

XXXIV.—*Malacone, a Silicate of Zirconium.*

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A RECENT paper by Kitchin and Winterson (Trans., 1906, **89**, 1568) has directed attention to malacone, and to the fact that it is the only mineral known to contain argon. It is radioactive, and these

authors were the first to find uranium in it, although Strutt (*Proc. Roy. Soc.*, 1904, **73**, A, 191) had previously suggested that this metal was present.

The identity of the zirconium was proved by Kitchin and Winterson, who prepared from the mineral a pure sample of zirconium oxychloride. The crude zirconium oxychloride gave a ratio of 1 : 1·824 for zirconium to chlorine, as against 1 : 2·01 for a sample of zirconium oxychloride of known purity, and it was only after thirteen recrystallisations from alcohol that they obtained a pure specimen of zirconium oxychloride. The authors found that their crude oxychloride contained some uranium, but the total uranium found in the mineral was insufficient to affect appreciably the purity of the zirconium oxychloride.

When the mineral had been separated into its constituents, Kitchin and Winterson found that the radioactivity emanated from the zirconia. This was a surprising observation, as the zirconia had been boiled with hydrochloric acid, which should have extracted any ordinary radioactive material, and zirconium salts are not themselves radioactive. It seemed, therefore, desirous that these facts should be further investigated.

EXPERIMENTAL.

A complete analysis of the mineral was not thought necessary, but, in the course of certain separations, values for the silica and zirconia were obtained which differed considerably from those given by Kitchin and Winterson. The results obtained, together with those of previous investigators, are given in the following table :

Locality of specimen.	Authority.	SiO ₂ .	ZrO ₂ .	SiO ₂ + ZrO ₂ .
1 Hitterö	Scheerer ¹	31·31	63·4	94·7
2 Ilmengebirge ...	Hermann ²	31·87	59·8	91·7
3 Chanteloupe ...	Damour ³	30·87	61·17	92·0
4 Chanteloupe ...	Rammelsberg ⁴	31·05	61·44	92·5
5	Kitchin and Winterson ⁵	22·53	67·8	90·3
6	Cumming	32·3	60·5	92·8

¹ Scheerer (*Pogg. Ann.*, 1844, **62**, 436).

² Hermann (*J. pr. Chem.*, 1851, **53**, 32).

³ Damour (*Ann. Chim. Phys.*, 1848, **24**, 87).

⁴ Rammelsberg (*Mineralchemie*, p. 891).

⁵ *Loc. cit.* The specimens examined by Kitchin and Winterson and by myself were obtained from the Christiania Mine Kompani.

The results obtained thus agreed well with those of early investigators and with the formula (ZrO₂,SiO₂) for the silicate, but differed widely from those of Kitchin and Winterson. The explanation probably lies in the unusual stability of zirconium silicate towards hydrofluoric acid. Repeated evaporations, usually about ten, are necessary to drive off all the silica. There is a possible source of error in this process, as it was found that zirconium was also readily

expelled unless a large amount of sulphuric acid was present. After treatment, the zirconium is left mainly as zirconium sulphate, and, if the quantity exceeds 0.5 gram, prolonged ignition is necessary to ensure complete reduction to oxide.

Identity of the Zirconium.—The change of sulphate to oxide on ignition was adopted as a test of the identity of the zirconium salts obtained from malacone. It was carried out as follows: a small unweighed sample of the oxychloride was placed in a platinum crucible, concentrated sulphuric acid added, the mixture evaporated gently to dryness, and weighed as sulphate. More sulphuric acid was then added, and again evaporated. The weight was usually unchanged. The residue was then strongly ignited until of constant weight, and weighed as oxide.

The results of some of the blank experiments were as follows:

Salt used.	Weight as sulphate.	Weight as oxide.	Oxide in sulphate, per cent.
Zirconium nitrate	1.0607	0.4518	42.6
Zirconium oxychloride.	0.3054	0.1315	43.2
	0.3804	0.1718	45.2
Uranium acetate	0.2118	0.1552	73.6

The theoretical percentage of oxide in pure zirconium sulphate is 43.4. It was found that values between 43.2 and 43.5 could always be obtained by starting from pure zirconium oxychloride. Expt. 3 is the result with a specimen to which a little uranium acetate had been added; it was further distinguished from a pure zirconium salt, as the oxide obtained was green, whilst pure zirconia is white. The results for pure uranium acetate agree with the probable change, that is, from uranyl sulphate, UO_2SO_4 , to uranyl oxide, U_3O_8 , the theoretical percentage of oxide being 74.8.

The oxide to sulphate ratio was thus proved to be a good test of the purity of a zirconium salt, particularly as regards uranium.

Partial Separation into Constituents.—After removal of the silica, a very convenient separation was effected by boiling for about one hour with concentrated hydrochloric acid containing a little nitric acid. The residue was found to be almost pure zirconia, and very little of the zirconia had dissolved. These two portions were examined separately, and are referred to later as the acid-soluble portion and part insoluble in acid respectively.

Part Insoluble in Acid.—9.986 Grams of this part were treated with hydrofluoric acid to remove most of the silica. After ignition, the weight was 7.22 grams. This was made into balls with wood charcoal and sugar, and the mixture heated in a covered crucible. The coke-like mixture was then ignited in a stream of chlorine saturated with carbon tetrachloride at about 60°.

A white, crystalline chloride was collected, which proved to be zirconium tetrachloride. This was washed with water, with which it reacted vigorously, and yielded on evaporation 7.2 grams of oxychloride.

The residue in the tube weighed 3.1 grams, part of which was the ash from the 15 grams of charcoal used.

The oxychloride was found to give all the ordinary tests for zirconium. A trace of iron was present, but no uranium could be detected. The equivalent was determined with the following result :

0.1664 gram of oxychloride gave 0.1920 gram of sulphate.

Weight as oxide = 0.0836 gram.

Oxide in sulphate = 43.6.

The theoretical value for zirconium is 43.4 per cent.

On account of the ash, it was useless to proceed further with this experiment. An attempt was next made to test the homogeneity of the part of malacone insoluble in acid by fractional chlorination.

For this purpose, 20 grams of the part insoluble in acid were evaporated once with hydrofluoric and sulphuric acids to remove the bulk of the silica. After ignition, the residue weighed 15.51 grams. This was mixed with sugar-carbon and chlorinated, but after five hours' chlorination the chloride obtained yielded only 0.62 gram of oxychloride (fraction A).

The sugar-carbon was burnt off, as it was evidently unsuitable, and wood charcoal, which had been boiled for some hours in concentrated hydrochloric acid, substituted.

The second chlorination yielded 4.52 grams of oxychloride (fraction B). The third chlorination yielded 7.95 grams of oxychloride (fraction C), and the fourth chlorination yielded 2.9 grams of oxychloride (fraction D). The carbon and silica were removed from the residue, which then weighed 2.1 grams (fraction E).

Fraction.	Total weight.	Weight of sample		Percentage oxide in sulphate.
		as sulphate.	as oxide.	
A	0.62	0.5196	0.2238	43.2
B	4.52	0.2047	0.0875	42.8
C	7.95	0.1302	0.0565	43.4
D	2.90	0.5025	0.2200	43.7

For zirconium, the amount of oxide in sulphate is 43.4 per cent. Each fraction gave all the zirconium tests, and in all cases the oxide obtained was pure white; a trace of iron was noticed in each case, and with fraction A a yellow colour was obtained with hydrogen peroxide, which probably indicated the presence of titanium in this fraction. In no case could uranium be detected, although it was carefully tested for, and could be readily recognised if a trace were afterwards added. Fraction E, the residue from the chlorinations,

was qualitatively examined and found to contain zirconia, a ferric salt, and a calcium salt, the latter being probably derived from the charcoal.

Radioactivity.—The part of malacone which did not dissolve in hydrochloric acid, that is, the zirconia and silica, was found to be non-radioactive. This was ascertained by placing 20 grams in a flask with some dilute hydrochloric acid and exhausting the flask. At the end of a week, some air was admitted and then pumped off in the usual manner, but no evidence of radioactivity was found. As a further test, 19 grams of the crude oxychloride collected in the various chlorinations were kept in an exhausted flask for seven days, and the flask washed out thoroughly with successive small quantities of air. The oxychloride proved so completely free from any radioactive material that this air did not affect the leak of an electroscope which had a period of eight hours per twenty divisions.

At first sight, this is in direct opposition to the experience of Kitchin and Winterson, who found that all the radioactive matter remained with the zirconia, but the explanation is probably to be found in the different previous treatment. In their case, the malacone had been fused with fusion mixture, and they mention that it was necessary to use ten times as much fusion mixture as mineral. It is very possible that this contained sufficient sulphate to transform any traces of barium, calcium, or strontium into sulphates, and these would carry down also the radioactive matter as radium sulphate, which would not dissolve in the hydrochloric acid, but would remain with the precipitated zirconia.

Part Soluble in Acid.—This part was found to contain all the radioactive matter. The emanation from the portion of 100 grams of malacone soluble in acid was collected and introduced into an electroscope in the usual manner.

Several measurements were made of the time taken for the activity to fall from its maximum to one-half, and the results varied between 3.5 and four days. In all cases, the activity had almost reached the maximum value two hours after introduction into the electroscope, and after three hours began to fall.

There seems, therefore, no reason to suspect the presence of any radioactive element other than radium, so that the presence of argon cannot be explained on this ground.

Summary.

The formula $\text{ZrO}_2, \text{SiO}_2$ corresponds more closely with the observed composition of malacone than does the formula $3\text{ZrO}_2, 2\text{SiO}_2$ which has been recently assigned to it. A detailed examination gave no

reason for doubting the identity of the zirconia, or to suspect the presence of an unknown impurity. The radioactivity can be sufficiently explained by the presence of radium.

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