

# ON HERDERITE.

BY F. A. GENTH.

(Read before the American Philosophical Society, October 17, 1884.)

In the American Journal of Science [3], xxvii, 135-138, in an article on Herderite, by William Earl Hidden and James B. Mackintosh, the latter published his analysis of this rare mineral from Stoneham, Me. In a letter to the editors of the "Neue Jahrbuch der Mineralogie, &c.," of 1884, ii, 134-136, Professor A. Weisbach gives the results of a comparative examination of the *original* herderite from Ehrenfriedersdorf, Saxony, and of that of Stoneham, Me., made at his suggestion by Dr. Cl. Winkler.

These investigations, showing remarkable discrepancies not only between Dr. Winkler's analyses of the herderite from the two localities, but also between those of the two analysts of the Stoneham mineral, it was desirable to re-examine this interesting species.

I am under great obligations to Mr. George F. Kunz, who has kindly furnished me with the material for this investigation, from which I was able to pick out over 2.5 grms. of pure crystals.

Referring to the occurrence of herderite, he has sent me the following communication, dated New York, October 14th, 1884 :

"On revisiting the Stoneham locality I found that the herderite had all been obtained from a vein of margarodite, four feet wide, about twenty feet long, worked to a depth of ten feet. This vein is on the side of the top of Harndon hill, about one hundred feet from the place where was found the topaz obtained by me (see Proceedings New York Academy of Science, November and December, 1882, and American Journal of Science, Feb., 1883), and not in the same pocket, as stated in the article, in the American Journal of Science, Jan. 7, 1884. The vein is almost entirely margarodite, occurring here in unexampled crystals. These at times cover spaces four or five inches square with distinct perfect crystals of margarodite, also altering to serpentine, and associated with it what is possibly topaz, altered into serpentine.

"The herderite occurs almost invariably in crystals, implanted on the margarodite, crystals of quartz, and in a few instances on columbite.

"Between the herderite vein and the topaz vein worked by me were found the large columbite and triplite. Two distinct crystals of triplite have been found recently.

"Signed,

GEORGE F. KUNZ."

The analysis of herderite presents great difficulties, and the following methods have been used in the different analyses :

I. A portion of the material was slightly yellowish, and probably contaminated with a trace of mica. 1.0334 grm. were slowly ignited to a bright red heat in a well covered platinum crucible, and lost 4.80 per cent ; after ignition, the lid and outside margin of the crucible were found coated with a film, which, when moistened with water, gave a strongly acid reaction.

About equal weights of silica and the mineral were fused with about six parts of sodium carbonate for one hour. The well-fused mass, which was greenish from a minute quantity of manganese, was lixiviated with water

and should now have contained *all* the phosphoric acid, and fluorine. The silica in the solution was precipitated by ammonium carbonate, and from its filtrate the remaining silica by zinc oxide, dissolved in ammonium carbonate and ammonia. From the filtrate of the zinc silicate after evaporation to dryness and dissolving in water, the greater portion of the sodium carbonate was neutralized with dilute nitric acid, then precipitated with silver nitrate, keeping the liquid slightly alkaline. In the filtrate the balance of the fluorine (which had not been expelled by ignition), was precipitated together with calcium carbonate by calcium chloride. The mixed precipitate was ignited, dissolved in acetic acid, evaporated to dryness, the calcium acetate dissolved out by water and the calcium fluoride determined. It gave 1.57 per cent which would give, with that driven off by ignition, about 6.4 per cent.

The zinc silicate precipitate was found to contain phosphoric acid.

The portion insoluble in water was dissolved in a little hydrochloric acid and the clear solution precipitated by ammonia, and this separation twice repeated, and washed, until the filtrate was free from lime. The precipitate was ignited and weighed. It gave over 37 per cent and contained a large quantity of phosphoric acid. It was then re-dissolved in hydrochloric acid, the excess driven off by evaporation, then dissolved in water and enough sodium hydrate added to re-dissolve the greater portion of the precipitate. From the filtrate of the insoluble portion the phosphoric acid was precipitated by baryum hydrate as baryum phosphate; in the filtrate from this the excess of baryum was removed by sulphuric acid, and from the filtrate of the baryum sulphate, the glucina and alumina were precipitated with ammonia. The residue insoluble in sodium hydrate contained about 4.5 per cent of lime, nearly 3 per cent of phosphoric acid, a little iron and glucina and alumina, which latter were added to the ammonia precipitate.

These were then re-dissolved in as little acid as possible, precipitated by ammonia, and the separation of glucina from alumina attempted by that method, recommended by the highest authorities as the most perfect, namely, boiling these hydrates with a concentrated solution of ammonium chloride. The strength of the solution was kept so, that on cooling a small quantity of ammonium chloride crystallized out. It was boiled briskly for a whole day, and did not show any bumping at all; a large insoluble residue remained. It had a slightly yellowish color from a little iron, but had not the slimy gelatinous appearance which alumina would have presented, but, on the contrary, it was, without being crystalline, more granular and resembled beryllium hydrate precipitated on boiling from a dilute solution in sodium hydrate. The filtrate was precipitated with ammonia and gave 5.61 per cent of ignited beryllium oxide. That portion insoluble in ammonium chloride dissolved readily in a minute quantity of dilute hydrochloric acid. Sodium hydrate was now added and the whole evaporated in a platinum dish to a pasty consistency, then diluted with cold water

and the little ferric hydrate filtered off, which was subsequently dissolved in hydrochloric acid, precipitated by ammonia. In washing the iron precipitate the filtrate became gradually more and more turbid. It was still more diluted with water and boiled for about one hour, when it was filtered off and washed; it gave 8.99 per cent.\* The filtrate was now acidulated with hydrochloric acid and precipitated by ammonia and gave 0.17 per cent of alumina, which was dissolved in hydrochloric acid and precipitated by ammonia and was found to be insoluble in ammonium carbonate.

The different constituents were added together and gave the results given below. A considerable quantity of phosphoric acid was lost probably in the zinc silicate before I was aware of the fact that this retained such a large portion of it, and only 41.76 per cent were obtained.

II. 0.8608 grm. of finely powdered perfect crystals, dried over one week over sulphuric acid, were fused with twice their weight of silica and sodium carbonate, and the mass treated as in I. It was found, however, that for this mineral this method, even with such an excess of silica, cannot be used advantageously, as the phosphoric acid, notwithstanding the most careful operations, was contaminating almost every precipitate and was largely contained in the zinc silicate. After the greater portion of the phosphoric acid was obtained, there was still about 4.5 per cent with the glucina and ferric oxide, from which it was separated by ammonium molybdate. The excess of molybdic acid was removed by precipitating the slightly acid solution by nitrate of lead. The excess of lead and trace of molybdenum were precipitated by hydrogen sulphide, and from the filtrate the glucina, ferric oxide and alumina separated by sodium hydrate as in I. I am afraid that a portion of the fluorine was lost in a similar way. The ignited calcium fluoride was treated with sulphuric acid and weighed as calcium sulphate, and, as probably a little silica was there which was volatilized as silicon tetrafluoride, it lost 1 per cent, and gave only 6.04 per cent of fluorine.

III. 0.3303 grm. of the same material as I, was intimately mixed with a known quantity of freshly ignited plumbic oxide, and put in a small platinum crucible with close cover, this was placed in a larger platinum crucible which had some magnesia in the bottom, it was then tightly

\* This unexpected behavior of glucina with a boiling solution of ammonium chloride induced me to make the following experiments: A quantity of beryllium carbonate, prepared from beryl, from Acworth, N. H., was dissolved in hydrochloric acid, to the strongly acid solution ammonia was added until it showed a slightly alkaline reaction. It was boiled briskly for one day, then filtered, the undissolved residue was again dissolved in an excess of hydrochloric acid, precipitated by ammonia and boiled for another day and filtered. The two filtrates were mixed and precipitated by ammonia and gave 0.1158 grm. of beryllium oxide. The insoluble residue was dissolved in just enough hydrochloric acid precipitated and redissolved by sodium hydrate, diluted with much water and boiled for one hour. The precipitate weighed after ignition 0.1422 grms. Both were converted into anhydrous sulphates, the first furnishing 0.4742 grm. containing  $\text{SO}_3 = 75.58$  and  $\text{BeO} = 24.42$ ; the second gave 0.5912 grm. sulphate of beryllium with  $\text{SO}_3 = 75.95$  and  $\text{BeO} = 24.05$ .

covered and gradually heated to a strong red heat, which was continued for twenty minutes. After cooling the small crucible had sustained a loss of 0.0020 grm., which would represent 0.61 per cent. The contents of the crucible were completely fused and the lid showed a slight film. As lead fluoride is slightly volatile, it is a question whether this very small loss may not be owing to this, and that the mineral is anhydrous.

The fused mass was dissolved in acetic acid and filtered, the residue, consisting mostly of lead phosphate and fluoride, was dissolved in diluted nitric acid. A pulverulent residue, containing amongst other substances calcium fluoride, was filtered off, the fluorine driven off by sulphuric acid and the sulphates added to the other portion of the analysis. It was found that a considerable portion of the lead phosphate had gone in solution, therefore all the liquids, from which the lead had been removed by hydrogen sulphide, were united and the analysis finished as under II.

IV. 0.5860 grm. of the very finely powered perfect crystals from another specimen with traces of albite was placed in a platinum crucible moistened with water, and then sulphuric acid was added and it was evaporated until copious fumes of sulphuric acid went off. It was dissolved in water and hydrochloric acid. A very slight portion, 0.0070 grm., escaped the decomposition and was therefore deducted from the original quantity. The solution was precipitated by ammonia which would precipitate all the glucina, alumina, ferric oxide and a part of the lime in combination, with all the phosphoric acid, and would leave the calcium which was in combination with the fluorine in solution. I found that 13.16 per cent had not been precipitated, which corresponds to 8.98 per cent of fluorine, which is probably more correct than 6.04 per cent as found by direct determination. The precipitate by ammonia was dissolved in nitric acid, the phosphoric acid precipitated by ammonium molybdate and the analysis finished as above.

To my four analyses I add for comparison those of Mr. Mackintosh and Dr. Winkler.

	Stoneham.				Ehrenfriedersdorf.		
	I	II	III	IV	Mackintosh.	Winkler.	Winkler.
P <sub>2</sub> O <sub>5</sub> =	41.76	— 43.01	— 43.38	— 43.43	— 44.31	— 41.51	— 42.44
BeO =	14.60	— 15.01	— 15.17	— 15.04	— 15.76	— 14.84	— 8.61
Al <sub>2</sub> O <sub>3</sub> =	0.17	— 0.22	— 0.09	— 0.20	— —	— 2.26	— 6.58
Fe <sub>2</sub> O <sub>3</sub> =	0.48	— 0.31	— 0.49	— 0.15	— —	— 1.18	— 1.77
MnO =	0.09	— 0.08	— 0.12	— 0.11	— —	— —	— —
CaO =	33.96	— 34.06	— 33.74	— 33.65	— 33.21	— 33.67	— 34.06
H <sub>2</sub> O =	— —	— —	? 0.61	— ? 0.61	— —	— 6.59	— 6.54
Fl =	— —	? 6.04	— —	— 8.93	— 11.32	— —	— —
				102.12	104.06		
Less O =				3.76	4.76		
				98.36	99.84		

Silicic acid and the alkalies belonging to the albite, etc., have not been determined, it should be remembered however that 0.20 alumina represents one per cent of albite.

The analysis made by Mr. Mackintosh and myself show that herderite is anhydrous beryllium-calcium phosphate and fluoride,—with traces only of alumina and ferric oxide and perhaps a little water. The traces of alumina are owing to slight admixtures of traces of mica and albite.

Somewhat doubtful is the exact quantity of fluorine which it contains. Mr. Mackintosh determined its quantity from the excess of lime which he found. A determination which I have made in the same manner gave me a far lower result, instead of 11.32, only 8.93 per cent. My direct fluorine determination is probably too low, owing to the incomplete decomposition of the mineral by fusion with silica and sodium carbonate and the difficulties in the separation of fluorine from such a solution. A doubt also exists as to the 0.61 per cent loss by fusion with plumbic oxide, whether it is water or lead fluoride.

As all my material was used up I could not attempt any other determination for clearing up these doubtful points.

It is to be regretted that the results of Dr. Winkler's two analyses are so very unsatisfactory, and that he has sacrificed the very precious Ehrenfriedersdorf herderite by employing incorrect methods for his analyses.

By ignition he has volatilized the greater portion of the fluorine, then by evaporation with nitric acid the rest may have gone (although nitric acid is less liable to drive off hydrofluoric acid than hydrochloric acid would be); therefore when he subsequently tested for fluorine, there was no more left than sufficient to give a *doubtful reaction*.

Although it is stated (Rose's Qual. Analyse, Leipzig, 1867, p. 212), incorrectly as I believe, that boiling with sodium acetate does not precipitate glucina, I am not aware that this method has ever been suggested to separate glucina from alumina by boiling a solution, nearly neutralized with sodium carbonate, with sodium acetate. It is a known fact (see Graham-Otto's Anorganische Chemie, by Michaelis, iii, 2 Hälfte, p. 694) that from a solution of beryllium chloride the glucina is precipitated on boiling with sodium acetate.\*

\* In order to show the value of the method used by Dr. Winkler for the separation of alumina and glucina, a quantity of beryllium carbonate was dissolved in hydrochloric acid, evaporated to dryness, diluted with about 150° of water, nearly neutralized with sodium carbonate, then about 2 grams of sodium acetate were added and the solution heated. At about 80° it became turbid, and after two hours boiling a considerable precipitate had formed, which was filtered off and washed. It was dissolved in dilute hydrochloric acid, then sodium hydrate was added to redissolve the precipitate, then it was diluted with much water and gave on boiling beryllium hydrate, which after ignition weighed 0.0855 grams. The filtrate from the precipitate produced by sodium acetate was precipitated by ammonia and gave 0.2705 grm. This shows that 24.3 per cent were precipitated by boiling, and that the method is worthless for the separation of glucina from alumina. By a greater dilution and a more strict neutralization perhaps all the glucina might have been precipitated.

Dr. Winkler does not state that he has tested his so-called *alumina* for its purity, which is unfortunate, or he would have found that a slight trace of it might have been present, but that the precipitate was nearly pure glucina. *There can be very little doubt that the Ehrenfriedersdorf and Stoneham mineral are identical in composition.* There is also a larger percentage of ferric oxide in Dr. Winkler's analysis than found by me. Might this not have come from the molybdic acid which he used? The ammonium molybdate—prepared from Merk's molybdic acid—which I use contains in 100<sup>cs</sup> 0.002 grms. ferric oxide. As I used measured quantities, a corresponding amount of ferric oxide was deducted.

UNIVERSITY OF PENNSYLVANIA, *Philadelphia, October 17, 1884.*