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Mereheadite, $Pb_2O(OH)Cl$: a new litharge-related oxychloride from Merehead Quarry, Cranmore, Somerset

M. D. WELCH, A. J. CRIDDLE AND R. F. SYMES

Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, UK

ABSTRACT

Mereheadite, ideally $Pb_2O(OH)Cl$, is a new mineral related to litharge and which is structurally similar to synthetic bismuth-oxyhalides. With other lead- and lead-copper oxychlorides, it occupies lenses and cavities in veins of manganese and iron oxide minerals which cut through a sequence of dolomitic limestones at Merehead quarry, Cranmore, Somerset (51°12′N, 2°26′W). Mereheadite is pale yellow to reddish-orange, transparent to translucent and has a white streak and a vitreous or resinous lustre. It is not fluorescent. Individual grains, up to a few mm across, cluster together in compact masses of 10–30 mm in size, but discrete crystals have not been observed. Specular reflectance data on randomly orientated grains from 400 to 700 nm are provided, and refractive indices calculated from these at 590 nm range from 2.19 to 2.28. $H = 3.5$, $VHN_{100} = 171$, $D_{(meas)} = 7.12(10)$ g/cm^3, $D_{calc} = 7.31$ g/cm^3. The mineral is brittle with an uneven, conchoidal to hackly fracture and has a perfect (001) cleavage which is parallel to the sheets of PbO and Cl. It is intimately associated with mendipite, blixite, cerussite, hydrocerussite and calcite in lenses and pods in the veins. Other minerals which occupy cavities in these veins include chloroxiphite, paralaurionite, parkinsonite and the borosilicate datolite. Mereheadite is monoclinic, space group *C*2/*c,* and its cell parameters, refined from powder X-ray diffraction are: $a = 5.680(2)$, $b = 5.565(3)$, $c = 13.143(9)$ Å, $\beta = 90.64(4)°$, $V = 415.4\ (8)$ Å^3, $Z = 4$. The ten strongest reflections in the X-ray powder diffraction pattern are [*d* in Å, (I, *hkl*)]: 2.930(10,113), 3.785(5,111,−111), 2.825(4,200), 6.581(4,002), 2.182(4,115), 2.780(4,020), 3.267(4,004), 1.980(3,−220), 1.695(3,224,132,117), 1.716(3,026). Its empirical formula is $Pb_8O_{4.19}(BO_3)_{0.51}(CO_3)_{0.62}(OH)_{0.76}Cl_{4.09}$. Although it is very similar chemically to blixite, it has notably different cell parameters. There is some uncertainty about the essential nature of boron and carbon in natural mereheadite. This stems from the impossibility of ensuring the purity of samples for wet-chemical analysis, and from the predominance of lead in the structure of the mineral which has meant that the location of boron and carbon within the mereheadite structure is unresolved. ^{11}B MAS NMR does show, however, that boron is present as BO_3 groups. The structure consists of alternating PbO sheets and layers of chlorine atoms. Each lead atom is coordinated to four chlorines and four O/OH in a square antiprism configuration. As such, it is structurally-related to nadorite, thorikosite and schwartzembergite. Comparisons with structurally analogous phases such as bismuth oxychlorides and bismutite ($Bi_2O_2CO_3$) suggest that the BO_3 and CO_3 groups are likely to replace chlorine in the layer between PbO sheets. The composition of natural mereheadite is defined by three end-members: the mereheadite end-member $Pb_2O(OH)Cl$, and two fictive end-members $Pb_2(OH)_2CO_3$ and $Pb_4O(OH)_3BO_3$.

KEYWORDS: mereheadite, litharge, Somerset, England, oxychloride.

Introduction

SPECIMENS from a secondary lead and copper oxychloride assemblage at Merehead Quarry, Cranmore, Somerset, England, include a new yellow-orange mineral close in chemical composition to blixite (Gabrielson *et al.*, 1958) which we have named mereheadite. The name and characteristic data for the mineral have been approved by the Commission on New Minerals and Mineral Names. The type specimen BM 1965,285 and polished mount E.1175 are registered at The

Natural History Museum, London, England. These were collected directly from manganese-rich pods along 'Vein 2' at Merehead Quarry (Symes and Embrey, 1977) and from loose blocks believed to have been derived from 'Vein 1'. In specimens from Vein 2 the mineral is typically coarsely crystalline to massive, and is associated with calcite in a matrix of manganese oxide 'wad' or pyrolusite. In Vein 1, mereheadite is associated with calcite, mendipite, cerussite and hydrocerussite, and in some cases with the red litharge-related, lead-molybdenum oxychloride parkinsonite, $Pb_7MoO_9Cl_2$ (Symes *et al.*, 1994; Welch *et al.*, 1996). Though individual grains of mereheadite rarely exceed 2 mm in size, they habitually cluster together to form compact polycrystalline masses up to 10 × 30 mm in size.

Physical and optical properties

Mereheadite is pale yellow (Methuen 3A3) to reddish orange (Methuen 7B7), transparent to translucent and has a white streak, a vitreous or resinous lustre and an uneven, conchoidal to hackly fracture; it is not fluorescent. $H = 3.5$, $VHN_{100} = 171_{10}$ (range 151–192), $D_{(meas)} = 7.12(10)$ g/cm^3. There is a perfect (001) cleavage that in hand specimen is difficult to distinguish from the striated plane crystal faces found in the massed clusters of grains. Attempts to obtain reliable optical constants for mereheadite using immersion liquids were hampered by its high refringence which exceeds 2.1. Its optical properties were, therefore, subjected to observation and measurement in reflected light. Three grains were separated from the type specimen and polished in E.1175. In plane-polarised reflected light, the mineral is a nondescript grey of modest reflectance and weak bireflectance. It is not pleochroic but the amber to light yellow internal reflections, which are ubiquitous, can mislead the untutored eye into believing that the variable effects of these reflections are the product of pleochroism. Similarly, between crossed polars, if the mineral is anisotropic, this is completely masked by the internal reflections.

Reflectance measurements were made between 400 and 700 nm relative to a Zeiss SiC reflectance standard, no 472, and using Zeiss oil $N_D = 1.515$ for immersion. The effective numerical apertures of the objectives used were adjusted to 0.15. It was impossible to orientate grains for measurement at clearly defined positions of extinction; instead they were positioned with respect to reflectance maxima and minima at 590 nm. The reflectance data (monotone from 400 to 700 nm) and colour values for the most bireflectant grain (Table 1) are consistent with the nondescript grey (blue-grey) observed by eye. Refractive indices calculated from the reflectance values at 590 nm (and assuming zero absorption) of 2.19 to 2.28, fall between those reported by Gabrielson *et al.* (1958) for blixite of 2.05 to 2.20 and those for damaraite of 2.29–2.34 (Criddle *et al.*, 1990).

TABLE 1. Reflectance spectra and colour values for mereheadite BM 1965.285

λ nm	R_1	R_2	$^{im}R_1$	$^{im}R_2$
400	17.20	17.95	5.07	5.65
420	16.50	17.40	4.69	5.28
440	15.90	16.90	4.40	4.99
460	15.50	16.50	4.17	4.77
470	15.20	16.30	4.07	4.67
480	15.10	16.10	3.98	4.58
500	14.90	15.80	3.83	4.43
520	14.50	15.50	3.70	4.30
540	14.30	15.30	3.61	4.19
546	14.20	15.30	3.59	4.17
560	14.10	15.20	3.53	4.11
580	14.00	15.00	3.47	4.05
589	13.90	15.00	3.44	4.02
600	13.90	14.90	3.43	3.99
620	13.80	14.80	3.39	3.96
640	13.80	14.80	3.37	3.93
650	13.70	14.70	3.37	3.91
660	13.70	14.70	3.34	3.90
680	13.60	14.65	3.32	3.88
700	13.60	14.60	3.30	3.86
Colour values for CIE illuminant C:				
x	0.3003	0.3011	0.2925	0.2942
y	0.3045	0.3055	0.2944	0.297
Y%	14.2	15.3	3.58	4.16
λd	474	474	473	474
Pe%	5	4.6	9	8.1

Chemistry

An initial semi-quantitative chemical survey was conducted using an Hitachi S-2500 analytical SEM in EDS mode (LINK systems) and this revealed that the only detectable elements were lead and chlorine. Electron microprobe analysis

(WDS) of mereheadite was performed on a CAMECA SX50 probe operated at 20 kV and 20 nA with a 1 μm focussed beamspot. PbO and NaCl were used as microprobe standards. Wet-chemical and electron microprobe data are given in Table 2. The average lead:chlorine ratio from 17 electron microprobe analyses is 1.93 ± 0.03 (1σ). Boron was originally detected in emission spectra from grains of the mineral hand-picked by G.C. Jones (NHM) from the type specimen BM 1965.285, and was quantified colorimetrically (Curcumin method) by the late Dr A. A. Moss. Boron particle-track analysis (Din and Henderson, 1982; Din *et al.*, 1986) was carried out on a polished section made from the type material (in which laths of mereheadite are intergrown in a matrix of blixite). The resulting boron particle-track map (Fig. 1*b*) clearly shows the presence of boron in mereheadite and its absence from blixite. The CO_2 and H_2O contents of the mereheadite sample were determined by CHN analysis (Perkin-Elmer 240 analyser) on part of the sample used for colorimetric analysis.

TABLE 2. Chemical data for mereheadite BM 1965.285

	Ideal	1	2
PbO	90.95	90.5	90.0(5)
Cl	7.22	6.8	7.4(1)
B_2O_3	–	0.6	n.a.
CO_2	–	1.4	n.a.
H_2O	1.83	0.7	n.a.
	100	100	97.4(5)
O = Cl	1.63	1.5	1.7
Total	98.37	98.5	95.7(5)
Pb/Cl	2	2.11	1.93

1. Wet chemical analysis by Dr A.A.Moss on hand-picked grains: CO_2 and H_2O by CHN analyser, B determined colorimetrically by the Curcumin method.
2. Average of 17 electron microprobe analyses obtained on a Cameca SX50 instrument operated at 20 kV, 20 nA with a 1–2 μm beam; PbO and NaCl standards. Numbers in brackets are 1σ of the mean and refer to the first decimal place.

n.a. = not analysed

Although we are confident that the boron analyses are accurate, and that boron is a definite component of mereheadite, we remain uncertain as to whether or not it is an essential component. The same holds true for carbon: though it was undoubtedly present in the analysed sample, the possibility that its presence was due to admixture of mereheadite with cerussite or hydrocerrusite cannot be ruled out. For these reasons we have opted for a boron- and carbon-free end-member formula $Pb_2O(OH)Cl$ for the mineral. This formula is very similar to that of blixite, $Pb_2[O(OH)]_{<2}Cl$ (Gabrielson *et al.*, 1958). However, mereheadite is monoclinic, not orthorhombic, and has significantly different cell parameters from blixite (see below).

X-ray crystallography

Mereheadite, $Pb_2O(OH)Cl$, is monoclinic but pseudo-orthorhombic and pseudotetragonal. Precession photographs were obtained on a single, optically continuous, somewhat tabular cleavage fragment approximately 0.1 mm on an edge and 0.05 mm thick. With the fragment mounted with the (001) cleavage normal to the X-ray beam the precession photographs appeared tetragonal; the smallest dimensions were determined as approximately 4.0 Å and the diagonals as approximately 5.6 Å. Close examination of the diagonals revealed them to be of slightly different lengths. These were then designated *a* and *b* for the new 'orthorhombic' cell. Zero-level photographs about the *y* axis (*h*0*l*) then showed the angle β to be 0.5° greater than 90°. This further reduced the symmetry to monoclinic.

X-ray powder diffraction data were obtained using an Enraf-Nonius position-sensitive-detector (PSD) diffractometer. As a limited amount of type material was available, an external Si metal standard was used to avoid specimen contamination. Our experience with the PSD has shown that the detector response is extremely stable over several days and that external standardization is very reliable when it is done within hours of collection of the sample's pattern. Unit-cell parameters were refined using the program LSUCRIPC (Garvey, 1986). Starting cell parameters used for refinement of the powder data were a = 5.67, b = 5.58, c = 13.15 Å and β = 90.5°, and are based upon the single-crystal data (Welch *et al.*, in preparation). The cell parameters derived from the powder data are a = 5.680(2), b = 5.565(3), c = 13.143(9) Å, β = 90.64(4)° and V = 415.4 (8) $Å^3$. There is good agreement between the cell parameters obtained by single-crystal and powder methods. A listing of *d*, I and *hkl* values is given in Table 3.

TABLE 3. *d*-spacings and peak intensities of X-ray reflections for mereheadite BM 1965.285 from powder diffraction data

I_{obs}	d_{obs} (Å)	d_{calc} (Å)	*h*	*k*	*l*
37	6.581	6.571	0	0	2
48	3.785	3.796	1	1	1
		3.813	−1	1	1
35	3.267	3.286	0	0	4
100	2.930	2.932	1	1	3
		2.955	−1	1	3
43	2.825	2.840	2	0	0
36	2.780	2.782	0	2	0
37	2.182	2.185	1	1	5
		2.190	0	0	6
10	2.148	2.137	2	0	4
21	2.118	2.123	0	2	4
33	1.980	1.987	−2	2	0
7	1.766	1.763	−1	3	0
11	1.745	1.744	−2	0	6
		1.748	−1	3	1
		1.747	1	3	1
10	1.732	1.734	−3	1	2
26	1.716	1.721	0	2	6
30	1.695	1.695	2	2	4
		1.702	1	3	2
		1.692	1	1	7
10	1.655	1.653	3	1	3
10	1.645	1.643	0	0	8
22	1.633	1.634	1	3	3
		1.638	−1	3	3
6	1.489	1.488	−3	1	5
6	1.471	1.474	3	1	5
7	1.463	1.462	1	3	5
		1.467	−1	3	5
		1.466	2	2	6
4	1.423	1.420	4	0	0
6	1.412	1.415	0	2	8
		1.415	2	0	8
6	1.391	1.391	−4	0	2
		1.391	0	4	0
4	1.369	1.370	−2	2	7
		1.370	1	3	6
4	1.365	1.367	1	1	9
5	1.310	1.309	−4	0	4
5	1.297	1.297	3	3	2
		1.298	4	0	4
9	1.286	1.288	−1	3	7
		1.290	3	1	7
		1.283	1	3	7
4	1.268	1.265	3	3	3
4	1.264	1.265	−4	2	0
4	1.261	1.261	2	2	8
4	1.249	1.249	−2	4	0
2	1.193	1.198	−4	0	6
		1.198	−2	0	10
2	1.187	1.188	2	0	10
		1.188	0	2	10
		1.187	−3	3	5
4	1.186	1.185	4	0	6
		1.184	−4	2	4
2	1.175	1.174	0	4	6
		1.176	4	2	4
4	1.098	1.098	0	2	11
		1.099	−5	1	2
4	1.092	1.092	2	2	10
		1.092	−1	5	0
4	1.090	1.091	4	2	6

A detailed structural description of mereheadite and its relations with other layered lead-oxychlorides is in preparation by Welch *et al.* In brief, the structure of mereheadite comprises a basic structural unit $Pb(OH,O)_4Cl_4$ in which lead is coordinated to an upper square of two hydroxyls and two oxygens and a lower square of four chlorines to form a square antiprism. The symmetry operators then act upon this unit to form (00*l*) sheets of linked units that are stacked obliquely along *z*. The β angle is the stacking angle. As such, mereheadite is a member of the family of PbO-related layered lead-oxychlorides that includes nadorite, thorikosite and schwartzembergite, all of which are characterized by the alternation of PbO sheets with layers of chlorine atoms (Sillén and Melander, 1948; Giuseppetti and Tadini, 1973; Rouse and Dunn, 1985; Dunn and Rouse, 1985).

Boron and carbon in mereheadite

The boron particle-track map shown in Fig. 1*b* clearly shows that boron occurs in mereheadite and not in the matrix blixite, further suggesting that the two minerals are distinct. That single-crystal structure determination did not locate boron or carbon in the mereheadite structure (Welch *et al.*, in prep.) is a result of the dominating effect of lead on the residual scattering which effectively masks the small contributions from the weak scatterers.

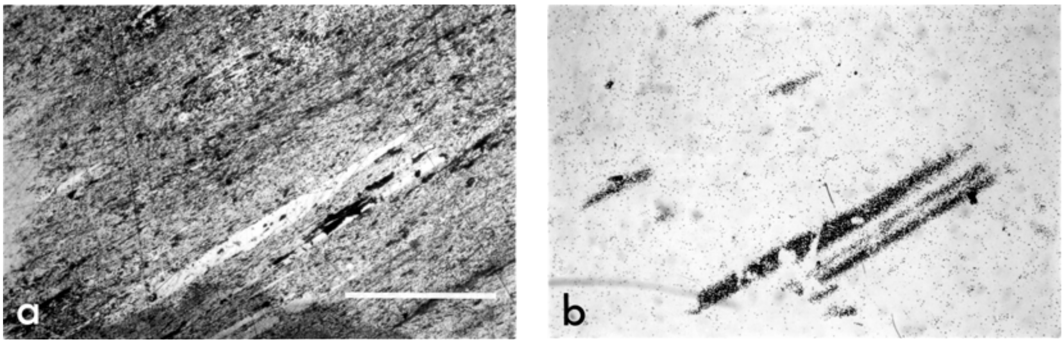

FIG. 1 (*a*) Optical photomicrograph (reflected light) of BM 1965.285 showing large mereheadite laths (good polish) within fine-grained blixite-rich matrix. (*b*) Boron particle-track map of the same area showing the preferential concentration of B in the mereheadite crystals relative to the matrix blixite. Scale bar is 1 mm and is the same for both micrographs.

However, some insights into the probable location of boron and carbon in mereheadite can be gained by examining the well-established structural similarities between the litharge-related lead oxychlorides and bismuth oxyhalides (Rouse and Dunn, 1985; Dunn and Rouse, 1985).

We have carried out ^{11}B MAS NMR spectroscopy on mereheadite BM 1965.285 which shows unequivocally that boron occurs as triangular BO_3 groups. The large size difference between boron/carbon and lead makes it very unlikely that boron or carbon replaces lead. It is, however, conceivable that BO_3 and CO_3 occupy the anion layers between PbO sheets in the same way as CO_3 lies between Bi_2O_2 sheets in bismutite, $Bi_2O_2(CO_3)$ (Lagerkrantz and Sillén, 1948). It is proposed that boron and carbon are incorporated into the mereheadite structure as layers of BO_3 or CO_3 replacing chlorine. As the amounts of boron and carbon are not well constrained for mereheadite (due to the dominance of the heavy atoms lead and chlorine) it is possible that the quantities involved are very small and do not result in a noticeable chlorine deficit.

Mereheadite, blixite and α-$Pb_4O_3Cl_2$

The compositions and physical properties of mereheadite and blixite are very similar. If, as seems possible, blixite has a PbO-related structure, the formula proposed by Gabrielson *et al.* (1958), $Pb_2(O,OH)_{1.7}Cl$, implies the presence of O/OH vacancies in the PbO sheets. The blixite formula is defined by two components: $Pb_2O(OH)Cl$ and $Pb_2O_{1.5}Cl$. The first is isochemical with mereheadite and the second may be a 'defect oxychloride' with oxygen vacancies in the PbO sheet. An anhydrous synthetic compound α-$Pb_4O_3Cl_2$ (orthorhombic) exists that has cell parameters a = 13.06, b = 5.58, c = 5.62 Å (JCPDS 6-405), which are close to those of mereheadite. The structure of α-$Pb_4O_3Cl_2$ is unknown, but the close correspondence to the cell parameters of mereheadite suggests that it may be the 'defect-oxychloride' end-member. If and how the two components are combined in blixite remains to be shown. Note that although we define the mereheadite end-member as $Pb_2O(OH)Cl$, this is an ideal formula that reflects the observed hydrous nature of BM 1965.285. The difficulty in getting sufficiently accurate OH contents for these minerals (due to the dominance of a very heavy element) opens up the possibility that natural mereheadites contain an anhydrous α-$Pb_4O_3Cl_2$-like component. Oxygen vacancies occur in the PbO sheet of kombatite (Cooper and Hawthorne, 1994) and this is compensated by the presence of the VO_4 apical oxygen. The presence of O/OH vacancies in mereheadite is a matter for conjecture.

Despite their similarities, mereheadite and blixite have rather different cell parameters: mereheadite is monoclinic (pseudo-orthorhombic) with a = 5.680, b = 5.565, c = 13.143 Å, β = 90.64°, whereas blixite is orthorhombic with a = 5.832, b = 5.694, c = 25.470 Å. Furthermore, the preferential occurrence of boron in mereheadite may also point to structural differences – the structure of mereheadite being able to accommodate boron, that of blixite not. The cell parameters are the most obvious means of distinguishing the two minerals.

Petrogenesis

It has been suggested that the lead oxychloride minerals at Merehead Quarry were produced by the interaction of brines with primary lead sulphides (Symes and Embrey, 1977). However, the geochemical details are not well understood. In several other localities around the world lead oxychlorides have formed by the interaction of brines with primary sulphides and have also been produced by the alteration of ancient lead slags by seawater at Laurion in Attike, Greece (Schnorrer-Köhler, 1986). In their experimental study of the effects of pH and Cl^- concentration (a_{Cl^-}) upon the stabilities of lead oxychlorides in the model system $PbO\text{-}HCl\text{-}H_2O$, Edwards *et al.* (1992) found that litharge is stable at pH >9.5 and $a_{Cl^-} < 10^{-4}$ M. Blixite is stable from pH 3 to pH 8 and over a wide range of a_{Cl^-} from 1 M to 10^{-6} M. Seawater has a pH of 8 and a_{Cl^-} of about 0.5 M. Edwards *et al.* (1992) proposed various reactions between H^+, Cl^- and lead oxychlorides to explain their origin from interactions with brines. Similar reactions can be written for mereheadite:

$$2PbO + H^+ + Cl^- = Pb_2O(OH)Cl \qquad (1)$$
$$2PbO + 2H^+ + CO_3^{2-} = Pb_2(OH)_2CO_3 \qquad (2)$$
$$4PbO + 3H^+ + BO_3^{3-} = Pb_4O(OH)_3BO_3 \qquad (3)$$
$$4PbO + 4H^+ + Cl^- + BO_3^{3-} = Pb_4(OH)_4BO_3Cl \qquad (4)$$

Carbonate and borate species are assumed to be present in the brine. Reactions between oxychlorides can occur in response to changing pH, a_{Cl^-} and temperature. The oxychlorides of equations (1) to (3) represent structural and chemical components that can be intercalated within the mereheadite structure as discrete layers. $Pb_2O(OH)Cl$ is our preferred ideal formula for the mereheadite endmember; $Pb_2(OH)_2CO_3$ is a fictive carbonate component and the analogue of bismutite in the lead-oxychloride system; $Pb_4O(OH)_3BO_3$ is the corresponding fictive borate component. All cases involve protonation of the PbO sheets to maintain charge balance.

Conclusion

The layered lead-oxychloride minerals are challenging to characterize structurally because of the strong pseudosymmetries between tetragonal, orthorhombic and some monoclinic cells. Mereheadite is particularly difficult because of the occurrence of very heavy and very light atoms in a structure that is dominated by the former. While it has not been possible to locate boron or carbon in mereheadite, a comparison with structurally-related synthetic bismuth oxyhalides and bismutite suggests that they occur as BO_3 and CO_3 groups replacing chlorine. Three end-member components are proposed: $Pb_2O(OH)Cl$ is the ideal mereheadite end-member and the other two are fictive borate and carbonate components and are analogous to bismutite. There is also the possibility that a vacancy-bearing α-$Pb_4O_3Cl_2$-like component occurs in natural mereheadites.

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