

Brianyoungite, a new mineral related to hydrozincite, from the north of England orefield

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Abstract

Brianyoungite, which is chemically and structurally related to hydrozincite, occurs as white rosettes (<100 μm) with gypsum on rubbly limestone within the oxidised zone at Brownley Hill Mine, Nenthead, Cumbria. The mineral contains (wt.%) 71.47 ZnO, 9.90 CO₂, 6.62 SO₃ and 10.70 H₂O⁺. Based on 29 oxygen atoms, the empirical formula is Zn_{11.73}[(CO₃)_{3.00}(SO₄)_{1.10}]_{4.10}(OH)_{15.88} or ideally Zn₃(CO₃,SO₄)(OH)₄. Brianyoungite is either orthorhombic or monoclinic with β very close to 90°. Cell parameters determined by electron diffraction and refined from X-ray powder diffraction data are $a = 15.724$, $b = 6.256$ and $c = 5.427$ Å. Density is > 3.93, < 4.09 g/cm³ (meas.) and 4.11 g/cm³ (calc.); Z = 4. Thermogravimetric analysis, IR and XRD powder data (23 lines) are presented.

KEYWORDS: brianyoungite, hydrozincite, Cumbria, new mineral.

Introduction

White rosettes (<100 μm) of brianyoungite are associated with gypsum on rubbly limestone, or black shaly coatings on limestone, within the oxidised zone at Brownley Hill Mine (NY 776 447), Nenthead, Cumbria. The specimens were collected underground by Mr Brian Young in the disused lead-zinc mine which is the type locality for alstonite. Apart from oxidising pyrite with accompanying goethite and iron staining, the only other minerals noted are the rare zinc analogue of ktenasite (Livingstone, 1991) and smithsonite. Brianyoungite developed as individual rosettes on the surface of specimens or within cavities, and as coalescences forming thin surface layers. Additionally, it may be encapsulated by gypsum. The new mineral developed from downward percolating waters transgressing rocks of the oxidised zone through which the mine entrance tunnel was driven.

The mineral is named after Brian Young (1947–), a field geologist and mineralogist with the British Geological Survey and author of numerous papers on the minerals of northern England, who initially brought it to the attention of one of the authors (A. L.). Brianyoungite has been confirmed on a specimen from Smalleleugh

mine, Nenthead, and from Vieille, Montagne, Hollogne, Belgium, by XRD, XRF and IR and has also been found associated with the zinc analogue of schulenbergit (Livingstone *et al.*, 1992) from the Bastenberg mine, Ramsbeck, Germany. Both the mineral and the name were approved by the I.M.A. Commission on New Minerals and Mineral Names before publication. Holotype material is deposited within the Royal Museum of Scotland Department of Geology, General Mineral Collection, under register number 1992.17.1 and co-type material under 1992.17.2-8.

Physical and optical properties

Extremely delicate brianyoungite rosettes (Fig. 1) consist of very thin (~1–2 μm) blades which taper to a sharp point in a similar manner to hydrozincite. Individual blades are vitreous and transparent. Accurate determination of the density proved difficult due to the small size of individual blades or entrapped air in the rosettes. After approximately two hours the air bubbles escaped from single rosettes that had been immersed in diluted Clerici solution contained in a cavity-mount microscope slide. A series of

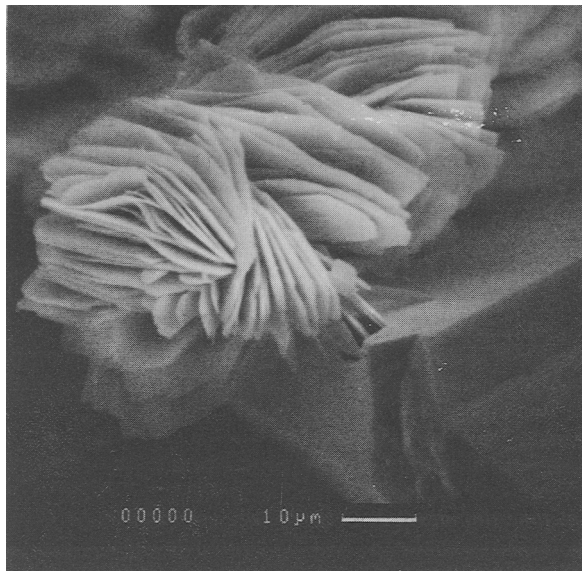


FIG. 1. SEM photograph of brianyoungite rosettes on gypsum. Scale bar = 10 μm .

diluted Clerici solutions of known densities were prepared and rosettes added to each solution. In this way it was found that rosettes remained in suspension in liquids of density >3.93 and <4.09 g/cm^3 . Because the grains always lay on the same face only two refractive indices could be measured, i.e. 1.635 and 1.650 in NaD, (± 0.003). Utilizing the calculated density and Gladstone-Dale constants of Mandarino (1981) the calculated refractive index is 1.747. The two measured refractive indices are therefore α and β respectively. All blades showed straight extinction. In dilute acids, rapid dissolution with effervescence occurred. The mineral does not fluoresce under long- or short-wave ultraviolet light. Because of the minute size of the crystals the hardness could not be determined.

Chemical, infrared and thermal studies

When analysed with a Camebax Cameca microprobe, X-rayed polished rosettes revealed only zinc and sulphur as major elements. Other elements detected include Cu, Mg, Al, Si, Ca and Fe, which summed to approximately 0.3 wt.%; however, one spot analysis revealed 0.54 wt. % Mg. EPMA results varied widely from 61–63 wt. % ZnO using a 10 μm line raster at 20 kV and 10 nA to 69–82% ZnO on spot analyses at 20 kV and 20 nA. These data reflect inherent difficulties when undertaking this mode of analysis on highly hydrated, carbonated material that is difficult to

polish. Utilizing 1 mg aliquots ICP/OES and XRF (EDS) analyses yielded 72.19 and 70.75 wt. % ZnO respectively (average 71.47 wt. %). For the XRF analysis, 1 mg of brianyoungite was dissolved in dilute HNO_3 acid and the solution absorbed on a small disc of filter paper. The method was standardised by preparing pure ZnO in the same way. The ICP/OES gave 6.62 wt. % SO_3 and a CHN analysis, on 1.115 mg, yielded 14.40 wt. % H_2O total, plus 9.90 wt. % CO_2 . Thermogravimetric analysis showed that absorbed moisture was 3.7 wt. %, which is a slightly high value, although Jambor (1964) suggested that the basic zinc carbonates may contain considerable absorbed water. From the following analysis—ZnO 71.47, CO_2 9.90, SO_3 6.62, and H_2O^+ 10.70 wt. % (total 98.69 wt. %), on the basis of 29 oxygens, the empirical formula is $\text{Zn}_{11.73}(\text{CO}_3)_{3.00}(\text{SO}_4)_{1.10}(\text{OH})_{15.88}$. The ideal formula— $\text{Zn}_{12}(\text{CO}_3)_3(\text{SO}_4)(\text{OH})_{16}$ theoretically requires ZnO 73.26, CO_2 9.91, SO_3 6.01, and H_2O 10.82 wt. %. This composition, if CO_3 and SO_4 are combined, is similar to hydrozincite— $\text{Zn}_3(\text{CO}_3)_2(\text{OH})_6$, viz ZnO 74.12, CO_2 16.03, and H_2O 9.85 wt. %. However, the possibility remains that sulphate is substituting for carbonate. The ideal formula would then reduce to $\text{Zn}_3(\text{CO}_3, \text{SO}_4)(\text{OH})_4$. On this basis, from the empirical formula, one quarter of the CO_3 sites are filled by SO_4 .

The infrared spectrum (Fig. 2) reveals OH, CO_3 and SO_4 absorptions. The spectrum bears a

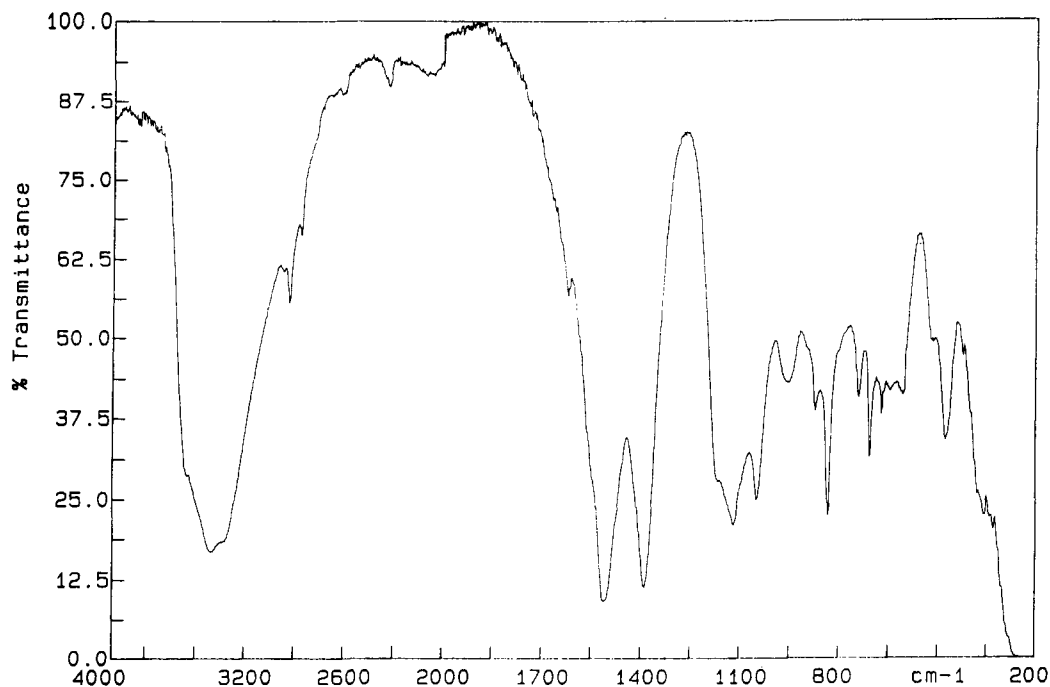


FIG. 2. Infrared spectrum of brianyoungite.

remarkable similarity to that of hydrozincite although the OH absorptions of brianyoungite are significantly shifted ($\sim 100 \text{ cm}^{-1}$) towards higher wavenumbers. Comparison of the two spectra reveals that brianyoungite is also a double carbonate structure with major CO_3 absorptions at ~ 1500 and 1380 cm^{-1} .

Thermogravimetric analysis (Fig. 3) revealed a series of overlapping regions of weight loss. The first loss (3.7 wt.%) up to 240°C is solely due to absorbed water. A major loss occurs between 320 – 450°C and is due to simultaneous evolution of water and some carbon dioxide. The next three losses between 450 and 900°C involve both carbon dioxide and sulphur dioxide. Total recorded loss is 36.8 wt.%.

X-ray and electron diffraction studies

Several rosettes mounted on a spindle yielded the X-ray powder data given in Table 1. Individual rosettes produce the same pattern which is characterised by very sharp lines. This sharpness markedly contrasts with that of hydrozincite and other basic zinc carbonates (Jambor, 1964; 1966). Sections of the X-ray powder pattern show similarities to those of hydrozincite, but there are extra reflections that could not be indexed using the cell parameters of hydrozincite.

Because the crystals of brianyoungite were too small for single crystal XRD, we used electron diffraction in order to determine the unit cell parameters and to obtain information on the space group. Rosettes were crushed in distilled water and sedimented onto an electron microscope grid that was covered with a supporting film of carbon. The sample was placed in a double-tilt ($\pm 60^\circ$, $\pm 45^\circ$) holder and examined in a Philips EM430 electron microscope operated at 300 kV. The grains showed no signs of degradation in the electron beam under these conditions.

In the TEM the crushed fragments appeared bladed and were of uniform thickness (Fig. 4a). At zero tilt, the grains always gave a diffraction pattern identical to that shown in Fig. 4b. Thus the grains always lie on the same perfect cleavage face. The straight edges parallel to the length of the grains suggests that brianyoungite has a second good cleavage.

The d -spacings, corresponding to the two shortest reciprocal lattice vectors in Fig. 4b, were calculated using an internal standard (i.e. by evaporating pure gold onto the sample). Assuming that, by analogy with hydrozincite, the perfect cleavage is (100), $d_{(010)} = 6.24 \pm 0.04$, $d_{(001)} = 5.40 \pm 0.04 \text{ \AA}$, $\alpha^* = 90^\circ$. With this indexing, the crushed grains are elongated parallel to [010] and the second possible cleavage is (001).

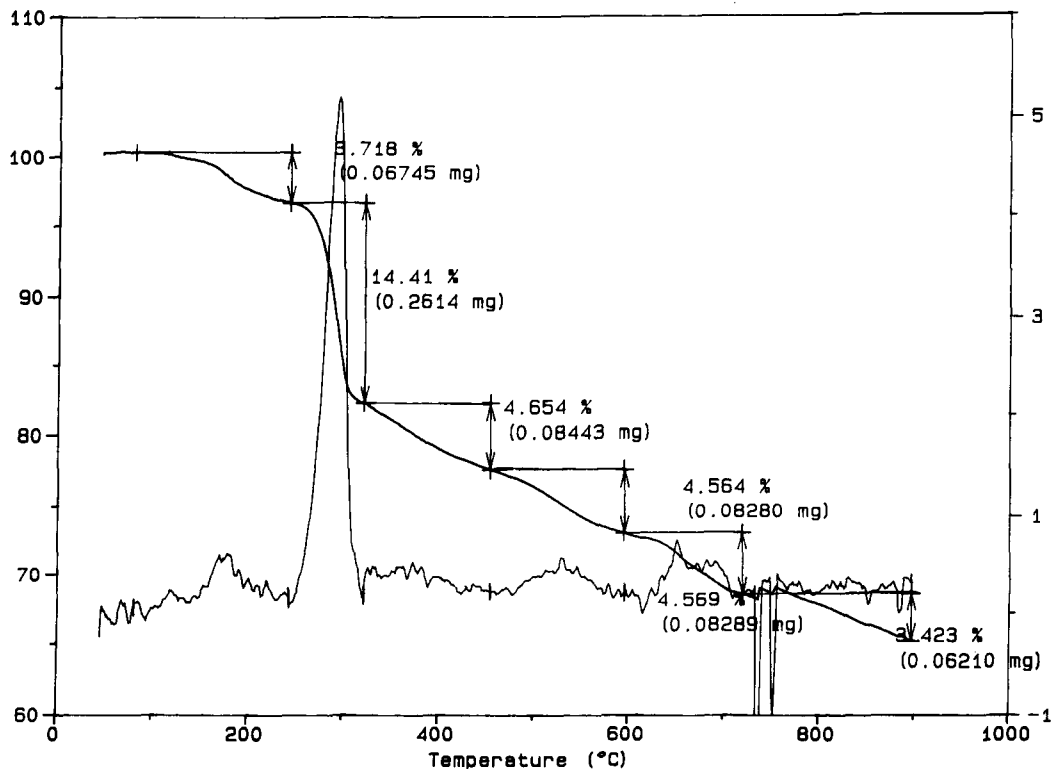


Fig. 3. Brianyoungite thermogravimetric analysis curve, heating rate $10^{\circ}\text{C}/\text{min.}$, in helium.

The specimen was tilted away from the exact zone axis about the two principal reciprocal lattice directions in the $[100]$ diffraction pattern. On tilting about b^* the $0k0$ reflections with k odd, which are weak in the $[100]$ pattern (Fig. 4b), disappeared. This suggests that the reflections are 'systematically absent' because there is either a screw diad parallel to $[010]$ or a b - or n -glide plane parallel to (001) and that the 'missing' reflections only appear in the $[100]$ pattern by double diffraction (e.g. $021 + 0\bar{1}\bar{1} = 010$). Tilting about c^* did not affect the intensities of the 001 reflections, so there is neither a screw diad parallel to $[001]$ nor a c - or n -glide plane parallel to (010) .

No Kikuchi lines were observed in the diffraction patterns and the tilting experiments did not reveal the Laue zones that would be expected of a perfect crystal. Rather, when the specimen was tilted about either of the principal reciprocal axes in Fig. 4b, the other principal reciprocal axis merely appeared to increase in length. These observations suggest that brianyoungite has some sort of disorder parallel to (100) , cf. hydrozincite.

When the grains were tilted about b^* and c^* no deviation from 90° could be detected in the angle

between the principal reciprocal axes. Thus we conclude that brianyoungite is either orthorhombic or monoclinic with a β angle very close to 90° . The (pseudo-)orthorhombic symmetry is also apparent in Fig. 4b in the distribution of intensity of the diffraction spots which shows $2mm$ symmetry. The lattice is primitive as there are no systematic absences in the hkl reflections. However, the comparative weakness of the spots with k odd in Fig. 4b, particularly at high angle, is an indication of pseudo C -face centring.

Using the b and c parameters derived by electron diffraction, it was possible to index the X-ray powder pattern as shown in Table 1. The refined cell parameters are: $a = 15.724(3)$, $b = 6.256(5)$, $c = 5.427(5)$ Å, $\beta \sim 90^{\circ}$, $V = 534.01(3)$ Å³, calculated density 4.11 g/cm³. The cell parameters for hydrozincite are: $a = 13.554$, $b = 6.297$, $c = 5.404$ Å, $\beta = 95.74^{\circ}$, $V = 458.92$ Å³ (Effenberger and Pertlik, 1985). The indexing of the powder pattern confirms the lattice type of brianyoungite as primitive and the absence of a 010 reflection, together with the lack of restrictions on $hk0$ reflections, indicates the presence of a screw diad parallel to $[010]$ rather than a glide

TABLE 1. X-RAY POWDER DATA FOR BRIANYOUNGITE

I est.	d meas. Å	d calc. Å	hkl
100	15.44	15.72	100
100	7.88	7.862	200
20	5.25	5.241	300
5	4.13	4.100) 4.018)	(011) (310)
5	3.944	3.931	400
10	3.128	3.128	020
10	2.976	3.068	120
10	2.907	2.906	220
10	2.802	2.809	510
40	2.714	2.714) 2.710)	(002) (021)
10	2.661	2.671	121
20	2.577	2.565) 2.562)	(202) (221)
5	2.478	2.489	012
20	2.397	2.407) 2.373)	(321) (212)
5	2.336	2.360	601
10	2.253	2.249	312
10	2.034	2.033	122
15	1.748	1.747) 1.744)	(900) (431)
30	1.565b	1.566) 1.564) 1.563)	(023) (040) (631)
10	1.547	1.543	812
10	1.484	1.496) 1.489) 1.476)	(141) (603) (241)
10	1.351		
5	1.024		

plane parallel to (001). There appear to be no other systematic absences.

Discussion

Brianyoungite is either orthorhombic or monoclinic with β close to 90° . If it is orthorhombic, the diffraction symbol is $mmm P_2$, which has only one possible space group, viz. $P2_212$, standard setting $P222_1$. If, on the other hand, the mineral is monoclinic the diffraction symbol is $2/m P12_1$ and there are two possible space groups— $P2_1/m$ and $P2_1$. The similarity between the properties of brianyoungite and hydrozincite is striking; their b and c cell-parameters are virtually identical, their IR spectra and X-ray

powder patterns are very similar, they both show a bladed habit and have perfect (100) cleavage, and both are disordered parallel to (100) (which is the result of both twinning and stacking disorder in the case of hydrozincite (Ghose, 1964; Effenberger and Pertlik, 1985). This suggests that the structures are closely related and that the space group of brianyoungite is probably either a subgroup or a supergroup of $C2/m$, the space group of hydrozincite. Of the possible space groups listed above, $P2_1/m$ and $P2_1$ are both subgroups, but $P222_1$ is not a supergroup of $C2/m$. However, definite identification of the space group must await a full structure determination.

Ghose (1964) found that, in hydrozincite, the octahedral zinc atoms form chains parallel to [001]. The chains are joined together by sharing an octahedral edge to form a sheet parallel to (100). Vacancies within the octahedral sheet are distributed on a rectangular $6.3 \times 5.4 \text{ \AA}$ ($b-c$) net. It seems highly probable that this same octahedral sheet-structure is present in brianyoungite.

The major difference between the cell parameters of brianyoungite and hydrozincite is in the value of a , being 15.724 \AA for the former and 13.554 \AA for the latter. The structure of hydrozincite consists approximately of layers of oxygen/hydroxyl ions parallel to (100). There are six such layers, each one contributing four O/OH per unit cell. As there are four more OH per unit cell in brianyoungite than in hydrozincite, this suggests that there is an extra layer of O/OH in the cell of the former than in the latter and this allows the coordination of the two extra Zn atoms in the unit cell of brianyoungite. The average spacing of the O/OH layers in hydrozincite is 2.26 \AA , which is roughly the difference between the a parameters of hydrozincite and brianyoungite.

In all three of the possible space groups the minimum number of equivalent positions in the unit cell is two. This suggests that the CO_3 and SO_4 groups occupy the same equivalent position, i.e. that the SO_4 substitutes randomly for CO_3 as happens in carboydite, $(\text{Ni,Cu})_{6.9}\text{Al}_{4.48}(\text{SO}_4, \text{CO}_3)_{2.78}(\text{OH})_{21.69}$ (Nickel and Clarke, 1976). The formula for brianyoungite can therefore be written: $\text{Zn}_3(\text{CO}_3, \text{SO}_4)(\text{OH})_4$; $Z = 4$.

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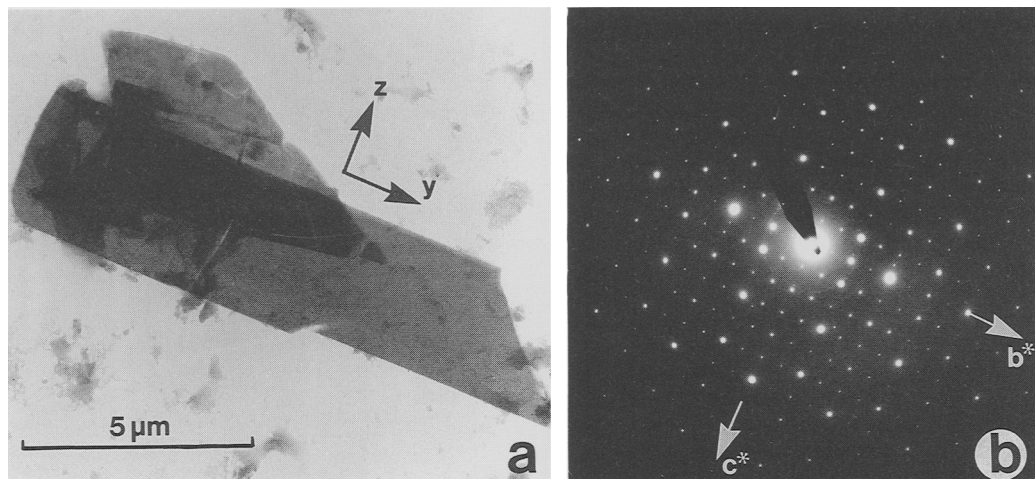


FIG. 4(a) Electron micrograph (300 kV) of two overlapping crushed grains of brianyoungite. (b) Electron diffraction pattern from the larger grain in (a) in the correct relative orientation.

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