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Cheralite, a new mineral of the monazite group.

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Introduction.

A GREEN mineral akin to monazite, derived from the State of Travancore in southern India, was investigated chemically during the first world war by the Imperial Institute, London, and was found to be exceptionally rich in thorium and uranium. No description of this unusual 'monazite' has hitherto been published.

The high content of radioactive elements in this mineral led the State Geologist, Mr. Venkitarama Mahadevan, to have a deposit opened up in 1945, in readiness for an assessment of the radioactive mineral resources of Travancore. At the invitation of the former Dewan, Sir C. P. Ramaswami Aiyar, K.C.S.I., K.C.I.E., this assessment was carried out by Dr. C. F. Davidson early in 1946. In an unpublished report to the Dewan, Dr. Davidson records that the mineral in question occurs sparsely distributed throughout a kaolinized pegmatite dike outcropping on a small hill at Kuttakuzhi (lat. 8° 18′ 11″ N., long. 77° 15′ 48″ E.) in Kalkulam taluk, about 23 miles ESE. of Trivandrum. In the pegmatite it is associated with a little black tourmaline, small greenish-yellow crystals of chrysoberyl, partly-metamict dark zircon with a radioactivity equivalent to 0·1 % U_3O_8, and considerable smoky-quartz. A few crystals of brown monazite occur in washings from the same pegmatite. The thorium-rich green mineral is also found sparsely in the adjacent wall-rock (kaolinized granitic gneiss) as well as in surface wash and in the gravel of adjacent streams. The occurrence has no economic potentialities, only an ounce or two of 'monazite' being obtainable from

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each cubic yard of pegmatite. We are indebted to Dr. Davidson for
the material on which this present study is based.

The green mineral has been found to be a member of the monazite
group near $(TR,Th,Ca,U)(P,Si)O_4$ in composition, where $TR =$ Ce, La,
Pr, Nd, &c. It is proposed that it be called cheralite from Chera, the
ancient Dravidian kingdom which corresponded roughly to the modern
territory of Travancore.

Physical properties.

Cheralite occurs as brittle masses up to two inches across, seldom
showing crystal faces. It is pale to dark green in colour with a resinous
to vitreous lustre, an uneven fracture, and a white streak. The hardness
is 5, and specific gravity, determined by the pyknometer method in
carbon tetrachloride, is 5.3 ± 0.1.

In thin section cheralite is pale green in colour, and it gives a positive
biaxial interference figure. The indices of refraction are α 1.779, β 1.780,
γ 1.816. The optic axial angle 2V measured on different fragments of
the mineral ranges from 17.4° to 19.0°, the average of some twenty
determinations being 18.1°—a figure which is in good agreement with
the calculated value of 17.9°. Pleochroism is faint with α and β green,
γ green with a yellow tinge. Dispersion of the optic axes is not per-
ceptible. The cleavage directions and optical orientation appear to be:
cleavages (010) distinct, (100) difficult, parting on (001) poor; $\alpha = b$,
and $\gamma:c = 7°$. These data are tentative, since it has not been possible
to identify the crystal faces on the available material with any certainty.

Chemical composition.

The material chosen for analysis was purified by passing the crushed
and washed mineral through a Frantz electromagnetic separator, traces
of superficial ferruginous matter then being removed by immersion in
hot dilute hydrochloric acid. In table I, the new analytical data are
compared with an unpublished analysis carried out about 1916 by
Mr. S. J. Johnstone of the Imperial Institute, which Mr. G. E. Howling
of Colonial Geological Surveys kindly brought to our notice when the
present paper was read. Mr. Johnstone's material was collected by
Mr. E. Masillamani, then State Geologist, Southern District, Travan-
core, from a locality described as Cootykad Pothay in Vilavancod taluk
—the adjoining taluk (or 'parish') to that from which our specimens
were derived. It is uncertain whether there are two localities for the
mineral (possibly both on the same pegmatite dike) or whether the

original find was wrongly localized. The material analysed by Mr. Johnstone was not specially purified before analysis and may have been somewhat contaminated by iron and quartz. The other two analyses in table I are of a high-grade monazite concentrate from the Travancore beaches, which form one of the principal commercial sources of this mineral, and of a thorium-rich monazite from Ceylon, which is discussed below.

The recalculation of the new cheralite analysis in terms of atomic proportions (table II) shows that the composition corresponds closely with the formula ABO_4, where $A = TR$, Th, Ca, U, and $B = $ P, Si.

TABLE I.   Chemical analyses of cheralite and monazite.

	1.	2.	3.	4.
P_2O_5	26·80	25·90	26·82	20·20
SiO_2	2·10	1·15	0·90	6·09
ThO_2	31·50	29·45	10·22	28·20
U_3O_8	4·05	6·56	(0·37)	—
Ce_2O_3	14·21	13·98	31·90	20·65
$(La,Pr,Nd)_2O_3$	13·35*	13·26	28·00	21·63
Yt_2O_3		0·19	0·46	0·94
Fe_2O_3	trace	2·50	1·50	1·13
Al_2O_3	trace	—	0·17	0·29
CaO	6·30	5·73	0·20	0·10
PbO	0·92	0·07	—	—
$H_2O +$ ...	0·06	0·30	0·46	—
	99·29	99·59	101·00	99·23

1. Cheralite, Kuttakuzhi, Travancore. Analysis by Radiochemical Division, Chemical Research Laboratory, Teddington.   * Major constituents: La, Pr, Nd; minor constituents: Gd, Sm, Yt.
2. 'Green monazite' (= cheralite), from a locality given as 'Cootykad Pothay, Vilavancode taluq, Travancore'. Unpublished analysis by S. J. Johnstone, Imperial Institute, London, 1915 or 1916. Also contains MnO 0·18, TiO_2 0·32 %. Free silica 0·16 % has been omitted.
3. Monazite concentrate from beach sand, Travancore. Analysis by S. J. Johnstone, Journ. Soc. Chem. Indust., 1914, vol. 33, pp. 55–59. Value for U_3O_8 by Radiochemical Division, Chemical Research Laboratory, Teddington.
4. Monazite pebble, Ratnapura, Ceylon. Analysis by S. J. Johnstone, ibid. Specific gravity 5·47.

In almost all monazite samples that have been studied chemically, some thorium and a little uranium are present replacing the cerium-lanthanum earths in the crystal lattice of the mineral; but in cheralite this substitution has been carried very much further than in normal monazites. The increase in cationic charge is compensated for by a similarly large substitution of calcium for the cerium-lanthanum earths, aided by the replacement of a little phosphorus by silicon. The result

TABLE II.   Analyses of cheralite (table I, 1) and Ratnapura monazite (table I, 4) recalculated as atomic ratios to 16 oxygens.

Ionic radii (Å).*		Cheralite				Ratnapura monazite			
0·99	Ca^{2+}	...	1·084			Ca^{2+}	...	0·018	
1·07	Ce^{3+}	0·836				Ce^{3+}	1·286		
1·14	La^{3+}					La^{3+}			
1·06	Pr^{3+}	0·780	1·616			Pr^{3+}	1·335	2·707	
1·04	Nd^{3+}					Nd^{3+}			
0·92	Yt^{3+}			4·030		Yt^{3+}	0·086		4·023
1·02	Th^{4+}	1·151				Th^{4+}	...	1·092	
0·97	U^{4+}					U^{4+}	—		
0·80	U^{6+}	0·139	1·330			U^{6+}	—		
1·20	Pb^{2+}	0·040				Pb^{2+}	—		
0·64	Fe^{3+}	—				Fe^{3+}	...	0·206	
0·52	Al^{3+}	—				Al^{3+}	...	0·057	
0·42	Si^{4+}	...	0·337	3·979		Si^{4+}	...	1·035	4·000
0·35	P^{5+}	...	3·642			P^{5+}	...	2·908	

* After L. H. Ahrens, Geochim. Cosmochim. Acta, 1952, vol. 2, pp. 155–169.

is that in cheralite the sum of the thorium, uranium, and calcium atoms exceeds the total rare-earth atoms in the ratio of three to two.

Carried to the limit, the replacement of rare earths by calcium and thorium would result in the hypothetical end-member $CaTh(PO_4)_2$, and an attempt was therefore made to synthesize this compound. The synthesis was carried out using thorium orthophosphate, $Th_3(PO_4)_4.4H_2O$, kindly prepared for us by the Radiochemical Division of the Chemical Research Laboratory, mixed in equimolecular proportions with tri-calcium orthophosphate, $Ca_3(PO_4)_2$. In one experiment the reagents were fused in an oxygen and coal-gas flame, and in another the mixture was heated in an electric furnace at 1400° C. The product obtained by the latter method was found on X-ray analysis to consist of a single phase isostructural with monazite. In the product of the former experiment, a ThO_2 phase was also present, suggesting that dissociation occurs at a high temperature.

In searching the literature relating to monazite, we have only been able to trace one other reliable analysis showing a thoria content comparable to that of cheralite; this is given as analysis 4 in table I, and in terms of atomic proportions in table II. Here the increased cationic charge due to the introduction of thorium is balanced solely by the replacement of phosphorus by silicon, the calcium remaining negligible. The end-member of this type of substitution is the mineral huttonite,

the monoclinic form of $ThSiO_4$. The role of the iron in the analysis of this monazite is uncertain.

It may be mentioned in passing that the 'chemical' age of the cheralite, derived from Wickman's graph,[1] is 492 million years. In the absence of an isotopic analysis of the lead, this apparent age is open to question.

X-ray powder data.

Spacings derived from powder photographs of cheralite, of beach-sand monazite from Travancore, and of synthetic $CaTh(PO_4)_2$ are compared in table III with data published by Pabst[2] for monazite from South

TABLE III. X-ray powder data in Å.

hkl.	Monazite South Korea. d.	Int.	Monazite Travancore. d.	Int.	Cheralite Travancore. d.	Int.	CaTh(PO₄)₂ Synthetic. d.	Int.
$\bar{1}01$	5·23	4	—	—	5·20	vvw	5·18	vvw
110, 011	4·72	4	4·72	w	4·68	w	4·67	vw
$\bar{1}11$	4·17	6	4·19	mw	4·14	ms	4·12	mw
111	3·52	5	3·52	w	3·49	mw	3·47	w
200	3·31	7	3·29	ms	3·26	s	3·24	s
120	3·09	10	3·10	vs	3·07	vs	3·05	vs
210	2·99	2	2·98	vvw	2·96	vvw	2·94	vvw
$\bar{1}12, 012$	2·88	7	2·87	m	2·86	s	2·83	vs
$\bar{2}02$	2·61	2	2·62	vvw	2·60	vvw	2·58	w
$\bar{2}12, 112$	2·45	3b	2·46	vvw	2·44	vvw	2·41	w
	2·19	4	2·19	mw	2·18	mw	2·16	w
	2·14	6	2·14	mb	2·13	mwb	2·11	mb
	1·969 1·963	5 } 1 }	1·970	vw	1·958	w	1·941	ms
	1·899	2b	—	—	—	—	1·872	vvw
	1·875	6b	1·874	mb	1·870	mwb	1·846	msb
	1·800	2	1·802	vvw	1·795	vvw	1·778	vw
	1·766	4	1·762	vvw	1·758	vvw	1·740	vw
	1·746	6	1·745	mwb	1·733	mw	1·718	ms
	1·695	4	1·699	vw	1·684	w	1·667	mw
	1·651	1 −	—	—	—	—	1·629	vvw
	1·630	1 −	—	—	—	—	1·608	vvw
	1·605	1	1·606	vvw	—	—	1·583	vvw
	—	—	—	—	—	—	1·556	vvw
	1·541	4	1·537	vvw	1·534	vw	1·517	mw

Order of decreasing intensities: vs, s, ms, m, mw, w, vw, vvw; b = broad.

[1] F. E. Wickman, A graph for the calculation of the age of minerals according to the lead method. Årsbok Sveriges Geol. Undersök., 1944, vol. 37, no. 7 (Avhandl. och Upps., Ser C, no. 458), pp. 1–6. [M.A. 9–69.]

[2] A. Pabst, Huttonite, a new monoclinic thorium silicate. Amer. Min., 1951, vol. 36, pp. 60–65. [M.A. 11–310.]

Korea. The indices given by Pabst for the first ten powder lines were derived from single-crystal photographs. The powder photographs for the present study were taken in a 9 cm. camera with Cu-$K\alpha$ radiation ($\lambda = 1\cdot5418$ Å.) using sodium chloride as an internal standard. The relative intensities were estimated visually.

There is a systematic decrease in corresponding spacings on going from monazite through cheralite to $CaTh(PO_4)_2$; this indicates a shrinkage of the unit cell due to the smaller ionic radii of calcium and thorium compared to cerium and lanthanum. By using the spacings for powder lines representing single reflections, the reciprocal lattices have been computed and the following approximate values thus derived for the unit-cell dimensions:

	a.	b.	c.	β.	Vol.
Monazite, Travancore ...	6·79	7·04	6·47	104·4°	299 Å.³
Cheralite, Travancore ...	6·74	7·00	6·43	104·6°	294
$CaTh(PO_4)_2$	6·69	6·93	6·38	104·4°	286

The density of cheralite corresponding to the unit-cell contents (table II) and the above dimensions is 5·41 g.cm.$^{-3}$, compared with the measured value of 5·3 g.cm.$^{-3}$.

Systematic relations.

The X-ray powder data presented here show that monazite, cheralite, and $CaTh(PO_4)_2$ are isostructural. Huttonite has already been shown by Pabst to possess the same structure. The relationship of cheralite to huttonite and monazite is shown in fig. 1, in which the unit-cell composition of cheralite (see table II) is plotted as point A in the monoclinic system $CePO_4$–$CaTh(PO_4)_2$–$ThSiO_4$. In this system cerium and thorium may be in part replaced by other rare earths and by uranium respectively.

It is proposed that the name cheralite be applied to minerals intermediate in composition between monazite and $CaTh(PO_4)_2$, the exact limits of the composition being as indicated in the diagram (fig. 1). The three regions of the diagram for which natural representatives are not yet known or well established are left unnamed.

It will be seen that the Ratnapura mineral plots just outside the field assigned to monazite (point B); if further work substantiates the original analysis, it might legitimately be referred to a new species intermediate between monazite and huttonite.
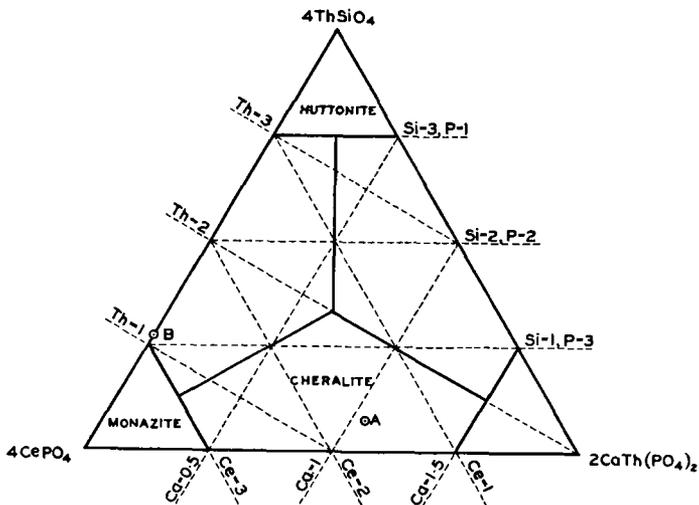
FIG. 1. Relationships in the monoclinic system $CePO_4$–$CaTh(PO_4)_2$–$ThSiO_4$.
Point *A*, cheralite, analysis 1; *B*, 'monazite', analysis 4.