A CHEMICAL AND MINERALOGICAL STUDY OF THE CELESTITE FROM THE PHOSPHATIC NODULES OF THE CRETACEOUS ROCKS OF TRICHY*

By N Jayaraman

Introduction —While working on the phosphatic nodules from the cretaceous rocks of Trichy, the author noticed the presence of a crystalline white mineral which filled up the septarian cracks in the nodules This mineral was also found to occur as fan-like radiating aggregates even in nodules which were free from the septarian cracks On examination it was identified to be celestite

The occurrence of celestite in the cretaceous rocks of Trichinopoly was first reported by Ramaswami Sivan[1] Except for the following remark with a photograph, which is reproduced in this paper for the sake of reference, he gives no further details He says, " Crystalline gypsum in flakes is abundant and characteristic of the locality, and celestine, chalk and belemnites are also found associated with the phosphatic nodules " Though Sivan remarks that celestine occurs in association with the phosphatic nodules, he does not, however, mention that it occurs within the nodules, and his photograph also indicates only lumps of celestite and not the mineral occurring in the nodule itself

Even though celestite is present in the nodules in fairly large quantities it has been very often wrongly considered as gypsum Blanford[2] of the Geological Survey of India on superficial examination considered the mineral to be selenite and he says that it occurs as nuclei and as infiltration-matter filling up cracks in the nodules. Rama Rao[3] in his paper on the phosphatic nodules from Utatur also regarded this mineral as gypsum Contrary to these findings, it can now be said that gypsum is found only occasionally in the body of the nodules, it is more often met with in the calcareous than in the phosphatic nodules Occasionally, gypsum is present in the nodules filling up the wide cracks

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which terminate at the surface It occurs very often also as a thick surface covering on the outer shell of the nodule

Megascopic and Microscopic properties —The celestite occurs as fairly thick veins and also as radiating and platy and acicular crystalline aggregates Its appearance is colourless to white and it is transparent to translucent with a vitreous to subvitreous lustre. It also occurs as scattered grains and blades or groups of radiating crystals spread out in a fan-like manner throughout the entire mass of the nodules, being particularly abundant in the dark interior Sometimes it is found concentrated in the centre of the nodules, suggesting so to say, pseudo-nuclei around which the nodules are built up The strontium infiltration product appears to have replaced the original nuclei of the phosphatic nodules The celestite is almost completely absent in nodules of very low phosphorus content This mineral is found associated with gypsum, calcite, dolomite, quartz and also an yellowish-brown mineral, collophanite or koninckite or a phosphate mineral related to these A thorough investigation of the mineral is now in progress The typically septarian type of nodules hold only a very small quantity of this mineral

On the average the celestite forms about three per cent of the total mass of the nodules although in some nodules it is so abundant as to form about 15 per cent Most of this celestite occurs as irregular masses and shapeless grains When examined under the microscope this celestite presented four sets of cleavages of which three were perfect and the fourth was rather imperfect Two of these three perfect sets were found to be parallel to the prism faces and these were found to cut each other at an angle of 76° The third one was parallel to *c* (001) and the fourth was parallel to *b* (010) Under the microscope thin plates of celestite show small rounded grains of a brownish-yellow mineral as inclusions, either isolated or in groups These grains are almost isotropic and appear to be made up of a phosphate mineral In many cases spherical inclusions of quartz in the celestite were found covered by a shell of this brownish-yellow mineral

Crystallography —Though perfectly developed crystals are

not usually met with, a few good crystals were obtained from a small cavity in a nodule These crystals were of three definite habits which were as follows —

(*a*) Poorly developed crystals which were tabular parallel to (001) and elongated parallel to the crystallographic axis *a* Five forms are observed on these crystals and they are as follows —*m* (110), *b* (010), *c* (001), *o* (011) and *d* (102) These crystals vary in length from 1 mm to nearly 12 mm and in thickness from 0 5 mm to 1 mm (Fig 1) Photograph 1, Fig 6

The interfacial angles are as follows —

$110 \wedge 1\bar{1}0 = 75°56'$, $110 \wedge 010 = 51°55'$, $001 \wedge 011 = 52°$, $010 \wedge 011 = 38°$, $001 \wedge 102 = 39°20'$, $102 \wedge 10\bar{2} = 78°40'$

Axial ratio = a b c = 0 7803 1 1 2799

Refractive indices (sodium light) $\alpha = 1\ 6219$,

$\beta = 1\ 6239$ and $\gamma = 1.6311$

$\gamma - \alpha = 0\ 0092$

Specific gravity (powder) = 3 9853.

Very often the values for the interfacial angles of these crystals were found to vary from crystal to crystal So for the purpose of calculating the axial ratio, ten measurements were made on different crystals and the average value was taken As these crystals were of the same chemical composition this variation in the interfacial angles must be due to some abnormality in the crystal structure as pointed out by Thaddeeff[1] Because, these crystals always have a tendency to form parallel growths or they are arranged in a fan-like manner, the axis of elongation of each crystal, viz , the *a* crystallographic axis forms an angle of 2° to 5° with that of the adjacent crystal Thaddeeff has discussed in detail the variations in the crystal angles of celestite and he comes to the conclusion that crystals of celestite are built up of smaller elements not exactly in a parallel position but in a fan-like arrangement about a particular zone axis

(b) Very poorly developed crystals, tabular parallel to (001) and equally developed in the directions of *a* and *b* crystallographic axes These crystals vary in thickness from very thin plates to about 5 mm.

thickness They are very poor in faces and the predominant form is the basal pinacoid Specific gravity 3.9785 (Photograph 1, Fig 6)

(c) Well-developed crystals with a prismatic habit developed parallel to (011) or the crystallographic axis *a* exhibiting the development of only two prominent forms, viz, the prism (110) and the brachy dome (011) (Fig 2). Only in a few cases were a poor development of (102) and (010) noticed. The crystals vary in length from 1 mm to nearly 2 cms. and in thickness from 0 2 mm to 5 mm (Photograph 3, Fig 6).

The interfacial angles are as follows —

$110 \wedge 1\bar{1}0 = 75°58'$, $011 \wedge 0\bar{1}1 = 104°5'$

Axial ratio, a b c 0 7808 1 1 2819.

Refractive indices (sodium light) α 1 6223,

$\beta = 1\ 6238$, $\gamma = 1\ 6313$

$\gamma - \alpha = 0\ 0090$

Specific gravity = 3.9811.

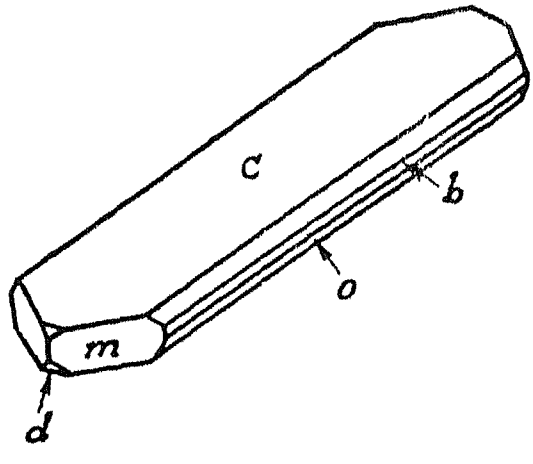


Fig 1

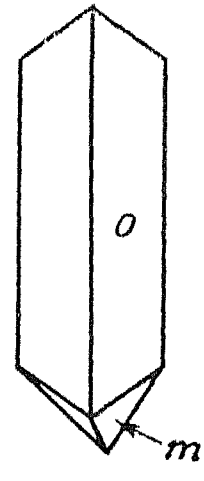


Fig 2

Celestite crystals

Basal cleavage flakes of these crystals when examined under the microscope show an elongated hexagonal outline, the longer axis of which coincides with the *a* axis and this is the direction of slow vibration *Z* As common in celestite, the optic axial plane was found to be parallel to (010), the Bx_o being perpendicular to (001) and Bx_a parallel to the crystallographic axis *a*

A thoroughly purified sample of the celestite was subjected to chemical analysis to determine the exact proportions of strontium, barium and calcium sulphates present therein

Preparation of the sample for examination —The phosphatic nodules containing a large quantity of celestite were roughly crushed and the small lumps of this mineral were picked out These lumps were then treated with dilute hot hydrochloric acid and then washed with distilled water It was then dried at 110° till free from moisture At this stage a small portion of this material was taken out and chemically analysed The analysis showed 94 per cent of strontium sulphate, 3 per cent of the sulphates of calcium and barium and 3 per cent of quartz The result of this preliminary study was first reported by me and Dr K R Krishnaswami in "Current Science," (December 1939) The remaining portion of the material was subjected to heavy liquid (methylene iodide) separation and the concentrate so obtained was examined under a low power microscope Traces of impurities, if present, were removed by picking The final concentrate was then chemically analysed as follows

Method of analysis —As the mineral was found to be insoluble in all acids, fusion with sodium carbonate was resorted to The fused mass was digested with hot water and filtered and the residue washed with hot dilute sodium carbonate solution Silica was determined both in the filtrate and in the residue after acidifying with hydrochloric acid and evaporating the acid solutions to dryness Sulphur as SO_3 was determined in the filtrate by precipitating it as barium sulphate Phosphorus was determined in a separate sample by the phosphomolybdate method

The insoluble residue after the removal of silica contained iron, calcium, strontium and barium Iron was estimated as follow : It was first precipitated with ammonia as hydroxide, filtered and the precipitate dissolved again in hydrochloric acid and the solution was then treated with thiocyanate and compared colorimetrically with solutions containing known amounts of iron.

The filtrate from the iron precipitation now held all the calcium, strontium and barium and the separation of these three metals offered some difficulty Correct values were not obtained when the calcium and strontium were determined by the oxalate method as recommended by Hillebrand[5] Secondly, after separating the barium at the initial stage by precipitating it as chromate, the strontium and calcium were at first precipitated as carbonates and then converted into nitrates The nitrates were then treated with 1 1 ether alcohol mixture and filtered Calcium was determined in the filtrate and strontium in the insoluble portion This method also was not found to be satisfactory So finally a reversed form of this method was adopted and it gave reliable results

The method is as follows —The filtrate obtained after the iron precipitation was evaporated to dryness and the ammonium salts were completely expelled by ignition The residue left after this was taken in dilute nitric acid and the solution was again evaporated to dryness in a small glass dish The nitrates thus obtained were dried for about an hour at a temperature of 135°C and allowed to cool They were then digested three or four times with small quantities of an ether alcohol mixture (1 1 mixture of pure dry ether and absolute alcohol) and then filtered. The filtrate was evaporated to dryness and the dry residue was taken in dilute hydrochloric acid and the calcium present in it was precipitated as oxalate and determined as usual The insoluble residue after the ether alcohol treatment contained both strontium and barium and these were separated by precipitating the barium as chromate in acetic acid solution[6] The filtrate from the barium chromate precipitation was evaporated to a small volume and the strontium present in it was precipitated as $SrSO_4$ observing the usual precautions.

TABLE I

The chemical composition of the celestite

Oxides	Per cent	Mol Proportions	Percentage composition of the various components
SiO_2	0 32		
Fe_2O_3	0 15		
CaO	0 46	0 0084 } 0 0040 / 0 0044	$CaSO_4$=0 60
BaO	0 78	0 0051	$BaSO_4$=1 19
SrO	54 67	0 5285	$SrSO_4$=97 01
SO_3	43 04	0 5380	
P_2O_5	trace		
Loss	0 12		
Total	99 54		

The results given in table I show clearly that the mineral is sufficiently pure, the total amount of impurities being very low If the mineral composition is calculated from the chemical analysis taking the SO_3 found as the basis, then all the SrO and BaO and part of the CaO are accounted for as being present as sulphates. The whole of the BaO is calculated as $BaSO_4$, because, this would be more in keeping with the mode of occurrence of this mineral than if the whole of the CaO is calculated as $CaSO_4$ and part of BaO left out The presence of $BaSO_4$ in the mineral would be more in keeping with the crystallographic data As this mineral occurs in a calcareous nodule which is more or less free from barium, it is reasonable to assume calcium rather than barium as an impurity

Origin —Nodules holding this mineral when broken open, show that the veins of this mineral are restricted to only the black interior portion of the nodules and do not extend to the light coloured outer shell The outer shell of the nodule, which is mostly made up of

calcium carbonate, is very poor in cracks, and cracks even if present are not filled up by celestite. So the celestite which occupies the inner core of the nodule is completely cut out from the outside. In this connection, it is interesting to note that the celestite occurs only in nodules where the phosphate content is high and the nodule is dark. Light coloured calcareous nodules are free from celestite. Further, the celestite occurs not only in the septarian and other stray cracks but also occurs interlaminated with the substance of the nodule.

The above findings indicate that the celestite must have formed either simultaneously with the phosphates under the same conditions or subsequent to the formation of the phosphates. As calcareous nodules with small cores of calcium phosphate are found in large numbers in the same locality, it can be assumed that the nodules originally formed were strictly calcareous ($CaCO_3$) and that they were later replaced by calcium phosphate. This process of replacement must have proceeded very slowly and was mainly confined to two definite stages. The first stage involved the infiltration of the phosphoric solution into the body of the calcareous nodule and the second stage involved the transference of this phosphorus towards the core of the nodule. Strontium compounds in solution must have entered the nodules along with the phosphatic matter and got accumulated within its body. Later it crystallised as the sulphate celestite either in the substance of the nodule or redissolved and redeposited in the septarian cracks.

The strontium required for this must have been derived from the surrounding area which is rather rich in this metal. Adopting Dinger's[7] view, it can be suggested that the origin of celestite is caused by the entry of strontium in solution into the nodule, probably as $Sr(HCO_3)_2$, from which it is precipitated as sulphate owing to interaction with the gypsum already present in the nodule. This assumption is supported by the fact that while the highly calcareous nodules have a high proportion of gypsum, the nodules rich in phosphorus are almost entirely free from it and they hold instead an almost equal quantity of celestite.

Summary.—After careful examination it was established that the white crystalline mineral, which occurs within the body of the

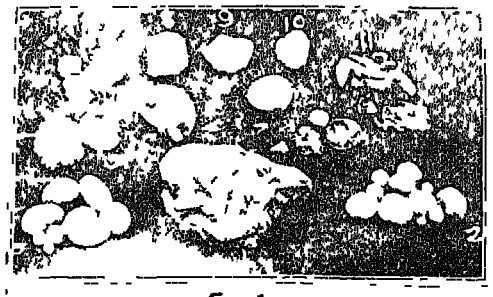


Fig 1

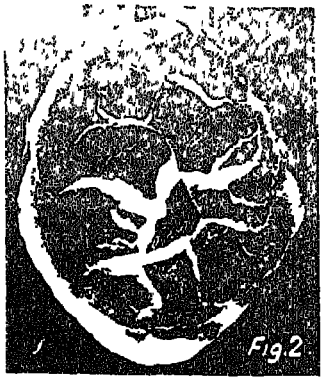
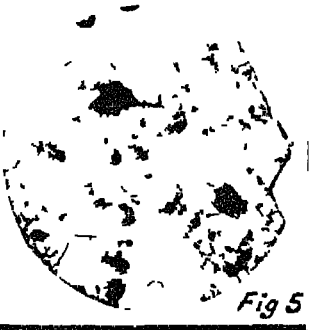


Fig 3



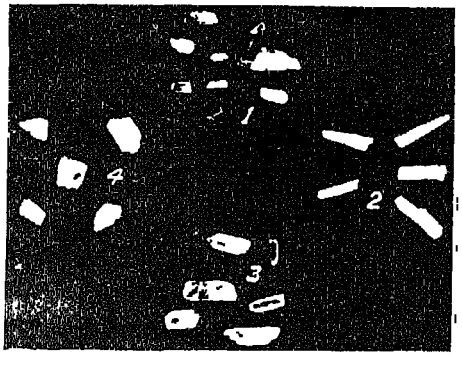


Fig. 6

Fig 7

FIG 1 Some geological specimens of the locality

(1) Phosphatic nodules, imbedded in yellow clay, *in situ* The nodules may be spherical (2) or ovul (3) The phosphatic nodules, when broken, give a peculiar crystalline fracture (4), which is absent in purely calcareous nodules (7) When the phosphatic nodules undergo weathering the dark core inside is seen (5) Sometimes the phosphates may be present in other forms than the septaria (6) The nodules are enclosed in a rind of hardened shale (10), sometimes chalk (9) Between the rind and the nodules, there is usually a layer of crystalline gypsum (8) The region of phosphatic nodules abounds in gypsum (11), celestine (12) and belemnites (13)

phosphatic nodules, is celestite and not gypsum or calcite as assumed by earlier workers

A crystallographic study of a few well developed crystals is given and it is shown that these crystals exhibit three definite habits

A chemical analysis of an average sample involving the careful separation of calcium, strontium and barium by suitable methods was carried out and it shows 97 per cent of $SrSO_4$, 1 2 per cent of $BaSO_4$ and 0 6 per cent $CaSO_4$

Finally it is pointed out that the celestite is of secondary origin and that the requisite strontium is derived from the surrounding strata

In conclusion the author wishes to express his grateful thanks to Dr K R Krishnaswami, D Sc, (London), F I C., for his keen interest and constant encouragement throughout the course of this work and also for much helpful criticism His thanks are also due to Sir C. V Raman, Kt., F R S, N L, of the Physics Department of this Institute, for allowing him to use the various optical instruments in his department

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PHOTOGRAPHS

Fig 1 —Photograph reproduced from Sivan's paper Specimen No 12 shows the lumps of celestine

Fig 2 —A phosphatic nodule cut across and polished showing the presence of white celestite veins—$\frac{3}{4}$ natural size

Fig 3 —A phosphatic nodule cut across showing a group of white radiating platy aggregates of celestite—$\frac{1}{1}$ natural size

Fig 4 —Shows a similar radiating group of celestite crystals as Fig 3, but the centre of crystallisation is not a single point but it is a curved line indicating the drifting of the centre—$\frac{1}{2}$ natural size

Fig 5 - Microphotograph of a basal cleavage flake of celestite showing very minute spherical grains (dark points) of a brownish yellow mineral which occur both as scattered grains and in groups Between parallel nicols

Fig 6 —Crystals of celestite gathered from a cavity in the phosphatic nodule

1 Crystals elongated parallel to the *a* axis and flattened parallel to *c* (001)

2 Crystals elongated parallel to *a* axis and without the development of any face

3 Well developed crystals elongated parallel to the *a* axis, and almost equally developed along *b* and *c* axes

4 Imperfectly developed crystals tabular parallel to *c* (001)

Fig 7 —A phosphatic nodule cut across showing the typical septarian cracks and the almost complete absence of celestite

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