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"Analysis of samarskite from a new locality"
Proceedings, Boston Society of Natural History

1875

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1874-5

ANALYSIS OF SAMARSKITE FROM A NEW LOCALITY. BY ELLEN
H. SWALLOW. Richards

Mr. T. T. Bouvé called the attention of the meeting to an analysis of a very rare and interesting mineral, the Samarskite, made by Miss Ellen H. Swallow of the Institute of Technology. He stated that this species was first found thirty or forty years since, near Miask in the Ural Mountains, where it occurred in very small quantity. The largest pieces obtained were only of the size of hazel nuts, and until recently no other locality of this mineral was known. Analyses of the Miask mineral have been made by a number of chemists, all of whom agreed in its being a columbate of uranium, iron and yttrium, whilst some of them found in it, also, notable quantities of the rare earths zirconia and thorium. Some ten or twelve years ago a small piece of a mineral, which turned out to be of the same species, was found in the loose soil in North Carolina and was analyzed by Dr. Hunt, the result being given in the American Journal of Science.

Last year Col. Joseph Willcox of Philadelphia, discovered a locality of Samarskite in Mitchell Co., North Carolina, occurring in a pocket of small size, but from which he was able to procure a number of good specimens, two of which I procured from him, one for my own cabinet and one for that of the Society. He also presented me with a very pure piece for analysis, if I should wish to have one made in Boston. This I placed in the hands of Miss Swallow, who appears to have done herself great credit by the thoroughness with which she performed the analysis, and by the full account given of her method.

The sample on which all the the tests were made was a perfectly compact, homogeneous piece handed to me by Mr. Bouvé. It weighed nearly seven grammes. Color black. Streak dark reddish-brown.

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Lustre vitreous like obsidian. Fracture conchoidal. G. 5.755, H. 5.5. The characters as determined by the blowpipe corresponded to those given under Samarskite in Dana's Mineralogy.

Two portions were treated according to the method described by Hermann in the Journal für Prakt. Chemie, 107 Band (1869), p. 139, which was the latest available research on this mineral. This treatment was undertaken in order to ascertain whether tungsten, titanium, thorium and zirconium were present.

No test was obtained for thorium, and the precipitates which might contain the other elements gave only the reactions for columbic acid, which probably escaped precipitation on account of the degree of concentration of the first solution. These precipitates amounted to only one or two tenths per cent.

One portion was also treated according to the method given by Dr. Hunt in the American Journal of Science and Arts, Vol. 14 (1851), p. 341, in the account of the only analysis of American Samarskite. The mineral was decomposed by sulphuric acid, the columbic acid separated by filtration, all the remaining constituents precipitated by ammonia, and the precipitate so obtained treated with carbonate of ammonia, to dissolve the uranium. The insoluble portion was dissolved in chlorhydric acid and the cerium and yttrium precipitated by oxalic acid. But this specimen of Samarskite from Mitchell Co. was decomposed by sulphuric acid with great difficulty; moreover, as Dr. Hunt says, yttrium and cerium, especially yttrium (see Graham-Otto's Chemie, Band II, page 912), are soluble in excess of carbonate of ammonia (although an insoluble double salt soon forms), and the oxalates are readily soluble in chlorhydric acid and the addition of oxalic acid increases the acidity of the solution; therefore it was deemed best to decompose the mineral by fusion with bisulphate of potash, and to precipitate the cerium and yttrium by oxalate of ammonia before separating the uranium by carbonate of ammonia.

The analysis given was made on 0.9091 gramme of the powdered mineral which lost nothing on drying at 100°. Another portion weighing 1.07365 grammes gave results which confirm those given below. The analysis by Dr. Hunt and the analysis of a specimen of the same specific gravity from Miask by Hermann are given for comparison.

		<i>Mitchell Co., N. Carolina, 1875.</i>	<i>Rutherford Co., N. Carolina, Dr. Hunt, 1852.</i>	<i>Miask, Ural, Hermann, 1869.</i>
The metallic acids of the Tantalie Group		54.96	54.81	56.36
Oxide of Tin	SnO ₂	.16		
Oxide of Uranium	UO	9.91	UO ₂ 17.03	16.63
Oxide of Iron	FeO	14.02	14.07	8.87
Oxide of Manganese	MnO	.91		1.20
Oxide of Cerium (La, Di)	CeO	5.17	3.95	2.85
Yttria	YO	12.84	11.11	13.29
Magnesia	MgO	.52		.50
Insoluble residue from the oxalate of Cerium		1.25		
Loss on ignition66 ¹	.24	.33
		100.40	101.21	100.03

The quantity at hand was too small to warrant an attempt at separating the metallic acids of the tantalie group. It is to be hoped that enough may be found to enable some one this side the Atlantic to undertake the investigation. Hermann yet maintains the existence of Ilmenium in Samarskite, Aeschnite and the Columbite from Haddam, Conn. (See Journal für Prakt. Chemie. 1870).

The final analysis was made by the method detailed below, which is essentially that of Hermann, with the omission of the tests which gave negative results in the preliminary examination and with addition of such precautions and modifications as could be gathered from the methods of separation given under the different elements in Graham-Otto's Chemie, and Rose's Analyse Quantitative, and the experience of the preceding tests. The weighed portion was fused with an excess of bisulphate of potash, treated with 400 c.c. distilled water and allowed to remain forty-eight hours, as the fused mass is very slowly decomposed. The solution (and residue) was then heated to about 90° C. and after half an hour the columbic acid was allowed to settle out and was filtered off and well washed with warm water. It was treated on the filter with warm sulphide of ammonium to dissolve the tin. The solution so obtained was evaporated and ignited in a platinum crucible, again ignited with chloride of ammonium and the tin calculated from the loss.

The columbic acid was slightly blackened by the sulphide of ammonium and was consequently digested with very dilute chlor-

¹ Determined on another sample.

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hydric acid, filtered, and the filtrate added to the first filtrate. The columbic acid was then ignited and weighed. It was light yellow while hot, and white when cold.

The filtrate was evaporated somewhat, boiled with nitric acid and precipitated by ammonia. The filtrate so obtained was evaporated to dryness, ignited, dissolved in the least possible quantity of chlorhydric acid, and the manganese was then precipitated by ammonia. The magnesia was precipitated as phosphate in the filtrate; it was free from manganese.

The precipitate by ammonia was dissolved in dilute chlorhydric acid, reprecipitated, and the third time dissolved in slight excess of acid, and oxalate of ammonia added in quantity just sufficient to precipitate. It was allowed to stand twelve hours. The white flocculent precipitate had then settled to a fine powder and was filtered, washed, dried, ignited, dissolved in chlorhydric acid, and reprecipitated; this was repeated three times and the filtrates evaporated and tested each time. The weight of the oxides of cerium and yttrium was taken as a check upon the subsequent separation. The chlorhydric acid solution of the two oxides was treated with a hot saturated solution of sulphate of potash and a crystal put in to ensure complete saturation. The whole bulk of the liquid was about 10 c.c. After twelve hours the double salt of cerium and potash was filtered off, washed with cold sulphate of potash and dissolved in water; in the duplicate analysis it was precipitated in the very dilute solution by oxalate of ammonia, and this showed a loss of oxide of cerium; in the analysis given, the dilute solution was first precipitated by ammonia, and this precipitate, well washed, dissolved in chlorhydric acid, and reprecipitated by oxalate of ammonia, gives the correct per cent. as shown by the check weight.

There was a small residue insoluble in water and in chlorhydric acid, which in fusing with bisulphate decomposed into a soluble portion, which gave all the reaction of cerium, and a white powder, which may have been titanitic acid but which gave reaction of columbic acid. This residue was too small to obtain satisfactory results; it was about 1 per cent. of the mineral. The solution of yttria in sulphate of potash was diluted, precipitated by oxalate of ammonia, ignited and weighed. The filtrate from the precipitated oxalates of cerium and yttrium was just neutralized with ammonia, boiled, and carbonate of ammonia added. After twelve hours the solution of uranium was filtered off, evaporated to a small bulk and precip-

itated by ammonia, dissolved, neutralized, and treated with carbonate of ammonia. This was repeated three times, as also in the same manner the iron precipitate, and thus the separation of the uranium was nearly or quite complete.

Mr. Bouvé also presented a paper by Miss Swallow upon the occurrence of Boracic Acid in mineral waters, with the results of numerous analyses made by her of waters not before analyzed. This, too, will be found by chemists and geologists to be a very valuable contribution to our knowledge of mineral waters.

ON THE OCCURRENCE OF BORACIC ACID IN MINERAL WATERS.
BY ELLEN H. SWALLOW.

In May, 1872, a small bottle of water from Bitlis, Turkey, was given me to analyze. In making the qualitative tests I found boracic acid in considerable quantity. I do not remember what led me to test for it; probably it was a suggestion of Prof. Ordway. The presence of boracic acid in this water caused me to make special test for it in all the mineral waters that I had occasion to analyze.

It occurred in the hot spring of Idaho, Colorado, in Chicken Soup Spring and Bath Spring, both hot waters of Elko, Nevada, and in a cold water from Laramie Plains, Wyoming. These all belong to the class of alkaline waters. It was also found in a chalybeate spring in Albany, Maine, which is in the tourmaline region, and probably that fact may account for its presence in the Albany spring as well as in a spring of very pure water on Pike's Hill, Norway, Maine. It was observed in one of the Spa Springs, Wilmot, Nova Scotia, which belongs to the class of calcic waters, and it occurred in considerable quantity in the mud of another of the Spas. It will be remembered that ulexite and other borates are frequent in the gypsum of Nova Scotia.

The query is at once suggested what are the properties of boracic acid and what are its effects upon the system when taken internally. There seems to be little known as regards its effect in mineral waters, but by comparing the medicinal properties as given in medical treatises with the reputed effects of noted springs which are known to contain boracic acid, we may hope to get a hint of the value of this constituent. Externally applied, borax is very effective in allaying

irritation and healing skin diseases. Taken internally it acts especially on the mucous membranes of the respiratory and digestive organs, consequently it is very beneficial in internal catarrhs and hæmorrhoids. It is especially adapted to sensitive temperaments and nervous constitutions, hence is potent in female diseases. It is very highly extolled in nephritic and calculus complaints.

If we now consider the waters which are known to contain either borax or borate of magnesia in respect to the diseases which they are celebrated for curing, we shall find a noteworthy coincidence, to say the least.

The following statements concerning foreign waters are taken from "Balneotherapie," edited by Dr. Valentiner, and those referring to American Springs from Walton's "Mineral Springs of the United States and Canada."

Eilsen, among the sulphur waters, is beneficial in catarrh, and the mud baths are still more noted as curative agents and are said to be somewhat different in their action from the Nenndorf baths, without any apparent cause. St. Sauveur, used for bathing, has "a very marked sedative effect on the skin, and is the most noted bath for women in France." Eaux Bonnes, "the only drinking water among the several springs, has a very marked effect, even on the first day. . . . this action is not to be expected according to the chemical analysis. Its great fame lies in the cure of bronchitis, catarrh, and tuberclose phthisis." Among the alkaline waters, Fachingen, Nassau, is very effective in all bronchial diseases, blennorrhœa, and catarrh, of the urinary organs with gravel and stones; it contains of borax 0.03 part in 100,000, according to Fresenius. Giessübel, a mile from Carlsbad, is much used for the same diseases. The famous Vichy and Carlsbad waters contain traces of boracic acid, as also nine out of the fifteen springs at Saratoga, and the Balston Spa. Others less known are St. Leon Springs, Canada, the Tuscan Springs, Shasta Co., California, and the Gettysburg Springs which contain 0.032 grain of borate of magnesia in a gallon. The latter water has great reputation in gravel, calculus, and catarrh of the bladder and stomach.

Now as it is acknowledged by the best authorities in all schools of medicine that it is often the substances present in small quantity in mineral waters that are the most efficacious, and as many springs are curative in their action without any apparent reason, it may be possible that the remedial virtue lies in the presence of the neglected constituents like that one under consideration.

A table of the analyses of the mineral waters of which there is no known previous analysis, is appended. The results are expressed in parts per 100,000.

	<i>Itaho, Colorado.¹</i>	<i>Laramie Plains, Wyoming.</i>	<i>Chicken Soup Sp'g, Elko, Nevada.</i>	<i>Bath Spring, Elko, Nevada.²</i>	<i>Albany, Maine.³</i>	<i>Pike's Hill, Norway, Maine.</i>	<i>Bitlis, Turkey.</i>
SiO ₂	6.15	3.00	9.80	6.40	1.85		
Fe ₂ O ₃ + Al ₂ O ₃38	trace			.90	.56	6.70
CaO	2.24	40.00	6.71	8.29	.55	.44	32.50
MgO	22.20	10.00			traces		6.50
Na ₂ O	45.93	32.00	16.50	11.50	undet.	undet.	22.60
K ₂ O	5.69	1.30	1.68	13.50	"	"	13.08
SO ₃	20.20	80.00	4.29	6.63	"	"	18.27
B ₂ O ₃	2.66	undet.	undet.	undet.	"	consid.	6.50
CO ₂	2.40	22.00	5.23	21.34	"		115.60
Cl	4.97	4.00	2.40	2.00	"		11.82
P ₂ O ₅	traces						
H ₂ S		1.93					

¹ B₂O₃ found in the Tufa.

² B₂O₃ found in the Tufa.

³ Much iron was deposited and filtered from the water on which the determinations were made.

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