

The zinc analogue of schulenbergite, from Ramsbeck, Germany

A. LIVINGSTONE, B. JACKSON AND P. J. DAVIDSON

Department of Geology, Royal Museum of Scotland, Chambers Street, Edinburgh EH1 1JF

Abstract

A blue-green scaly coating on a slaty specimen from the Bastenberg mine, near Ramsbeck, Germany, yielded an X-ray powder pattern akin to schulenbergite. Chemically it is the zinc analogue of schulenbergite. Electron-probe data, XRF and ICP/OES analyses are presented which demonstrate two distinct zinc-rich compositions. Thermogravimetric analysis, together with CHN results, suggest the phase may contain 3–4 water molecules. Powder data are indexed on a hexagonal cell with a 8.293(2) Å, c 7.247(4) Å and cell volume 431.6(2) Å³, with $Z = 1$.

Introduction

A SLATY specimen, approximately $16 \times 12 \times 5$ cm collected from the Bastenberg mine, near Ramsbeck, Nord-Rhein Westfalen, Germany, is partially coated with a pale blue-green flaky mineral. The X-ray powder photograph gave a schulenbergite-type pattern, whereas three instrumental techniques demonstrated the dominance of zinc over copper. Schulenbergite $(\text{Cu,Zn})_7(\text{SO}_4, \text{CO}_3)_2(\text{OH})_{10} \cdot 3\text{H}_2\text{O}$ was first described by Hodenberg *et al.* (1984) from dumps at the Glücksrad mine, Oberschulenberg, Harz mountains. Schulenbergite has been reported from three localities in the U.K. (Livingstone *et al.*, 1990).

Physical and X-ray data

The Ramsbeck zinc analogue of schulenbergite is pale blue-green with a pearly lustre. It is extremely soft (H est. 1–2) and forms hexagonal and trigonal-shaped plates which individually measure approximately $150 \times 100 \times 50 \mu\text{m}$ although they tend to adhere to form larger scales (up to 0.3 mm) within the coating. Two cleavages have been observed with $\{0001\}$ perfect and the second (good) parallel to the trigonal prism faces. Under long or short-wave ultraviolet light the mineral does not fluoresce. In sodium (D) light the zinc analogue of schulenbergite has ω 1.650 and ϵ 1.634 (± 0.003) which are 0.01 greater than corresponding schulenbergite indices. From the empirical formula E (Table 2) the calculated density is 3.27 g/cm³, whereas the measured value

is 3.25 g/cm³. Empirical formulae A–D yield a calculated value of 3.33 g/cm³, somewhat higher than the determined value. Hodenberg *et al.* (1984) encountered a similar situation which possibly results from enhanced buoyancy due to entrapped air in the flaky material.

Table 1 details 18 lines for the powder pattern

TABLE 1
X-ray data for the
zinc analogue of schulenbergite

I est	d meas	d calc	hkl
10	7.255	7.247	001
2	5.064	5.101	101
5	4.156	4.147	110
7	3.623	3.623	002
		3.599	111
7	3.236	3.235	102
8	2.719	2.728	112
		2.715	210
8	2.542	2.542	211
1	2.404	2.394	300
1	2.285	2.290	103
5	2.172	2.172	212
2	1.992	1.993	221
		1.992	310
5	1.806	1.804	213
2	1.747	1.746	312
		1.743	401
1	1.659	1.660	114
1	1.610	1.608	402
		1.607	321
5	1.567	1.567	410
3	1.530	1.532	411
4	1.507	1.507	214

Camera diameter 114.6mm; FeK α radiation; Mn filter.

TABLE 2

Chemical composition and empirical formula (21 oxygens) of the zinc analogue of schulenbergite

	1	2	3	4	1S	2S	3S	4S	5	6	7
ZnO	45.07	43.25	46.81	38.58	38.25	38.32	41.93	37.51	46.04 ⁺	47.96	50.46
CuO	31.72	29.94	25.86	28.32	26.92	26.53	23.17	27.54	15.37 ⁺	16.01	17.91
SO ₃	21.46	20.99	20.45	18.87	18.21	18.60	18.32	18.35	15.16	15.79	15.16
H ₂ O ⁺	-	-	-	-	16.62	16.55	16.58	16.60	17.21 ⁺	17.92	-
H ₂ O ⁻	-	-	-	-	-	-	-	-	0.91	0.95	-
CO ₂	-	-	-	-	-	-	-	-	1.32	1.37	-
	98.25	94.18	93.12	85.77	100.00	100.00	100.00	100.00	96.01	100.00	83.53

A	(Zn _{4.09} Cu _{2.94})Σ _{7.03} (SO ₄) _{1.98} (OH) _{10.10} · 2.98H ₂ O
B	(Zn _{4.09} Cu _{2.89})Σ _{6.98} (SO ₄) _{2.02} (OH) _{9.92} · 3.01H ₂ O
C	(Zn _{4.48} Cu _{2.53})Σ _{7.01} (SO ₄) _{1.99} (OH) _{10.04} · 2.99H ₂ O
D	(Zn _{4.01} Cu _{3.01})Σ _{7.02} (SO ₄) _{1.99} (OH) _{10.06} · 2.98H ₂ O
E	(Zn _{5.07} Cu _{1.73})Σ _{6.80} (SO _{41.70} , CO _{30.27}) _{1.97} (OH) _{9.66} · 3.74H ₂ O

1 & 2	Electron probe microanalyses, separate grains.
3 & 4	XRF analyses on approximately 2 mg samples.
1S - 4S.	H ₂ O calculated stoichiometrically using determined atomic ratios of Zn:Cu:S.
5+	Analysis on same bulk sample, Zn, Cu and Ca by ICP/OES and H ₂ O+ by CHN analyser; all corrected for 1.1 wt% gypsum as sample contained 0.34% CaO. SO ₃ is average of corrected ICP/OES result and tga result.
6	Analysis 5 to 100%.
7	Average of 14 electronprobe microanalyses, single spot per grain. Range of ZnO 44.71-53.72%, CuO 15.79 - 19.35% and SO ₃ 14.32 - 16.20%.
A-D	Empirical formulae of 1S-4S.
E	Empirical formula of 6.

which are indexed by analogy with that of schulenbergite. Cell parameters, as refined from the powder data, are a 8.293(2) Å and c 7.247(4) Å and cell volume 431.6(2) Å³, $Z = 1$.

Chemistry

X-rayed grains, consisting of numerous plates, were polished and analysed with a Cameca Camebax electron microprobe utilizing a defocused beam with copper and zinc metals, and celestine, as standards. The extreme softness, when combined with the high water content, presented considerable analytical difficulties. However, results showed dominance of zinc over copper although metal to sulphur ratios were

incorrect for most analyses. From sixteen microprobe analyses on X-rayed grains only two generated satisfactory metal to sulphur ratios of close to 3.5:1; consequently two XRF(EDS) analyses on approximately 2 mg samples were undertaken.

Results from both techniques are detailed in Table 2. A second sample prepared for the microprobe produced data incompatible with the first results for they revealed a Zn:Cu ratio close to 3:1. Utilizing a third bulk sample (approximately 8 mg) for ICP/OES and CHN analysis it yielded ZnO 45.76, CuO 15.28, SO₃ 14.46, CaO 0.37, H₂O 17.45, and CO₂ 0.3%. This sample contained a small quantity of a 10 Å phase which may possibly be namuwite and also from the

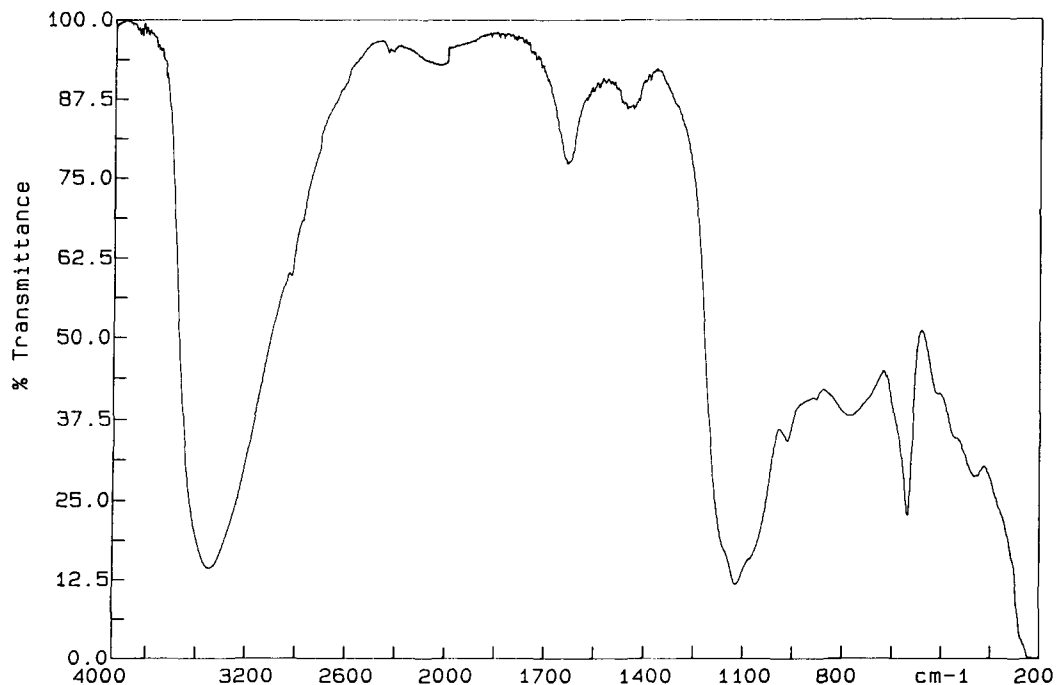


FIG. 1. Infrared scan of sample used for thermogravimetric analysis.

calcium content a 1.1% gypsum impurity. Wide inter sample variation cannot be satisfactorily reconciled with narrow intra sample differences. Possibly the zinc analogue of schulenbergite may possess two distinct chemical compositions which reflect variations at the time of formation, both being physically indistinguishable and non uniformly distributed over the sample surface. If namuwite occurs in small amounts then large chemical variations detected cannot be explained by its presence as an aliquot impurity.

Infrared spectrophotometry on small samples highlighted slight variations in anion ratios also which cannot be attributed to admixtures. Sulphate absorptions at 1116 cm^{-1} are always considerably greater than CO_3 absorptions at 1418 cm^{-1} (Fig. 1). Thermal analysis (on 2.37 mg), Figs. 2A and 2B, utilising a DuPont 951 TG instrument with a $15^\circ\text{C}/\text{min}$ heating rate in argon revealed a 0.91% surface water loss up to approximately 30°C . Water of crystallisation, expelled between 30 and 110°C amounted to 8.76%. A two-stage loss, totalling 11.92%, occurred between 260 and 370°C , with 5.29% H_2O lost up to 330°C and thereafter 6.61% lost between 330 and 370°C . Theoretically $(\text{Zn,Cu})_7(\text{SO}_4)_2(\text{OH})_{10}\cdot 3\text{H}_2\text{O}$ contains 10.37% water as (OH) hence the first loss (Fig. 2B) may be

attributed to $5(\text{OH})$ and the second to simultaneous evolution of (OH) and CO_2 thus from TGA CO_2 tenor is 1.32%. Between 600 and 830°C 16.31% SO_3 was evolved. For synthetic, hexagonal zinc-rich namuwite compositions Gilbert (1977) obtained a similar thermal curve which demonstrated a two-stage water loss between about 270 and 400°C , with SO_3 being evolved at about 800°C .

Interpretation

In view of the chemical variations detailed five empirical formulae, based on 21 oxygens, are given in Table 2. Apart from varying Zn:Cu ratios the last formula exhibits a higher hydration with nearly $4\text{H}_2\text{O}$ molecules present. Theoretically the Zn analogue of schulenbergite contains 16.5% H_2O whereas Hodenberg *et al.* (1984) reported 17.4% H_2O in the Glücksrad material which converts to 3.43 H_2O molecules in their empirical formula. (Thermal data for schulenbergite has not been found in the literature.)

Assuming the space group is the same as that for schulenbergite, i.e. $P3$ then three Zn sites are possible. From empirical formula E (Table 2) the site occupancy may well be Zn (site 1), $(\text{Zn}_{2.07},$

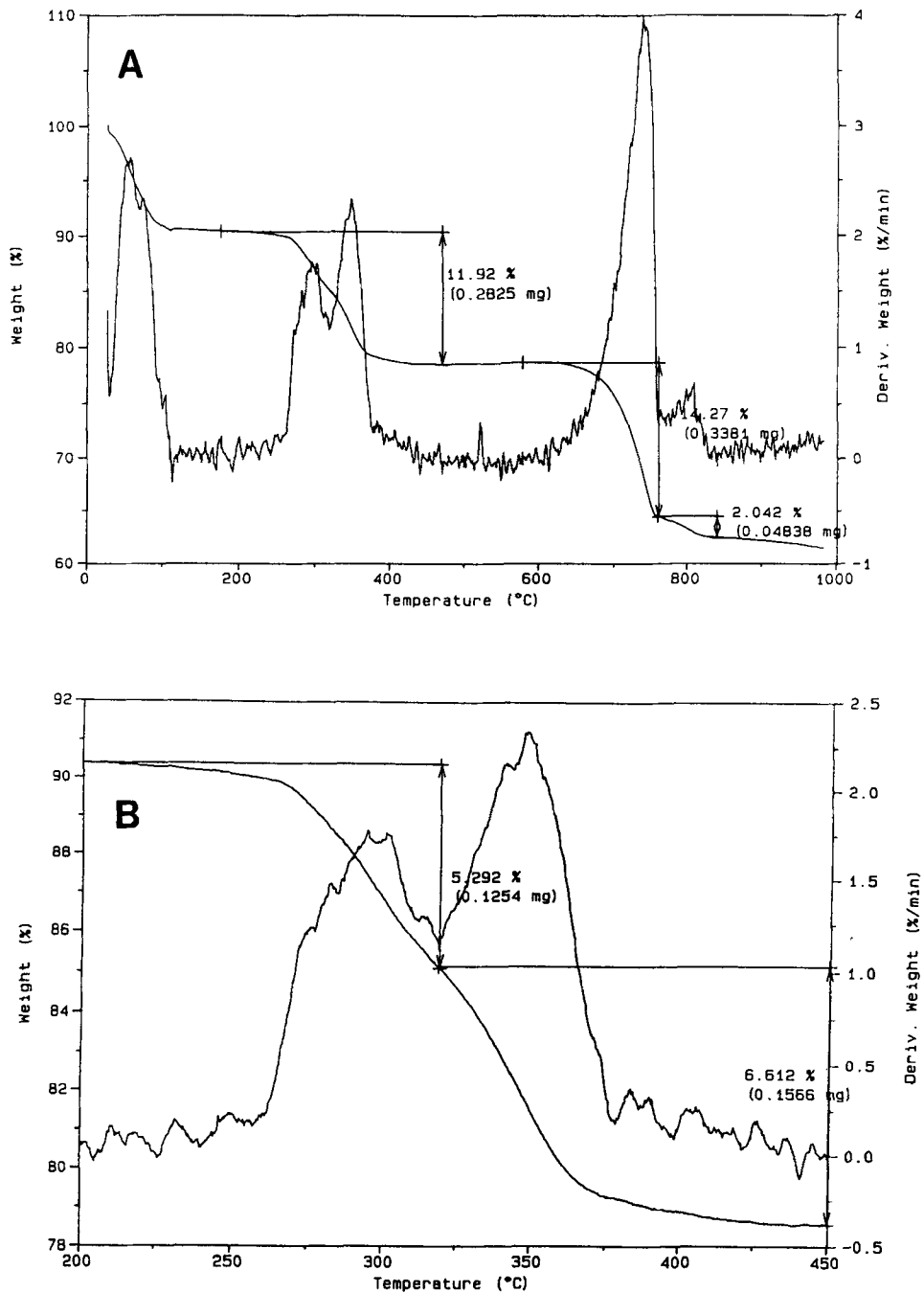


FIG. 2. (A) Thermogravimetric curve of the zinc analogue of schulenbergite showing water of crystallisation, two-stage OH-CO₂ evolution, and SO₃ loss. (B) Computer evaluation of the OH-OH/CO₂ region.

Cu_{0.93}) (site 2) and (Zn_{2.0},Cu_{0.80}) (site 3). Solutions to the above dilemmas must await a structural determination of both schulenbergite and its zinc analogue.

Acknowledgements

The authors are indebted to Mr. C. Chaplin for preparation of the electron-probe microanalysis samples and to Mr. V. K. Din for the CHN analysis.

References

Gilbert, J. (1977) Les sulphates basiques mixtes de cuivre et de zinc. *Bull. Soc. Chem. Belg.*, **86**, 1-9.

Hodenberg, R. Von, Krause, W., and Täuber, H. (1984). Schulerbergite, $(\text{Cu,Zn})_7(\text{SO}_4,\text{CO}_3)_2(\text{OH})_{10}\cdot 3\text{H}_2\text{O}$ ein neues Mineral. *Neues Jahrb. Mineral., Mh.*, 17-24.

Livingstone, A., Bridges, T. F., and Bevins, R. E. (1990) Schulerbergite and namuwite from Smallcleugh Mine, Nenthead, Cumbria. *J. Russell Soc.*, **3**, 23-24.

[Manuscript received 1 September 1991]