

SHORT COMMUNICATIONS

A bismuth-bearing variety of bindheimite.

IN 1792 J. J. Bindheim¹ reported the results of his analysis of a 'Bleiocher' from Nerchinsk, Siberia, from which he concluded that it was a hydrated arsenate of lead. Since this time other workers have analysed similar minerals from the same locality, and concluded that they were dealing with an antimonate, not an arsenate, of lead. D. L. G. Karsten² gave the name Blei Niere to this mineral, but later it became known as bleinierite: Dana, however, thinking this name unsuitable, renamed it bindheimite.³ Today bindheimite is a yellow earthy mineral composed of lead and antimonic oxides and water: it has the pyrochlore structure, and a variable composition.⁴ With the exception of the discoverer (Bindheim) every investigator has found that antimony is present and has assumed it to be in the pentavalent state, although no evidence has been advanced in support of this.

An X-ray powder photograph of a 'bismuthic ochre' from Otjimboyo East, Karibib, South West Africa (B.M. 1929, 1843) showed it to be a well-crystallized fibrous bindheimite and a spectrographic examination indicated the presence, in addition to lead and antimony, of bismuth, iron, and calcium, together with very small amounts of aluminium, arsenic, sodium, and indium.

Chemical analysis gave the following results: Bi_2O_3 9.7 %, PbO 41.1, Sb_2O_5 30.0, CaO 1.0, Fe_2O_3 3.0, Na_2O 0.2, As_2O_5 0.1, loss in weight on ignition (850°C .) 4.5 %, residue (insoluble in HBr and HClO_4) 8.0 % (SiO_2 6.4 %), total 97.6 %. No tests were made to determine accurately the state of oxidation, although it was apparent that some of the elements were in their higher valency states since bromine was released on addition of hydrobromic acid. Had the mineral been decomposed completely by hydrobromic acid it would have been possible to determine the degree of oxidation of the mineral in the manner described below for bindheimite from Endellion. However, the mineral resisted attack by all reagents tried except hot concentrated sulphuric acid or a mixture of hydrobromic and perchloric acids, used in equal proportions, in which it dissolved on gentle warming. The antimony was determined, after reduction, by titration with standard potassium permanganate solution and the antimony was separated from the other metals either by distillation of antimony bromide at $160\text{--}180^\circ\text{C}$. from a solution of the

mineral in hydrobromic and perchloric acids,⁵ or by treatment of the mixed sulphides with yellow ammonium sulphide. Bismuth and lead were estimated as oxybromide and chromate respectively. We are unable to account for the low summation but derive consolation from some other published analyses of bindheimite.⁶

To test further the method of analysis, a bindheimite from Endellion, Cornwall (B.M. 26757), was analysed and gave: PbO 43.0 %, Bi₂O₃ nil, Sb₂O₅ 43.7, FeO 2.3, As₂O₅ 0.5, residue 1.7, and loss of weight on heating (850° C.) 8.2 %; total 99.4 %. This mineral was easy to deal with, being readily soluble in cold hydrobromic acid in contrast to the related bismuth-bearing mineral just described. This fact made it a straightforward matter to ascertain the state of oxidation of the mineral and this was carried out in the following manner: the mineral (about 200 mg.) was transferred to a glass-stoppered flask followed by 1 g. potassium iodide dissolved in about 2 ml. of water; 5 ml. HBr were poured in and the flask swirled to hasten the dissolution of the mineral. When the mineral had dissolved, 5 ml. of chloroform were added to the flask and the liberated iodine titrated with decinormal sodium thiosulphate solution. If the liberated iodine is calculated in terms of Sb₂O₅, the result agrees with that obtained by direct titration of antimony with potassium permanganate, indicating that the iron was wholly in the ferrous condition, although, of course, the possibility exists that the mineral contains ferric iron and an equivalent amount of trivalent antimony. The Cornish bindheimite is just as indefinite in composition as are other specimens of this mineral; the atomic ratio of lead to antimony in the bismuth-bearing bindheimite, however, is close to unity.

The fibrous bindheimite has a cell dimension of $10.4480 \pm 0.0004 \text{ \AA}$. and is highly oriented with the [110] axis along the fibre. The Cornish bindheimite, on the other hand, is microcrystalline and the fibres un-oriented, in which respect it conforms with other bindheimite specimens examined. The high degree of crystallinity in this fibrous bindheimite may be the reason for its resistance to chemical attack (cf. monimolite).⁷ It would appear, therefore, having regard to the high degree of crystallinity and orientation, that this bismuth bearing bindheimite may be pseudomorphous after a fibrous bismuth-bearing lead antimony mineral such as kobellite.

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References.

- ¹ Schriften Ges. naturf. Freunde, Berlin, 1792, vol. 10, p. 368.
- ² Mineralogische Tabellen, Berlin, 1800, pp. 50, 77.
- ³ System of Mineralogy, 5th edn, 1868, p. 591.
- ⁴ B. Mason and C. J. Vitaliano, *Min. Mag.*, 1955, vol. 30, p. 102.
- ⁵ Some bismuth bromide also passed into the distillate.
- ⁶ See, for example, E. V. Shannon, *Econ. Geol.* (Chicago), 1920, vol. 15, pp. 92, 93.
- ⁷ B. Mason and C. J. Vitaliano, *loc. cit.*

Cahnite from Capo di Bove, Rome.

CAHNITE, $\text{Ca}_2\text{B}(\text{OH})_4\text{AsO}_4$, is the textbook example of a mineral crystallizing with point symmetry $\bar{4}$ and is thus better known than its rarity would suggest. The type locality is Franklin, New Jersey (Palache and Bauer, 1927), and the Klodeborg mine, Arendal, Norway (Bügge, 1952), is the only other recorded locality; cahnite is the last-formed mineral at both places.

A specimen labelled 'Gismondite, Capo di Bove, near Rome, Italy' was obtained by F. N. Ashcroft in 1906 from J. R. Gregory and Co. and later presented to the British Museum (Natural History) with the identity of the gismondine queried. My optical examination showed the refractive indices (ω 1.662) to be much too high for a zeolite, and that the mineral was probably cahnite; because the paragenesis is so unexpected, the identification has been confirmed by X-ray powder photograph and qualitative chemical analysis. The specimen, B.M. 1914, 339, a dark grey leucitic lava, has on one side part of a cavity lined with rounded aggregates of glassy phillipsite and a few white hemispheres of chabazite. Parts of the cavity, between the zeolites, are coated with a thin drusy layer of calcite on which are several dozen flattened sphenoids of cahnite. The crystals are clear and glassy, and of fairly uniform size (about $\frac{1}{3}$ mm.); the habit is dominated by slightly curved faces of $\{111\}$, the corners of the sphenoids being truncated by much smaller faces of $\{\bar{1}11\}$ (indices of Palache), and I have not seen any other form. None of the crystals examined was truly single, even when there were no external traces of another individual, but at the same time no true twin was observed goniometrically; between crossed nicols the extinction positions of the components differ by $1-2^\circ$. Despite careful searching, I have found no cahnite on other similar specimens in the Museum from Capo