

SAMARSKITE FROM NELLORE DISTRICT

Part II. Chemical Composition

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INTRODUCTION

IN Part I¹ it was pointed out by the authors that Tipper's identification of the mineral, Samarskite, occurring in the Nellore District was based only on its megascopic characters and qualitative analyses carried out by Blyth. It was shown that Samarskite occurs often closely intergrown with Columbite-Tantalites. The Uranium and "Earth Acid" contents of a number of samples were reported.

The object of the present paper is to report on the chemical composition of a typical sample of samarskite. The specimen chosen weighed about 820 gm. It has indistinct crystal faces developed on one side but is mostly irregular, massive and partially intergrown with felspar. The latter is also seen as fine veins shot through the samarskite. These, however, are quite superficial. The mass appears otherwise perfectly homogeneous. The specimen was cut through and the cut surfaces polished. There was no evidence of intergrowth with any other mineral as noticed in some other specimens of samarskite from the same area.¹ Autoradiographs of the polished specimens using ordinary photographic plates also failed to detect any lack of homogeneity in the specimen. The general physical properties of the specimen are as follows: Colour, Velvet black; Streak, Dark brown; Lustre, Vitreous and splendent; Hardness, about 6; and Specific gravity, 5.625.

It is well known that the rare earth minerals always contain a number of rare earths in varying proportions. The points of special interest in the analytical study of samarskite are: (a) the thorium content, (b) the presence of cerium, (c) uranium in the quadrivalent and hexavalent states, and (d) the lead content.

Thorium is not one of the rare earths but is generally associated with them. Spencer² states that it is quite probable that many of the rare earth minerals in which thorium has not been reported, do actually contain it, although in very small quantities, for the rare earths may be regarded as

the ultimate disintegration products of thorium. The thorium content is also of interest in the calculation of the age of the mineral.³ J. L. Smith,⁴ and Allen,⁵ do not report any thoria in their samples of samarskite from North Carolina, but others report amounts varying from 1.73 to 6% as shown in the table below (Spencer, *loc. cit.*).

Authors	Source of Samarskite	ThO ₂ %
Finkener and Stephans	.. Minsk	6.0
Hillebrand	.. Colorado	3.64
Chroustschoff	.. Urals	1.73

Smith (*loc. cit.*) did not find any cerium in N. Carolina samarskite while Allen (*loc. cit.*) reported a minute quantity, and Wells⁶ found 0.2% cerous oxide in a sample presumably of American origin.

Uranium occurs both in the quadrivalent and hexavalent states in samarskite and these can be separated as the insoluble green uranous and the soluble uranyl fluorides, using hydrofluoric acid (J. L. Smith's method), but it is doubtful, as pointed out by Wells (*loc. cit.*) if the results obtained represent the composition of the mineral exactly. The actual content of uranium is of interest in the calculation of the age of the mineral as well as the radium content (*cf.* Part I).

The lead content enters into the calculation of the age of the mineral but its accurate determination is considerably difficult. The possible presence of lead of non-radioactive origin in the mineral itself as well as lead in the reagents used, vitiates the results. Further, unless the specimen is fresh and unaltered, the figure is of no value.

CHEMICAL ANALYSIS

Chemical analysis was carried out on the same general lines as in the J. L. Smith method (*loc. cit.*) involving the decomposition of the mineral with hydrofluoric acid. The insoluble portion contains mainly the rare earths and quadrivalent uranium while the soluble portion contains the "Earth Acids", hexavalent uranium, iron and manganese. Minor constituents such as tin, tungsten and titanium go exclusively with the "Earth Acids" while lead, calcium and magnesium are found mostly in the insoluble portion. This separation into two groups is not clean cut as can be seen from the data given by Wells (*loc. cit.*).

Actual analysis was carried out according to Giroto's⁷ procedure modified suitably as follows:—(a) thorium was separated and estimated by the

hexamine method,⁸ (b) cerium isolated by the iodate method and estimated by ignition to ceria by way of the oxalate,⁸ (c) the cerium and yttrium group of earths were separated by the double sulphate method using potassium sulphate and independently estimated by conversion to oxalates and ignition to the oxides,⁸ and (d) the major portion of the "Earth Acids" was precipitated directly by dilution and boiling while the rest was recovered from the filtrate by the tannin method from alkaline tartrate solution after removal of iron as sulphide.⁸

RESULTS

All the major constituents of the specimen were determined. The results obtained are reported in Column I in the following table:—For comparison results obtained by Smith, Miss Swallow and Allen are also reported in Columns II, III and IV respectively (*cf.*, Smith, *loc. cit.*).

	I	II	III	IV
1 Earth acids ..	57.4	55.13	54.98	55.8
2 Thoria ..	1.98
3 Cerium Earths :	(1.2)	4.24	5.17	4.25
(a) Ceria ..	0.4
(b) Lanthanum Earths ..	0.8*
4 Yttria Earths ..	16.9*	14.49	12.84	14.45
5 UO ₂ ..	8.4	} 10.96	9.91	12.46
6 UO ₃ ..	Nil		14.02	10.90
7 FeO ..	9.1	11.74	14.02	10.90
8 PbO ..	2.25†
9 CaO ..	1.1	0.55
10 Loss on ignition ..	0.87	0.72	0.52	1.12
11 MnO	1.53	1.09	0.75
12 MgO	Trace
13 WO ₃	} 0.31	[0.16	0.08
14 SnO ₂			
15 ZrO ₂
16 TiO ₂
17 Insoluble residue from "Cerium oxides"	1.25	..
Total ..	99.20	99.12	99.72	100.36

* Uncorrected for peroxidic oxygen.

† This value is unreliable as lead-free reagents could not be secured.

Several attempts to precipitate hexavalent uranium, if any, from the H. F.-soluble portion by the usual procedure failed to yield the yellow ammonium diuranate and hence it must be presumed that either hexavalent uranium is absent or is present in minute quantity. Other points of interest are the presence of 1.98% thoria and 0.4% ceria.

Calculation of Radium content according to the formula of L.D. Roberts.⁹

$$U\% \times 3.4 = \text{mg. Ra. per ton.}$$

$$7.406 \times 3.4 = 25.19 \text{ mg. Radium per ton.}$$

i.e., 1 gr. in 39.71 tons.

It is nearly as rich as the Katanga Carnotite.¹⁰

SUMMARY

1. A typical sample of samarskite has been analysed and the results reported.
2. The thoria content of the sample is 1.98%.
3. The percentage of cerium earths present in this sample is relatively much smaller than found in samples from North America. Our sample contains 0.4% ceria.
4. Hexavalent uranium has not been found in the sample but this is of no special significance.
5. The radium content is 1.0 gr. in 39.71 tons and the Nellore samarskite is nearly as rich as Katanga Carnotite in this element.

REFERENCES

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| 1. Karunakaran and Neelakantam | <i>Proc. Ind. Acad. Sci.</i> , 1947, 25 A, 404. |
| 2. Spencer | .. <i>The Metals of the Rare Earths</i> , 1919, 13. |
| 3. | .. <i>Physics of the Earth</i> , 1931, 4, 99. |
| 4. J. L. Smith | .. <i>Am. J. Sci.</i> , 1877, 13, 359. |
| 5. Allen | .. <i>Ibid.</i> , 1877, 14, 128. |
| 6. Wells | .. <i>J. Am. Chem. Soc.</i> , 1928, 50, 1017. |
| 7. Giroto | .. <i>Chemical Abstracts</i> , 1941, 3557. |
| 8. Schoeller and Powell | .. <i>The Analysis of Minerals and Ores of the Rarer Elements</i> , 1940. |
| 9. L. D. Roberts Scott | .. <i>Standard Methods of Chemical Analysis</i> , 1939, 1, 767. |
| 10. Karunakaran and Neelakantam | <i>J. Sci. Ind. Res.</i> , 1946, 5 B, 36. |