Hereroite and vladkrivovichevite: two novel lead oxychlorides from the Kombat mine, Namibia

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ABSTRACT

Two new lead oxychloride minerals, hereroite $[Pb_{32}(O, \Box)_{21}](AsO_4)_2((Si,As,V,Mo)O_4)_2Cl_{10}$ and vladkrivovichevite $[Pb_{32}O_{18}][Pb_4Mn_2O]Cl_{14}(BO_3)_8$ ·2H₂O occur in association with asisite, damaraite, kombatite, sahlinite, copper, quartz, barysilite, Mn silicates and a number of Mn oxyhydroxide minerals on a specimen from the Kombat mine in Namibia. The minerals formed as late-stage products of hydrothermal reworking of primary sulfide minerals.

Hereroite is monoclinic, C2/c with a = 23.14(1), b = 22.65(1), c = 12.39(1) Å, $\beta = 102.00(5)^{\circ}$, V = 6351.6(41) Å³ from powder-diffraction data and a = 23.139(4), b = 22.684(4), c = 12.389(2) Å, $\beta = 102.090(3)^{\circ}$, V = 6358.8(18) Å³ from single-crystal data. It is bright orange, with white streak and adamantine lustre. It is brittle with no observed parting or cleavage and has a conchoidal fracture. The calculated density is 8.15 g cm⁻³. The mean refractive index in air at 589 nm is 2.38. The six strongest reflections in the X-ray powder diffraction pattern [d in Å, (I), (hkI)] are as follows: 2.982(100)(551); 2.795(47)(802); 1.986(24)(882); 1.641(24)(11.5.5); 3.512(23)(612); 3.901(21)(511). Hereroite is named for the Herero people, one of the indigenous tribal groupings in the region where the Kombat mine is located.

Vladkrivovichevite is orthorhombic, *Pmmn* with a = 12.87(5), b = 27.7(4), c = 11.46(3) Å, V = 4080.1(5) Å³, from powder-diffraction data and a = 12.759(1), b = 27.169(4), c = 11.515(1) Å, V = 3992.0(9) Å³, Z = 2, from single-crystal data. It is pale greenish yellow, with white streak and adamantine lustre. It is brittle with no observed parting or cleavage and has a conchoidal fracture. The calculated density is 7.40 g cm⁻³. The mean refractive indices in air at 589 nm are 2.30 and 2.34. The six strongest reflections in the X-ray powder diffraction pattern [*d* in Å, (*I*), (*hkl*)] are as follows: 2.860(100)(370); 2.733(84)(073); 3.707(49)(073); 3.068(37)(401); 2.075(32)(473); 1.601(32)(3.14.3). Vladkrivovichevite is named in honour of Prof. Dr Vladimir Gerasimovich Krivovichev (b. 24.04.1946), Head of the Department of Mineralogy, Geological Faculty, St Petersburg State University.

The crystal structures of hereroite and vladkrivovichevite consist of alternating litharge-like O–Pb double layers and chlorine sheets and both are structurally related to other layered lead oxychlorides. In hereroite, tetrahedral AsO₄ and (Si,As,V,Mo)O₄ groups locate in defects within the O–Pb block, which combines square 'symesite-type' and double-square 'kombatite-type' cavities in its crystal structure. The structure of vladkrivovichevite is based on O–Pb derivative blocks with the interlayer occupied by Cl⁻ anions and oxocentred OPb₄Mn₂ octahedra whose eight triangular faces are capped by triangular borate anions, BO_3^{3-} .

Keywords: hereroite, vladkrivovichevite, Kombat mine, layered lead oxychlorides, lead oxyhalides, Namibia, new mineral species, new structures, OPb₄ tetrahedra, oxocentred units.

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Introduction

THE mineralogy of Pb oxyhalides with structures derived from tetragonal PbO (litharge) is very rich in terms of both chemical diversity and structural variability (Welch *et al.*, 1996, 1998, 2000, 2001; Welch, 2004; Lepore and Welch, 2010). Recent research on the Pb oxyhalides of the Mendip Hills, England, (Turner, 2006; Rumsey, 2008; Siidra *et al.*, 2008b; Krivovichev *et al.*, 2009; Turner and Rumsey, 2010; Rumsey *et al.*, 2011) has increased our understanding of these minerals, and led to a wider examination of deposits that contain similar minerals including Långban in Sweden, the Mammoth-St Antony mine in the USA and the Kombat mine in Namibia.

An unusual specimen from the Kombat mine in Namibia was found by one of the authors (RT) on sale at the Munich Mineral Show in October 2009. Labelled as 'red asisite' the specimen clearly contained a variety of minerals, and on examination yielded the two new species described here: hereroite (IMA 2011-027), and vladkrivovichevite (IMA 2011-020). Both have been approved by the IMA Commission on New Mineral Names and Classification. Hereroite is named after the Herero people, one of the indigenous tribal groupings in the region where the Kombat mine is located. This name is in keeping with similar minerals from Kombat mine, which are named after other local features and peoples (e.g. asisite, damaraite, johninnesite, and kombatite). Vladkrivovichevite is named in honour of Prof. Dr Vladimir Gerasimovich Krivovichev. (b. 24.04.1946) Head of the Department of Mineralogy, Geological Faculty, St Petersburg State University. Although a single name eponym would be preferable, krivovichevite already exists; it honours Prof. Dr Sergey Krivovichev. Among his many diverse contributions to the fields of mineralogy and geochemistry, Prof. Dr Vladimir Krivovichev has made a significant contribution to the mineralogy of manganese deposits and the naming of a new Pb-Mn oxychloride borate in his honour is particularly appropriate.

The original hand specimen was approximately $25 \times 15 \times 15$ mm in size and was broken up for examination. The largest and richest fragment has been designated as the holotype specimen for both species and is stored at the Natural History Museum in London under catalogue number BM2010, 101.

Occurrence

The Kombat mine orebodies contain primary Pb-Cu-Zn(-Ag) sulfides, and are similar to other deposits in the Otavi Mountainland, such as those at Tsumeb and Berg Aukas. The sulfide minerals were originally emplaced hydrothermally as fracture fillings; they were subsequently modified by epigenetic, hydrothermal and metasomatic replacement events associated with the Damaran Orogeny, including a phase of Fe-Mn silicification. These events created a range of Pb-Mn-Fe silicate minerals in the Kombat deposit, and a variety of late-stage Pb-oxyhalide minerals including hereroite and vladkrivovichevite. For further detailed descriptions of the Kombat deposits see Cairncross (1997) and Innes and Chaplin (1986).

There is little data available on the specific conditions that existed when the Kombat oxychlorides crystallized, but our work in the Mendip Hills, where similar minerals are found, indicates that the oxychlorides are formed at the end of the paragenetic process, at low (epigenetic) temperatures and over a wide range of pH conditions (Turner, 2006; Turner and Rumsey, 2010). Given the mineralogical similarities it is reasonable to suggest that similar conditions prevailed at Kombat mine when hereroite and vladkrivovichevite crystallized.

Appearance

Hereroite is relatively abundant on the type specimen (Fig. 1) as transparent to translucent intergrown glassy orange grains. The individual grains are generally <1 mm in size and they form aggregates up to ~3 mm. On one corner of the specimen hereroite forms relatively well defined crystals to ~0.5 mm; this may represent part of a small open cavity.

Vladkrivovichevite occurs on the type specimen in one pale green glassy region 1×1.5 mm across (Fig. 1) but is found more typically as grains <0.1 mm in size within the granular groundmass. It is visually very similar to asisite and the two minerals cannot be easily distinguished by visual methods; X-ray diffractometry is required for a reliable identification.

Hereroite and vladkrivovichevite are associated with other oxyhalide minerals including asisite, damaraite, kombatite and sahlinite. On the type specimen, asisite is most abundant as glassy greenish yellow crystalline masses up to 3 mm

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FIG. 1. A portion of the holotype specimen of hereroite (BM 2010,101) showing bright orange hereroite (top right) and a glassy greenish yellow grain of vladkrivovichevite (top left). The quartz matrix also contains greenish asisite and orange-brown kombatite. The black minerals are manganese oxides. Field of view ~15 mm.

across. Kombatite also occurs as orange-brown aggregates of grains (<1 mm across) which are visually very similar to hereroite.

The matrix of the specimen is made up of clear to white granular vein quartz containing irregular grains of oxychloride minerals, barysilite, abundant manganese silicates, rare native copper and minute grains of Mn oxyhydroxide minerals. The Mn oxyhydroxide minerals occur as small <0.2 mm grains. They have not been identified due to their small size, but other oxychloride specimens from the Kombat mine typically contain a mixture of hausmannite, jacobsite and manganite and there is no reason to suppose that this specimen is different.

Physical and optical properties

Hereroite is bright orange with a white streak and an adamantine lustre. It is brittle with no obvious cleavage or parting and has a conchoidal fracture. Vladkrivovichevite is pale greenish yellow with a white streak and an adamantine lustre. It is also brittle with no obvious cleavage or parting and has a conchoidal fracture.

The density could not be measured directly for either mineral due to a lack of material. The calculated densities on the basis of the empirical formulae are 8.15 and 7.40 g cm^{-3} for hereroite and vladkrivovichevite, respectively.

Hereroite and vladkrivovichevite are non metallic, but they have the high refractive indices (RIs) that are typical of lead oxychlorides, and their optical properties were characterized using the methods common for metallic minerals to avoid toxic RI liquids. In reflected light hereroite is grey with a bluish tint. Any possible bireflectance is masked by internal reflections, which are yellowish orange. Vladkrivovichevite is slightly bluish grey with a weak bireflectance and a weak anisotropy. The internal reflections are colourless. Reflectance values for both minerals are listed in Table 1. The mean RIs in air at 589 nm calculated from the Fresnel equation (assuming k = 0) are 2.30 and 2.34 for vladkrivovichevite, the mean RI for hereroite is 2.38. These values are similar to other Pb-oxychloride minerals.

Chemical composition

For hereroite and vladkrivovichevite 20 and 15 analyses, respectively, were obtained using a Cameca SX100 microprobe in wavelength-dispersive spectrometry (WDS) mode, operating at 20kV accelerating voltage and 20nA beam

Wavelength	Hereroite	Vladkrivovichevite	
(nm)	R'	R_1	R_2
400	20.4	22.0	23.2
420	19.4	19.5	20.2
440	18.6	18.4	19.0
460	18.1	17.5	18.2
470 (COM)	17.9	17.2	17.9
480	17.7	17.0	17.7
500	17.4	16.6	17.2
520	17.1	16.1	16.7
540	16.9	15.8	16.3
546 (COM)	16.9	15.7	16.3
560	16.8	15.6	16.2
580	16.7	15.6	16.2
589 (COM)	16.6	15.5	16.1
600	16.55	15.5	16.1
620	16.4	15.4	16.0
640	16.3	15.3	16.0
650 (COM)	16.3	15.4	16.1
660	16.2	15.4	16.2
680	16.3	15.7	16.8
700	16.4	16.2	17.7

TABLE 1. Reflectance values for hereroite and vladkrivovichevite.

Reflectance values measured in air using SiC as a standard.

The abbreviation COM denotes a standard point of measurement as defined by the Commission on Ore Mineralogy.

current with a beam diameter of 20 μ m, at the Natural History Museum, London. The analyses (Table 2) were made on a number of separated monomineralic grains, which gave consistent results. The elements P, Mg, Mn, Cu, Al and Fe were sought, but were below detection limits.

Forty further analyses of three different grains of vladkrivovichevite were obtained using a Camscan-4DV scanning electron microscope (SEM) with an AN-10000 energy-dispersive X-ray (EDX) spectrometer, operating at 30 kV accelerating voltage and 0.7 nA beam current with a 3 μ m beam diameter, at the Radium Institute, St Petersburg; PbL α , MnK α , and ClK α were used as analytic lines. The spectrum of the PbM α line was subtracted to get the correct chemical formula because of its overlap with the ClK α line (peak overlap correction). All calculations were made using AF4/FLS software.

For hereroite, H_2O and CO_2 could not be determined directly due to the small amount of material that was available, but analytical totals close to 100 wt.% combined with crystallographic data suggest that they are absent. For vladkrivovichevite, H_2O and BO_3 were calculated on the basis of structural considerations as insufficient sample was available for the determination of H_2O and BO_3 using CHN or any other type of conventional light-element analysis.

The empirical formula for hereroite assuming 32 lead atoms per formula unit (a.p.f.u.) is $[Pb_{32}O_{20.70}](AsO_4)_2((Si_{0.48}As_{0.29}V_{0.15}Mo_{0.09}) O_4)_2Cl_{9.84}$ which gives a simplified formula which

Constituent	— Hereroite —		Vladkrivovichevite		Probe standard(s)	
	Mean (wt.%)	Range	Mean (wt.%)	Range		
PbO	91.90	91.57-92.32	91.15	91.08-91.20	Pyromorphite, vanadinite, PbTe	
MnO	_	_	1.34	1.27 - 1.39	Elemental Mn	
As ₂ O ₅	3.81	3.64-4.15	_	_	GaAs	
SiO ₂	0.74	0.67 - 0.79	_	_	Fayalite	
V ₂ O ₅	0.35	0.28 - 0.41	_	_	Vanadinite	
MoO ₃	0.31	0.22 - 0.36	_	_	Mo metal	
Cl	4.49	4.16-4.55	5.59	5.29-5.81	Pyromorphite, vanadinite	
$O = Cl_2$	-1.01	-(0.94 - 1.03)	-1.29	_		
B_2O_3 (calc)*	_		3.13	_		
H_2O (calc)*	—	_	0.84	_		
Total	100.59	100.13-101.11	100.76			

TABLE 2. Chemical composition of hereroite and vladkrivovichevite.

These data were obtained by WDS analysis at the Natural History Museum, London.

* Calculated on the basis of stoichiometry from single-crystal data.

can be written $[Pb_{32}O_{21-x+y}](AsO_4)_2$ $((Si_x(As,V)_{1-x-y}Mo_y)O_4)_2 Cl_{10}$, with x = 0.48and y = 0.08. The ideal formula is $[Pb_{32}(O,\Box)_{21}](AsO_4)_2((Si,As,V,Mo)O_4)_2Cl_{10}$. The substitutions within the formula imply that hereroite may form a series with a number of hypothetical endmembers, and therefore it is possible that other phases may be found with varying but related formulae (see also Table 3). The empirical formula for vladkrivovichevite calculated on the basis of (Pb + Mn) =38 a.p.f.u. is $Pb_{36,32}O_{19}Mn_{1.68}Cl_{13.99}$ $(BO_3)_8:2H_2O$, and the ideal formula is $[Pb_{32}O_{18}]$ $[Pb_4Mn_2O]Cl_{14}(BO_3)_8:2H_2O$.

X-ray diffraction data and crystal structure

X-ray powder diffraction data were obtained using MoK α radiation on a Stoe Image Plate System at the Department of Crystallography, St Petersburg State University and are listed in Tables 4 and 5. Single-crystal X-ray diffraction studies were performed on both minerals. Hereroite is monoclinic, *C2/c* with *a* = 23.14(1), *b* = 22.65(1), *c* = 12.39(1) Å, β = 102.00(5)°, *V* = 6351.6(41) Å³ (from powder-diffraction data); and *a* = 23.139(4), *b* = 22.684(4), *c* = 12.389(2) Å, β = 102.090(3)°, *V* = 6358.8(18) Å³ (from single-crystal data). Vladkrivovichevite is orthorhombic, *Pmmn* with *a* = 12.87(5), *b* = 27.7(4), *c* = 11.46(3) Å, *V* = 4080.1(5) Å³ (from powder-diffraction data); and

a = 12.759(1), b = 27.169(4), c = 11.515(1) Å, V = 3992.0(9) Å³, Z = 2 (from single-crystal data).

The structural details of both minerals will be reported separately, and only a brief overview is given here. Vladkrivovichevite belongs to the 1:1 type of layered lead oxyhalides, whereas hereroite belongs to the 2:1 type. Their structures consist of alternating O-Pb double layers and chlorine sheets. In hereroite, tetrahedral AsO4 and (Si,As,V,Mo)O₄ groups locate in defects within the O-Pb block, this block contains square 'symesite-type' and double-square 'kombatitetype' cavities. Hereroite thus provides a structural link between symesite and mereheadite and kombatite, parkinsonite and sahlinite, a relationship not previously determined. The structure of vladkrivovichevite is unusual among Pb oxyhalides. It is based upon O-Pb derivative blocks with the interlayer occupied by Cl⁻ anions and oxocentred OPb₄Mn₂ octahedra whose eight triangular faces are capped by triangular borate anions, BO_3^{3-} .

Relationship to other species

Hereroite and vladkrivovichevite are related to other layered Pb oxyhalides that contain layers of oxocentred OPb₄ tetrahedra derived from tetragonal PbO (litharge). This group of minerals includes asisite, blixite, kombatite, mereheadite, parkinsonite, sahlinite, schwartzembergite and

TABLE 3. A comparison of the compositions of hereroite and the phase reported by Rouse *et al.* (1988).

Constituent	Hereroite (ideal) (wt.%)	Hereroite (actual) (wt.%)	Rouse <i>et al.</i> (1988) (wt.%)*
PbO	91.02	91.90	92.46
As ₂ O ₅	2.93	3.81	2.55
$V_2 \tilde{O}_5$	_	0.35	_
MoO ₃	_	0.31	_
SiO ₂	1.53	0.74	0.81
Cl	4.52	4.49	4.30
OH	_	_	0.66
Subtotal			100.78
$O = Cl_2$			-0.97
O = OH			-0.31
Total	100.00	100.59	99.50

* The chemical composition of the unknown phase described by Rouse *et al.* (1988) was provided by CJS, who was part of the team that described the then new mineral asisite. These data were not published at the time.

I _{rel}	$d_{\rm qbs}$	d_{calc}	h	k	l
	(A)	(A)			
6	11.8725	11.801	0	0	ī
3	9.8346	9.855	1	0	1
1	9.0666	9.039	1	1	1
2	7.9326	7.984	2	2	0
5	7.6161	7.561	0	3	0
4	6.8260	6.798	3	ī	ī
8	6.0331	6.021	3	2	ī
9	5.6781	5.671	0	4	0
5	5.3383	5.339	3	3	0
5	5.1715	5.177	3	3	ī
5	4.9791	4.997	1	2	2
5	4.8352	4.841	2	4	1
5	4.5129	4.519	2	2	2
6	4.2938	4.301	4	2	2
21	3.9013	3.915	5	1	1
23	3.5121	3.510	6	1	2
3	3.2657	3.266	7	ī	ī
100	2.9821	2.989	5	5	1
47	2.7950	2.797	8	0	2
2	2.6286	2.628	5	3	4
3	2.5028	2.505	1	9	0
8	2.2509	2.249	8	6	2
2	2.1269	2.132	7	8	0
1	2.1014	2.102	10	4	0
1	2.0443	2.044	8	7	1
24	1.9863	1.991	8	8	2
1	1.8853	1.886	12	0	0
1	1.8101	1.810	12	3	3
14	1.7580	1.769	8	10	2
4	1.7167	1.717	3	10	4
24	1.6411	1.641	11	5	5
12	1.5978	1.598	5	13	1
5	1.5652	1.566	8	12	2
4	1.5512	1.551	2	7	7
4	1.5373	1.538	15	1	2
5	1.4888	1.489	6	11	4
5	1.3960	1.396	11	11	4
3	1.3616	1.362	14	4	3
3	1.3070	1.307	14	2	4
4	1.2736	1.272	15	5	3
9	1.2529	1.257	18	0	0
10	1.2423	1.242	7	3	15
2	1.1891	1.190	12	6	6
4	1.1477	1.148	2	18	4
1	1.0897	1.090	14	10	8
3	1.0619	1.063	19	5	7

TABLE 4. X-ray powder diffraction data for hereroite.

The six strongest lines are indicated in bold face.

 TABLE 5. X-ray powder diffraction data for vladkrivovichevite.

$I_{\rm rel}$	d _{obs} (Å)	$d_{ m calc}$ (Å)	h	k	l
4	8.8506	8.874	0	2	1
6	6.4251	6.380	2	0	0
13	5 8127	5 775	2	2	Ő
6	5 5396	5 581	2	õ	1
4	5.4670	5.467	2	1	1
- 0	5 2181	5 248	1	0	2
6	4 0057	1 806	1	2	2
0	4.9037	4.090	1	1	2
8	4.2441	4.202	3	1	2
9	4.21/3	4.133	1	4	2
1	4.0728	4.077	2	2	2
9	3.9383	3.952	0	2	2
49	3.7069	3.713	1	1	0
3	3.5573	3.516	2	6	1
19	3.3594	3.349	3	2	0
9	3.2041	3.156	1	8	1
37	3.0681	3.074	4	0	1
100	2.8600	2.867	3	7	0
84	2.7329	2.729	0	7	3
7	2.6432	2.628	3	4	3
5	2.6194	2.608	4	6	0
1	2.5724	2.586	3	8	1
8	2.5040	2.509	2	7	3
6	2.4454	2.443	4	1	3
5	2.2255	2.224	2	9	3
3	2.1910	2.172	2	7	4
8	2.1257	2.127	6	0	0
32	2.0746	2.074	4	7	3
13	1.9385	1.941	0	14	0
15	1.9225	1.928	1	12	3
4	1.8991	1.920	0	0	6
3	1.7657	1.773	3	12	3
2	1.7464	1.750	6	5	3
15	1.7064	1.716	1	14	3
20	1.6774	1.676	6	7	3
23	1.6483	1.640	7	7	0
32	1.6008	1.604	3	14	3
28	1.5950	1.595	3	7	6
3	1 5464	1 547	7	6	3
2	1 4615	1 457	4	15	3
6	1 4283	1 434	6	14	0
6	1.3691	1 365	0	14	6
4	1 3322	1 3 3 4	2	14	6
4	1.3322	1.554	10	0	0
т 14	1.2730	1.276	7	14	2
0	1.2340	1.230	2	21	0
7	1.2277	1.236	2	21	0
2	1.2105	1.225	0	7	9
∠ 5	1.2130	1.213	10	7	7 2
5	1.1494	1.130	10	21	3 2
4	1.1393	1.144	4	21 7	3
2	1.1295	1.130	4	/	9
3	1.1119	1.094	9	/	6
2	1.1061	1.063	10	0	6
3	1.0048	1.062	6	21	3
2	1.0557	1.055	6	/	9
1	1.0496	1.047	7	0	9

symesite. Hereroite is most closely related to symesite and mereheadite (and an as yet unnamed phase that is probably a carbonate-bearing variant), and to kombatite and sahlinite and related minerals (Turner and Rumsey, 2010).

Vladkrivovichevite is structurally unique in the Pb oxyhalides as it contains oxocentred OPb₄Mn₂ octahedra. It can be considered to be related compositionally to chloroxiphite, Pb₃CuO₂(OH)₂Cl₂ (Spencer and Mountain, 1923; Finney et al., 1977; Siidra et al., 2008b); rickturnerite, Pb₇O₄[Mg(OH)₄](OH)Cl₃ (Rumsey et al., 2011); and philolithite, [Pb₂O]₆ [Mn(Mg,Mn)₂(Mn,Mg)₄(OH)₁₂(SO₄)(CO₃)₄]Cl₄ (Kampf et al., 1998; Moore et al., 2000). These minerals are similar to vladkrivovichevite in that they contain structural units based upon oxocentred OPb₄ tetrahedra (Siidra and Krivovichev, 2008; Siidra et al., 2008a, 2011). However, the structures of chloroxiphite, rickturnerite and philolithite are based upon chains of edge-sharing OPb4 tetrahedra, whereas in vladkrivovichevite the OPb4 tetrahedra link via common edges to form continuous two-dimensional layers, relating it structurally to symesite and mereheadite, and to kombatite and sahlinite and related minerals.

It is likely that hereroite is the phase described by Rouse et al. (1988) in close association with asisite as "...another, unnamed, oxychloride phase, which is currently under investigation." The chemical composition of this phase as determined at the time is close to that of hereroite (Table 3). The calculation in Table 3 for the ideal formula of hereroite assumes that (Si,As,V,Mo)O₄ is all present as SiO₄ and as such, it represents one potential endmember. Thus the compositional differences between the hereroite analysis and the phase of Rouse et al. (1988) are likely to be explained as mineral grains with slightly different compositions within this series. Unfortunately, Rouse et al. (1988) did not state whether or not they analysed for Mo and V, and it is impossible to comment on exactly how significant this compositional difference may be.

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