

Siidraite, $\text{Pb}_2\text{Cu}(\text{OH})_2\text{I}_3$, from Broken Hill, New South Wales, Australia: the third halocuprate(I) mineral

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Abstract: Siidraite, $\text{Pb}_2\text{Cu}(\text{OH})_2\text{I}_3$, is a new mineral from the Broken Hill deposit in New South Wales, Australia. It occurs as an extremely rare secondary phase alongside marshite, other lead and copper secondaries and supergene cuprite on a single specimen, BM 84642 preserved in the collection of the Natural History Museum, London. Siidraite is yellow and occurs in crystalline grainy aggregates up to 0.3 mm around relict galena. The mineral is translucent with a vitreous lustre and yellow streak, no cleavages or forms have yet been observed. It is non-fluorescent in mixed-wavelength UV light. The calculated density is 6.505 g cm^{-3} . Siidraite is orthorhombic, space group $Fddd$, $a = 16.7082(9) \text{ \AA}$, $b = 20.846(1) \text{ \AA}$, $c = 21.016(1) \text{ \AA}$, $V = 7320.0(8) \text{ \AA}^3$ and $Z = 32$. The empirical formula derived from a combination of electron-microprobe analysis and structure determination is $\text{Pb}_{2.06}\text{Cu}_{0.89}(\text{OH})_2\text{I}_{2.97}$, the ideal formula has (in wt%) 8.01 Cu_2O , 50.01 PbO , 42.65 I and 2.02 H_2O . The five strongest lines in the calculated X-ray powder diffraction pattern are $[(hkl), d_{\text{obs}} (\text{Å}), I/I_{\text{max}} (\%)]$: $[(246), 2.746, 100]$, $[(404), 3.270, 81]$, $[(264), 2.738, 77]$, $[(315), 3.312, 76]$, $[(351), 3.296, 69]$. The crystal used for structure determination had minor pseudomerohedral twinning on $[0\bar{1}1]$ and the structure was refined taking this into account to $R_1 = 0.037$, $wR_2 = 0.052$, $\text{Goof} = 1.016$, based upon 1368 unique reflections having $I > 2\sigma(I)$. The structure of siidraite is a framework comprising an alternation of two structural elements, a cubane-like $[\text{Pb}_4(\text{OH})_4]^{4+}$ group and a $[\text{Cu}_2\text{I}_6]^{4-}$ dimer of edge-sharing CuI_4 tetrahedra with non-equivalent Cu. Six halocuprate groups surround each $[\text{Pb}_4(\text{OH})_4]^{4+}$ nucleus, and each halocuprate group is shared between six adjacent $[\text{Pb}_4(\text{OH})_4]^{4+}$ groups, five long Pb–I bonds are required to complete the co-ordination of each Pb atom. The resulting $\text{Pb}(\text{OH})_3\text{I}_5$ polyhedra are centred on a tetrahedron of O atoms to form a $\text{Pb}_4(\text{OH})_4\text{I}_{16}$ cluster. Siidraite has a unique composition and structure. It is the third naturally occurring halocuprate(I) after marshite and nantokite. A compositionally similar synthetic compound $\text{Pb}_2\text{Cu}_2(\text{OH})_2\text{I}_2\text{Br}$ has been described that has cubane and CuI_4 groups, but a very different structural topology from that of siidraite. Bideauxite, $\text{Pb}_2\text{Ag}(\text{OH})\text{FCl}_3$, which has the $[\text{Pb}_4(\text{OH})_4]^{4+}$ group, shares some topological features with siidraite.

Key-words: siidraite; new mineral; halocuprate(I); $[\text{Pb}_4(\text{OH})_4]^{4+}$ group; iodine; Broken Hill.

1. Introduction

Halocuprate(I) compounds characteristically contain monovalent copper and have been studied extensively in the form of organometallic structures, which have technologically significant properties including photoluminescence, magnetism and semiconductivity. As far as we are aware, there is only one inorganic lead-bearing halocuprate(I), $\text{Pb}_2\text{Cu}(\text{OH})_2\text{BrI}_2$, which occurs only as a synthetic compound (Hu *et al.*, 2011). Here, we report the discovery and characterisation of a related new inorganic halocuprate(I) mineral, siidraite, $\text{Pb}_2\text{Cu}(\text{OH})_2\text{I}_3$, having a very different crystal structure from $\text{Pb}_2\text{Cu}(\text{OH})_2\text{BrI}_2$. It is only the third halocuprate(I) mineral after marshite CuI and nantokite CuCl , both of which are rare minerals.

Siidraite was found during investigation of iodine-bearing minerals in the collection of the Natural History Museum, London (henceforth NHM). It is known from

just one specimen, registered as marshite, obtained from the mineral dealer Dr. A.E. Foote of Philadelphia in 1899. The specimen has abundant orange marshite on cavity-ridden cuprite and is from the Broken Hill Mining Area in Australia, it is registered in the mineral collection as BM 84642. A search for further specimens in the collection of the NHM and the Museum Victoria, Melbourne, Australia was unsuccessful.

Siidraite (“сийдрайт”) is pronounced “see-dra-ite” and named after Russian mineralogist and crystallographer Oleg I. Siidra (b. 1981) for his extensive work on secondary lead oxysalts and, in particular, on synthetic iodine-rich phases (Siidra *et al.*, 2013a, b, and c). The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2016-038) and there is no similar material on the valid or invalid unnamed minerals lists (Smith & Nickel, 2007; IMA-CMNMC website).

Holotype material constitutes the original specimen, BM 84642, and the polished probe block and single-crystal mount removed from it, both registered under the new number BM 2016,1 at the NHM.

2. Occurrence

Sample BM 84642 is from the Broken Hill deposit in New South Wales, Australia, a classic supergene enrichment deposit. The deposit has been extensively studied for decades and a detailed description of the geology and its relevance to mineral collecting and mineral specimens was summarized in Birch (1999).

Due to the entry date of the specimen into the NHM collection, the nature of recording information at that time and the fact it came to the NHM through a mineral dealer, the specific locality within the deposit is unknown. However, it is suggested that, as it was obtained not long after Broken Hill was first mined (1885), the specimen is likely to be from the upper oxidation zone levels of the mine (S. Mills, personal communication).

The specimen is a mass of cuprite and native copper, pervaded by cavities in which cuprite has grown as well-formed octahedra. Occasionally within the cuprite and the cavities there are small relict blebs and broken shards of the characteristic Broken Hill galena–Mn-silicate ore and quartz. Some cavities host a complex suite of secondary minerals that is dominated by orange/pale-brown translucent marshite tetrahedra, blue linarite and connellite, green brochantite and tsumebite, white anglesite, traces of plumbogummite-group minerals and, occasionally, where relict galena occurs in very close proximity to marshite and cuprite, tiny yellow granular aggregates of the new mineral siidraite.

Considering the coexisting minerals present, it is suggested that siidraite formed from the secondary alteration of cuprite that was at one time part of an area of supergene enrichment within the Broken Hill deposit. Mineralising fluids were extremely rich in iodine and not strongly oxidizing. Siidraite formed only due to the local availability of Pb mobilized from the small galena “blebs” and shards present, and it is this feature that determines the scarcity of the phase.

3. Physical properties

Siidraite occurs on the holotype specimen in patches up to 2 mm in size, although the individual aggregates of siidraite crystals within these areas are no more than 0.3 mm across (Fig. 1). Siidraite is translucent in various shades of yellow; the variation in colour is apparently due to its small size and adjacency and/or intergrowth with nearby brochantite, anglesite, cuprite and marshite. When strongest yellow and presumably purest, the colour is most similar to HTML colour codes FFFF66 and FFFF33.

Individual crystals have not been clearly observed in hand specimen or during optical microscope work. When small areas were disaggregated for single-crystal diffraction

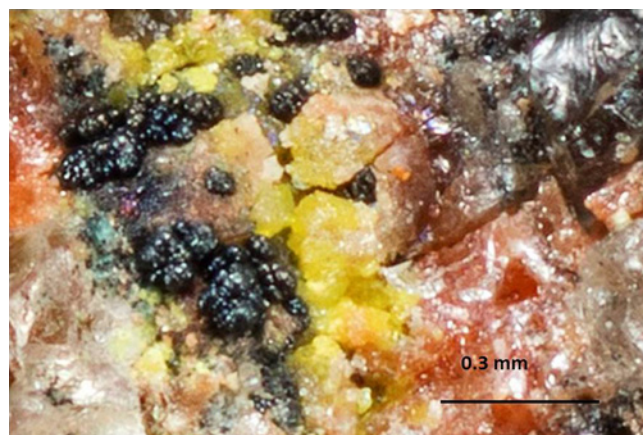


Fig. 1. A close-up of the richest area of siidraite on specimen BM 84642 from Broken Hill, Australia. Showing yellow crystalline areas of siidraite associated with deep red cuprite, white anglesite, orange marshite, glassy silicates and blackened galena.

studies, the crystal shape and any forms were still indistinct, though seemingly equant with a vitreous lustre. The largest single crystals removed were up to 0.1 mm long.

Where material was sampled from the holotype specimen, the powdered remains indicate that the streak is the same yellow colour as the mineral. No cleavages or parting were observed and fracture and tenacity were impossible to assess accurately on such small crystals.

Siidraite is non-fluorescent in both short- and long-wave UV light, the size of the crystals and overall paucity of material precluded the determination of both Mohs hardness and density by direct measurement. By analogy with similar materials (bideauxite, marshite, miersite), the hardness of siidraite is likely around 2.5–3.5 on the Mohs scale. The density calculated for the empirical formula is 6.505 g cm^{-3} and for the ideal formula is 6.465 g cm^{-3} .

Due to the nature and paucity of the material, no quantitative optical properties could be obtained. The calculated mean refractive index based on the ideal formula is 2.18.

4. Chemical composition

A sample containing siidraite was analysed using a Cameca SX100 electron microprobe in wavelength-dispersive mode at the NHM in London using an accelerating voltage of 20 kV, a beam current of 20 nA and a beam diameter of 0.01 mm. The elements (with relevant standard) Cu (Cu metal), Pb ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$), I (KI), Ag (Ag metal), Fe (Fe_2O_3), Sb (Sb metal), V ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$), Mn (MnTiO_3), Cl (NaCl), Br (KBr), K (orthoclase) and S (ZnS) were sought. All elements apart from Cu, I and Pb were found to be below detection limits. It is of note that an earlier analysis of a different subsample using a Zeiss EVO 15LS scanning electron microscope operated with 20 kV accelerating voltage and 3 mA beam current, coupled with an Oxford Instruments XMax 80 (EDS), revealed traces of Br.

Table 1. Analytical data (wt%) for siidraite obtained by EMPA.

Constituent	Mean	Range	SD	Standards
Cu_2O	7.22	6.96–7.35	0.12	Cu
PbO	51.8	50.1–53.4	1.03	PbVO_4
I	42.5	42.2–42.8	0.19	KI
H_2O	2.03	1.99–2.08		Calculated
Total ($-\text{I}=\text{H}_2\text{O}$)	100.94	98.89–102.65		Calculated

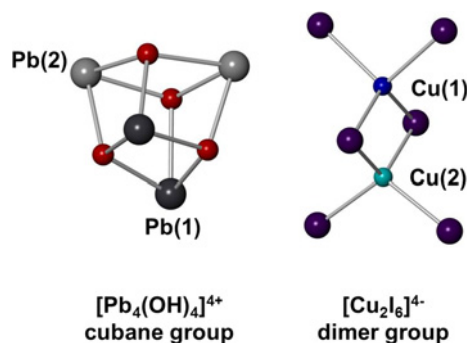


Fig. 2. The two structural components of siidraite. The $\text{Pb}_4(\text{OH})_4$ cubane group contains four oxygens and two non-equivalent Pb atoms. The Cu_2I_6 dimer unit comprises two non-equivalent Cu sites coordinated to six I atoms. The crystal structure consists of a checkerboard pattern of alternating cubane and dimer units.

There was not enough material on the holotype specimen to perform CHN analysis or to quantify water content directly by any means other than based on stoichiometry from the structural refinement. The average values for 10 spot electron-microprobe analyses are reported in Table 1. The empirical formula calculated on the basis of five anions (including two OH), according to the crystal-structure study, is $\text{Pb}_{2.08}\text{Cu}_{0.90}(\text{OH})_2\text{I}_3$. The corresponding ideal formula $\text{Pb}_2\text{Cu}(\text{OH})_2\text{I}_3$ has 8.01 wt% Cu_2O , 50.01 wt% PbO, 42.65 wt% I and 2.02 wt% H_2O .

5. Crystal structure

Full details of the crystal structure determination of siidraite are reported by Welch *et al.* (2016). However, a summary of the structure is given here. A Crystallographic Information File (CIF) containing details of the data collection and structure refinement is deposited with the journal. A list of structure factors is also deposited with the journal. They are freely available online as Supplementary Material linked to this article on the GSW website of the journal: <http://eurjmin.geoscienceworld.org/>. Several small yellow transparent crystals of siidraite were examined for structure determination using an XcaliburE four-circle diffractometer, EOS detector and $\text{MoK}\alpha$ radiation (Rigaku Oxford Diffraction). Siidraite has orthorhombic symmetry, space group *Fddd*. Unit-cell parameters derived from single-crystal X-ray diffraction are: $a = 16.7082(9)$ Å, $b = 20.846(1)$ Å, $c = 21.016(1)$ Å, $V = 7320.0(8)$ Å³ ($Z = 32$), and final

agreement indices for structure refinement are $R_1 = 0.037$, $wR_2 = 0.052$, $\text{Goof} = 1.016$, based upon 1368 unique reflections with $I > 2\sigma(I)$.

The structure topology of siidraite is unique and consists of two structural elements that alternate in a checkerboard motif: (1) a $\text{Pb}_4(\text{OH})_4$ “cubane” group and (2) a Cu_2I_6 dimer in which a pair of CuI_4 tetrahedra share an edge. These two components are shown in Fig. 2. Despite their very similar individual geometries, the two constituent $\text{Cu}(1)\text{I}_4$ and $\text{Cu}(2)\text{I}_4$ tetrahedra of the Cu_2I_6 dimer have very different next-nearest-neighbour environments.

6. Raman spectroscopy

Details of the collection of the Raman spectrum and peak assignments for a single crystal of siidraite that was part of the crystal separated from BM 84642 are reported by Welch *et al.* (2016). Peaks below 400 cm^{-1} were assigned to modes of the cubane (Jensen, 2002) and Cu_2I_6 dimer units, and internal modes of the CuI_4 tetrahedra (Ouslati *et al.*, 2013). Two peaks occur in the OH-stretching region at 3443 and 3455 cm^{-1} and are assigned to the two non-equivalent OH groups known to be present in siidraite from the structure determination. The presence of two non-equivalent OH groups is consistent with the *Fddd* structure, but not the tetragonal (*I4₁/acd*) structure, which has only one symmetrically non-equivalent OH group.

7. Powder X-ray diffraction

Due to the very small quantities of siidraite available, it was not possible to collect X-ray powder diffraction data. An attempt was made to collect a pseudo-powder pattern using a quasi-Gandolfi movement on a Rigaku Rapid II curved image-plate diffractometer (®Rigaku Oxford Diffraction) for the single crystal for which the structure was determined. However, diffraction from this very small crystal was so weak that no usable pattern was obtained after a 2-day collection. Consequently, X-ray powder diffraction data for siidraite were calculated from the crystal structure and are given in Table S1 in Supplementary Material.

8. Discussion

Siidraite is only the third halocuprate(I) mineral. A synthetic compound with similar stoichiometry $\text{Pb}_2\text{Cu}(\text{OH})_2\text{I}_2\text{Br}$ has been described (Hu *et al.*, 2011). This phase

has the $\text{Pb}_4(\text{OH})_4$ cubane group, but has chains of corner-sharing CuBr_2I_2 tetrahedra rather than isolated edge-sharing Cu_2I_6 pairs, resulting in a very different structural topology. As far as we are aware, siidraite and synthetic $\text{Pb}_2\text{Cu}(\text{OH})_2\text{I}_2\text{Br}$ are the only Pb-based cuprous oxyhalides.

Topological variants for $\text{Pb}_2M^+(\text{OH})_2X_3$ stoichiometry may occur that depend upon the halogen motif, which itself may be dependent upon halogen type (size). The novel structure described here hints at the possibility of synthesizing a new class of *inorganic* halocuprates based upon the cubane-type $\text{Pb}_4(\text{OH})_4$ cluster and CuI_4 tetrahedra having varying degrees of tetrahedral polymerization of the latter that could be engineered by modifying halogen composition. A synthetic methodology for controlling structure topology could be found through better understanding of the paragenesis of siidraite within the natural environment. With this possibility in mind, it is noteworthy that the $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster has a role in controlling Pb mobility in aqueous system, but its occurrence is limited to near and just below neutral pH conditions (Ronay & Seff, 1993; Grimes *et al.*, 1995). The rarity of minerals containing the $\text{Pb}_4(\text{OH})_4$ cluster is likely due to the transient nature of pH conditions favouring its stabilisation, as more alkaline conditions develop and new products arise from the continued oxidation of original galena.

For maricopaite (Rouse & Peacor, 1994), a mineral with $\text{Pb}_4(\text{OH})_4$ groups incorporated into a mordenite-type aluminosilicate framework, it has been suggested that the framework crystallised around the aqueous $[\text{Pb}_4(\text{OH})_4]^{4+}$ cation from a near-neutral pH solution. Further insight might also be gained from studying bideauxite, $\text{Pb}_2\text{Ag}(\text{OH})\text{FCl}_3$, space group $Fd\bar{3}m$, which has some structural similarity to siidraite (Cooper *et al.*, 1999). The structure of bideauxite is composed of a checkerboard framework of alternating AgCl_6 octahedra and $\text{Pb}_4(\text{OH}_{0.5}\text{F}_{0.5})_4$ cubane-type groups. The Cl motif is different from the I motif of $\text{Pb}_2\text{Cu}(\text{OH})_2\text{I}_3$ and results in octahedral (rather than tetrahedral) sites being occupied by the monovalent cation (Ag). The cubane group in bideauxite is bonded to 18 Cl atoms to give a $\text{Pb}_4(\text{OH}_{0.5}\text{F}_{0.5})_4\text{Cl}_{18}$ cluster. Two extra halogen atoms enter the coordination sphere of the cubane group of bideauxite compared with the $\text{Pb}_4(\text{OH})_4\text{I}_{16}$ cluster of siidraite. Although bideauxite and siidraite are very rare minerals, their existence suggests that further cubane-like halide “cluster” compounds may occur.

Acknowledgements: The authors would like to thank Tony Wighton of the NHM for specimen preparation and Dr. Stuart Mills (Museum Victoria, Australia) for his opinions on the origin of the specimen. An anonymous reviewer and Dr. Tony Kampf are thanked for their reviews of this paper.

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Received 25 January 2017

Modified version received 3 May 2017

Accepted 19 June 2017