Ashoverite, a new mineral, and other polymorphs of $Zn(OH)_2$ from Milltown, Ashover, Derbyshire

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Abstract

Four polymorphs of $Zn(OH)_2$ have now been recorded from an oxidised vein exposure near Milltown, Ashover, Derbyshire; sweetite, wülfingite, γ-$Zn(OH)_2$, and ashoverite. The last is a new mineral, a tetragonal modification of $Zn(OH)_2$ containing minor quantities of Pb, Cd and Ca. Its unit cell dimensions are a 6.825(2) and c 33.36(4) Å, giving V = 1554 Å^3; Z = 32; space group $I4_1/amd$, $I4_1 md$, or $I\bar{4}2d$; $D_{meas.}$ 3.3, $D_{calc.}$ 3.44 g cm^{-3}. Ashoverite occurs as colourless platy crystals associated with fluorite; it is uniaxial positive with ω 1.629(2), ε 1.639(2). The chemical composition of sweetite is compared with that of ashoverite.

KEYWORDS: ashoverite, new mineral, zinc hydroxide, sweetite, Milltown, Derbyshire.

Introduction

VARIOUS polymorphs of $Zn(OH)_2$ have been prepared artificially (Roy and Mumpton, 1956; Aigueperse et al., 1960; Giovanoli et al., 1966). Of these, only ε-$Zn(OH)_2$ has so far been described in both a mineral and synthetic form. Schmetzer et al. (1985) have found the phase, which they named wülfingite, as a natural weathering product of zinc-bearing slags in the Richelsdorf Mountains, Hesse, Germany. Schnering (1964) stated that the ε-phase is the only stable form of $Zn(OH)_2$, but Baneyeva and Popova (1969) have shown that the α-form is stable up to 600 °C below 110 kbar and that β-$Zn(OH)_2$ is produced at 110–120 kbar and 400 °C.

A tetragonal $Zn(OH)_2$ phase, not so far reported as a synthetic compound, was described by Clark et al. (1984) as the mineral sweetite. It occurs in oxidised vein exposure at the disused Milltown limestone quarry, 200–300 m north-west of the village of Milltown, near Ashover, Derbyshire. Further examination of specimens from this vein sent to the British Museum (Natural History) by Mr S. A. Rust has shown that a small quantity of a white radiating acicular mineral (Rust specimen 28A, BM 1986,513) is associated with sweetite. X-ray powder diffraction examination showed this phase to be γ-$Zn(OH)_2$ (Giovanoli et al., 1966). Another specimen (Rust 14A) contained a small star-like cluster of colourless crystals which has

proved, by X-ray examination, to be a second occurrence of wülfingite.

Some of the specimens from Milltown show clusters of platy colourless crystals which were thought originally to be baryte until their X-ray powder diffraction pattern was examined and could not be matched with any known mineral or inorganic compound. These crystals have proved to be a further tetragonal polymorph of $Zn(OH)_2$; sufficient material was available to enable the mineral to be characterized fully. The data and name ashoverite (for the nearby town) have been approved for this mineral by the Commission for New Minerals and Mineral Names of the International Mineralogical Association (86-08). This paper describes ashoverite and compares its chemical composition with that of sweetite. The studies have been carried out on crystals from specimens registered in the British Museum (Natural History) mineral collection as BM 1982,5 (ashoverite) and BM 1982,4 (sweetite).

During the final stages of the preparation of this manuscript, a second occurrence of ashoverite was reported (Schnorrer-Köhler, 1988), in slag from the Harz Mountains.

Optical and physical properties

Ashoverite occurs as groups of square plates about 0.5 mm across, scattered over colourless fluorite crystals. Individual crystals of ashoverite

TABLE 1. Electron probe analyses of ashoverite and sweetite
from Milltown, Derbyshire (wt.%)

	1	2	3	4	5	6	7	8	Ave.	Ideal Zn(OH)$_2$
Ashoverite	Core				Rim					
ZnO	84.65	83.70	84.27	83.39	86.03	84.03	84.51	84.53	84.46	81.87
PbO	2.05	2.12	1.78	2.00	1.96	1.71	2.50	2.39	2.06	-
CdO	0.72	0.63	0.82	0.71	0.81	0.87	0.58	0.51	0.71	-
CaO	0.18	0.11	0.10	0.13	0.14	0.10	0.10	0.31	0.15	-
H$_2$O	-	-	-	-	-	-	-	-	[14.9]*	18.13

	1	2	3	4	5	6	7	8	Ave.	
Sweetite	Core				Rim				Core	Rim
ZnO	91.96	88.06	85.05	84.27	86.95	87.12	87.05	88.19	87.34	87.33
PbO	0.35	0.57	0.44	0.49	0.28	0.50	0.43	0.18	0.46	0.35
CdO	0.15	0.68	0.44	0.67	0.01	0.07	0.16	0.20	0.49	0.11
CaO	0.40	0.57	0.69	0.60	0.30	0.24	0.29	0.31	0.57	0.29
H$_2$O	-	-	-	-	-	-	-	-	[17.0]+	

H$_2$O by elemental analyser: *this paper; +Clark et al., 1984.

thin markedly towards their edges. Many intersect in stellate groups at angles of 60–70°. They are generally colourless and translucent, but become progressively milkier towards the centre. Their lustre is dull to vitreous and the streak white. The mineral fluoresces bluish-white in short-wave ultra-violet light.

In plane polarised light crushed ashoverite fragments are colourless and exhibit a single perfect cleavage parallel to (001). Consequently, only the refractive index corresponding to the ordinary ray vibration direction could be measured from such fragments in oil; $\omega = 1.629(2)$ for sodium light (589 nm); $\varepsilon = 1.639(2)$*. However, because of the cleavage morphology, most fragments dispersed in oil yielded close to centred optic figures in conoscopic illumination. Ashoverite is uniaxial positive. Some fragments have a brownish colouration due to fluid inclusion.

The density of ashoverite was determined on a Berman balance, using a crystal weighing 0.9 mg. The average value of nine determinations was 3.3 g cm^{-3}, in good agreement with the value calculated from the chemical analysis and unit cell dimensions, 3.44 g cm^{-3}.

Chemical analysis

Electron probe analyses were made using a Cambridge Instruments Geoscan fitted with a Link

* Determined on a crystal of ashoverite in thin section cut perpendicular to (001).

Systems energy-dispersive analyser. The elements detected in both ashoverite and sweetite were Zn, Pb, Cd and Ca; the last three are present only as minor constituents. Eight analyses of each mineral were obtained using 15 kV excitation potential, four each on the core and rim of each crystal; the analyses presented in Table 1 show that ashoverite crystals are uniform in composition, whereas sweetite shows slight enrichment in Cd and Ca at the core. More importantly, there is a marked difference in the concentrations of Ca, Cd and Pb between the two minerals. Ashoverite is enriched in Pb and Cd relative to sweetite, while the latter shows a significantly higher concentration of Zn and Ca than ashoverite.

The water content of ashoverite was determined on a CHN elemental analyser; a single 0.5 mg grain gave 14.9 wt. % H$_2$O. From the same instrument a figure of 12.1 wt. % CO$_2$ was obtained on the same grain, but this is thought to be due to heavy liquid contamination of the crystal used, since an electron probe determination using a suitable wavelength-dispersive multilayer crystal gave no carbon peak.
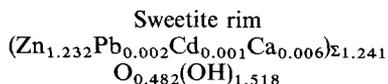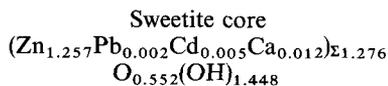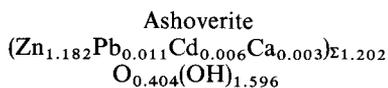
The electron probe determinations indicate that water is lost from both ashoverite and sweetite under electron bombardment and heating, resulting in enhanced cation values. There is evidence that the minerals become permanently dehydrated, as repeated analyses of the same grains over several months showed steadily increasing cation totals,

TABLE 2. X-ray powder diffraction data for ashoverite

h k l	d calc.	d obs.	I obs.	h k l	d calc.	d obs.	I obs.	h k l	d calc.	d obs.	I obs.
n.i.		12.21	<1	307	2.053	2.046	<1	422	1.520	1.518	<1
101	6.69	6.60	<1	2.1.13	1.964 }	1.959	<1	n.i.		1.493	<1
103	5.817	5.787	2	2.0.14	1.954 }			426	1.472	1.470	19
105	4.771	4.772	4	309	1.939	1.928	<1	2.4.10,			
008	4.171	4.176	<1	321	1.890 }	1.886	<1	2.0.22	1.388	1.387	6
107	3.908	3.912	5	1.0.17	1.886 }			2.2.20	1.373	1.373	4
202	3.343	3.332	11	n.i.		1.854	<1	4.0.16	1.321	1.321	3
109	3.256	3.250	<1	2.2.12	1.822 }			1.2.23,			
204	3.158	3.154	<1	325	1.821 }	1.819	33	1.0.25	1.311	1.3096	<1
211	3.040	3.031	13	3.0.11	1.820 }			n.i.		1.2626	<1
n.i.		2.990	1	400	1.706 }			440	1.207	1.2050	7
206	2.909	2.902	100	3.0.13	1.702 }	1.702	21	2.4.18	1.179	1.1789	4
215	2.776 }	2.777	<1	1.0.19	1.701 }			n.i.		1.1199	<1
1.0.11	2.772 }			404	1.672	1.674	<1	606	1.115	1.1142	5
2.0.10	2.386	2.380	7	411	1.653 }	1.652	<1	3.5.12	1.079	1.0798	<1
224	2.318	2.315	9	2.1.17	1.651 }			n.i.		1.0777	5
301	2.270	2.271	<1	406	1.631 }			264	1.071	1.0706	6
305	2.153 }	2.150	2	2.0.18	1.629 }	1.631	7	4.4.16	1.045	1.0458	4
2.1.11	2.152 }			n.i.		1.601	<1	2.6.12	1.006	1.0063	13
228	2.089 }	2.086	3	408	1.579	1.578	<1	n.i.		0.9843	4
0.0.16	2.085 }			n.i.		1.556	<1				

Indexed on a tetragonal cell with a 6.825(2), c 33.36(4) Å, d in Å, Philips 11.46 cm diameter powder camera, Fe-Kα radiation; n.i. = not indexable. Some indices not affected by the space group have been omitted because they did not appear on single crystal photographs [Weissenberg and precession].

eventually approaching that equivalent to ZnO. However, a set of analyses obtained on a Microscan 9 wavelength-dispersive electron probe gave cation ratios very similar to the energy-dispersive values, but with enhanced totals, due to the longer beam exposure time required. The average of the analyses for the two minerals from the Geoscan determinations give the following empirical formulae, following recalculation to 2(O,OH):

Ashoverite

$$(Zn_{1.182}Pb_{0.011}Cd_{0.006}Ca_{0.003})_{\Sigma 1.202}$$
$$O_{0.404}(OH)_{1.596}$$

Sweetite core

$$(Zn_{1.257}Pb_{0.002}Cd_{0.005}Ca_{0.012})_{\Sigma 1.276}$$
$$O_{0.552}(OH)_{1.448}$$

Sweetite rim

$$(Zn_{1.232}Pb_{0.002}Cd_{0.001}Ca_{0.006})_{\Sigma 1.241}$$
$$O_{0.482}(OH)_{1.518}$$

X-ray diffraction studies

A single crystal study of ashoverite showed the mineral to be tetragonal body-centred with a 6.825, c 33.36 Å. From a combination of an a-axis rotation photograph, zero and upper layer Weissenberg photographs, and a stack of a- and c-axis precession photographs, the following reflection conditions were observed:

$$hkl: h+k+l = 2n$$
$$hk0: h,(k) = 2n$$
$$(0kl: k+l = 2n)$$
$$hhl: 2h+l = 4n.$$

These lead to three possible space groups, namely $I4_1/amd$, $I4_1md$, and $I\bar{4}2d$. Since no $hk0$ reflections with $h(k) \neq 2n$ occur, $I4_1/amd$ cannot be ruled out and may even be the most likely space group for ashoverite. In addition, hkl reflections with $h+k \neq 2n$ occur as sharp spots superimposed on streaks parallel to c*, indicating that ashoverite probably has a layered structure parallel to (001) with layer stacking displacements of the order of $a/2$. For tetragonal symmetry, two equivalent choices of $a/2$ layer stacking displacement direction exist; the superimposition of sharp spots on hk streaks indicates that crystal domains are probably present with their $a/2$ stacking fault vectors perpendicular to each other.

The indexed X-ray powder diffraction pattern is given in Table 2.

Gladstone–Dale relation

Using the averaged analysis for ashoverite (Table 1) and the revised Gladstone-Dale constants of Mandarino (1981), the calculated value of K_p is 0.1803. The value of K_c from the refractive indices (Mandarino, 1976) and calculated specific gravity is 0.1850. This gives a compatability

index $(1 - K_p/K_c)$ of 0.026, which Mandarino (1981) categorizes as 'excellent' (the second point on his proposed scale of five categories).

Discussion

We are at present unable to define the stability fields for sweetite and ashoverite or any common structural elements for the two tetragonal modifications of $Zn(OH)_2$. The zoning found in sweetite supports the evidence of the earlier examination (Clark *et al.*, 1984) of another crystal, which indicated that the mineral nucleated as zinc oxide and developed as tetragonal bipyramids about a zinc-rich core. Ashoverite, with its platy habit, shows less evidence of changes in composition of the crystallizing solutions than sweetite.

The minor elements lead and cadmium reported here in ashoverite and, for the first time, in sweetite, are typical for minerals formed as secondary products in lead–zinc veins. The occurrence of wülfingite (Schmetzer *et al.*, 1985) as a weathering product of zinc-bearing slags suggests that zinc hydroxides only form under intense oxidizing conditions.

Acknowledgements

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