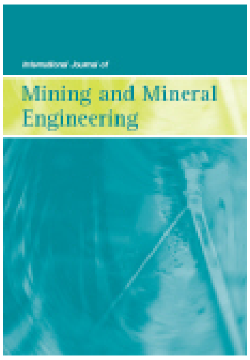

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Mineralogical studies of Cretaceous phosphatic nodules of Nambakuruchi block of Tiruchirappalli District, Tamil Nadu, India

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Abstract: The Cretaceous phosphatic nodules of study area are found in different sizes and shapes. Elliptical, cylindrical, globular, conical and irregular, with veins containing calcite, gypsum and celestite and minor amount of the montetrisaite are the common shapes. The thin section, X-ray diffraction and scanning electron microscope (SEM) studies show that the carbonate fluorapatite (CFA) is the main phosphate mineral of apatite family. Minerals like calcite, quartz, feldspar, kaolinite, chlorite, montimorlinite are the minor constituents. The crystal of the phosphate is brown to grey colour with bryozoan fragments. The fine phosphatic grains of nodules with silt size are embedded in fine matrix. Fragments of the fossils and others small carbonate particles show light to dark lamination. Coated grains, peloids, and fine detrital grains are found in these nodules. The shape of the peloids is rounded and having no well-defined structure which indicates fluctuating/or high energy environmental conditions. Micro cracks with microbial mat are also common with algal structure. Presence of organic matter, calcite, quartz and feldspar minerals is strongly supporting oxic to suboxic environmental conditions.

Keywords: phosphatic nodules; Cretaceous; Nambakuruchi; carbonate fluorapatite; CFA; mineralogy; India.

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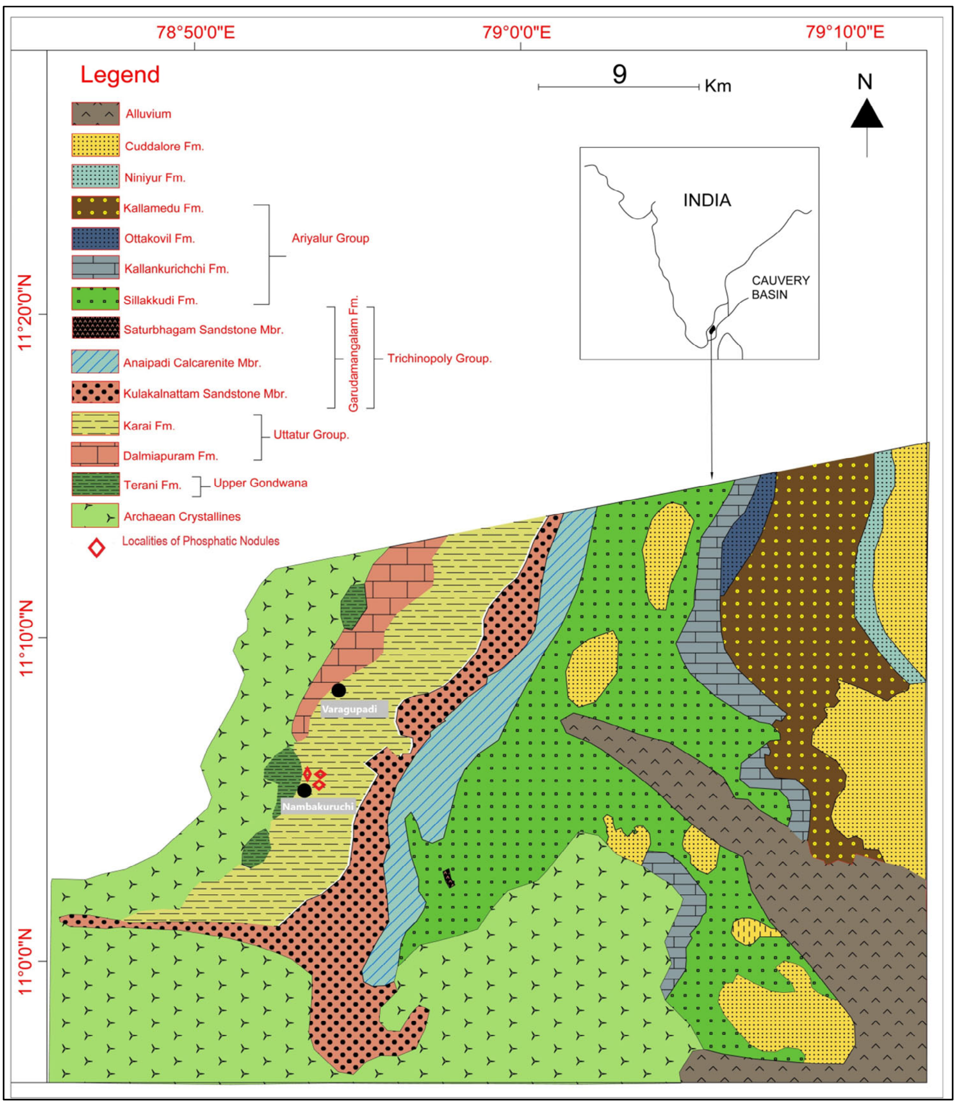
1 Introduction

Cauvery basin is one of the largest sedimentary basins located at the Eastern Coast of South India. In recent years, exploration activities are being carried out in parts of Tamil Nadu state and offshore of Bay of Bengal. In the western margin of this basin Cretaceous sediments are found in the form of isolated patches. One of the outcrops is located adjacent to Tiruchirappalli, which is the largest being studied in details. The presence of 4 to 6 km thick sedimentary succession has been confirmed by the drilling of exploratory wells. The age of this succession is early Cretaceous to recent. The extent of basin is from Pondicherry in the north to Tuticorin in the south. On the west side it is bound by Indian craton and the Sri Lankan massif and their subsurface continuations, below the Bay of Bengal are beyond Karaikal offshore defining its eastern limits.

The onshore Cretaceous marine sedimentary sequence of the phosphatic nodules is exposed in Tiruchirappalli District of Tamil Nadu. The Uttatur group of the Cretaceous period in this district is one of the important sources of rock phosphate in India. Cretaceous phosphorite deposit is one of the major deposits in the world. The phosphatic nodules in the Nambakuruchi is the part of the Cauvery basin of South India, which lies in the Uttatur group of the Karai formation and was first reported by the Worth (1893). The area has been investigated by previous workers on different aspects as lithosptratigraphy, biostratigraphy, paleooceanography, phosphatic nodules, depositional environment and flora and fauna (Rao et al.,, 2002, 2007; Banerjee, 1986; Sundaram and Rao, 1979; Rama Rao, 1958; Blanford, 1862). The present research paper deals mineralogical studies based on thin section, scanning electron microscope (SEM) and X-ray diffraction (XRD) have been carried out to investigate the size, mineralogical characteristics, nature, optical behaviour and texture of phosphate minerals and associated gangue in order to delineate their depositional environment of phosphatic nodules of Nambakuruchi Varagupadi Block of Tiruchirappalli District, Tamil Nadu, India.

Figure 1 Geological map of the Cretaceous of Cauvery basin (see online version for colours)

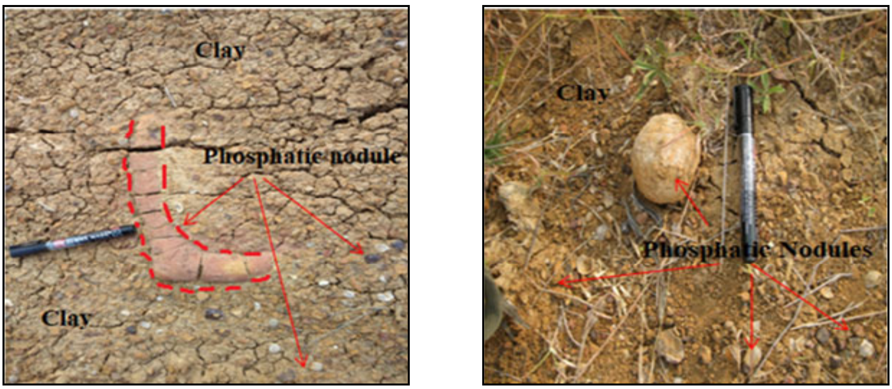


Source: Nagendra and Reddy (2017)

2 Geological setting

The Cauvery basin is a NE – SW trending rift basin that was formed during the late Jurassic to early Cretaceous. It is large basin with an approximate aerial extension of 25,000 square kms, consisting of well-preserved sedimentary sequence of Tamil Nadu, India. The structural framework (skeleton) of the basin is of horst and graben type comprising of ridges and depression. A boundary fault along the western margin is probably responsible for the development of the faulted basin (Nagendra and Reddy, 2017).

Figure 2 Field photograph showing phosphatic nodules, Nambakuruchi block of Tiruchirappalli, Tamil Nadu, India (see online version for colours)



The Nambakuruchi Varagupadi block of Tiruchirappalli District, Tamil Nadu, India is a part of Cauvery basin which lies in south part of the India. The geographic location of Nambakuruchi (latitude 11°5′30″; longitude 78°52′15″) and Varagupadi (latitude 11°8′50″; longitude 78°54′00″); and phosphatic nodules occur in an area about 27.52 square kms. The largest exposure of Cretaceous rocks in Tamil Nadu has been found in Tiruchirappalli District extending over 500 square kms. The Cretaceous successions of Cauvery basin consist of Precambrian basement overlain by Uttatur, Trichinopolly, Ariyalur and Niniyur groups. The phosphatic noudules have been marked in the Uttatur group of Karai Formation in shale bed. The lower contact is Kallakkudi Limestone of Nambakuruchi Varagupadi block of Tiruchirappalli District, Tamil Nadu which is exposed on the surface (Figure 1). The size of the nodules ranges from 5 to 25 cm in length and 2 to 10 cm in width with spherical, elliptical circular, cylindrical shape. The colour of the nodules surface is yellow to reddish ferruginous with light to dark brown phosphate content having veins of calcite, gypsum and celestite (Figures 2 and 3).

Generally, Uttatur group comprises grey shale, which is lower-most and oldest unit overlain by Kallakkudi Limestone (Dalmiapuram Formation) comprising Coral Algal Limestone, Marl Bedded Limestone and Marl Limestone which is overlain by Karai Shale. Dalmiapuram Formation is well exposed in the Kallakkudi Limestone and belongs to Uttatur Group.

The Uttatur group of the Cretaceous period in this district is one of the important sources of rock phosphate in India. The Cretaceous rocks have been divided into four group; Uttatur, Trichinopoly, Ariyalur and Niniyur, based on the lithological, faunal and stratigraphic characteristics. The phosphatic nodules are found to occur mostly confined to the lower and the middle formation of the Uttatur group which extends over an area of about 153 square kms (60 square miles) and exposed along a belt trending roughly NE – SW for a distance of about 25.76 kms (13 miles) between Uttatur village on the south and Chitalai village on the north, overlapped by the Tiruchirappalli group on the east and flanked on the west by the Archean comprising the gneisses and charnockites, and the upper Gondawanas.

Table 1 Lithostratigraphic classification of Cauvery basin of Tiruchirappalli, Tamil Nadu

Period	*Epoch*	*Age*	*Group*	*Formation*	*Member*
			Alluvium		
			Cuddalore		
			Niniyur		
Cretaceous	Upper	Maastrichtian	Ariyalur	Kallamedu	Kallamedu Sandstone
				Ottakkovil	Ottakkovil Sandstone
				Kallankurichchi	Kallankurichchi Limestone
		Campanian		Sillakkudi	Sillakkudi Sandstone
		Santonian	Trichinoplolly	Saturbugam	Saturbugam Sandstone
				Anaipadi	Anaipadi Sandstone
		Coniacian		Garudamangalam	Kulakkalnattam Sandstone
		Turonian	Uttatur	Karai phosphatic nodules#	Karai Shale/ Maruvattur Clay
		Cenomanian			
	Lower	Albian			
		Aptian		Dalmiapuram	Kallakkudi Limestone
				Arogyapuram	Gray shale
		Neocomian	Upper Gondwana	Terani	Terani beds
					Boulder conglomerate
Precambrian				Basement	

Note: #Indicate the location of phosphatic nodules.

Source: Venkateshwarlu and Nagendra (2016)

3 Materials and methods

The phosphatic nodules were collected from the Nambakuruchi block of Karai Formation, Uttatur Group Tiruchirappalli, Tamil Nadu (Figure 1). The sampling was carried out from different locations with different shape and size. The representative samples were selected for XRD, thin sections and SEM images analysis. The first cut the nodules in two equal halves. One half was used for thin section studies to identify texture/structures and mineral constituents. The other half was powdered for XRD. The powder was scanned from 3° to 60° 2θ at 0.5° 1/min, using nickel filtered Cu Kα radiation at the department of Mechanical Engineering AMU Aligarh. The minerals constituents of veins were first separated from the veins with the help of pencil knife and then powdered for XRD analysis and checked with hydrochloric acid with three dimensional microscopic studies for identification. The XRD data have been identified by 2θ to d values tables of National Bureau of Standards, 10 series of US Department of Commerce, and also used JCPDS cards and Match3 for the identification of minerals. The fresh broken phosphatic nodules were observed under JEOL/EO 6510 JSM SEM at USIF AMU Aligarh.

Figure 3 Photograph of the phosphatic nodules of Nambakuruchi block of Tiruchirappalli, Tamil Nadu, (a)–(l) shape and size variation in hand specimen (m)–(o) veins in the nodules (see online version for colours)

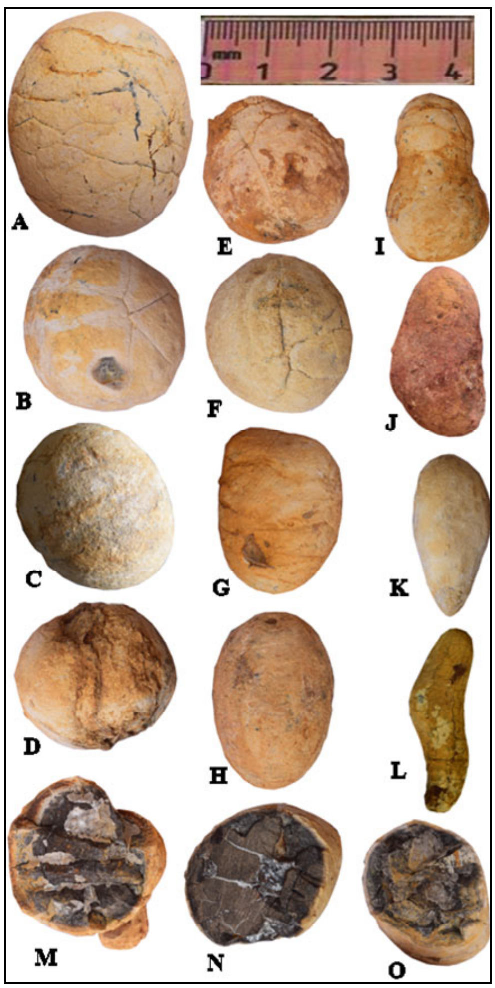
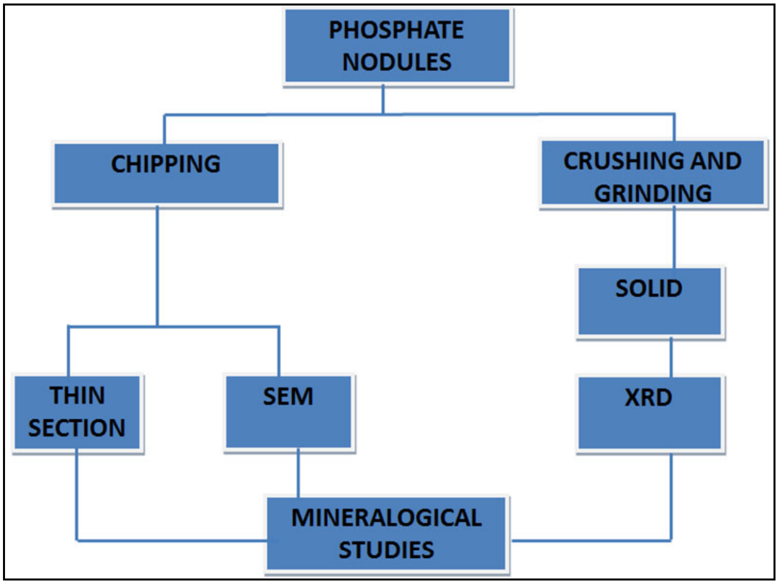


Figure 4 Flowchart of methodology adopted for the mineralogical study of phosphate nodules of the study area (see online version for colours)

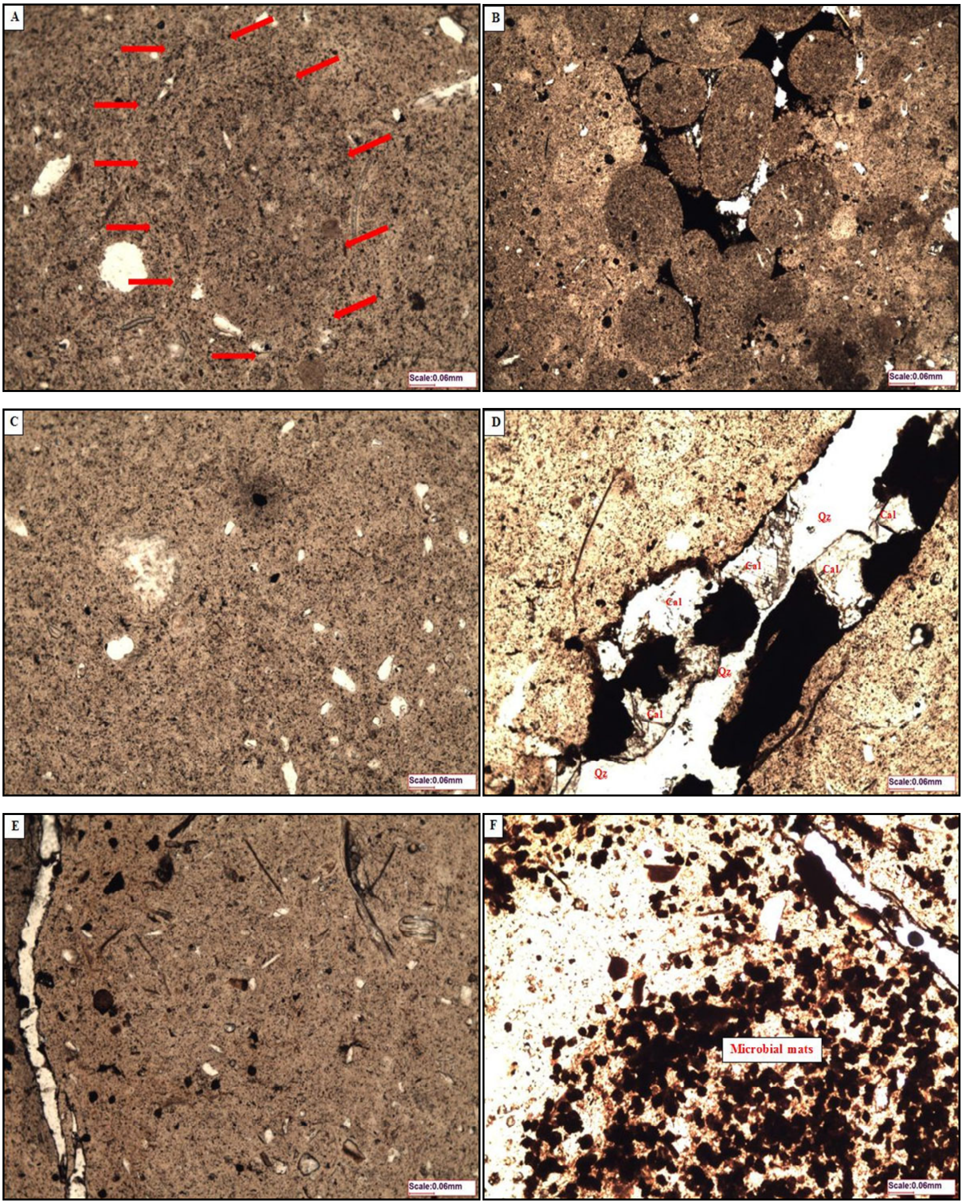


4 Results

The phosphatic nodules of the Nambakuruchi have different shapes and size. Their surface is yellow or white to reddish colour with different veins with crystal contact (Figure 3). The crystal of the phosphate is brown to grey colour with bryozoan fragments. Thin sections of the nodules indicate that the fine phosphate grains are of silt size with fine grain matrix. Fragments of the foraminifera and others small carbonate particles are marked with light to dark lamination. There are coated grains, peloids, and fine detrital grains with cavities (Figure 5). The shapes of peloids are rounded and structurless may have been formed in high energy environments [Figure 5(b)]. Micro cracks with microbial mat are also common with algal structure. The veins/cracks cut in nodules in different directions are of gypsum, calcite and celestite with silt size detrital particles [Figure 5(d)].

SEM shows that the main constituents of the phosphate are carbonate fluorapatite (CFA) with fine grained matrix [Figure 6(a)]. The SEM images also justify the major and minor minerals in the phosphatic nodules with the quartz and others microbial fragments of 6 μm size [Figure 6(b)]. The coated grains with smooth surfaces are also found in the SEM images [Figure 6(c)]. The microbial filaments are homogeneous forms with fragments of the planktic foraminifera. They are showing uniform composition. The laminae resemble with microbial filaments, which demark hollow [Figure 6(d)]. Figure 6(e) shows cavities which were formed by dissolution of the particles with phosphate crystals. The CFA crystal consists of quartz in central with globular phosphatised particles [Figure 6(f)]. Globular microbial mats with cavities are found in Figure 6(g). In the last figure the laminated phosphatised shows the development of the phosphate grains with the microbial filaments.

Figure 5 Photomicrographs of phosphatic nodules, (a) coated grain (b) peloids (c) fine lamination of phosphate (d) veins in the nodules (e) algal structure (f) microbial mats (see online version for colours)



The XRD studies revealed that the CFA is the major phosphate mineral in the nodules and calcite, quartz, feldspar, kaolinite, chlorite and montimorlinite are the minor constituents [Figures 7(a)–7(c)]. The composition of the vein/crack are of gypsum; calcite, celestite with minor amount of the montetrisaite [Figure 7(d)]. The same mineral composition has been reported earlier by Rao et al. (2007) in phosphorite samples of Nambakuruchi block of Tiruchirappalli, Tamil Nadu.

Figure 6 SEM images of the phosphatic nodules, (a) CFA crystal (b) CFA with quartz and other fragments (c) coated grains (d) uniform microbial filaments (e) cavities filling mat structures (f) CFA crystal with quartz grains (g) globular microbial mat with cavities (h) lamination (see online version for colours)

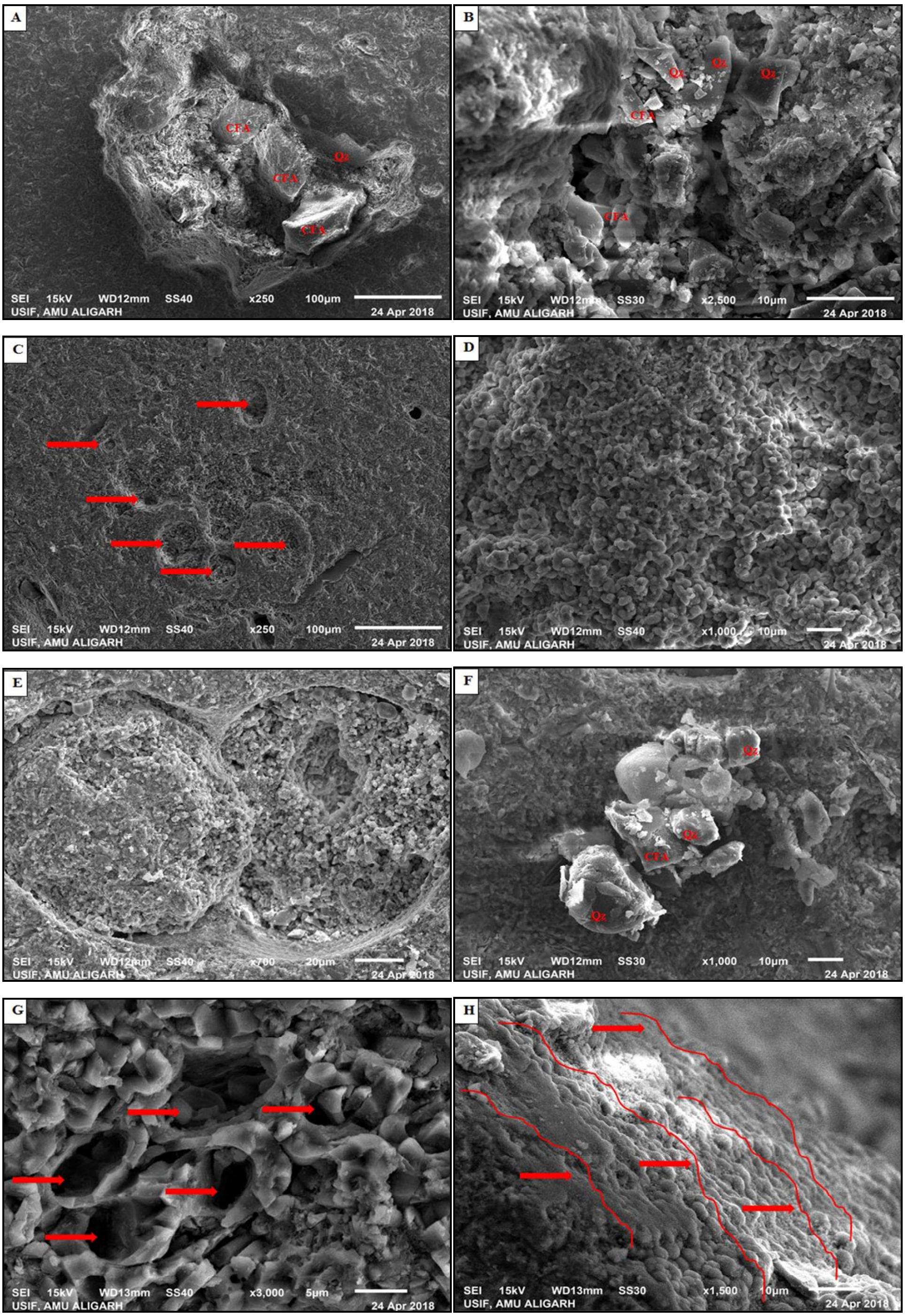
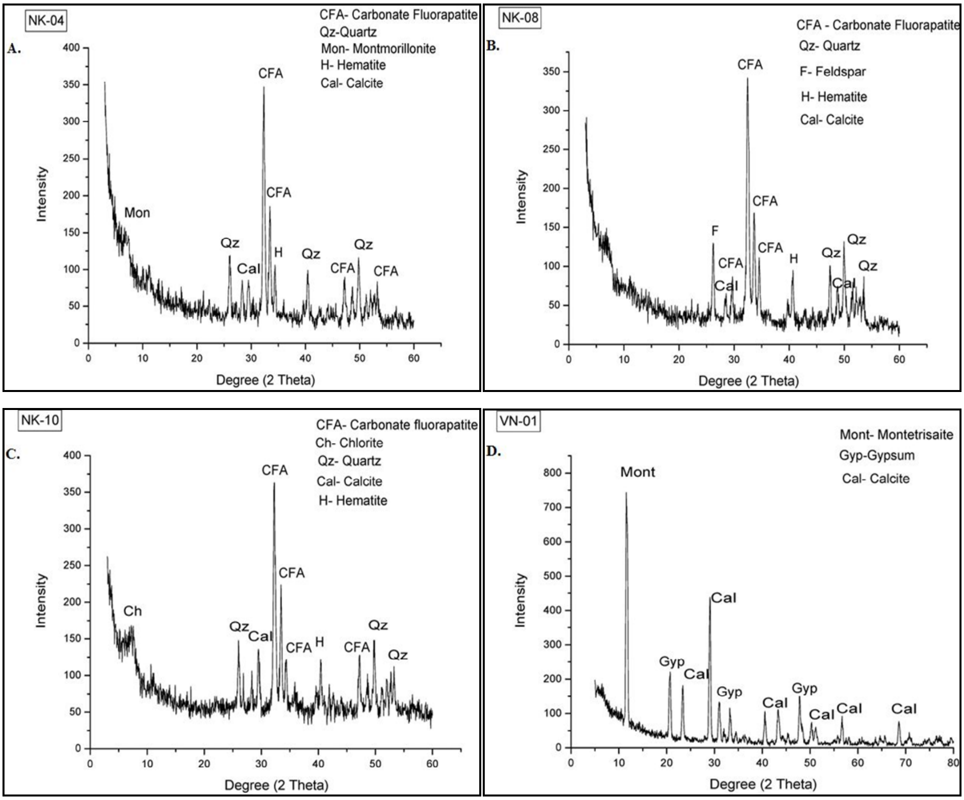


Figure 7 XRD patterns of phosphatic nodules of Nambakuruchi block of Tiruchirappalli, Tamil Nadu, (a)–(c) hole-posphatic nodules (d) only veins (cracks) composition



5 Discussion

Majority of phosphorite deposits which are distributed globally were deposited in Cretaceous period through process of phosphogenesis (Notholt et al., 1986). There is a large scale variation in the varieties of phosphorite, ranging from laminated beds with intercalated glauconites, nodular deposits to boulder conglomerates, or mud-dominated deposits to grain-dominated deposits. Several phosphorites from the Cretaceous contain peloids made of phosphorus. One can argue that peloids are either reworked or arthigenic in origin (Baioumy and Tada, 2005; Glenn and Arthur, 1990). Additionally, the primary mechanism underlying the extensive phosphogenesis that occurred during the Cretaceous has not yet been determined. There are different views on phosphorites, but the genesis of sedimentary phosphorites can be explained by three dominant processes (Follomi, 1994; Notholt and Jarvis, 1990; Burnett and Riggs, 1986). These three important processes are replacement of carbonates at the sea floor by phosphates, diagenetic precipitation from pore waters and precipitation by microbial activity and bacteria. Precipitation of phosphate on microbial bodies was mainly during the metabolic activity of micro-organisms or an early process just after their death, as per the empty microbial filaments/cell-based phosphate structure. Thus, it is considered that these formations are the syn-sedimentary phosphatised remains of cyanobacteria that form mats. Therefore, the nodule's nucleus is made up of phosphate clasts that were torn away from primary phosphorites produced by microbial mat during high-energy episodes. According to Walter (1976), the distinguishing characteristic of stromatolites is the binding and trapping of detrital particles by mineral precipitation and a microbial mat brought on by metabolic activity. Phosphate stromatolites are therefore represented by the phosphate clasts in the nucleus. The phosphate stromatolites which are discussed here, however, do not show many features (like macroscopic, columnar habit) of ancient stromatolitic phosphorites of Proterozoic and Cambrian age (Cook and Shergold, 1986). This finding is also confirmed the peninsular India and Himalayan phosphogenic province (Banerjee, 1986; Valdiya, 1972). Monty (1976) proposed that stratiform stromatolites having laminae are equivalent to cryptalgal laminites. The Phosphate stromatolites formed in shallow water conditions during the Quaternary (Rao et al., 2000), Paleogene (Soudry and Panczer, 1994) and Paleozoic (Bertrand-Sarfati et al., 1997) and in pelagic conditions during Mesozoic along the northern margin of the Mediterranean Tethys (Martin-Algarra and Sanchez-Navas, 1995; Follomi, 1989; Krajewski, 1981; Krajewski et al., 1994) were reported. They proposed that the authigenic phosphate deposit's fabric and structure are both defined by the apatitic stromatolites, which typically consist of tiny microlaminated units.

Mineralogical studies of the phosphatic nodules shows that the most dominant phosphatic constituents is CFA, with texture/structures like peloids, coated grains, micro-laminations with microbial filaments. The source of the microbial mat may be micro-organism. Peloids structures formed due to the mechanical accretion. According to Walter (1976) the binding and trapping of detrital particles by a mineral precipitation and microbial mat due to of metabolic activity is the characteristic feature of stromatolites. Therefore the phosphate clast is organic origin. Phosphate stromatolites during Mesozoic in pelagic setting (Krajewski et al., 1994). Micro-cracks filled with celestite, calcite, gypsum indicates shallow environmental conditions. Presence of celestite indication the evaporative conditions (Taberner et al., 2002). This shows that the microbial mats are formed in evaporative conditions. Krumbein (1986) described in carbonates, coated grains similar structures in Negev phosphorites (Soudry and Champetier, 1983). The nuclei of nodules in carbonate grains related to the phosphate stromatolites formed intertidal environmental conditions (Rao et al., 2007). According to McConnell (1973) dominance of CFA as the primary mineral in the phosphorites shows major elemental composition together with subordinate quartz, calcite, clay minerals and feldspar.

5.1 Uses and application of phosphatic nodules

For extracting phosphatic nodules different separation methods and flow sheets are applied to separate phosphate from gangue minerals in phosphate nodules. The nodules of Tiruchirappalli District, Tamil Nadu, are composed primarily of fluorapatite, quartz, and organic matter as predominant minerals. If the phosphate nodules contain a lot of organic matter, the phosphate content is separated using a combination of low-temperature roasting (400–600°C) and dry magnetic separation. In addition, when quartz is present as a gangue mineral, Anastassakis (2013) recommends using high-intensity electrostatic separation. As a result, both separation procedures will work for separating phosphate materials from gangue to the area's nodules. A weak phosphoric acid

(40–55%) is produced by the wet method (reaction of rock phosphate with sulphuric acid), which is employed in the production of a variety of liquid and solid fertilisers. Single and triple superphosphates and ammonium phosphates are the most important. Rock phosphate is used as a fertiliser in India, where finely powdered rock phosphate with 16% P_2O_5 is applied directly to the soil. The chemical composition and structure of the rock have a role in this application. Direct application is best for pastures and feed crops, as well as acidic soils, according to the Indian Bureau of Mines. The solubility of rock phosphate in acidic soil determines whether it may be used directly as a fertiliser.

6 Conclusions

On the basis of the presentation and interpretation of mineralogical findings and discussion it may be concluded:

1. The presence of the microbial mats, pelloids, coated grain, fossils wrap with association of CFA, calcite, quartz, chalorite suggest oxic to suboxic environmental conditions. The presence of organic matter, calcite, quartz and feldspar minerals in the study area strongly supports the oxic to suboxic and alkaline environmental conditions.
2. The source of the organic matter may be the microbial mat formed on Kallakkudi Limestone bed indicating deposition of phosphatic nodules in oxic to sub-oxic shallow marine intertidal environmental conditions.
3. Presence of laminated, fragmented and peloids with coated grains of phosphorite deposits may be due to high energy tidal conditions. The constituents of phosphatic nodules may have been derived from microbial bodies from the sea and the precipitation of the phosphate during metabolic process was early stage of burial (micro-organisms).
4. The process of phosphatisation suggest that the microbial filaments and cell structures observed here are empty, implying that phosphatisation took place during their early stages of decay followed by association of algal mats which may be as one of the original sources of phosphate.

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