

# STUDIES ON SOUTH INDIAN RADIOACTIVE MINERALS

## II. Allanite from Madura

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### ABSTRACT

Allanite, a cerium-bearing epidote occurring in the pegmatites of Kavarkattumalai, Madura District, has been studied in detail. The investigations comprise the determination of physical and optical characters, chemical composition, mineral formula, and autoradiographic studies. Attempts have been made from a study of the data on metamict and non-metamict allanites to formulate the changes that allanite undergoes when it becomes metamict. Evidence has been collected to show that the allanite from Madura had become metamict and is hence of dubious value as an age index.

### INTRODUCTION

MUTHUSWAMI<sup>8</sup> reported the occurrence of allanite in the pegmatites intrusive into the Archæans of Kavarkattumalai, Madura District, and this discovery opened up a new source of data to determine the sequence of Peninsular Archæans. The Archæans in this area consist of bands of quartz-magnetite rocks, garnetiferous biotite gneisses, norites and pyroxenites. As the contemporaneity or otherwise of this group of rocks with their counterparts in the coastal Circars and Mysore has long been in question, an attempt has been made to solve the problem by dating the Madura pegmatitic cycle and interpreting it with the available geo-chronological evidence.

### EXPERIMENTAL AND RESULTS

#### *Physical Characters*

The specific gravity of the mineral is 3.63. The specimen is roughly tabular and is probably parallel to (100). Lustre is sub-metallic. Colour is black. Fragments from the core of the mass are velvety black and lustrous but the outer portions are dull black in colour. The allanite is traversed by a small vein of a different mineral, which stands in contrast by its very pale yellow colour. Small flakes of mica can be seen adhering to the mineral.

### *Optical Characters*

The mineral has a brownish yellow body colour and is pleochroic. It is traversed by a network of cracks in the major portion of the section. Adjacent to the region where parallel cleavages are developed, the mineral changes to a colourless one with an extinction angle of  $10^\circ$ . It is significant that the cleavage systems in the two cases are similarly oriented. This associated mineral is most probably clinozoisite.

The clinozoisite shows the presence of bright red ochery material. The deposition of this material appears to have been effected through the cleavages, as the latter have a reddish border running adjacent to them and terminating in lumps of ochery material. There are inclusions, presumably solid, in allanite, which are systematically spaced.

### *Chemical Composition*

The mineral was chemically analysed by the well-known methods of Schoeller and Powell<sup>11</sup> and A. F. Williams.<sup>12</sup> The methods used in the estimation of rarer elements are briefly described below.

(1) *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  $\text{ThO}_2$ .

(2) *Cerium and Yttrium Earths*.—The rare earths are precipitated as oxalates in the hydrochloric acid medium. A broad separation between cerium and yttrium earths is effected by double sulphate precipitation. Cerium is separated from cerium-earths by potassium iodate procedure.

The values for the various constituents are recorded here, along with values given by other workers for Allanite.

It appears from the analytical data that the mineral is similar to the specimen from Llano County, Texas, studied by Marble.<sup>5</sup>

A variation graph has been drawn on the basis of the analytical data, which are relatively modern and more reliable. The author's results have been plotted on the graph and they have been found to be within the limits.

### *Autoradiographic Studies*

The autoradiograph was obtained for allanite by exposing it for 35 days, as suggested by Marble. The following observations have been made:

TABLE I

		A	B	C	D	E
SiO <sub>2</sub>	..	30.12	32.20	30.42	33.73	29.89
Al <sub>2</sub> O <sub>3</sub>	..	18.06	17.18	17.00	16.09	19.09
FeO	..	7.62	10.38	11.96	3.87	8.49
Fe <sub>2</sub> O <sub>3</sub>	..	8.03	3.79	5.45	10.68	6.41
TiO <sub>2</sub>	..	0.70	0.74	..	0.80	0.89
MgO	..	0.14	0.69	..	0.18	0.15
CaO	..	9.60	11.95	13.38	16.18	8.48
SrO	..	..	n.d.	..	..	..
MnO	..	0.72	0.26	0.80	0.06	..
ThO <sub>2</sub>	..	1.56	1.05	2.37	..	0.82
Ce <sub>2</sub> O <sub>3</sub> } La <sub>2</sub> O <sub>3</sub> }	..	20.21*	18.30	16.40	15.55	22.55
Y <sub>2</sub> O <sub>3</sub>	..	0.97*	0.72	1.42	1.10	0.81
U <sub>3</sub> O <sub>8</sub>	..	..	..	..	..	..
P <sub>2</sub> O <sub>5</sub>	..	n.d.	..	..	..	..
Na <sub>2</sub> O+K <sub>2</sub> O	..	0.12	0.02	..	..	0.24
PbO	..	n.d.	..	..	..	..
H <sub>2</sub> O	..	1.90	2.18	0.73	1.69	1.84
		99.75	99.46	99.93	99.93	99.66

\* Uncorrected for peroxidic oxygen.

A. Metamict allanite from Madura.

Analyst: Aswathanarayana, U.

B. Allanite from Wilmot Pass, Fiordland, New Zealand.

Analysts: Seelye and Hutton.<sup>3</sup>

C. Allanite from Madagascar.

Analyst: Carrobbi.<sup>3</sup>

D. Allanite from Michalkowo (Russia).

Analyst: Kostov.<sup>3</sup>

E. Allanite from Barringer Hill, Llano Country, Texas.

Analyst: J. P. Marble.<sup>5</sup>

(a) Inclusions are present but their distribution appears to be sporadic and confined to the border zones of the mineral.

(b) A number of irregular cracks are present which might have facilitated the processes of leaching and enrichment.

(c) The outer rim of the mineral shows a high photographic density which, as a rule, is associated with higher radioactive content. This is indicative of the leaching of the mineral, resulting in the segregation of a mineral, richer in radioactivity, towards the periphery of the mineral. Most likely the secondary mineral may be gummite or one belonging to that group.

#### DISCUSSION

*Nature of Association.*—Muthuswami,<sup>8</sup> who has reported the occurrence of Madura Allanite, did not record the existence of any other rare earth mineral in association with Allanite. On the strength of the theoretical work of Quirke and Kremers<sup>10</sup> on the associational aspects of rare earths, it may be said wherever Allanite is found, “more rare earths might have combined with most, if not all, of the phosphate in the magmatic solutions and hence may be found as Monazite in the higher temperature phases of the same rock assemblage.” Thus it can be reasonably presumed that Monazite may be found somewhere in the vicinity of the recorded occurrence of allanite. It is suggested that it is not unlikely that the transition may be effected through Nagetelite, a silicate and phosphate of rare earths and a member of the epidote group.

Under the microscope, the mineral shows the association with clinozoisite. The epidote group to which both allanite and clinozoisite belong forms an isomorphous series and both allanite and clinozoisite can be derived by simple replacement of constituent elements—monovalent Ca by Fe and trivalent Al by Fe. Both of them are monoclinic. Thus the association of allanite and clinozoisite is quite understandable. The transition between allanite and clinozoisite is apparently sharp. In some regions allanite has developed a lighter colour in comparison with the deep colour of the rest of the section and this coincides with the development of cleavage system, parallel to that of clinozoisite. This suggests that probably these small patches have effected the transition from allanite to clinozoisite.

*Formula.*—There appears to be considerable diversity of opinion regarding the usage of terms orthite and allanite. “The term allanite was originally intended to denote those small unaltered crystals that were tabular parallel to the orthopinacoid, whereas orthite was reserved for large crystals of prismatic habit, whose analyses showed a considerable degree of hydration and leaching.”<sup>3</sup> Hutton<sup>3</sup> recently discussed the nomenclature adopted by Lokka, Mountain, Simpson, Marble and Geijer and expressed himself in favour

of abandoning the term orthite, and using allanite to signify the cerium-bearing members of the epidote group, without regard to the crystal habit or degree of metamictisation—a view which is bound to be popular in view of its simplicity of approach.

Nandi and Sen<sup>9</sup> have recently presented the various formulæ suggested for allanite by Groth, Marble, Takuba and Yukawa. The monoclinic members of the epidote group of which allanite is one, are believed to form a solid solution series. The role of the hydroxyl, ferric and ferrous radicals and the nature and extent of molecular replacements among the elements involved appear to be responsible to the discordance in the chemical formulæ suggested for allanite.

Winchell<sup>13</sup> is uncertain whether allanite and other minerals of the epidote group have frame works of (Si, Al) O<sub>2</sub> or not, but suggests they have to be provisionally placed in that group for lack of more accurate data.

The author suggests the following formula on the basis of his analytical results:  $5 \text{AO} \cdot 2 \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \cdot 9\text{SiO}_2$ , where A = Fe'', Mn, Ca, Mg; B = Ce, Y, Fe''', Al. Another arrangement has been worked out, grouping Ca and Ce on the basis of the similarity of their ionic nuclei and this has given a formula:  $2(\text{Ca}, \text{Ce}) \text{O}, 3(\text{Al}, \text{Fe}, \text{Y}, \text{Mn}, \text{Mg}) \text{O}, 5 \text{SiO}_2 \cdot \text{H}_2\text{O}$ .

#### *Metamictisation of Allanite*

The following evidence is adduced to show that Madura allanite had become metamict:

(1) The appreciable H<sub>2</sub>O content (1.9%) which the mineral exhibits is generally associated with alteration and hydration.

(2) The low specific gravity of the mineral (3.63) is of the same order as that recorded by Marble<sup>5</sup> for the metamict allanite from Barringer Hill, Texas (3.54). It is clearly different from the anisotropic varieties with a specific gravity of 4.0. The low specific gravity of Madura Allanite can be explained to have resulted from the leaching of heavier elements like Ur, Th and rare earths and introduction of water.

(3) The low refractive index<sup>8</sup> is particularly significant. Most of the anisotropic fresh allanites gave a refractive index of  $1.80 \pm 0.02$ , while the metamict types gave an R. I. of  $1.70 \pm 0.01$ .

(4) The isotropy of the allanite is indicative of its alteration. The original anisotropic mineral gradually gets altered and becomes isotropic, as has happened in the case of Madura allanite. A few anisotropic specks here and there, observed in this case, do not alter the situation appreciably.

(5) *Effect of Concentrated HCl*.—The mineral undergoes rapid decomposition when treated with small quantities of hot concentrated HCl and the resulting solution rapidly sets into a jelly. This behaviour compares favourably with that noted by Osborne Hutton in the case of metamict allanites from Albany, Wyoming and Barringer Hill, Texas.

The significance of this property of Madura allanite can be best appreciated, when contrasted with the behaviour of non-metamict and fresh allanites on similar treatment. An extreme case is the allanite from Wilmot Pass, New Zealand,<sup>3</sup> which has been found to decompose only after the most drastic treatment, *i.e.*, prolonged heating with fuming sulphuric or perchloric acids. The Yosemite Park allanite, however, is readily soluble in hot concentrated hydrochloric acid, with the separation of pulverent silica, which does not set into a jelly. It may be mentioned, by the way, that this conspicuous difference in the behaviour of two types of non-metamict allanites has been found to be dependent upon whether the octahedral positions in the lattice are dominantly occupied by aluminium or by iron and/or manganese.<sup>2</sup>

The author has made a critical study of the data on metamict and non-metamict allanites occurring all over the world and suggests the following differences between metamict and non-metamict allanites:

	<i>Metamict</i>	<i>Non-metamict</i>
1. H <sub>2</sub> O content	.. High ( $1.8 \pm 0.2\%$ )	Low ( $0.9\%$ )
2. Refractive index	.. Low ( $1.69 \pm 0.01$ )	High ( $1.80 \pm 0.02$ )
3. Optical characters	.. Isotropic	Anisotropic
4. Specific gravity	.. Low ( $3.5 \pm 0.1$ )	High ( $4 \pm 0.1$ )
5. Action with HCl	.. Readily decomposes on treatment with hot conc. HCl and rapidly sets into a jelly.	Some decompose relatively easily but with the separation of pulverent silica. Others decompose only with difficulty on treatment with sulphuric and perchloric acids.

#### *Autoradiographic Studies*

The autoradiograph of allanite is suggestive of the alteration it has undergone, thus making the mineral useless as an age-index. The processes of leaching have taken place to an unknown extent.

#### CONCLUSION

A study of the physical and optical characters, chemical composition and behaviour on the addition of concentrated hydrochloric acid, distinctly

points to the conclusion that Madura allanite had become metamict and hence is of dubious value, if not useless, as an age-index. Such a situation precludes the possibility of dating the Madura pegmatitic cycle which, when interpreted with the ages of other pegmatitic cycles, would have given us a clearer picture of relative positions of Peninsular Archæans.

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