

in this field. Oftentimes with some substances, what seem to be wholly fortuitous cases of crystallization, will occur in liquids at rest, under such conditions that a very large mechanical shock would be required to accomplish the same result. As to the nature of these influences but little can be said at the present time. Investigations are under way which it is hoped may throw some light on the subject. Also the researches upon the mechanical stimulus are being extended.

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## BISMUTH OCHERS FROM SAN DIEGO CO., CALIFORNIA.

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*Introduction.*—The bismuth ochers which are herein described were found at several of the mines yielding lithium minerals in San Diego Co., California. Native bismuth occurs sparingly, as a primary component, in several of the pegmatite bodies which have produced gem tourmalin, lepidolite, etc. From this metallic mineral, a number of secondary alteration products have formed and it is the purpose of this paper to briefly describe these. The presence of these bismuth ochers, which have been called bismite, has been noted by Kunz<sup>1</sup> and also by the writer.<sup>2</sup> A recent paper by Rogers<sup>3</sup> notes the occurrence of bismite in distinct crystals, agreeing in form and angle with the artificial  $\text{Bi}_2\text{O}_3$ . The correctness of the determination of these crystals as bismite ( $\text{Bi}_2\text{O}_3$ ) was not verified by chemical data and, in the light of the facts set forth in this paper, it seems not at all sure that the material is the oxide of bismuth ( $\text{Bi}_2\text{O}_3$ ). These ocherous oxidation products are found coating the quartz and other minerals of the pegmatite, as gray, yellow, or green pulverulent masses, usually in very limited quantities. Examination under the microscope showed them all to be amorphous, and not transparent. Nothing indicated, however, that they were not homogeneous.

*Yellow Bismuth Ocher, Stewart Mine.*—The yellow powder is the most abundant and nearly a gram of it was obtained for analysis from specimens found in the Stewart Mine, at Pala. About a quarter of it was sacrificed for qualitative tests which showed the presence of an insoluble residue (mostly quartz and feldspar), and, in the solution, of abundant bismuth and vanadium with very small quantities of silica, alumina and lime. A small amount of water was given off when the ocher was heated in a closed tube. No carbon dioxide was given off on dissolving the

<sup>1</sup> G. F. Kunz, "Native Bismuth and Bismite from Pala, California," *Am. J. Sci.*, [4] 16, 398 (1903).

<sup>2</sup> W. T. Schaller, "The Tourmaline Localities of Southern California," *Science*, 19, 266 (1904).

<sup>3</sup> A. F. Rogers, "Minerals from the Pegmatite Veins of Rincon, California," *School of Mines Quart.*, 31, 208 (1910).

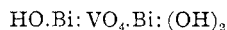
mineral in hydrochloric acid, and bases other than those mentioned could not be detected in the solution.

The quantitative analysis of the yellow bismuth ocher from the Stewart Mine gave the following values; the ratios obtained therefrom are also given.

## ANALYSIS AND RATIOS OF YELLOW BISMUTH OCHER, STEWART MINE, PALA, CALIFORNIA.

	Bi <sub>2</sub> O <sub>3</sub> .....	64.43	0.139 or 2 × 0.0695
	V <sub>2</sub> O <sub>5</sub> .....	12.11	0.067 or 1 × 0.067
Gang	{ sol. in HNO <sub>3</sub> .....	2.27	
	{ insol. in HNO <sub>3</sub> .....	17.63	
H <sub>2</sub> O	{ at 107°.....	0.32	
	{ at 210°.....	0.24	0.204 or 3 × 0.068
	{ on ign.....	3.43	
		<hr/>	
		100.43	

The ratios yield sharply the formula 3H<sub>2</sub>O.2Bi<sub>2</sub>O<sub>3</sub>.V<sub>2</sub>O<sub>5</sub> which may be interpreted as BiVO<sub>4</sub>.Bi(OH)<sub>3</sub>, forming a basic hydrous bismuth vanadate. This is also structurally interpretable, Professor F. W. Clarke suggesting the following:



Based on the evidence so far shown, one would be almost justified in describing the yellow ocher from the Stewart Mine as a distinct new mineral species with the formula just given. In fact, many new (supposed) species have been proposed on evidence weaker than that here given. On extending the investigation of these ochers, however, results were obtained that show conclusively that the above analyzed bismuth ocher is not uniform in composition, does not possess the formula deduced and is, in all probability, a mixture of bismuth vanadate and bismuth hydroxide.

*Yellow Bismuth Ocher, Pala Chief Mine.*—A sample of coherent yellow ocher was found at the Pala Chief Mine, which resembled that from the Stewart Mine in almost every way. An analysis of this was made in order to verify the composition deduced from the analysis just given. Very unexpectedly the composition of the second sample of ocher was found to be different from the first and to agree in composition with pucherite, BiVO<sub>4</sub>. A fifth of a gram gave, on analysis, the results shown below.

## ANALYSIS AND RATIOS OF YELLOW BISMUTH OCHER, PALA CHIEF MINE, PALA, CALIFORNIA.

	Bi <sub>2</sub> O <sub>3</sub> ....	66.14	0.143
	V <sub>2</sub> O <sub>5</sub> .....	25.80	0.142
	Insol. gang.....	7.37	.....
H <sub>2</sub> O	{ at 107°.....	0.21	.....
	{ at 240°.....	0.32	.....
	{ on ign.....	0.84	.....
		<hr/>	
		100.68	

The ratios yield sharply the formula  $\text{Bi}_2\text{O}_3 \cdot \text{V}_2\text{O}_5$ , which is the mineral pucherite. This appears to be the first noted occurrence of pucherite in the United States and the first time that amorphous pucherite has been found. The small amount of water retained above  $107^\circ$  may have come from the insoluble gang. Massive pucherite probably also occurs at the Tourmaline Queen Mine, Pala, but its quantity is entirely insufficient for any quantitative work.

*Gray Bismuth Ocher, Stewart Mine.*—One specimen of quartz collected from the Stewart Mine, Pala, showed a small coating of a grayish material containing a few yellow spots scattered through it. A quantity of the material was scraped off with a knife but only 0.0953 gram substance could be obtained. An analysis made on this small amount gave the following values:

ANALYSIS OF GRAY BISMUTH OCHER, STEWART MINE, PALA, CALIFORNIA.

	$\text{Bi}_2\text{O}_3$ .....	64.9
	$\text{V}_2\text{O}_5$ .....	0.8
Gang	{ sol. in $\text{HNO}_3$ .....	9.5
	{ insol. in $\text{HNO}_3$ .....	13.5
$\text{H}_2\text{O}$	{ at $107^\circ$ .....	0.4
	{ at $240^\circ$ .....	0.3
	{ on ign.....	11.4
		<hr/> 100.8

As the analysis shows, only a small amount of vanadium is present and this is doubtless due to the presence of a little pucherite as shown by the small yellow spots in the original sample. Beside the gang, only bismuth oxide and water are present and this gray bismuth ocher is doubtless a bismuth hydroxide. Before considering the ratios, however, a little water should be deducted for the gang soluble in nitric acid, which is probably a clay comparable to the halloysite occurring here so abundantly. This halloysite, as shown by my analysis,<sup>1</sup> contains nearly 19 per cent. of water, of which one-third is given off at  $107^\circ$ . However, assuming that the 9.5 per cent. of soluble gang was ignited halloysite, there would be about 2.2 per cent. of the total water belonging to this gang. As some water was also given off by the insoluble gang, it may be safely assumed that nearly 3 per cent. of the total water found belonged to the gang and not to the bismuth ocher. Readjusting the analysis on this basis we have the following values.

The ratios agree fairly well with the formula  $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , considering the quality and quantity of material and the uncertain nature of the assumptions made with regard to the water of the gang. The gray bismuth ocher may then be classed as a bismuth hydroxide,  $\text{Bi}(\text{OH})_3$ ,

<sup>1</sup> W. T. Schaller, "Notes on Some California Minerals Halloysite," *Am. J. Sci.*, [4] 17, 191 (1904).

and the yellow ocher from the Stewart Mine is simply a mixture of  $\text{Bi}(\text{OH})_3$  and  $\text{BiVO}_4$ , the apparent rationality of the molecular ratios being only accidental.

READJUSTED ANALYSIS AND RATIOS OF GRAY BISMUTH OCHER, STEWART  
MINE, PALA, CALIFORNIA.

$\text{Bi}_2\text{O}_3$ .....	64.9	$0.140 - 0.004 = 0.136 = 1.0$
$\text{V}_2\text{O}_5$ .....	0.8	$0.004 - 0.004 =$
$\text{H}_2\text{O}$ (ocher).....	9.1	$0.506 = 0.506 = 3.7$
$\text{H}_2\text{O}$ (gang).....	3.0	
Gang.....	23.0	
	<hr/>	
	100.8	

*Conclusion.*—The appearance of most of the samples of bismuth ocher that I have from this general locality is such as to suggest that most of them are mixtures of the hydroxide and vanadate of bismuth. They certainly are not bismite ( $\text{Bi}_2\text{O}_3$ ). The presence of considerable vanadium in these yellow ochers was also established qualitatively for specimens from the Tourmaline Queen Mine at Pala, and from the Victor Mine at Rincon. Moreover, all the yellow specimens from the Stewart Mine, at Pala, that were tested showed the presence of vanadium. The source of the vanadium is probably to be found in the surrounding altered gabbro.

*Method of Analysis.*—The method of analysis was as follows: The mineral was heated in a porcelain crucible at different temperatures (as given) to constant weight and finally ignited by a low flame. The water was thus determined by loss, but its presence and the absence of carbonic acid was determined qualitatively for each sample analyzed. The ignited mass was dissolved in nitric acid, the insoluble residue filtered off and the bismuth precipitated by hydrogen sulfide. The bismuth was finally precipitated as carbonate and weighed as  $\text{Bi}_2\text{O}_3$ . The combined filtrates containing the vanadium were evaporated to dryness and the vanadium and soluble gang weighed as a check on the subsequent determinations. The vanadium was then separated by a current of dry hydrochloric acid gas, the vanadium oxychloride formed was collected in water and, after evaporating down with sulfuric acid, was reduced and titrated with permanganate. The residue from which the vanadium was driven off by hydrochloric acid gas, was ignited and weighed as the residue soluble in nitric acid. It consisted chiefly of silica and alumina with some lime.

*Composition of Bismite.*—A review of the literature on bismite or bismuth ochers free from carbonate shows only two analyses on which the existence of the natural anhydrous oxide of bismuth is based. The first is by Suckow<sup>1</sup> (1848) who gives the composition of bismuth ocher, free from water and carbonic acid, as follows:  $\text{Bi}_2\text{O}_3$ , 96.5;  $\text{As}_2\text{O}_3$ , 1.5;

<sup>1</sup> See C. Hintze, *Handbuch d. Mineralogie*, 1, 1246 (1904), for references.

brown iron ore, 2.0; total, 100. The analysis is certainly far from satisfactory. The second analysis is by Carnot<sup>1</sup> who gives 96.70 per cent.  $\text{Bi}_2\text{O}_3$  with the remainder distributed over eight compounds, including 0.95 per cent.  $\text{H}_2\text{O}$ , also  $\text{SO}_3$ ,  $\text{HCl}$ ,  $\text{CO}_2$ , etc. While indicating the probable presence of  $\text{Bi}_2\text{O}_3$ , the existence of the simple oxide can hardly be considered as established by the analysis of Carnot. As the first natural crystals of bismite described do not agree<sup>2</sup> with those artificially prepared, it seems doubtful whether  $\text{Bi}_2\text{O}_3$  actually occurs in nature. The apparent identity of the natural crystals described by Rogers<sup>3</sup> with the artificial crystals of  $\text{Bi}_2\text{O}_3$  is rendered somewhat questionable by the lack of chemical data on his crystals and by the evidence of the composition of the San Diego County ochers, as shown in this paper.

*Summary.*—The chief points brought out in this paper may be briefly summarized as follows:

- (1) The existence of natural  $\text{Bi}_2\text{O}_3$  has not been established.
- (2) Natural bismite or bismuth ocher, when pure, is more probably a bismuth hydroxide.
- (3) The bismuth ochers from San Diego County, California, are either a bismuth hydroxide or bismuth vanadate, pucherite, or mixtures of these two.
- (4) Pucherite has been found noncrystalline and determined for the first time in the United States.

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## RECENT WORK IN INORGANIC CHEMISTRY.

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The problem of chemical formulas and nomenclature of inorganic compounds, with especial reference to indexing, is discussed by M. K. Hoffmann,<sup>4</sup> and the system used in his recently published *Lexicon der anorganischen Verbindungen* is described. Without attempting changes which can be considered radical, a logical and unambiguous system is worked out, which deserves general consideration.

The solubility of gases in metals has been studied by Sieverts.<sup>5</sup> Nitrogen dissolves in no metals, but reacts with several, forming nitrides. Carbon monoxide dissolves in both solid and fused nickel and also in cobalt, but not in copper. Sulfur dioxide is soluble in fused copper but insoluble in solid copper. Oxygen is soluble in silver but not in gold. Hydrogen is the most generally soluble of gases, but is not soluble in silver, gold, tin, and many other metals. Its solubility in copper is in-

<sup>1</sup> See Hintze's Handb., *loc. cit.*, for references.

<sup>2</sup> W. T. Schaller and F. L. Ransome, "Bismite," *Am. J. Sci.*, [4] 29, 173 (1910).

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Chem.-Ztg.*, 34, 73.

<sup>5</sup> *Z. physik. Chem.*, 68, 115; 74, 277. *Ber.*, 43, 893. *Z. Elektrochem.*, 16, 707.