to hereroite where one of the sites is partially vacant (Siidra *et al.*, 2013a).

Average <T–O> bond lengths in the tetrahedral groups demonstrate very similar values (Table 6) which is interpreted as both T1 and T2 sites having mixed occupancies of V⁵⁺, Si⁴⁺, Mo⁶⁺ and As⁵⁺, unlike hereroite where <T–O> bond lengths are different and one site is exclusively occupied by As⁵⁺. Refined site-scattering values for the T1 and T2 sites in erikjonssonite are very similar: 26.45 and 27.60. Taking into account complex heterovalent cationic substitutions at both sites, it is sensible to assume equal occupation for the ideal structure, which is broadly in accordance with the microprobe data discussed above. Relatively high bond-valence sum at the T1 site (Table 5) tentatively indicates concentration of Mo⁶⁺ at this site.

6. Discussion

Comparative data for erikjonssonite and hereroite are given in Table 7. Both minerals are similar in X-ray diffraction characteristics, but differ markedly in reflectance data because of significant differences between Gladstone–Dale constants for As₂O₅ and V₂O₅ (0.162 and 0.340, respectively; Mandarino, 1981).

Erikjonssonite is a new representative of a relatively large family of layered lead oxychloride minerals with structural lead oxide blocks derived from that of litharge PbO (Boher & Garnier, 1984) which alternate with layers of chloride ions (Krivovichev *et al.*, 2009). A structural and chemical

Table 5. Atom coordinates, bond-valence sums (BVS) and equivalent displacement parameters (U_{eq} , in \AA^2) for erikjonssonite.

Atom	Site	BVS	x	y	z	U_{eq}
Pb1	8f	1.91	0.02381(3)	0.33085(3)	0.11211(5)	0.01591(15)
Pb2	8f	1.99	-0.13868(2)	0.33133(2)	-0.05641(5)	0.01216(13)
Pb3	8f	1.85	0.24278(3)	0.16753(3)	0.00195(5)	0.01579(16)
Pb4	8f	1.90	-0.03659(3)	0.55678(3)	0.37428(5)	0.01376(15)
Pb5	8f	1.86	-0.30238(3)	0.33475(3)	-0.22000(5)	0.01629(15)
Pb6	8f	1.98	0.08107(2)	0.16459(3)	-0.17232(5)	0.01233(14)
Pb7	8f	1.96	-0.19194(3)	0.66878(3)	-0.28152(5)	0.01550(15)
Pb8	8f	1.87	-0.07939(2)	0.44381(3)	0.15068(5)	0.01460(15)
Pb9	8f	1.81	-0.19745(2)	0.44567(3)	-0.26128(6)	0.01521(15)
Pb10	8f	1.85	-0.02252(3)	0.04940(3)	-0.11711(6)	0.01726(15)
Pb11	8f	1.91	0.03161(3)	0.16536(3)	0.11001(5)	0.01981(17)
Pb12	8f	1.92	-0.24020(3)	0.55449(3)	-0.48621(5)	0.01435(15)
Pb13	8f	1.90	-0.08168(2)	0.67085(3)	0.17240(5)	0.01537(15)
Pb14	8f	1.93	0.18392(3)	0.05259(3)	-0.23272(5)	0.02004(16)
Pb15	8f	1.76	0.13775(3)	0.05504(3)	0.03925(6)	0.01996(16)
Pb16	8f	1.87	0.14398(3)	0.16528(3)	-0.43805(6)	0.01776(15)
T1	8f	5.56*	0.09431(10)	-0.06751(12)	-0.1570(2)	0.0190(8)
T2	8f	5.21*	-0.13542(9)	0.56963(11)	-0.0553(2)	0.0167(7)
Cl1	4d	0.88	$-\frac{1}{4}$	$\frac{1}{4}$	0	0.0232(15)
Cl2	8f	0.81	0.14066(17)	0.2368(2)	0.0556(4)	0.0235(8)
Cl3	8f	0.87	-0.02713(17)	0.24914(17)	-0.1117(4)	0.0255(11)
Cl4	8f	0.79	-0.07808(17)	0.2583(2)	0.1642(3)	0.0244(10)
Cl5	8f	0.85	-0.30144(16)	0.75129(18)	-0.2269(4)	0.0247(11)
O1	8f	2.14	0.0912(5)	0.0026(5)	-0.1669(10)	0.032(3)
O2	8f	2.08	0.0419(5)	-0.0951(6)	-0.0995(14)	0.055(4)
O3	8f	2.06	-0.4001(5)	0.3977(5)	-0.2795(10)	0.029(3)
O4	8f	2.08	-0.3407(4)	0.4077(5)	-0.0712(9)	0.025(3)
O5	8f	1.88	-0.0738(9)	0.5955(7)	0.0409(15)	0.092(7)
O6	8f	1.90	-0.1345(5)	0.4945(5)	-0.0575(12)	0.038(3)
O7	8f	2.15	-0.1178(9)	0.5959(7)	-0.1696(14)	0.094(7)
O8A	8f	2.13	-0.1873(12)	0.5926(13)	0.011(3)	0.075(11)
O8B	8f		-0.2050(14)	0.5940(14)	-0.105(3)	0.041(11)
O9	8f	1.86	0.2275(5)	0.1156(5)	-0.3515(11)	0.031(3)
O10	8f	1.97	-0.0492(4)	0.3887(4)	0.0174(8)	0.012(2)
O11	8f	2.00	-0.2252(4)	0.3918(5)	-0.1281(8)	0.015(2)
O12	8f	1.94	0.0564(4)	0.1104(5)	-0.0237(8)	0.015(2)
O13	4e	2.06	0	0.1053(6)	$-\frac{1}{4}$	0.019(4)
O14	8f	1.99	-0.1593(4)	0.3887(4)	0.0930(8)	0.013(2)
O15	8f	1.99	0.1696(4)	0.1085(5)	-0.0947(9)	0.018(2)
O16	8f	1.83	0.2218(4)	0.1116(5)	0.1408(9)	0.017(3)
O17	8f	1.97	-0.1169(4)	0.3895(4)	-0.2103(9)	0.014(2)
O18	4e	1.90	0	0.3851(6)	$\frac{1}{4}$	0.022(4)
O19	8f	1.93	0.1071(4)	0.1042(5)	-0.3271(9)	0.017(3)
O20	4e	1.94	0	0.6199(6)	$\frac{1}{4}$	0.019(4)

*Calculated for V^{5+} -O bonds.

feature of all minerals belonging to this family is the presence of additional oxygen atoms (Krivovichev *et al.*, 2013) being central in the oxocentered OPb_nA_{4-n} ($A = \text{metal}$) tetrahedra (Siidra *et al.*, 2008). The [PbO] blocks may have different types of “defects” (*i.e.*, cavities) obtained by the removal of individual atoms or atomic groups in the parent ideal (Fig. 5) tetragonal [PbO] layers. Chloride layers may also have different substitutions and cavities relative to the idealized chloride layer (Fig. 6i).

In rumseyite $[Pb_2OF]Cl$ (Turner *et al.*, 2012b), the electroneutrality of the formula is achieved by partial substitution of O^{2-} by F^- . In perite $[PbBiO_2]Cl$ (Gillberg, 1960) and nadorite $[PbSbO_2]Cl$ (Giuseppetti & Tadini, 1973),

ordered substitution of a half of Pb^{2+} cations by Bi^{3+} and Sb^{3+} , respectively, takes place. The $[Pb_2OF]^+$, $[PbBiO_2]^+$ and $[PbSbO_2]^+$ blocks are topologically identical to the [PbO] block in litharge. In rumseyite, perite and nadorite, each anion-centred tetrahedron in the [PbO]-like block shares four of $A-A$ edges ($A = \text{metal cation}$) and four A corners with eight neighbouring anion-centred tetrahedra in such a way that the resulting layer does not contain cavities (Fig. 6a). In order to classify the layered Pb oxychloride minerals (Table 8), we suggest to introduce the concept of a “DN”, which is the number of O^{2-} ions removed from the ideal [PbO] block per “defect” (cavity) area (Fig. 5). Thus in rumseyite, perite and nadorite DN is equal to 0

Table 6. Selected interatomic distances (in Å) in the structure of erikjonssonite.

Pb1–O10	2.266(9)	Pb5–O16	2.280(10)	Pb9–O17	2.240(9)	Pb14–O15	2.213(11)
Pb1–O18	2.271(8)	Pb5–O11	2.307(10)	Pb9–O11	2.257(10)	Pb14–O19	2.246(10)
Pb1–O7	2.717(19)	Pb5–O3	2.651(11)	Pb9–O16	2.391(10)	Pb14–O9	2.423(13)
Pb1–O5	2.95(2)	Pb5–O4	2.763(12)	Pb9–O6	2.865(13)	Pb14–O1	2.706(11)
Pb1–Cl4	3.060(4)	Pb5–Cl5	3.240(4)	Pb9–O8A	3.01(3)	Pb14–O8B	2.88(3)
Pb1–Cl4	3.246(4)	Pb5–Cl2	3.256(5)				
Pb1–Cl3	3.344(4)	Pb5–Cl1	3.353(1)	Pb10–O13	2.229(8)	Pb15–O12	2.266(9)
				Pb10–O19	2.303(10)	Pb15–O15	2.303(10)
Pb2–O14	2.396(10)	Pb6–O13	2.349(8)	Pb10–O12	2.391(9)	Pb15–O16	2.450(10)
Pb2–O11	2.441(10)	Pb6–O12	2.387(10)	Pb10–O2	3.004(15)	Pb15–O3	2.797(12)
Pb2–O10	2.459(9)	Pb6–O15	2.436(10)	Pb10–O1	3.009(13)	Pb15–O1	2.824(12)
Pb2–O17	2.460(11)	Pb6–O19	2.535(11)	Pb10–O1	3.026(11)		
Pb2–Cl4	3.257(4)	Pb6–Cl2	3.311(5)			Pb16–O19	2.248(10)
Pb2–Cl5	3.301(4)	Pb6–Cl3	3.321(4)	Pb11–O12	2.246(10)	Pb16–O9	2.304(12)
Pb2–Cl1	3.3665(7)	Pb6–Cl3	3.369(4)	Pb11–O2	2.318(12)	Pb16–O4	2.420(11)
Pb2–Cl3	3.377(4)	Pb6–Cl5	3.541(3)	Pb11–O3	2.351(11)	Pb16–Cl5	3.301(5)
				Pb11–Cl2	3.195(4)	Pb16–Cl1	3.3377(7)
Pb3–O16	2.276(10)	Pb7–O9	2.240(11)	Pb11–Cl3	3.388(4)	Pb16–Cl3	3.473(4)
Pb3–O15	2.295(10)	Pb7–O14	2.281(10)	Pb11–Cl4	3.480(4)		
Pb3–O8A	2.34(3)	Pb7–O7	2.57(2)	Pb11–Cl4	3.493(4)	T1–O1	1.598(11)
Pb3–O8B	2.59(3)	Pb7–O8B	2.83(3)			T1–O2	1.658(13)
Pb3–Cl2	3.033(4)	Pb7–Cl4	3.305(4)	Pb12–O11	2.230(11)	T1–O3	1.742(12)
Pb3–Cl5	3.384(5)	Pb7–Cl1	3.3221(8)	Pb12–O14	2.319(9)	T1–O4	1.747(10)
Pb3–Cl5	3.394(4)	Pb7–Cl5	3.339(4)	Pb12–O9	2.411(12)	<T1–O>	1.69
		Pb7–Cl2	3.531(4)	Pb12–O4	2.500(10)		
Pb4–O10	2.235(10)			Pb12–O6	2.991(13)	T2–O7	1.667(18)
Pb4–O17	2.290(9)	Pb8–O14	2.227(9)			T2–O8A	1.68(3)
Pb4–O20	2.390(9)	Pb8–O10	2.299(9)	Pb13–O20	2.255(8)	T2–O8B	1.70(3)
Pb4–O5	2.702(18)	Pb8–O18	2.394(8)	Pb13–O17	2.274(10)	T2–O6	1.706(11)
Pb4–O6	2.837(13)	Pb8–O7	2.725(17)	Pb13–O5	2.398(17)	T2–O5	1.760(16)
		Pb8–O6	2.873(13)	Pb13–Cl3	3.265(5)	<T2–O>	1.70
				Pb13–Cl3	3.323(4)		
				Pb13–Cl5	3.422(4)		
				Pb13–Cl2	3.551(4)		

(Fig. 6a). Identical DN0 topology but with complex disordered substitutions is observed in the related minerals: thorkosite $[(\text{Pb}_3\text{Sb}_{0.6}\text{As}_{0.4})(\text{O}_3\text{OH})]\text{Cl}_2$ (Rouse & Dunn, 1985), schwartzembergite $[\text{Pb}_5\text{I}^{3+}\text{O}_6\text{H}_2]\text{Cl}_3$ (Welch *et al.*, 2001), asisite $[\text{Pb}_7\text{SiO}_8]\text{Cl}_2$ (Welch, 2004), parkinsonite $[\text{Pb}_7\text{MoO}_9]\text{Cl}_2$ (Lepore & Welch, 2010), and janchevite $[\text{Pb}_7\text{V}^{5+}(\text{O}_{8.5}\square_{0.5})]\text{Cl}_2$ (Chukanov *et al.*, 2018a). In the formulae, we place the *host* [PbO]-like block with the *guest* atomic or anionic species in square brackets or in additional braces (for more complex mineral formulae of hereroite, erikjonssonite and ecdemite). Various [PbO]-derived blocks known, and their corresponding DN are shown in Fig. 5a–g, whereas ideal and defect chloride layers are represented in Fig. 6i–l.

In the structure of blixite $[\text{Pb}_8\text{O}_5(\text{OH})_2]\text{Cl}_4$ (Krivovichev & Burns, 2006), three oxygen atoms are removed per each cavity, which results in the formation of the $[\text{Pb}_8\text{O}_5]^{6+}$ layer shown in Fig. 6b. In this mineral, OH^- groups occupy DN3 cavities, and the monoclinically distorted chloride interlayer is defect-free (Fig. 6i).

In symesite $[\text{Pb}_{10}\text{O}_7(\text{SO}_4)]\text{Cl}_4(\text{H}_2\text{O})$ (Welch *et al.*, 2000), DN4 square cavities (Fig. 6c) are occupied by sulfate tetrahedra. Symesite is one of three Pb oxychloride minerals in which chloride interlayer also has cavities (Fig. 6j).

In addition, in this mineral a portion of Cl^- anions is replaced by H_2O molecules.

In kombatite $[\text{Pb}_{14}\text{O}_9(\text{VO}_4)_2]\text{Cl}_4$ (Cooper & Hawthorne, 1994) and its arsenate analogue sahlinitite $[\text{Pb}_{14}\text{O}_9(\text{AsO}_4)_2]\text{Cl}_4$ (Bonaccorsi & Pasero, 2003), DN7 double square cavities (Fig. 6d) occur in the $[\text{Pb}_{14}\text{O}_9]^{10+}$ blocks.

Large, cross-shaped DN12 cavities (Fig. 6e) were found in the oxocentred block in the structure of vladkrivovichevite $[\text{Pb}_{32}\text{O}_{18}\text{Mn}_2(\text{BO}_3)_8]\text{Pb}_4\text{OCl}_{14}(\text{H}_2\text{O})_2$ (Siidra *et al.*, 2013c). Four borate groups and one Mn atom are located at each cavity. In the complex $[\text{Pb}_4\text{OCl}_{14}(\text{H}_2\text{O})_2]^{8-}$ interlayer a part of Cl is replaced by other atoms (Fig. 6k). Each OPb_4 group in this layer has an almost flat configuration and replaces five Cl atoms. The cavities formed around the Pb^{2+} cations are a result of the stereochemical activity of the $6s^2$ lone electron pairs. Finally, water molecules are inserted into partially occupied sites located between Cl atoms.

The $[\text{Pb}_{32}\text{O}_{21}]^{22+}$ block in hereroite $\{(\text{Pb}_{32}\text{O}_{20}(\text{O},\square))(\text{AsO}_4)_2(\text{Si},\text{As},\text{V},\text{Mo})\text{O}_4\}_2\text{Cl}_9$ (Siidra *et al.*, 2013a) and erikjonssonite $\{(\text{Pb}_{32}\text{O}_{21})[(\text{V},\text{Si},\text{Mo},\text{As})\text{O}_4]_4\}\text{Cl}_9$ contains two types of defects: DN4 and DN7 (Fig. 6f). In these minerals, different tetrahedral anionic species are located within both cavities. The chloride interlayer in hereroite and

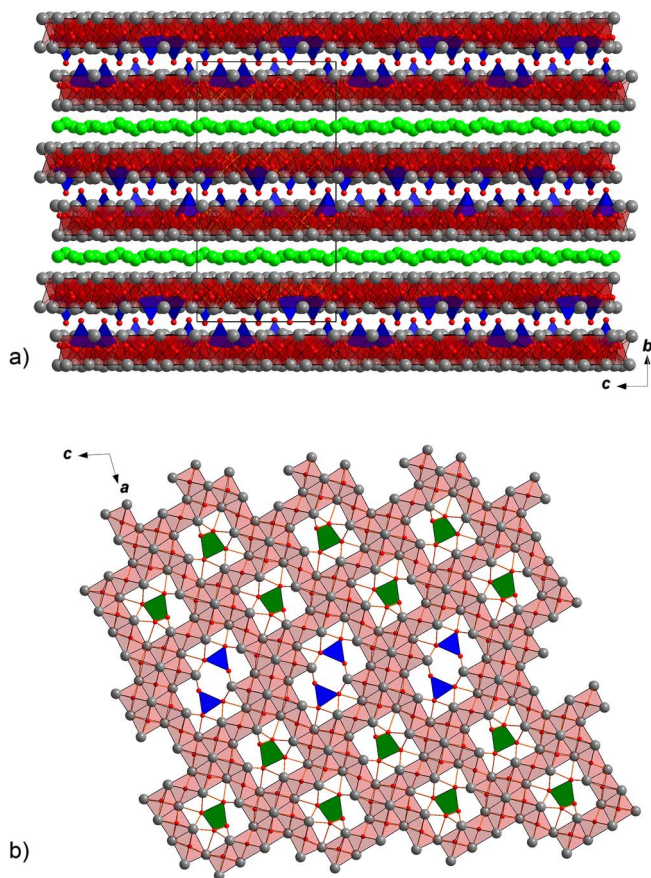


Fig. 4. General view of the erikjonssonite crystal structure: (a) projection along the **a** axis; two $[\text{Pb}_{32}\text{O}_{21}]^{22+}$ oxocentred blocks formed by OPb_4 tetrahedra (red) with inserted tetrahedral groups (blue) alternate with one chloride sheet (green) and (b) projection of the $[\text{Pb}_{32}\text{O}_{21}]^{22+}$ layer along the **b** axis with tetrahedral anions (T1O_4 tetrahedra in blue, T2O_4 tetrahedra in green) inserted in single-square or double-square shaped cavities.

erikjonssonite is the most common parent type without cavities (Fig 6i).

As in hereroite and erikjonssonite, two kinds of cavities are formed in the oxocentred block of mereheadite $[\text{Pb}_{44}\text{O}_{24}(\text{OH})_{13}(\text{BO}_3)_2(\text{CO}_3)]\text{Pb}_3\text{Cl}_{25}$ (Krivovichev *et al.*, 2009). The DN4 and DN2 cavities are occupied by the carbonate and borate groups and by OH^- anions, respectively. Additional Pb atoms are inserted in the chloride inter-layer (Fig. 6l).

The variability of cavities in the $[\text{PbO}]$ -derived structures shows that many other kinds of defects may exist in related structures. Limits to the sizes and spatial distribution of cavities are restricted by the conditions beyond which the basic $[\text{PbO}]$ -derived layer would lose its integrity. This situation is observed in the recently described crystal structure of ecdemite $\{[\text{Pb}_4\text{O}]\text{Pb}_2(\text{AsO}_3)_2\}\text{Cl}_4$ (Perchiazzi *et al.*, 2019). In this mineral, chloride interlayer is the most basic form (Fig. 6i), but oxocentred OPb_4 tetrahedra are isolated (Fig. 6h) and embedded in a lead-arsenite $\text{Pb}_2(\text{AsO}_3)_2$ matrix. Despite strong transformations and the disintegration of the $[\text{PbO}]$ block, the structural architecture of ecdemite

Table 7. Comparative data for erikjonssonite and hereroite.

Mineral	Erikjonssonite	Hereroite
Formula	$\{(\text{Pb}_{32}\text{O}_{21})[(\text{V},\text{Si},\text{Mo},\text{As})\text{O}_{414}]\text{Cl}_9$	$\{(\text{Pb}_{32}\text{O}_{20}(\text{O},\square))(\text{AsO}_4)_2[(\text{Si},\text{As},\text{V},\text{Mo})\text{O}_{412}]\text{Cl}_9$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
<i>a</i> (Å)	23.200	23.139
<i>b</i> (Å)	22.708	22.684
<i>c</i> (Å)	12.418	12.389
β (°)	102.167	102.090
<i>V</i> (Å ³)	6395	6359
<i>Z</i>	4	4
Strong lines of the powder	3.501 (24) 2.980 (100)	3.901 (21) 3.512 (23)
X-ray diffraction pattern:	2.794 (45)	2.982 (100)
<i>d</i> , Å (<i>I</i> , %)	1.990 (24) 1.977 (21) 1.648 (33)	2.795 (47) 1.986 (24) 1.641 (24)
Reflectance data:	470 (20.4/18.9)	470 (17.9)
λ , nm ($R_{\text{max}}/R_{\text{min}}$)	546 (19.0/17.6)	546 (16.9)
or λ , nm (R_{mean})	589 (18.5/17.1)	589 (16.6)
	650 (18.0/16.6)	650 (16.3)
Density, $\text{g} \cdot \text{cm}^{-3}$	7.967 (calc.)	7.40 (calc.)
Sources	This work	Turner <i>et al.</i> (2012a); Siidra <i>et al.</i> (2013a)

undoubtedly belongs to the family of layered lead oxychlorides.

As can be seen from Table 8, all layered lead oxychloride minerals are structurally related. In particular, many of the discussed minerals with defect $[\text{PbO}]$ blocks, including erikjonssonite, exhibit distinct tetragonal pseudosymmetry. However, strong differences in crystallographic parameters and symmetry, as well as wide variations in chemical composition prevent the creation of a new mineral group or supergroup of layered lead oxychlorides.

Structural regularities (including DN and shape of cavity) similar to those described above for Pb oxychloride minerals (Fig. 6) have been found in many synthetic compounds (Krivovichev *et al.*, 2006; Siidra *et al.*, 2013b, 2016). For example, DN4 cavities first described in the structure of symesite are quite common and have been found in the $[\text{PbO}]$ -like blocks in synthetic Pb oxyhalides of different composition: $\text{Pb}_{31}\text{O}_{22}\text{X}_{18}$ ($\text{X} = \text{Br}, \text{Cl}$) (Krivovichev *et al.*, 2006), $[\text{Pb}_{22}\text{O}_{16}][\text{PbO}](\text{OH})\text{I}_{10}(\text{I},\text{Br})(\text{H}_2\text{O})$ (Siidra *et al.*, 2013b) and $[\text{Pb}_{18}\text{O}_{12}]\text{Pb}(\text{BO}_2\text{OH})_2\text{Cl}_{10}$ (Siidra *et al.*, 2016). In all these compounds, DN4 cavities are organized within various $[\text{PbO}]$ -derived blocks in different ways not observed yet in crystal structures of minerals (Siidra *et al.*, 2016).

Erikjonssonite formed as a consequence of regional metamorphism of a primary, Pb–Mn–(As–Ba)-rich, chemically heterogeneous, volcanic hydrothermal assemblage (Innes & Chaplin, 1986). This and several related assemblages from the Mn–(Fe) oxide ore unit at Kombat bear a remarkable similarity to some assemblages from the Långban mine, Sweden (*cf.* Nysten *et al.*, 1999), as well as ore occurrences related to metasomatic rocks of the orogenic zone at the contact of meta-rhyolites and dolomitic marbles belonging

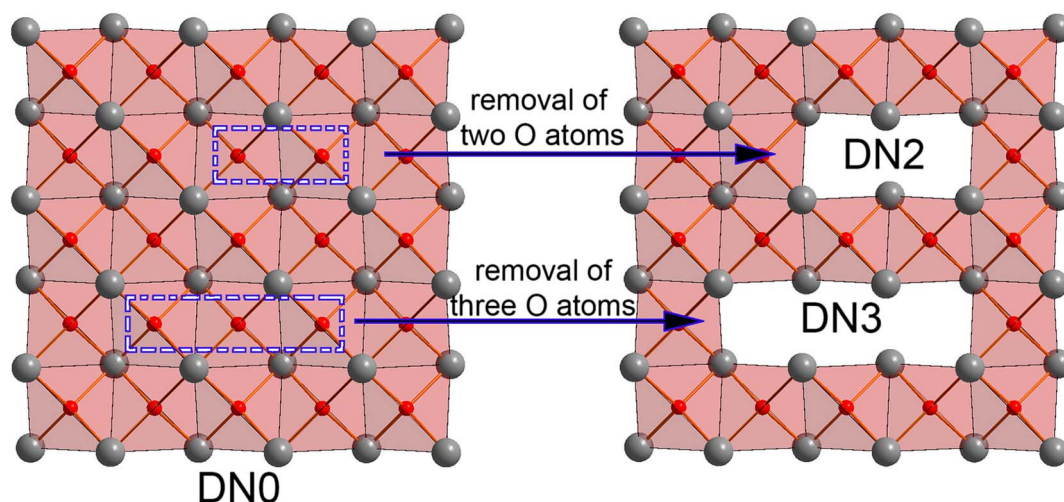


Fig. 5. Formation of cavities in the ideal (left) [PbO] block due to removal of O atoms. “Defect numbers (DN)” corresponds to the number of removed O^{2-} ions per cavity or “defect” area (right).

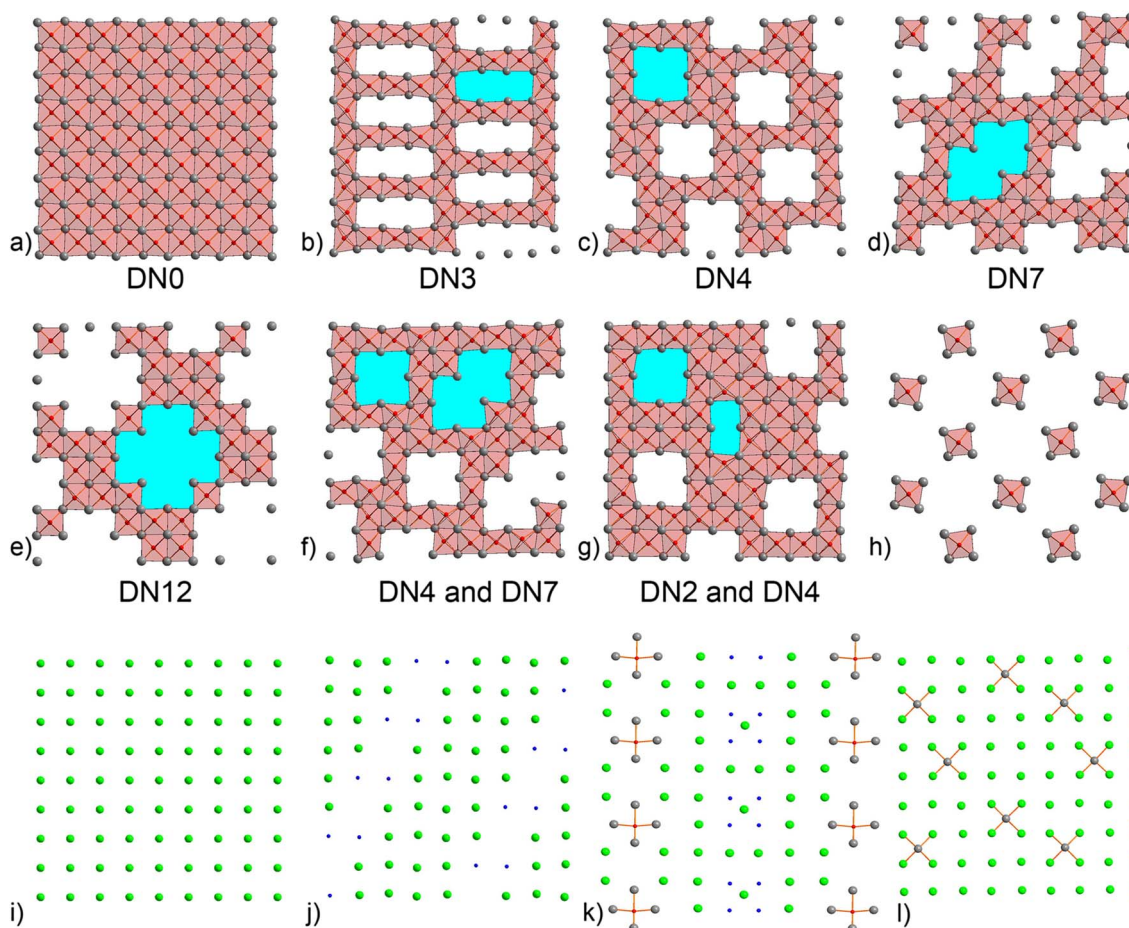


Fig. 6. Litharge-derived oxocentred blocks with various cavities (marked by blue) (a–g) and chloride interlayers (i–l) in the structures of layered lead oxychloride minerals. Defect numbers (DN) are labelled under each type of [PbO]-derived blocks: rumseyite, schwartzembergite, parkinsonite, asisite, nadorite, perite, thorikosite and janchevite (a); blixite (b); symesite (c); kombatite and sahlinitite (d); vladkrivovichevite (e); hereroite and erikjonnsontite (f); mereheadite (g). Disintegrated [PbO]-derived block in ecdemite contains only isolated OPb_4 tetrahedra (h). In most of Pb oxychloride minerals, the Cl interlayer is identical in topology and defect-free (i) with some exceptions: symesite (j); vladkrivovichevite (k) and mereheadite (l). See the text and Table 8 for details.

Table 8. Crystallographic data, “defect numbers (DN)” and characterization of chloride interlayer for layered Pb oxychloride minerals structurally related to litharge. See the text and Fig. 6 for details.

Mineral name	Chemical formula	Space group	DN	Chloride interlayer	Reference
Rumseyite	[Pb ₂ OF]Cl	<i>I4/mmm</i>	0	Defect-free	Turner <i>et al.</i> (2012b)
Perite	[PbBiO ₂] Cl	<i>Bmmb</i>	0	Defect-free	Gillberg (1960)
Nadorite	[PbSbO ₂]Cl	<i>Cmcm</i>	0	Defect-free	Giuseppetti & Tadini (1973)
Thorikosite	[(Pb ₃ Sb _{0.6} As _{0.4})(O ₃ OH)]Cl ₂	<i>I4/mmm</i>	0	Defect-free	Rouse & Dunn (1985)
Schwartzembergite	[Pb ₅ I ³⁺ O ₆ H ₂]Cl ₃	<i>I4/mmm</i>	0	Defect-free	Welch <i>et al.</i> (2001)
Asisite	[Pb ₇ SiO ₈]Cl ₂	<i>I4/mmm</i>	0	Defect-free	Welch (2004)
Parkinsonite	[Pb ₇ MoO ₉]Cl ₂	<i>I4/mmm</i>	0	Defect-free	Lepore & Welch (2010)
Janchevite	[Pb ₇ V ⁵⁺ (O _{8.5} □ _{0.5})]Cl ₂	<i>I4/mmm</i>	0	Defect-free	Chukanov <i>et al.</i> (2018a)
Blixite	[Pb ₈ O ₅ (OH) ₂]Cl ₄	<i>C2/c</i>	3	Defect-free	Krivovichev & Burns (2006)
Symesite	[Pb ₁₀ O ₇ (SO ₄)Cl ₄ (H ₂ O)]	<i>B1</i>	4	Defect	Welch <i>et al.</i> (2000)
Kombatite	[Pb ₁₄ O ₉ (VO ₄) ₂]Cl ₄	<i>C2/c</i>	7	Defect-free	Cooper & Hawthorne (1994)
Sahlinite	[Pb ₁₄ O ₉ (AsO ₄) ₂]Cl ₄	<i>C2/c</i>	7	Defect-free	Bonaccorsi & Pasero (2003)
Vladkrivovichevite	[Pb ₃₂ O ₁₈ Mn ₂ (BO ₃) ₈]Pb ₄ OCl ₁₄ (H ₂ O) ₂	<i>Pmmm</i>	12	Defect	Siidra <i>et al.</i> (2013c)
Mereheadite	[Pb ₄₄ O ₂₄ (OH) ₁₃ (BO ₃) ₂ (CO ₃)]Pb ₃ Cl ₂₅	<i>Cm</i>	2, 4	Defect	Krivovichev <i>et al.</i> (2009)
Hereroite	[Pb ₃₂ O ₂₀ (O,□)](AsO ₄) ₂ ((Si,As,V,Mo)O ₄) ₂ Cl ₉	<i>C2/c</i>	4, 7	Defect-free	Siidra <i>et al.</i> (2013a)
Erikjonssonite	{(Pb ₃₂ O ₂₁)[(V,Si,Mo,As)O ₄] ₄ }Cl ₉	<i>C2/c</i>	4, 7	Defect-free	This work
Ecdemite	{[Pb ₄ O]Pb ₂ (AsO ₃) ₂ }Cl ₄	<i>P2₁</i>	*	Defect-free	Perchiazzi <i>et al.</i> (2019)

*[PbO]-derived block is disintegrated which precludes usage of the DN concept.

to the “Mixed Series” metamorphic complex situated in the Pelagonian massif near the Nežilovo village, about 25 km WSW of the city of Veles, Republic of Macedonia (Chukanov *et al.*, 2015). A characteristic feature of all these assemblages is the occurrence of chalcophile elements as components of oxygen-bearing minerals.

At the Kombat deposit, primary sulfide minerals were partly decomposed during epigenetic, hydrothermal and metasomatic replacement events associated with the Damaran Orogeny (Turner *et al.*, 2012b). A possible role of high barium activity in the immobilization of sulfur in sulfide-free endogenous ore occurrences with chalcophile elements was discussed elsewhere (Chukanov *et al.*, 2018b).

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