

Observations on the alteration products of stibnite.

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IN the mineralogical literature, stibnite is usually stated to change by oxidation into kermesite and finally into valentinite or senarmonite. Another alteration product is described as antimony ochre, a term loosely applied to several minerals, viz. cervantite, stibiconite, and volgerite (Dana, System of mineralogy, 6th edit., 1892, p. 203).

In my metallurgical experience with stibnite ores, I have never met with kermesite or valentinite. Whenever I have encountered altered stibnite in ores from widely separated localities, it showed a yellowish to buff coating which I took to be cervantite. After spending two years in central China where I examined hundreds of tons of stibnite ores from Hunan province,¹ I had to purchase a specimen of kermesite from a mineral dealer in order to become acquainted with the mineral. The locality of the specimen was given as Bräunsdorf, Saxony.

I have a fine specimen, weighing 4 lb., of more or less completely oxidized stibnite from Shi-kuang-shan, Sinhoa district, Hunan. It is an aggregate of coarse radiating prismatic crystals, the largest of which measures 18 cm. in length. The crystals have the typical morphological appearance of stibnite, but are pseudomorphous; a few fractured crystals exhibit a thin core of unaltered sulphide. The superficial colour of the crystals is buff, but here and there a fracture reveals paler inner layers, greyish-white to cream-coloured.

In an endeavour to identify the oxide mineral, I removed one of the smaller crystals, seemingly free from stibnite. It gave specific gravity 4.160 and hardness $4\frac{1}{2}$ –5. In the closed tube much water was given off and a minute red sublimate was formed, the latter proving the presence of a very subordinate amount of sulphide. The powder was insoluble

¹ W. R. Schoeller, Notes on Chinese antimony ores, crude and regulus. Journ. Soc. Chem. Industry, London, 1913, vol. 32, pp. 260–262. Oxygen and metallic antimony in crude antimony. Ibid., 1914, vol. 33, pp. 169–170. In the liquated sulphide produced in Hunan, sulphur was found to be too low for Sb_2S_3 , and oxygen was determined by fusing the material in a current of dry H_2S and weighing the water formed.

in hot hydrochloric acid, but soluble on addition of stannous chloride; heated with hydrochloric acid and potassium iodide, it liberated considerable iodine. Hence the specimen is not cervantite (which is anhydrous), nor valentinite or senarmontite (which are soluble in acid).

For the antimony determination 0.2 g. of the finely powdered mineral was boiled in a 300-ml. flask with 3 g. KHSO_4 , 12 ml. of strong H_2SO_4 , and 0.25 g. of tartaric acid until the mass was quite colourless, leaving a little silica. About one hour's boiling was required. After cooling, 50 ml. of water and 12 ml. of strong HCl were added. The flask was gently heated until solution was complete. When quite cold, 60 ml. of cold water was added, and the solution titrated with KMnO_4 solution (1.75 g. KMnO_4 in 1000 ml.) standardized against sodium oxalate.

Chemical analysis gave: Sb 70.54, H_2O 4.50, SiO_2 1.94, Fe_2O_3 0.16, S 0.16 %. If the sulphur is calculated to Sb_2S_3 and the balance of the antimony to Sb_2O_5 , the analysis sums up to approximately 100 %:

Sb_2O_5 ...	93.17	÷	323.52,	molecular ratio	0.288
H_2O ...	4.50	÷	18.016,	,, . ,,	0.25
Sb_2S_3 ...	0.57				
SiO_2 ...	1.94				
Fe_2O_3 ...	0.16				
	100.34			Sp. gr.	4.160.

The molecular ratios approximate to a mineral of the composition $\text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O}$, whereas Dana (loc. cit.) gives the following data for the 'ochres':

Cervantite, Sb_2O_4 , sp. gr. 4.084.

Stibiconite, probably $\text{Sb}_2\text{O}_4 \cdot \text{H}_2\text{O}$, sp. gr. 5.1-5.28.

Volgerite, perhaps, $\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$.

'White antimony ochre', $\text{Sb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$.

Hence the mineral from Shi-kuang-shan does not correspond to any of the 'ochres' listed by Dana. These minerals appear to be ill-defined.

The information on cervantite given in Dana is rather unsatisfactory: no crystallographic data and no chemical analyses are given. The mineral is stated to be soluble in hydrochloric acid, whereas Sb_2O_4 is substantially insoluble. The specific gravity seems very low compared with that of the hydrous mineral stibiconite and the sesquioxides (senarmontite 5.22-5.30, and valentinite 5.566). Dana gives a long list of localities for cervantite, including four British ones; I am wondering

whether the minerals from these localities have been proved to be cervantite by chemical analysis; otherwise I cannot help thinking that some at least of these occurrences of 'cervantite' are in reality hydrous alteration products of stibnite.

The specimen from Shi-kuang-shan described in this communication has been presented to the British Museum of Natural History. Another specimen of native antimony oxide has been presented to the museum by Mr. E. W. Leighton. It is a water-worn pebble weighing 21 lb., representative of several hundred tons of antimony ore found stored in a warehouse in Kowloon old city near Hong Kong, and shipped to England. The exact locality of this ore is unknown, but it was undoubtedly brought down the Si-kiang river via Canton, hence it originated from Kwangsi province. This most unusual shipment of alluvial antimony ore consisted entirely of very hard, brown, smooth rounded pebbles, weighing from over 30 lb. down to a few ounces. Mr. Leighton kindly sent me a few of the smaller pebbles, one of which I broke and partly crushed. The powder was found to contain 4.46 % of water by direct determination, hence the antimony mineral is not cervantite. I hardly think that a more complete chemical analysis of this obviously impure mineral would lead to its identification; the average antimony content of the shipment was in the neighbourhood of 55 %.

At Dr. W. R. Schoeller's suggestion work is now proceeding in the Department of Mineralogy, British Museum, on both specimens referred to in his paper and also a stibiconite from Sonora, Mexico, and artificial preparations of antimonic acid. X-ray powder photographs of the altered stibnite from Shi-kuang-shan, the Kwangsi pebble ore, and stibiconite from Sonora, Mexico, are identical.
