STUDIES ON SOUTH INDIAN RADIOACTIVE MINERALS

Part I. Samarskite from Nellore

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ABSTRACT

Samarskite, a radioactive niobotantalate occurring in the Nellore pegmatites, has been studied in detail. The investigations comprise the determination of physical and optical characters, chemical composition, autoradiographic studies, distribution pattern, calculation and interpretation of age. The available data on Nellore Samarskite has been critically examined and it has been shown that the controversy raised by Holmes concerning the age of the Eastern Ghats can be solved, if the samarskite specimen analysed by Sarkar and Sen Sarma is understood to belong to the Gaya group of minerals, as has been later suggested. A tentative Archæan succession table has also been suggested.

INTRODUCTION

SAMARSKITE, occurring as it does in the pegmatites intrusive into the Nellore schists, is of unique importance in the determination of the age of the Eastern Ghats and ultimately in the solution of Archæan Correlation problems like the continuity of Eastern Ghats and its relationship with Satpuras, the contemporaneity or otherwise of Nellore schists with the Dharwarian schists of Mysore, etc.

PREVIOUS LITERATURE

The literature on Nellore samarskite may be broadly divided into two parts: (i) which treats samarskite as a chemical entity and deals with its nature of association, physical and optical characters, chemical composition formulæ, etc., and (ii) which utilises this data for geochronological studies. Bain,[1] Ellsworth,[2] Goldschmidt,[5] Karunakaran and Neelakantam,[8, 9, 10] Nandi and Sen,[14] Palache *et al.*,[15] Sarkar and Sen Sarma,[16] Yagoda,[17] have contributed to the first part of the studies and Holmes[16, 17] and Fermor[4] to the second part.

EXPERIMENTAL AND RESULTS

As the specific gravity is an index of the purity of the mineral, two determinations were made on two chips of the mineral. The lustrous fragment has a specific gravity of 5·75 and another chip with a coating of ochery material 5·36. Unaltered fragments have a lustrous velvet black colour, the lustre decreasing with alteration. Streak is brown with reddish tinge but when intergrown with non-radioactive columbate-tantalates develops a decided steel-grey tinge. Fracture is conchoidal.

Optical Characters

It is opaque even in thinnest slices. There is not even a faintest suggestion of its orthorhombic character. It is brown in reflected light.

Chemical Composition

Initially, the sample is broken into bits and the lustrous fragments are separated by hand-picking. They are then cleaned with a weak solution of nitric acid, washed repeatedly with distilled water, dried and powdered.

The mineral is chemically analysed by the well-known methods of Schoeller and Powell[17] and A. F. Williams.[18] The methods used in the estimation of rarer elements and lead are briefly described below:

1. *Columbium and Tantalum.*—The mineral is fused with potassium bisulphate and leached with tartaric acid solution. The earth acids are precipitated with tannin and finally ignited as $(Cb, Ta)_2O_5$.

2. *Uranium.*—The mineral is fused with bisulphate and leached with cold dilute hydrochloric acid. After a series of extractions, a chloride solution of U rare earths and aluminium is obtained. The rare earths are got rid of by double oxalate precipitation and alumina by double ammonium carbonate precipitation. Finally U is weighed as U_3O_8.

3. *Thorium.*—The mineral is fused with KOH and treated with dilute hydrochloric acid. The rare earths and thorium are separated by double oxalate precipitation and finally thorium is isolated from rare earths by precipitation with potassium iodate, converted into oxalate, ignited and weighed as ThO_2.

4. *Cerium and Yttrium earths.*—The rare earths are precipitated as oxalates in the hydrochloric acid medium. A broad separation between Ce and Yt earths is effected by double sulphate precipitation. Cerium is separated from Ce-earths by potassium iodate procedure.

5. *Lead.*—It is determined by the procedure evolved by Nandi and Sen.[14] The mineral is decomposed with hydrochloric acid and repeatedly

evaporated to dryness. Lead is precipitated as sulphide in the hydrochloric acid medium, converted to sulphate and extracted with ammonium acetate. The soluble lead acetate is converted into sulphate and weighed as such.

The values for the various constituents are recorded here, along with those given by other workers for Nellore samarskite (Table I).

TABLE I

	I	II	III	IV
Nb_2O_5 + Ta_2O_5 ..	56·29	52·57	57·40 (with TiO_2)	58·65 (with TiO_2)
TiO_2 ..	0·37	1·62	..	
SiO_2 ..	..	0·22	..	0·60
SnO_2 ..	..	1·48	..	0·50
FeO ..	9·30	14·77*	9·10	12·40*
CaO ..	1·41	0·94	1·10	1·03
MgO ..	..	0·03	..	0·75
Al_2O_3 ..	0·34	0·79	..	0·62
ThO_2 ..	1·32	1·21	1·98	1·33
Ce_2O_3† ..	1·51	0·81	1·20	1·54
Y_2O_3† ..	17·30	13·93	16·90	14·16
MnO ..	0·22	1·60	..	0·34
PbO ..	2·16‡	2·04	2·25	0·58
UO_2 ..	8·68	6·93	8·40	4·62
Na_2O+K_2O ..	0·26	0·50	..	..
Loss on ignition ..	0·63	0·29	0·87	1·12
	99·79	99·73	99·20	98·24

* Fe_2O_3.
† Uncorrected for peroxidic oxygen.
‡ Uncorrected for lead introduced by reagents.
I Samarskite from Kothandarama Mine, Nellore District. Analyst: Aswathanarayana, U.
II Samarskite from Sankara Mine, Nellore District. Analysts: Nandi, S. K. and Sen, D. N.[14]
III Samarskite from Nellore: Analysts: Karunakaran, C. and Neelakantam, K.[9,10]
IV Samarskite from Nellore (?). Analysts: Sarkar, P. B. and Sen Sarma, R. N.[16]

A variation graph has been drawn on the basis of analytical values of nine well-known samarskites and the author's results have been plotted on it. The values have been found to be within the expected limits.

TABLE II

	UO_2	ThO_2	PbO	Holme's Formula (Crude Age)	Lawson's Formula (Corrected Age)	Log Formula	Holmes-Lawson's Formula
I	4·62	1·33	0·58	911	856	853	841
II	8·40	1·98	2·25	1976	1739	1726	1687
III	6·93	1·21	2·04	2212	1915	1911	1872
IV	8·68	1·32	2·16	1889	1675	1658	1621

I Sarkar, P. B. and Sen Sarma, R. R. N.[16]
II Karunakaran, C. and Neelakantam, K.[9,10]
III Nandi, S. K. and Sen, D. N.[14]
IV Aswathanarayana, U.

AUTORADIOGRAPHIC STUDIES

An autoradiograph was obtained for a lustrous fragment of the mineral by exposing it for a week. The autoradiograph shows uniform photographic density, which suggests that the mineral has not suffered any alteration or enrichment.

DISCUSSION

Geological Setting

Bain,[1] after a detailed study of some occurrences of radioactive minerals and on the basis of certain theoretical considerations, has formulated the following principles, governing their distribution pattern.

(1) Refractory minerals are distributed rather generally through most crystalline rocks, except those in the centre of the shields.

(2) The centre of the shields is generally free from U-minerals.

(3) The principal uranium metalliferous provinces are on the periphery of shields and in large persistent massifs.

The shield area in India has an extensive spread in the southern Peninsula. "This shield border is fringed with pegmatites containing Uranium-minerals but presents a set of conditions inimical to lodes."

The pegmatites of Nellore District are characterized by concentrated mineralisation in a few favoured localities and diffuse mineralisation in most. Such a state of mineralisation is naturally incompatible with large-scale development of lodes, which alone are capable of producing a steady and continuous supply of radioactive minerals.

It has been shown that the radioactive minerals of refractory type appear in elongate or orogenic crystalline masses. Bain predicts that no economic deposit can be expected to occur in such a structure even where such places have produced large quantities of columbate-tantalate minerals. Apparently the Nellore occurrence of samarskite and other radioactive minerals fit into this theory well, as the Nellore schist belt is believed to be the schistose facies of elongate Eastern Ghat belt. In point of fact, however, concentrates of samarskite with columbo-tantalates have been reported from a number of mines and it is only the detailed prospecting by geophysical methods including radiometric surveys, that can disclose the actual potentialities, which incidentally will throw some light on the universal applicability of Bain's theory.

Significance of Physical and Optical Characters

The lustrous fragment has a specific gravity which approaches the highest recorded for the mineral and hence may be taken as one of high purity. The relatively low specific gravity of another sample shows that it is slightly altered.

The samarskite specimen examined is massive and isotropic, as almost all the recorded occurrences are, except one that has not been verified. It may be mentioned that this general observation has been satisfactorily explained by the theories of Yagoda[19] and Goldschmidt.[5] Yagoda[19] suggests that the mineral developed originally as an anisotropic crystal and has since become amorphous, possibly as a result of prolonged bombardment of crystal lattice and the recoil of atoms from the decay of uranium and thorium. If this theory were to hold good, every uranium-thorium mineral should be amorphous, which, of course, is not the case. Crystals of radioactive minerals like monazite have been reported from Bihar, Rajaputana, Mysore, Travancore and several other places in the world and similar is the case with thorianite from Ceylon. Goldschmidt's theory[5] appears to explain this anomaly more satisfactorily. From an extensive study of metamict minerals, he concluded that the presence of radioactive constituents is not the primary cause of destruction of the crystal structure but that a re-arrangement of outer electrons takes place in crystals composed of weak acid and weak basic constituents. Thus, minerals like thorianite, monazite and broggerite remain crystalline owing to strong lattice binding despite the high uranium and thorium contents. When the structure is initially weak, as in minerals containing Nb and Ta, they become amorphous because of degeneration into Y_2O_3, Cb_2O_5. Yagoda's theory of bombardment by radiations together with Goldschmidt's ideas on the weakness of chemical bonds in the Nb-Ta grouping, explains the observed amorphous nature of the samarskite sample.

Formula

Palache *et al*[15] gave the formula of samarskite as (Y, Er, Ce, U, Ca, Fe, Pb, Th) $(Cb, Ta, Ti, Sn)_2O_6$. According to them it is essentially an oxide (or columbate-tantalate) principally of rare earths, Ca, Fe, U and Th with columbium, tantalum and titanium. "The formula is probably AB_2O_6 with A = Y, Er, Ce, La, U, Ca, Fe^{2+}, Pb, Th; B = Cb, Ta, Ti, Sn, W. Water and SiO_2 are usually reported but are believed to be due to alteration and admixture."

Nandi and Sen[14] have recently discussed the formulæ of samarskite given by Rammelsberg, Groth, Doelter, Hess and Wells. The formula that the former[14] have arrived on the basis of analytical data on Nellore samarskite, is similar to the one obtained by Limori and Hata for Korean samarskite, $R_3''[(Nb, Ta)O_4]_2$, $2R'''(Nb, Ta)O_4$, $R''(Nb, Ta)_2O_7$. Nandi and Sen concluded that the samarskite corresponds to a composite salt consisting of two molecules of orthoniobotantalate and one molecule of pyroniobotantalate. The analysis of Glastonbury samarskite by Wells yields a formula $(Y, Er, Ce, La, Di, Ca, Fe^{2}, Mn, U, Th)_2(Cb, Ta, Fe, Ti)_3O_{11}$.

Palache and Frondel[15] believe that the difficulties in assigning a formula to this complex mineral are due principally to the uncertainty of the role of iron. The ferric iron, according to them, undoubtedly substitutes for parts of Cb, Ta while ferrous iron probably substitutes for the elements, U, Th, rare earths, Ca and Mn.

The formula worked out by the author on the basis of his analytical data—Ao B_2O_5 where A = Fe, Mn, Ca, Mg, Th, U, Ce, Y; B = Nb, Ta—is similar to the one given by Palache and Frondel. However, it must be said that unless the role of iron is understood, no formula can claim perfection and this formula is no exception. X-ray studies on the distribution of ferrous and ferric iron and autoradiographic studies on the distribution of uranium in the crystal lattice of samarskite, which are proposed to be taken up, may probably lead to some important conclusions on the subject.

Autoradiography

The uniform photographic density of the autoradiograph points out to the conclusion that the samarskite has not undergone any leaching or enrichment.

Age of the Eastern Ghats Pegmatitic Cycle and Archæan Correlation

Holmes, while trying to work out the Archæan succession,[6, 7] pointed out the enormous discrepancy in the ages of Nellore samarskite calculated from the values given by Sarkar and Sen Sarma[16] on one hand and Karunakaran and Neelakantam[9, 10] on the other. He, however, agreed (personal communication to Professor Neelakantam) that the latter value is likely to be nearer to the correct value.

The rationale behind such a conclusion can be easily understood. The Satpura belt, as has been dated by Gaya minerals is 955 ± 40 M.Y. old. All the available geological evidence points out to the fact that the Eastern Ghat belt, whose schistose facies are believed to constitute the Nellore schists, is older than Satpuras. The age given by Sarkar and Sen Sarma[16] to the Eastern Ghats pegmatitic cycle is less than the accurately determined age of the Satpuras and hence unlikely to be correct. The age calculated from the analytical data of Karunakaran and Neelakantam[9, 10] is at least consistent with geological evidence.

Recently Nandi and Sen,[14] while explaining the high lead content of their samarskite specimen when compared with the corresponding value given by Sarkar and Sen Sarma,[16] suggested that the samarskite analysed by the latter might have possibly belonged to the Gaya group of minerals. This suggestion is particularly significant, coming as it does from the colleagues of Prof. P. B. Sarkar, who was the author of the earlier paper and satisfactorily explains the discrepancies.

It appears that the specimens studied by Sarkar and Sen Sarma were not collected by them but were given to them from the G. S. I. collections, soon after the reopening of the museum. These collections were evidently not properly classified and the specimens taken up presumably belonged to the Gaya group, though they were mistakenly thought to have been obtained from Nellore area. The fact that P. B. Sarkar from his later studies on Nellore samarskite gives a value of 1760 M.Y. (quoted by Holmes,[7] as a personal communication from P. B. Sarkar) only confirms the surmise that the apparent discrepancy was due to an unfortunate mistake regarding the locality from which the specimen was collected.

If we exclude the analysis of Sarkar and Sen Sarma, the picture becomes less confusing. The ages calculated on the basis of the rest of the analyses, (Table II) though not same, are at least of comparable order of magnitude. All this data go to show that the Eastern Ghats pegmatitic cycle (1600 ± 50 M.Y.) is undoubtedly older than that of Satpuras (955 ± 40 M.Y.) and

Krishnan's observations in Orissa on the strike directions of Eastern Ghats add weight to this conclusion.

Though Fermor[4] was strongly against the idea of drawing any conclusions on the basis of cutting of the strike lines, he did not disapprove the principle of tentative correlation on the basis of parallelism of strike lines. The strike directions of Eastern Ghats, measured at several places along the east coast by the research workers of the Andhra University Geology Department, is roughly N.E.-S.W. This direction coincides with that of Aravalli belt on one hand and Shillong series on the other and on this basis they may be tentatively correlated. The Aravallis and the Shillong series have not yet yielded any radioactive minerals and hence such a correlation will naturally remain tentative, until sufficient data has accumulated on the ages of pegmatitic cycles of the two formations.

Further Krishnan,[12] while discussing the present state of Archæan correlation, has placed the Shillong Series in the Upper Dharwars. It has also been noted that parts of Shillong series show Satpura strike and as such it will not be surprising if further researches show that parts of Shillong series are Upper Dharwarian and parts lower.

If Eastern Ghats and Aravallis are understood to be of comparable antiquity, Satpuras becomes younger than both—a sequence which Holmes favoured but could not conclusively establish in view of the discrepancy in the ages of Nellore samarskite.

The recently reported occurrence of a radioactive mineral (Allanite ?) in the pegmatites intrusive into the khondalites of Anakapalli area (personal communication of Mr. V. Vijayaramamurthy to Professor C. Mahadevan) is of particular interest to all students of Eastern Ghats, as it is valuable in the solution of the Eastern Ghats continuity problem. Work is in progress on these collections. A mass of evidence[13] has already accumulated to show the contemporaneity of Khondalites, Bezwada gneisses, quartz magnetite rocks and Nellore schists, which constitute the various facies of Eastern Ghats and are believed to belong to the same orogenic cycle. The age of radioactive mineral from Anakapalli will add further information on the subject.

Holmes[7] is now engaged in an attempt to date the monazite occurring in the pegmatites intrusive into the Peninsular gneisses of Bangalore area. The age of the monazite, when interpreted with the age of the Nellore samarskite, will throw some light on Fermor's[3] views on the contemporaneity of Nellore mica schists and the Dharwarian schists of Mysore.

The following tentative correlation is suggested:

Vindhyan
Delhi cycle 735 M.Y.
Satpura cycle 955 ± 40 M.Y. (= Upper Shillong Series ?)
Eastern Ghats cycle 1600 ± 50 M.Y. (= Aravalli ?) (= Upper Shillong ?)
Dharwar cycle
Older gneissic complex

The magnitude of the time-lag between the Satpura pegmatite cycle and the Eastern Ghats pegmatitic cycle clearly suggests that the sequence is incomplete. It is hoped that clearer picture will emerge with the accumulation of some more data on the subject.

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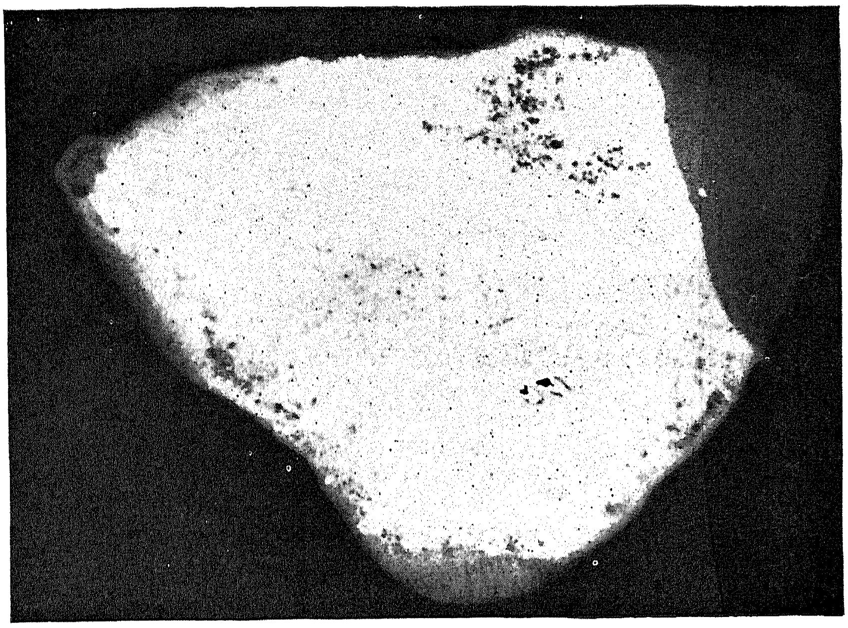
SAMARSKITE



AUTORADIOGRAPH