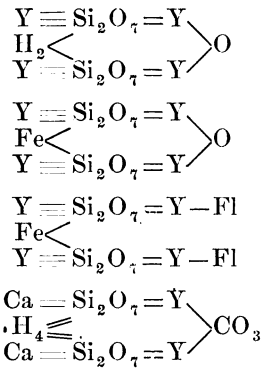
ART. XIII.—*The Composition of Yttrialite with a Criticism of the formula assigned to Thalénite;* by W. F. HILLEBRAND.

IN a paper describing the new yttrium silicate thalénite,* the author, C. Benedicks, casts doubt on the formula assigned by Hidden and Mackintosh† to their mineral yttrialite from Llano Co., Texas, for which they deduced the formula R_2O_3 $2SiO_2$ or $R_2Si_2O_7$, in which R_2O_3 includes the sesquioxid equivalents of very considerable percentages of monoxides and dioxides. Benedicks would assign yttrialite to a group of which rowlandite is the prototype and to which he believes thalénite and kainosite belong, being either plain basic salts of $H_6Si_2O_7$ of the type $R''\ R'''_4Si_4O_{15}$ or derivatives in which the fifteenth oxygen atom is replaced by its equivalent in fluorine (rowlandite) or CO_3 (kainosite), as shown below.



Benedicks says: "Dem Yttrialit, von Hidden and Mackintosh beschrieben, sollte die Formel R_2O_3, $2SiO_2$ zukommen, worin R hauptsächlich Ytter-und Thorerde ist. Dabei wird aber ca. 4% Eisenoxydul in der Analyse vernachlässigt. Wird dies nebst etwas Kalk und Bleioxyd mitgerechnet, so bekommt man die Formel $Fe''O$, $2R_2O_3$, $4SiO_2$, analog mit der des Thalénits, welche besser die Zusammensetzung des Yttrialits wiedergibt, obgleich die Ubereinstimmung gar nicht gut ist."

It is, however, not true that Hidden and Mackintosh neglected to take account of the ferrous iron, etc., of their analysis. It was regarded in the derivation of their empirical formula $R_2Si_2O_7$. How wholly unwarranted was the substitution by Benedicks of his formula for yttrialite is shown by the molecular ratio for $RO : R_2O_3 : SiO_2$, which he gives as 1 : 2 : 4 instead of 1 : 3·25 : 7·42 as calculated by me from Mackintosh's figures, wherein for a sound reason I have converted his UO_3

* Bull. Geol. Inst. Upsala, iv, 1, 1898. † This Journal, xxxviii, 477, 1889.

into UO_2, thus throwing it with the ThO_2, where it naturally belongs. The agreement is indeed "gar nicht gut."

Benedicks has made the grave mistake of counting Mackintosh's monoxide bases a second time, thus making a basic salt $R''R'''_4Si_4O_{15}$ instead of the normal one $R'''_4Si_4O_{14}$, to which Mackintosh's results closely conform.

Discussion of Benedicks' formula for Thalénite.

Moreover, in the light of the data furnished by Benedicks himself it cannot be admitted that the formula $H_2Y_4Si_4O_{15}$ for thalénite is established.

Water was determined by him according to Penfield's method,* but without any hint as to the particular modification employed. If, as seems probable, the water expelled from the mineral was caused to recondense in the cooler part of the ignition tube, the latter being then weighed and again after driving the condensed water out, two serious sources of error have to be considered: (1) The CO_2 present in the mineral, which would count in part as water unless a very careful correction was made, as provided for by Penfield. No mention is made by Benedicks of any such correction. (2) Nitrogen and helium are said to comprise 1·4 per cent of the mineral by weight. If so, these would introduce an error in the above water determination of contrary sign to that due to CO_2, and if the proportion of helium were large this error might be of very considerable magnitude.

In an appendix to his paper Benedicks gives an analysis of what he considers to be a very pure form of thalénite. He makes no comparison of this with his earlier analysis, nor does he deduce a molecular ratio, which I find to be 1 : 2·6 : 5·15, or 1 : 3·03 : 6·02 if small amounts of lime, magnesia, and soda are neglected, instead of 1 : 2 : 4 as required by his formula. There being no CO_2 in this purer material, the value for water (if determined as above surmised) may be supposed to be affected only by the error due to nitrogen and helium. It will be seen that the neglect to regard lime, magnesia, and soda in his second analysis affects the ratio very seriously. This neglect may be justified in figuring on his first analysis because of an approximate balancing by CO_2, but it would be by no means so in the other in spite of the very satisfactory ratio obtained and leading to the empirical formula $R''R'''_6Si_6O_{22}$, which is susceptible of a variety of interpretations. It may represent a basic salt of diorthosilicic acid $R''R'''_5(R'''O)'Si_2O_7)_3$ or of metasilicic acid $R''R'''_2(R'''O)'_4(SiO_3)_6$, or possibly even of other acids.

* This Journal, xlviii, 31, 1894.

Finally, if the values for nitrogen and helium are really anywhere near so great as given, an additional argument against the validity of his formula is furnished. For, in the light of Kohlschütter's recent researches* and my own less conclusive work of a much earlier date,† it is in the highest degree probable that nitrogen and helium are not occluded in uraninite and other minerals but are in chemical combination. Now, if this is so, in a mineral containing as much as 1·4 per cent of nitrogen by weight this must, quite irrespective of its form of combination, play so important a role in the molecule as to utterly invalidate any formula based on calculations from which it is omitted. If the above percentage is made up in large part of helium, its effect, because of its low atomic weight, must be vastly greater than that of nitrogen.

Until light is thrown on the nature of the combinations these two gases form in minerals, no very positive conclusions can be reached as to the formulas to be assigned to those minerals which contain them in more than traces.

Chemical investigation of Yttrialite.

At the earnest request of Mr. W. E. Hidden, the discoverer of yttrialite, I undertook to reanalyze the mineral in order if possible to settle definitely the question of its composition. This seemed especially desirable since a large quantity of very fine material was available.

The appearance and behavior of the mineral agreed in all respects except one with those of the original description.‡ It is there stated that the strongly ignited mineral is insoluble in acid. This is a mistake, for when powdered the solubility in hydrochloric acid is even then perfect, although not rapid.

Careful examination of thin sections under the microscope showed a condition that augured ill for decisive analytical results despite the apparently fine quality of the large specimens. Distinctly foreign mineral fragments were as good as absent except for insignificant coatings of a white alteration product, presumably a carbonate, but considerable shading was apparent in the slides, indicative of alteration or intimate contamination in the mass of the mineral itself. However, after treatment with hot dilute hydrochloric acid (whereby much yttrialite was dissolved) followed by dilute sodium carbonate, the clear glassy residue appeared to be improved in appearance and the specific gravity of two samples, each composed of small grains uniform in size for each sample, had risen from 4·596 and 4·590 to 4·654

* Ann. der Chem., cccxvii, 158, 1901.
† Bull. U. S. Geol. Surv., No. 78, pp. 76–78, 1891.
‡ This Journal, xxxviii, 477, 1889.

at 23½° C and 4·646 at 26° C. respectively. The two sizes were then mixed, giving one sample of about 4·65 sp. gr. at 25° C. That of the unpurified material analyzed by Mackintosh was 4·575.

Qualitative tests showed the absence of zirconium, glucinum, and aluminum and the presence of a little more than a trace of fluorine, of a very little carbon dioxide, besides some other gases which were set free by treatment with acids and by fusion with an alkali carbonate.

Silica was separated by two evaporations with hydrochloric acid; lead was then thrown out by hydrogen sulphide.

The earths when finally collected together free from all iron, manganese, uranium, titanium, phosphorus, calcium, and magnesium, were ignited and weighed. No filtrate from a precipitate of earth-oxalates was ever regarded as free from earths till after evaporating, igniting, and retesting. This is a needed precaution in all similar analyses.

The combined earths were dissolved in nitric acid and evaporated to dryness. A saturated solution of potassium sulphate was poured upon the dry mass, which wholly dissolved but almost at once began to deposit double sulphates. Solid potassium sulphate was then added in crystals. After twenty-four hours the precipitate was collected on a filter and washed with the precipitant solution. Twice was this precipitation repeated after first dissolving the double salts in acid, precipitating by potassium hydroxide, washing, redissolving in nitric acid, and evaporating. Then only was the extraction of the yttrium-erbium group practically complete. From the combined filtrates the soluble earths were thrown out, reconverted into nitrates, and again treated with potassium sulphate, whereby a little further insoluble matter was obtained. Yttrium-erbium oxides obtained from the oxalates gave a light-colored mixture of 265·6 Mol. W. (108·8 At. W.), which furnished a pink nitrate solution showing the erbium absorption bands strongly marked, with very faint indications of the strongest band of the didymium components.

The insoluble sulphates were converted into chlorides and thrice treated with potassium hydroxide and chlorine to precipitate thorium and cerium. From the filtrates the soluble earths were recovered and subjected to a repetition of this treatment. Their oxides after purification were light dirty brown when heated over the Bunsen flame, but grayish white when blasted. Their Mol. W. was 335·5 (At. W. 143·7); their nitrate solution was pink and gave the characteristic didymium component absorption bands altogether free from those of the erbium constituents.

Cerium and thorium were separated by a combination of the

ammonium oxalate and thiosulphate methods. The weighed thoria was pure white, the ceria of a pale salmon color.

The condition of the uranium was shown by its precipitability as tetrafluoride on dissolving the mineral in hydrofluoric acid. This reaction afforded a ready means of estimating with exactness the ferrous iron by permanganate after rapidly filtering off the fluorides precipitated in an atmosphere of carbon dioxide. Solution of the mineral in a sealed tube with dilute sulphuric acid allowed of finding the oxygen value of both UO_2 and FeO by permanganate. The result thus found for OU_2 agreed marvelously well with that calculated from the U_3O_8 found gravimetrically in a separate portion.

Analyses of Yttrialite.

	Hillebrand.		Mol. Ratios.		Mackintosh.		Mol. Ratios.
SiO_2	29·63		·4938		29·17		·4861
TiO_2	·05				——		
ThO_2	10·85		·0470		12·00		·0483
UO_2	1·64	(1			·79	(1	
Ce_2O_3	3·07				1·86		
La_2O_3, etc.	5·18	(2			2·94	(2	
Y_2O_3, etc.	43·45	(3			22·67	(3	
"					5·30	(4	
"			·1930		4·50	(5	·1864
"					14·03	(6	
Al_2O_3	——				·55		
Fe_2O_3	·76				——		
FeO	1·96				2·89		
MnO	·88				·77		·0655
PbO	·80				·85		
CaO	·67		·0608		·60		
MgO	·16						
H_2O+105 C.	·32						
H_2O-105 C.	·04				·79		
CO_2	·11						
P_2O_5	·12						
N, He, Fl, Alk	Diff. ·31						
	100·00				99·75		

1) Volumetrically. Gravimetrically 1·62%.
2) At. W. 143·8 (Mol. W. 335·6).
3) At. W. 108·8 (Mol. W. 265·6).

1) Given as $·83UO_3$ by Mackintosh.
2) At. W. 162 (Mol. W. 372).
3) At. W. 110·3 (Mol. W. 268·6).
4) At. W. 110·53 (Mol. W. 269·06).
5) At. W. 114·9 (Mol. W. 277·8).
6) At. W. 120 (Mol. W. 288).

Nitrogen (?) and helium (?) were obtained quantitatively by fusing the mineral with sodium-potassium carbonate in a current of carbon dioxide and collecting the gases in a nitrometer over potassium hydroxide. The volume was between one and two cubic centimeters per gram of yttrialite. The gases were not further examined.

The analysis is given above, together with that of Mackintosh for comparison.

The ratios of Mackintosh's analysis as calculated above by me are certainly wrong in so far as they are affected by the value for iron, which he assumed to be wholly ferrous. If corrected in accordance with the statement of my analysis, or, what amounts to the same thing for the purpose of illustration and is simpler, if my ratio is altered to conform to his statement for RO and R_2O_3 bases it becomes ·0644 : ·1882, a very close agreement.

It is altogether probable that Mackintosh's separations of the earths were not so far reaching as mine, and this belief is borne out by the differences in the experimental molecular weights for the lanthanum and yttrium groups, mine being more in accordance with what might be expected and, moreover, agreeing almost exactly with those which were found by me for rowlandite in 1893, namely, 336·8 and 266·2 respectively.*

It is of course impossible to say what disposition should be made of the small amounts of firmly held water, phosphorus, carbon dioxide, fluorine, and alkalies. The ratios of my analysis are, therefore, to a slight extent incorrect, but probably not enough to influence any conclusions that may be drawn. One thing is apparent, that the preliminary purification by acid has had no pronounced effect on the composition of the mass acted on, otherwise Mackintosh's and my analyses should show far greater differences in the main constituents.

The crude empirical formulas deducible from the ratios of the two analyses are nearly

* The three minerals gadolinite, yttrialite, and rowlandite occur in Llano County in most intimate association, suggestive of close community of origin, a suggestion which is emphasized by the marvelous agreement for gadolinite and yttrialite, not only in the relative proportions of the trivalent earth metals but in their absolute amounts as well.

	Ce_2O_3	La_2O_3, etc.	Y_2O_3, etc.
Gadolinite (Genth)	2·65	5 22	44·35
" "	2·66	5·01	44·45
" (Eakins)	2·62	5·22	41·55
Yttrialite (H'b'd.)	3·07	5·18	43·45
Rowlandite (")	5·06	9·34	47·70

This concordant testimony of three analysts may be regarded as strong evidence of the correctness of the earth separations made by them in these cases. Nearly the same relation is shown by the trivalent earth-metals of rowlandite, as seen in the table above.

Hbd.	R''_{61}	R'''_{386}	R''''_{47}	$(Si_2O_7)_{247}$
Mack.	R''_{65}	R'''_{373}	R''''_{48}	$(Si_2O_7)_{243}$

there being a slight *deficiency* of oxygen atoms in each case for the radical Si_2O_7, which is increased by allowing for the CO_2 and P_2O_5.

In so far then as the character of the acid radical is concerned the results of Mackintosh's analysis are fully confirmed and there is absolutely no ground for accepting Benedicks' basic formula, which as I have already shown (p. 145) is based on a palpable error. But the ratios are not at all such as to lend themselves to ready resolution into isomorphous salts of the acid $H_6Si_2O_7$. By doing quite unwarranted violence to the analytical data the above formulas might be reduced to

$$R''\ \ R'''_6\ \ R''''\ \ (Si_2O_7)_4$$

which can be readily represented structurally as a single complex molecule or as a mixture of molecules like $3R'''_2Si_2O_7 + R''R''''Si_2O_7$. In neither case, however, is the type of the rowlandite molecule approached, which requires an altogether different ratio of monoxide, dioxide, and trioxide bases, nor, if the second be accepted, is it at all clear that the two molecules would be mineralogically equivalent, that is, isomorphous.

An alternative hypothesis is to regard the mineral as a mixture containing the anhydrous thorite molecule. Proceeding on this assumption and deducting all thorium and uranium and the proper amounts of silicon and oxygen, the crude empirical formulas become

Mack.	R''_{65}	R'''_{373}	Si_{438}	O_{1501}
Hbd.	R''_{61}	R'''_{386}	Si_{447}	O_{1533}

which may be interpreted as basic salts of metasilicic acid:

	R''_{65}	R'''_{185}	$(R'''O)'_{187}$	$(SiO_3)_{438}$
	R''_{61}	R'''_{194}	$(R'''O)'_{192}$	$(SiO_3)_{447}$
or	R''	R'''_3	$(R'''O)'_3$	$(SiO_3)_7$

this last being easily susceptible of symmetrical representation in graphic form.

On the whole I prefer to leave the constitution of yttrialite unsettled until further evidence can be gathered, either from analyses of allied minerals or from yttrialite itself of more certain purity than any that has yet been discovered.

It must not be forgotten that the gases other than CO_2 contained in the mineral may be the cause of the inability to arrive at satisfactory conclusions in the case of this and all other minerals which contain them, as I have already pointed out on p. 147.

My excuse for such a lengthy publication on a matter still unsettled is the desire to prevent general acquiescence in the grouping under one type of minerals which can by no means be regarded as proven to belong to that type, and to which yttrialite certainly does not belong.

Summary.

The empirical formula of Hidden and Mackintosh for yttrialite is confirmed, and it is shown that the basic formula of Benedicks rests on error and has no standing.

The formula of Hidden and Mackintosh is not, however, susceptible of representation as a simple salt of the acid $H_6Si_2O_7$. On the purely hypothetical assumption of admixture of anhydrous thorite, the remaining constituents afford ratios conforming quite closely to those of a basic metasilicate $R''R'''_3(R'''O)'_3(SiO_3)_7$.

It is shown for two reasons fully discussed that the formula proposed by Benedicks for thalénite is to be regarded as doubtful.

Laboratory U. S. Geol. Survey,
Washington, D. C., Nov. 19th, 1901.