On the Chemical Composition of Zirkelite.

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IN a previous paper (*Min. Mag.* XI. 1895, p. 80), the result was given of an analysis of the new mineral, Zirkelite, which was discovered by Dr. Hussak in association with baddeleyite in the decomposing magnetite-pyroxenite of Jacupiranga, S. Paulo, Brazil.

In that analysis only a small amount of material (less than a quarter of a grm.) was used, and no very serious attempt was made to separate small percentages of rare earths in the main zirconia precipitate. The individual numbers also which resulted from an attempt to separate the titanium and zirconium by Bailey's hydrogen peroxide method were given provisionally, and stated to be regarded only as approximate. A subsequent examination of the precipitates showed that the mineral contained cerium, and that (owing mainly to the impurity and want of concentration of the hydrogen peroxide employed) the attempt at separating the titanium and zirconium had been a failure, so that the number giving the percentage of titanium was much too high. A note to this effect would have been inserted in this Magazine had no further material been available for analysis; but, fortunately, through the zeal of Dr. Hussak, a larger supply of the mineral was soon forthcoming, sufficient for the more complete analysis, of which the result is given below.

In this analysis only material which sank in thallium-silver nitrate was used.

A re-determination of the density, made on ·6893 grm. of such material, gave as the weight of 1cc. at 17° C. 4·741.

Result of Analysis :—

		Molecular ratios.
ZrO_2 =	52·89	·433
TiO_2 =	14·95	·182
ThO_2 =	7·31	·028
Ce_2O_3 =	2·52	·008
(Y_2O_3 ?) =	0·21	·001
UO_2 =	1·40	·005
FeO =	7·72	·107
CaO =	10·79	·193
MgO =	0·22	·005
Loss on ignition (from preliminary analysis) =	1·02	
	99·03	

Weight of material used in analysis, 0·4716 grm. The molecular ratios correspond approximately to the formula $RO.2(Zr,Ti,Th)O_2$.

Method of Analysis.—The mineral (very finely powdered by grinding in an agate mortar and moistening with absolute alcohol) was decomposed by fuming hydrofluoric acid.[1] By diluting and filtering, a rough separation was at once effected between the soluble (Zr,Ti,Fe...) and the insoluble (Th,Ca,Ce...) fluorides. The solution (A) and the insoluble residue on the filter (B) were then treated separately.

(A) The solution was evaporated nearly to dryness, and the fluorides decomposed by sulphuric acid, the excess of which was removed by heating gently. On adding cold water, a clear solution was obtained. After nearly neutralising with sodium carbonate, the Zr and Ti were precipitated by sodium thiosulphate, and the Fe in the filtrate, after separating sulphur, by ammonia. After weighing, the mixed ZrO_2 and TiO_2 were again brought into solution, and the TiO_2 determined by Weller's colorimetric method (*Ber. Deutsch. Chem. Ges.* XV. 1882, p. 2592).

(B) The insoluble fluorides were decomposed by sulphuric acid, and the resulting sulphates brought into solution in cold water. In this solution hydrogen peroxide failed to produce any coloration, thus showing the absence of TiO_2. On boiling, however, a precipitate (ThO_2) was deposited. This was filtered hot, washed, dried and weighed. Its weight was ·0294 grm., corresponding to 6·2 p.c. In the filtrate the Ce_2O_3, &c. was

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[1] Lawrence Smith, *Original Researches in Mineralogy and Chemistry*, p. 352.

separated from CaO by a double precipitation with ammonia. On testing the moist ammonia precipitate with dilute hydrofluoric acid, a large proportion was found to be soluble (some ZrO_2 had been retained in the insoluble fluorides). The hydrofluoric acid was expelled by sulphuric acid, and the solution reprecipitated by ammonia. This precipitate was washed, dried and weighed. It was then, together with the ThO_2 precipitate, again brought into solution by fusion with acid sulphate of potassium. From this solution a precipitate was obtained by means of sodium thiosulphate, which on ignition weighed ·0646 grm., corresponding to 13·70 p.c. In the filtrate the cerium and uranium were precipitated by ammonia; this precipitate was redissolved and the cerium separated by precipitation with oxalic acid. The filtrate was evaporated to dryness and ammonia salts expelled before precipitating the uranium. A small portion of this precipitate gave with microcosmic salt a good uranium bead. The oxalic acid precipitate (Ce_2O_3) was ignited and weighed. It was again brought into solution, and the Ce_2O_3 precipitated by potassium sulphate. In the filtrate, oxalic acid gave a slight precipitate, which, on ignition, yielded an oxide (Y_2O_3?), only faintly yellow, and thus distinct from the reddish-buff oxide (CeO_2) obtained from the potassium sulphate precipitate.

The sodium thiosulphate precipitate was found to consist of almost equal parts of ThO_2 and ZrO_2. After ignition and weighing, it was brought into solution by means of hydrofluoric and sulphuric acids. The solution was divided into two equal parts, and each treated separately. In one part the sulphuric acid was neutralised by potash, and the ZrO_2 and ThO_2 thrown down by boiling with potassium sulphate. From this precipitate hydrochloric acid separated the ThO_2, leaving most of the ZrO_2 undissolved. The hydrochloric acid solution was evaporated to dryness. The residue gave a clear solution with cold water, from which the ThO_2 was precipitated by oxalic acid added in considerable excess. The other half of the solution of the thiosulphate precipitate was treated with ammonia until a permanent precipitate formed; oxalic acid in excess was then added. A clear solution resulted, but on adding hydrochloric acid most of the ThO_2 was precipitated. The filtrate from the precipitate was evaporated to dryness, and the ammonia salts expelled. The residue was dissolved in hydrochloric acid, the excess of acid expelled, and the remainder of the ThO_2 precipitated by excess of oxalic acid. The ZrO_2 in the filtrate was precipitated with ammonia. The combined ThO_2 precipitates, after ignition and weighing (·0313 grm.), were dissolved in sulphuric and hydrofluoric acids, the solution evaporated to dryness, and the excess of sulphuric acid expelled: the residue was dissolved in cold water, and the ThO_2 again precipitated with excess of oxalic acid. The resulting oxide weighed 0·0299 grm., and gave a sulphate weighing 0·0492 grm., corresponding to a molecular weight of about 250.