ART. X.—*On the chemical composition of Herderite and Beryl, with note on the precipitation of aluminum and separation of beryllium and aluminum;* by S. L. PENFIELD and D. N. HARPER.

1. *Composition of Herderite.*

THE rare material for carrying on the present investigation of herderite was given to us by Mr. L. Stadtmüller and Professor George J. Brush. The crystals were carefully picked by hand and freed as far as possible from all foreign matter. They were then crushed and sifted and suspended in the Thoulet solution; only the material whose specific gravity was greater than 2·95 was used for analysis. By this means there was separated from the hand-picked crystals a little questionable material, which was used in making a sort of preliminary analysis, and we were able to obtain over five grams of very pure material. Before making the separation with the Thoulet solution we carefully took the specific gravity of some of the purest crystals by taking the specific gravity of the solution in which they were suspended without floating or sinking. This we found to be from 3·012 to 3·006, the heaviest being the specific gravity of a very clear transparent crystal, while the more opaque and cracked crystals were a trifle lighter. The mineral is so much heavier than the quartz and feldspar to which the crystals were attached, that we feel very confident of the purity of the material which we analyzed.

The analysis was made after we had had considerable experience in the determination of beryllium and had made some experiments in determining it in presence of phosphoric acid. The method which we adopted gave good satisfaction, and we give it here somewhat in detail. The mineral was dissolved in nitric acid, the solution concentrated to a small volume, sulphuric acid was added, and the gypsum crystals after being collected by filtering through a rubber funnel were ignited and weighed as $CaSO_4$. The filtrate was concentrated in a platinum dish and gently ignited to drive off all hydrofluoric acid and the excess of sulphuric acid. The residue was dissolved in hydrochloric acid, a basic acetate precipitation of a part of the beryllium and phosphoric acid was made in the cold with ammonium acetate, and a little calcium precipitated from the acetic acid filtrate by ammonium oxalate, which was ignited and weighed as CaO. The beryllium in the filtrate from calcium oxalate was precipitated as a phosphate by means of ammonia, filtered, and the phosphoric acid in the filtrate precipitated with magnesia mixture. The two precipitates containing the beryllium as phosphate (the basic acetate precipitate contained the bulk of the beryllium) were ignited in the same crucible and fused with sodium carbonate. The fused material was soaked out in water, phosphoric acid obtained in the solution by the usual method, while the insoluble beryllium oxide was dissolved in hydrochloric acid, precipitated with ammonia, weighed, and the trace of P_2O_5 contained in it separated with ammonium molybdate. The P_2O_5 and bases in analysis III, on which we place the greatest confidence, were separated and determined in the above manner.

Other determinations are given to show the accuracy of the method. The CaO in II was all obtained in the filtrate from the basic acetate precipitation and was not partially precipitated as gypsum. The BeO in the same analysis was tested for Al_2O_3, but not more than a questionable trace could be detected. The P_2O_5 in I was from a direct determination with ammonium molybdate, but a very slight mechanical loss was incurred. The fluorine was determined in III by driving off the silicon fluoride and titrating the hydrofluosilicic acid by means of a standard alkali.* After making the determinations, fresh U-tubes were connected with the apparatus and the aspiration carried on for several hours, but no more silicon fluoride was driven off. As our alkali had just been standardized by means of sodium carbonate and test experiments on fluor spar, we feel very confident that the fluorine determination is correct. The water determinations are somewhat surprising. Mackintosh† made no tests for water, and considered the mineral to be an anhydrous phosphate with fluorine. Winkler‡ made no determination of fluorine and obtained no satisfactory tests for that element by etching glass. He obtained a loss by ignition, however, of 6·59 per cent in the Stoneham mineral by strong ignition, which he regards as water. Genth§ obtained 6·04 per cent of fluorine by direct determination, and 0·61 per cent of water by heating the mineral with lead oxide to bright redness. Mackintosh‖ obtained good tests for fluorine by etching and found a loss of 6·03 per cent by strong ignition. He proved conclusively that fluorine was given off by strong ignition, and concludes that it is replaced in part at least by oxygen. We are scarcely willing to believe that such a reaction would take place on heating an anhydrous phosphate containing fluorine. Our first water determination was made by weighing out the mineral in a boat, placing it in a combustion tube containing a layer of dry sodium carbonate, igniting the tube to full redness and collecting the water in a weighed chloride of calcium tube. We obtained 0·69 per cent; afterward the mineral was dissolved, and analysis II completed

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* Am. Chem. Journal, i, 27.

† This Journal, III, xxvii, 135.

‡ Neues Jahrbuch für Mineralogie, 1884, ii, 134.

§ Proc. Amer. Phil. Society, xxi, 1884, 694.

‖ This Journal, III, xxviii, 401.

from the same material. After almost completing our analysis and finding only 5·27 per cent of fluorine we tried the following experiments. A little herderite powder was placed in a hard glass tube, sealed at one end and ignited; at first only a slight film of water condensed in the cold part of the tube; by strong ignition over the blast lamp, however, there was a sudden evolution of hydrofluoric acid, which etched the glass very perceptibly near the mineral and deposited a film of silica and very acid water, as marked as in an ordinary reaction for fluorine in a closed tube with acid sulphate of potash. In our experience we have never seen any hydrous fluoride which gives off such strongly acid water and such a marked fluorine reaction. Some of the powdered mineral was placed in a closed glass tube, covered with a layer of dry sodium carbonate and strongly ignited; neutral water was given off and condensed as a ring, which indicated more than a trace of water. The water was obtained in the following way. About two grams of calcite were ignited over the blast lamp till a constant weight was obtained. The mineral was then weighed into the same crucible, the lime was slaked with water, the contents of the crucible were carefully dried and then ignited till constant weight was obtained, the water being calculated from the loss of weight. The slaking of the lime makes an intimate mixture of the mineral with the lime, and a preliminary experiment proved to us that only neutral water was driven off. In I there was a slight mechanical loss in slaking the lime, which caused the water determination to be too high, the P_2O_5 too low. In III the water was obtained from a larger quantity of mineral. No sublimate was formed on the cover of the crucible by the volatilization of any fluoride. The analyses were made on air-dry powder which lost 0·10 per cent by drying for one hour at 100° C. The beryllium precipitates were always of a light cream color after ignition, indicating that not more than a minute trace of iron was present.

The following quantities of mineral were used in making the analyses: I. ·4552 grams; II. 1·0029; III. P_2O_5 and bases ·7336, F ·9692, H_2O 1·1612.

	I.	II.	III.	Ratio.			Calculated.
P_2O_5	43·47	- --	43·74	·308		1·	43·83
BeO	----	15·28	15·51	·620		2·01	15·44
CaO	----	33·61	33·67	·601		1·95	34·57
F	----	----	5·27÷38	·138	·343	1·11	5·86
H_2O	4·37 ?	----	3·70	·205			2·77
			101·89				102·47
O equivalent of F			2.22				2·47
			99·67				100·00

The ratio of $P_2O_5 : BeO : CaO : (F_2+H_2O) = 1 : 2 : 2 : 1$ nearly. The high temperature at which the water is driven off indicates that it is not water of crystallization, but is very firmly united in the mineral as hydroxyl, every H_2O representing two hydroxyl groups, and the OH being probably isomorphous with F. The ratio of F : OH is nearly 1 : 1, or more nearly 3 : 4 in our analysis. In the calculated analysis we have used the ratio F : OH=1 : 1, but recognize that it is probably simply a case of isomorphism. The composition of herderite is, therefore, an isomorphous mixture of $CaBeFPO_4$ with $CaBe(OH)PO_4$, which may be written $CaBe(FOH)PO_4$, or a salt of phosphoric acid, two of whose hydrogen atoms have been replaced by a bivalent element, and the third likewise by a bivalent element whose other free affinity has been satisfied by a fluorine atom or hydroxyl. This is the same composition as that proposed by Mackintosh, except that he regarded the mineral as simply the fluorine compound and did not detect the water. Chemically herderite is closely related to the three minerals—wagnerite, triplite and triploidite, whose compositions are respectively Mg_2FPO_4, $(FeMn)_2FPO_4$ and $(FeMn)_2(OH)PO_4$. These three minerals offer the best illustration we have of the isomorphism of F and OH, and we feel that we have in herderite another strong proof of the correctness of this interesting relation. In crystallization the minerals vary, herderite being orthorhombic, triplite questionable, and wagnerite and triploidite monoclinic. The latter two have, like herderite, a prismatic angle of nearly 120°.

2. *Analysis of beryl.*

In 1884 one of us* published a series of analyses which showed that alkalies are present in beryl sometimes to quite a large extent, and that water is always given off by ignition. At the time the analyses were made the author had had little experience in the determination and separation of beryllium and used the ammonium carbonate method, which seemed to him to be the most accurate. Our experience has taught us that the method used in the manner described in the above mentioned article gives too low results for beryllium, and the analyses are only of value as showing to what extent alkalies and water are present in beryl. Since the publication of the article it has always been the author's wish to make a series of experiments on the separation of aluminum and beryllium and renew the investigation.

We have considered it best not to make a long series of

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* S. L. Penfield. This Journal, III, xxviii, 25.

beryl analyses, but to select some very pure beryl and make an analysis of it as carefully as possible. The analysis was made according to the method described at the end of this article, and we feel assured from our experience that the results of the analysis represent the composition of the mineral very closely. The beryl which we selected for analysis was a very pure transparent aqua marine from Stoneham, Maine, furnished to us by Mr. George F. Kunz of New York. The mineral was crushed and ground in a steel mortar and the fine powder boiled in dilute hydrochloric acid, washed and dried at 100° C. Duplicate analyses were made by both of us, so that we might obtain a very fair average.

Specific gravity taken on a chemical balance, 2·706.

		Ratio.		
SiO_2	65·54	1·092		6·
Al_2O_3	17·75	·172	·173	0·95
Fe_2O_3	·21	·001		
FeO	·38	·005	·558	3·06
BeO	13·73	·541		
CaO	·06	·001		
Na_2O	·71	·011		
Li_2O	trace			
H_2O	2·01	·112		0·61
	100·39			

The ratio of $SiO_2 : Al_2O_3 : RO : H_2O = 6 : 1 : 3 : \cdot5$ nearly. The ratio of the first three is in the proportion required by the usually accepted formula for beryl. This conclusion was also arrived at by Baker* in a recent analysis made according to the same method which we used. As regards the alkalies, we have as yet no proof that they replace the beryllium, but that is probably the case. Analyses of beryls very rich in alkalies would best settle this question. The water is very constant, about two per cent, in all beryls which have come to our notice, with one exception—Aduntschilon, Siberia†—and must be in some way very firmly united in the molecule, as it is only given off by very strong ignition. As can be seen by our ratio, there is about one-half a molecule present. Beryls which show a higher percentage of water may, and in some cases which have come under our observation do, contain mechanical inclusions of water. Regarding the water as essential, we would have to add $\frac{1}{2}H_2O$ to the ordinary accepted formula of beryl, or write it $H_2Be_6Al_4Si_{12}O_{37}$. The theoretical composition according to the above formula is

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* American Chem. Journal, vii, 175.

† This Journal, III, xxviii, 29.

SiO_2	65·81
Al_2O_3	18·83
BeO	13·71
H_2O	1·65
	100.00

We can add also the alkali determinations in the following European beryls. The alkalies were determined by Smith's fusion method and calculated as sodium, although they all contained some lithia. Limoges, France, 0·73 per cent; Hühnerkobel near Bodenmais, Bavaria, 1·20 per cent; Habachthal, Tyrol, 2·26 per cent.

3. *On the precipitation and washing of aluminum.*

Before making the above investigations we tried a few experiments in the precipitation and handling of aluminum precipitates which may be of interest to some of our readers. A standard solution of aluminum chloride was first made containing ·1002 grams Al_2O_3 and 1 c.c. pure concentrated HCl in every 50 c.c. which were used in our experiments. The precipitation of the alumina was in all cases made in a volume of about 300 c.c. by neutralizing the solution with ammonia till the odor of ammonia could be distinctly obtained from the hot solution; the beaker was then placed upon a lamp stand and the solution brought to boiling, which was not continued more than one minute. The precipitates were in all cases washed without a pump, but suction tubes 7 inches long were attached to the funnels which cause a gentle suction, and if the filter papers are carefully fitted to the funnels very materially hasten the filtration.

The following facts were observed: that precipitates which were made in solutions containing large quantities of acid, either hydrochloric or nitric, filtered as well or better than those from solutions containing little ammonia salts, but on washing with boiling water the precipitates from solutions containing large quantities of ammonia salts became very sticky, washed slowly, so that it was almost impossible to free them from the last traces of ammonium chloride, and that very perceptible quantities of alumina settled out from the filtrates and washings on adding a few drops of ammonia and allowing the beaker to stand in a warm place. Further, that all of the alumina which ran through did so during the washing. The precipitates after they had become slimy and sticky seemed either to be quite soluble in the hot water or else got into such a condition that they readily passed through the pores of the paper and stopped them up, thus hindering the filtration. To make a successful precipitation and washing of alumina it is quite essential not to have very much ammonia salts present and even with the greatest care it is found that if the filtrates and washings are set away in a warm place, slight precipitates will almost invariably settle out. The above holds good for solutions containing ammonium chloride and nitrate. The fact that alumina passed through the filter only during the washing suggested to us that if we could wash the precipitate with a saline solution which would be completely volatile and do no harm to the precipitate we might avoid the passage of the alumina through the filter and it might also hinder the packing of the precipitate. Ammonium nitrate suggested itself to us as a salt which would be volatile on ignition and do no harm, and our experiments with it have been very satisfactory. The following strength of NH_4NO_3 has been used in all of our experiments—2 c.c. of pure concentrated HNO_3 neutralized with ammonia and diluted to 100 c.c. with water; this strength has proved so satisfactory that we have tried no other. Using this hot saline wash instead of hot water the precipitation can be made in solutions containing large or small quantities of ammonium salts and no very great care is needed in adding the ammonia. According to our experience, the precipitates from solutions containing a goodly quantity of ammonia salts, resulting we will say from 4 to 8 c.c. of pure concentrated hydrochloric or nitric acid, filter and wash better than precipitates from solutions containing less saline matter. After having made a large number of precipitations we can say that only in one or two cases have we found a trace of alumina in either the filtrate or washings, and that unless the precipitate becomes too dry and packs too firmly upon the sides of the funnel, the washing goes on as well at the end as at the beginning, and there is no difficulty in washing the precipitate free from all traces of chlorine.

Where large quantities of sodium or other fixed salts are to be removed and a second precipitation of the alumina is required, we recommend that the first precipitate after washing be dissolved in nitric instead of hydrochloric acid, then very little washing is enough to free the second precipitate from the last traces of chlorine and fixed salts.

Why ammonium nitrate acts in this way we are not able to state. It may be something on the same principle that sediment deposits much faster in saline than in fresh water. We are convinced that any one who has to handle troublesome alumina precipitates will find the above method of washing of great advantage.

4. *On the separation of aluminum and beryllium.*

Various experiments convinced us that the following methods are not satisfactory: pPrecipitation of the alumina as basic acetate, some beryllium being also precipitated; precipitation of the alumina with barium carbonate; solution of the beryllium in a boiling solution of ammonium chloride; by long boiling of a solution of ammonium chloride the solution becomes slightly acid and according to our own experience some alumina is dissolved, while Genth[*] found that the beryllium was not completely dissolved. Solution of the beryllium in and precipitation of the alumina with ammonium carbonate gives unreliable results, and the method, when carried out as described by one of us in making a series of beryl analyses,[†] gave too low results for beryllium.

We have made a large number of separations by dissolving the mixed chlorides in the least possible excess of caustic soda, diluting the solution largely and precipitating the beryllium by boiling. This method has recently been proposed by Genth[‡] as the most reliable of the known methods, and Baker[§] used it successfully in his analysis of beryl. Before using the method in our own work we made a series of experiments to determine its accuracy and to find out the best conditions for making the separation. A standard solution of beryllium chloride was made from purified K_2BeF_4 containing ·1107 grams BeO in every 50 c.c. Our standard solution of aluminum chloride contained ·1002 grams Al_2O_3 in every 50 c.c. Neither of the solutions contained any alkali and not more than traces of sulphuric acid.

The method was as follows: 50 c.c. of each solution were measured into a platinum dish and evaporated to dryness, the chlorides were dissolved in the least possible quantity of water, and a rather strong solution of pure soda, made from metallic sodium, was cautiously added till the precipitate which at first formed was completely dissolved. The contents of the dish were then rinsed with cold water into a beaker containing about 800 c.c. of boiling water and the contents of the beaker boiled for one hour, replacing from time to time the water which evaporated. The beryllium separates out as a granular precipitate which is easy to filter and wash. After acidifying and concentrating the filtrate the alumina was precipitated with ammonia. Our experience has taught us that the best results are obtained by dissolving the dried chlorides in the least possible quantity of water and using as little soda as possible for dissolving the aluminum and beryllium.

Below we have given in tabulated form the results of our experiments.

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[*] Proc. Amer. Phil. Society, xxi, 694, 1884.

[†] Loc. cit.

[‡] Loc. cit.

[§] American Chem. Journal, vii, 175.

	Weight of Al_2O_3.	Weight of BeO.
	·1041	·1093
	·1057	·1080
		·1096
	·1045	·1099
		·1107
	·1032	·1093
	·1037	·1093
	·1031	·1083
Average	·1040	·1093
Standard	·1002	·1107

The precipitates were in all cases ignited for a long time to full redness over a ring burner. It will be seen that the BeO is quite constant and the average only a little below the standard. The Al_2O_3 is in all cases too high. If the quantity of mixed beryllium and aluminum oxides be determined in any compound, and then the BeO separated according to the above method and the Al_2O_3 determined by difference, the results will be very nearly correct. The determinations of Al_2O_3 and BeO in beryl given earlier in this article were made in this way.

To account for the excess of Al_2O_3 we thought that perhaps appreciable quantities of silica were dissolved from the glass by boiling the alkaline solutions of the mixed oxides for one hour. We therefore in every case dissolved the oxides in hydrochloric acid and deducted from their weight a slight quantity of insoluble matter amounting to about ·0010 grams in the Al_2O_3 and ·0004 grams in the BeO. The excess of Al_2O_3 must, therefore, have come from some other cause than silica dissolved from the glass. The alkaline solutions are so dilute that the glass is very little acted on, and determinations made in a platinum dish convinced us that the separation can be made just as well in beakers. We have concluded that the beryllium is not completely precipitated from a solution in soda by boiling and that it is not possible to wash out all of the soda from the precipitate. The following experiments on the determination of BeO in beryl will show this. The first column gives the weight of BeO obtained by boiling the soda solution, the second the same oxide dissolved in hydrochloric acid, reprecipitated with ammonia and ignited.

·1476	·1440
·1464	·1422
·1330	·1300
·4270	·4162

The total BeO in these experiments weighed ·4270 on first precipitation, ·4162 on second, a loss of ·0108. Calculating by proportion the loss which would result from ·1107 grams BeO the quantity used in our first experiments we find

$$·4270 : ·1107 = ·0108 : x. \quad x = ·0027$$

that is, in the quantity of BeO which we used in making our experiments, the BeO was too heavy by about ·0027 grams, representing probably some soda compound which could not be removed by washing. The excess in the Al_2O_3 is due to the BeO which was not precipitated by boiling. If we take the sum of the Al_2O_3 and BeO in the average of our determinations ·2133 and deduct from it ·0027 we have ·2106 against ·2109, the sum of Al_2O_3 and BeO in our standard. The following determinations made from our standard solutions, the boiling of the soda solutions being done in platinum, confirm us in this. First weight of BeO ·1087 after solution and reprecipitation ·1068, weight of Al_2O_3 ·1041. ·1068 + ·1041 = ·2109, the weight of mixed oxides in our standard. We conclude therefore that the separation is not as perfect as our results would indicate. The error is however very constant, the amount of BeO which is not precipitated being almost exactly equal to the amount of soda which it seems impossible to remove from the precipitate by washing.

When phosphoric acid is present alumina may be separated from beryllium by boiling the solution of the mixed chlorides with barium hydroxide. The alumina goes readily into solution while the precipitate containing the barium phosphate and beryllium is easy to filter and wash. After dissolving the precipitate and separating the barium with sulphuric acid, a beryllium phosphate can be precipitated with ammonia. After weighing this the P_2O_5 may be determined by means of ammonium molybdate and the BeO by difference or the precipitate may be fused with sodium carbonate and the fusion soaked out with water which gives almost a complete separation of phosphoric acid from beryllium. If phosphoric acid is also to be determined it must be borne in mind that very perceptible quantities of it will be found in the barium sulphate precipitate.

We have also observed that when Al_2O_3 is ignited over a ring burner till a constant weight is obtained, then over a blast lamp there is a slight loss, amounting in the quantities which we have used in making the above experiments to about ·0010 grams. What this loss represents we are not able to say. Usually in practical work this error can not be avoided, because it is necessary to dissolve the ignited Al_2O_3 to test for traces of SiO_2 or iron, and it is almost impossible to dissolve Al_2O_3 which has been strongly ignited over a blast lamp. The same is true for ignited BeO. After strong ignition over a ring burner there is still a loss of about ·0013 in the quantities which we used, by igniting for five minutes over a blast lamp. This may be done however, as the ignited BeO is readily soluble in hydrochloric acid.

In closing we wish to express our thanks to Messrs. Geo. J. Brush, L. Stadtmüller and Geo. F. Kunz for the rare material which they kindly furnished for carrying out this investigation.

Mineralogical Laboratory, Sheffield Scientific School, May 28th, 1886.