A new British locality for beudantite: Sandford Hill, Somerset

By A. LIVINGSTONE and N. COGGER

Mineral Resources Division, Overseas Geological Surveys, London, W.C. 1

[Taken as read 9 June 1966]

Summary. A new British locality for beudantite $[PbFe_3(AsO_4)(OH)_6]$ is recorded. The mineral is intimately associated with goethite; chemical, d.t.a., and thermogravimetric analysis data for the mixture are presented and a possible paragenesis suggested.

THE sample to be described was collected by one of us (N. C.) from stalactitic limonite masses at the old workings on the southern slopes of the hill above the main Carboniferous Limestone at Sandford Hill quarry (O.S. 1-inch map, sheet 165, 421591), near Bristol, during the Geologists' Association Whitsun field meeting in 1960. An X-ray powder photograph of the material revealed it to be a mixture of beudantite and goethite in approximately equal proportions. Five similar specimens (2 to 5 in. long) collected from the same locality were also found to be beudantite-goethite mixtures; three of which also contained appreciable amounts of galena, especially towards the centre of the specimens.

Beudantite was first recorded as a British mineral in 1952 by Kingsbury from Penberthy Croft Mine, Cornwall; the only other British areas known for beudantite are Cornwall and the Lake District (Kingsbury and Hartley, 1957, 1960).

Both earthy brown-coloured powdery specimens and very small crystals, mainly acute rhombohedra, were found by Kingsbury and Hartley. In general, the cellular stalactitic samples from Sandford Hill range from dark chocolate brown to light yellowish-brown in colour. Dotted infrequently over the specimens are very small cerussite crystals, which become more abundant towards the galena; several are thinly coated with canary-yellow coloured mimetite.

Chemistry and mineralogical composition. The analysis (by N. Cogger) of a galena-free beudantite-goethite sample, which had only several minute cerussite crystals adhering to the surface, gave: PbO 14.57, Fe_2O_3

52·50, As_2O_5 7·71, SO_3 7·34, $H_2O + 10.04$, $H_2O - (200^{\circ} \text{C})$ 1·08, ZnO 1·77, CuO trace, P_2O_5 0·08, SiO₂ 2·40 (including 2·0 % insoluble SiO₂), TiO₂ 0·02, Al_2O_3 0·55, MnO 0·04, CaO 0·41, MgO 0·16, Na₂O 0·03, K₂O 0·43, sum 99·13.

For beudantite, which is rarely recorded, chemical analyses are very limited in number and the chemical variations within the mineral are little understood. The Sandford Hill beudantite may possibly be a zincbearing variety although a large cellular goethite sample, containing very small amounts of beudantite, was found to contain 2.8 % ZnO. Zinc-bearing beudantite has been reported by Chukhrov (1950) and zinc-bearing beudantite-plumbojarosite by Simpson (1938). In general, until more analytical data for beudantite is available, possible replacements within the structure that may be considered are Zn, Cu, Ca, and Mg for Pb, P for As, and Al for Fe³⁺.

From thermogravimetric data and using the theoretical composition for goethite, the sample contains approximately 40 to 45 % goethite, 45 to 50 % beudantite, and 2 % quartz by weight.

Thermal examination. Small portions of the beudantite-goethite mixture were placed in a pre-heated muffle, at fixed temperatures, for periods ranging from $\frac{1}{2}$ to $17\frac{1}{2}$ hours, and then X-rayed. It was found that the beudantite structure breaks down at approximately 450° C. Phases developed after the structural breakdown appear to be PbSO₄ and Fe₂O₃; the latter would also be formed after the goethite transformation. A powder pattern that closely fits PbO + Fe₂O₃ is obtained from material heated above approximately 760° C and up to 1100° C. Arsenic was found to remain abundantly in a sample ignited at 1050° C. For plumbojarosite, Kulp and Adler (1950) reported PbSO₄, Fe₂(SO₄)₃, and Fe₂O₃ as the breakdown products after the first endothermic peak. No evidence was found for Fe₂(SO₄)₃ or PbFe₄O₇ as beudantite breakdown products.

Differential thermal analysis (fig. 1) indicates an endothermic peak at 319° C for rather poorly crystallized goethite (well-crystallized goethite gives a single endothermic peak at $350-390^{\circ}$ C, Mackenzie, 1957). Beudantite endotherms occur at 462 and 913° C whilst for Kazakhstan beudantite Chukhrov (1950) reported endotherms at 465 and 875° C. Both the Sandford Hill and Kazakhstan curves display small exothermic peaks at about 600° C.

Thermogravimetric analysis indicates a weight loss of 1.3 % between 160° C and the end of the 200° C isotherm; this is adsorbed water. Between 240° C and the end of the 320° C isotherm 4.3 % was lost, which from d.t.a. is attributed to loss of goethite structural water. Between 360

1014

BEUDANTITE

and 490° C (the first beudantite endotherm) 4.5 % was lost whilst between 490° C and the 1100° C isotherm an additional 7.4 % weight loss was recorded.

From the X-ray, d.t.a., and thermogravimetric data we conclude that the first beudantite endotherm is a structural breakdown with loss of structural water, whilst the second endotherm is loss of SO_3 only.



FIG. 1. Differential thermal analysis curve for a beudantite–goethite mixture from Sandford Hill, Bristol.

Paragenesis. Hitherto arsenic-rich minerals recorded from the area have been limited to small amounts of mimetite and pyromorphite; galena occurs in pockets of soft iron oxides (beudantite-goethite mixtures?) in several Carboniferous Limestone quarries, and galena and smithsonite in the Triassic conglomerate (Kingsbury, 1941). If arsenic and iron-bearing solutions (possibly derived from Triassic rocks) percolated into the underlying limestones and encountered galena then beudantite may have formed. This paragenesis is similar to that observed by Kingsbury and Hartley (1960) who reported beudantite to have formed directly from galena; it is, however, in contrast to that noted by the same authors where beudantite formed as an intermediate alteration product after carminite, in the carminite-beudantite-plumbojarosite and carminite-beudantite-beaverite series.

Acknowledgements. The authors wish to express their thanks to Mr. J. A. Bain for d.t.a. and thermogravimetric data and to colleagues for constructive criticism at all stages of the work. Thanks are also due to the Mineral Resources Division for permission to carry out and publish the work.

References

[Сникнкоv (F. V.)], Чухров (Ф. В.) 1950. Докл. Акад. наук СССР (Compt. Rend. Acad. Sci. URSS), vol. 72, p. 115 [М.А. 11-247].

KINGSBURY (A. W. G.), 1941. Min. Mag., vol. 26, p. 67.

----- and HARTLEY (J.), 1957. Min. Mag., vol. 31, p. 700.

____, 1960. Ibid., vol. 32, p. 423.

KULP (J. L.) and ADLER (H. H.), 1950. Amer. Journ. Sci., vol. 248, p. 475.

MACKENZIE (R. C.), 1957. The oxides of iron, aluminium and manganese. In The differential thermal investigation of clays, London (Min. Soc.).

SIMPSON (E. S.), 1938. Journ. Roy. Soc. Western Australia, vol. 24, p. 107.

[Manuscript received 1 December 1965.]