

# Petro-mineralogical Studies of the Paleoproterozoic Phosphorites in the Sonrai basin, Lalitpur District, Uttar Pradesh, India

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The Paleoproterozoic phosphorites constitute an economically significant component of the Sonrai basin of Lalitpur district. These are associated with ferruginous shale, ironstone, limestone and quartz breccia. Petro-mineralogical studies of samples of the phosphorites, using X-ray diffractometry and scanning electron microscopy, reveal that the collophane (carbonate-fluorapatite) is the dominant phosphate mineral. Calcite, dolomite, quartz, mica and haematite are the dominant gangue constituents. The phosphate minerals occur as oolites mutually replaced by carbonate and silica. The presence of iron oxides has been found in most of the thin sections. There is meagre evidence of organic matter in the form of filaments of microbial phosphate laminae in the samples of phosphorite. The mineral assemblages, their texture and various forms in these phosphorites may be due to some environmental vicissitudes followed by replacement processes and biogenic activities.

**KEY WORDS:** Petro-mineralogy, Paleoproterozoic, Sonrai basin, Phosphorite, Carbonate-fluorapatite.

## INTRODUCTION

Phosphorite or rock phosphate is used mainly as intake for the manufacture of phosphatic fertilizers. To promote the modernisation of agriculture, phosphate deposits had been in great demand because they contain adequate concentrations of phosphorus (P) which is a critical and non-renewable element for fertilizer production upon which global fertility depends (Filippelli 2011; Khan et al. 2011a, b, 2012c; Dar 2013). Because of the paucity of natural phosphates, Lalitpur, Sagar and adjoining areas in India have been subjected to prospecting from time to time. The main phosphorite deposits are concentrated in the Sonrai basin of Lalitpur

district (Blatt and Tracy 1996; Daessle and Carriquiry 2008; Khan et al. 2012a, b; Dar 2013). Generally, a major proportion of P in the earth's crust occurs in the mineral apatite, which is a phosphate of calcium with fluorine and chlorine. The most widespread mineral species of phosphorite belong to the apatite family and they contain at least 1 %  $P_2O_5$ .

Earlier investigators have discussed various aspects of phosphorites and associated rocks at Sonrai basin of Lalitpur district such as geology, sedimentation, exploration strategy and origin (Srivastava 1989; Dar 2013), clay mineralogy (Jha et al. 2010), Precambrian phosphorites in the Bijawar rocks (Banerjee et al. 1982), lithotectonics (Banerjee 1982), petro-mineragraphy and mineral chemistry (Roy et al. 2004), geochemistry of phosphate bearing sedimentary rocks (Khan et al. 2012a, b), uranium concentration and genetic significance in phosphorites (Dar et al. 2014). In this paper, emphasis is laid on detailed mineralogical studies based on X-ray diffraction (XRD) and scanning electron microscope

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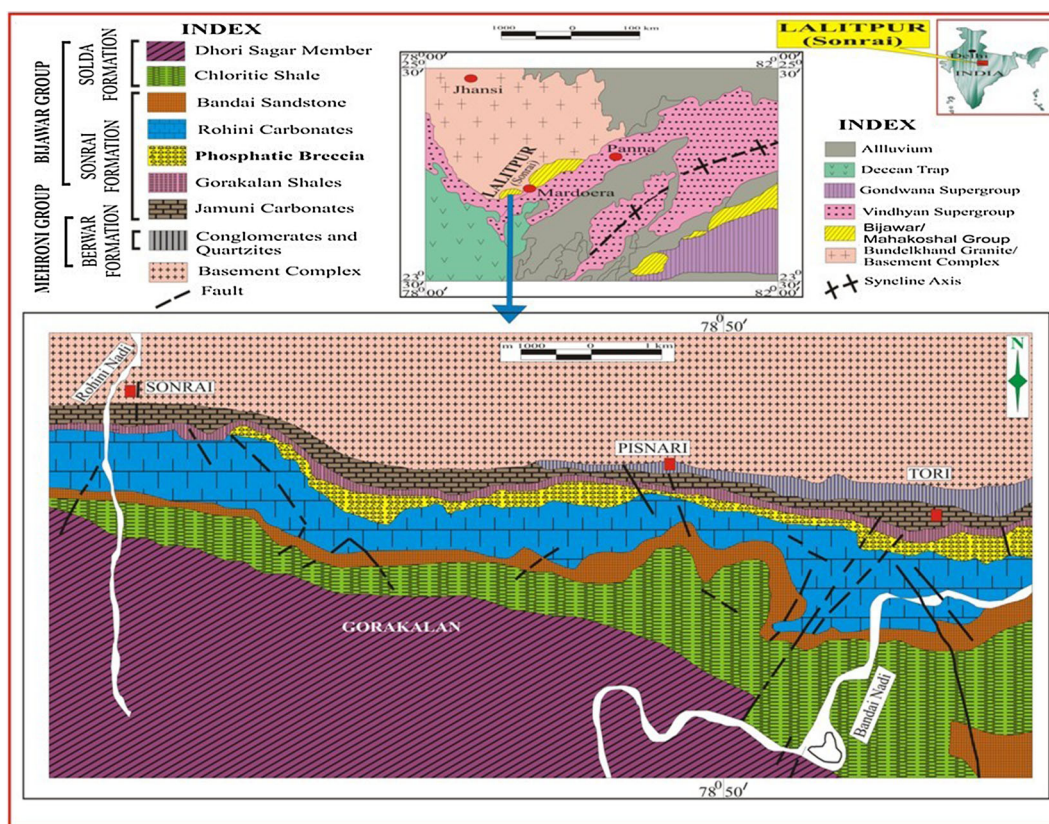
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(SEM) to investigate the nature and optical behaviour of phosphate bearing minerals, their distribution pattern and texture in order to delineate their formation in the depositional basin.

**GEOLOGICAL SETTING**

The Paleoproterozoic meta-sedimentary rocks of Bijawar Group, which rest upon the Archaean Bundelkhand Basement Complex, are overlain by the rocks of Vindhyan Supergroup. These meta-sedimentary rocks were deposited in small

intracratonic basins like the Sonrai, Hirapur and Gwalior Basins (Jha et al. 2010). The exploitable phosphorite deposits of Sonrai basin are associated with a variety of phosphatic breccia, limestones, shale, ironstone and quartzite with iron content and constitute a part of the Bijawar Group. The Bundelkhand Complex consists mainly of granitoids and enclaves of older metamorphic rocks, whereas the Vindhyan Supergroup, containing sedimentary rocks is overlain by Late Mesozoic to early Tertiary Deccan Traps (Fig. 1; Table 1) (Srivastava 1989; Roy et al. 2004; Dar 2013). The phosphorite deposits of Sonrai (24°18'00"N, 78°46'00"E) are associated



**Figure 1.** Modified geological map of Bijawar Group of the Lalitpur District, Uttar Pradesh, India (after Prakash et al. 1975; Roy et al. 2004; Khan et al. 2012a, b; Dar 2013).

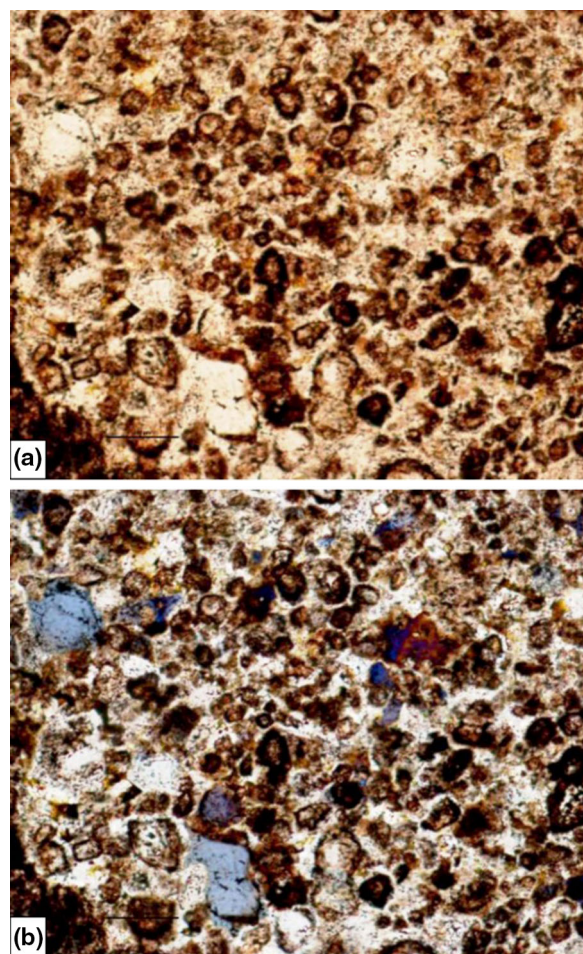
**Table 1.** Regional Stratigraphy (After Srivastava 1989; Dar 2013)

Deccan trap: (Cenozoic)	Basalts and related dykes
Vindhyan group (Late Proterozoic 1,400–600 my)	Sandstone, conglomerates and shale
Bijawar group (Early Proterozoic >1,800 my)	Quartz breccia, quartzite, shale, sandstone, limestone and ironstone
Berwar formation/Bundelkhand granite complex (Archaean)	Dykes, schists, gneisses, pegmatite, conglomerate and quartz veins

with the rocks of Tori and Shale members of the Sonrai Formation and are mainly concentrated in a stretch of 27 km with a width of 5 km between Pisanari (24°19'00"N, 78°44'30"E) and Berwar (24°18'30"N, 78°54'00"E) (Kothiyal et al. 2002).

The whole sequence at Sonrai is divided into five members, which in ascending order are (Table 2): (1) shale member consisting of dark grey, olive grey, reddish and black shales with carbonate rocks and phosphorite bands; (2) brecciated quartzite member comprising brecciated quartzite and lenticoid bodies of phosphorites with quartzite and phosphatic matrix cementing angular to subangular fragments of quartzite; (3) Tori Member with ferruginous massive quartzite and massive botryoidal and brecciated phosphorites; (4) Rohini Member (consisting of thinly bedded, light grey shaly dolomitic and pink sandy carbonate rocks) and its coeval Kurrat Member (lava); and (5) Bandai Member at the base consisting of sandstone and grits which are calcareous at places. The uppermost Solda Formation is divided into two members (Table 2): (1) the overlying Dhauri Sagar Member with tuffaceous shales; and (2) the uppermost Hadda Member comprising quartzite and shale intercalations.

The phosphorites of the Sonrai basin are found to occur as lenticular detached bodies, which are massive, laminated and brecciated. Individual bodies range from a few metres to about 4 km in length and the width varies from thin bands to about 125 m. The phosphorites are confined at four distinct stratigraphic levels. The first horizon, at the base, consists of massive to brecciated phosphorites and occurs within the lower reddish shales with at least

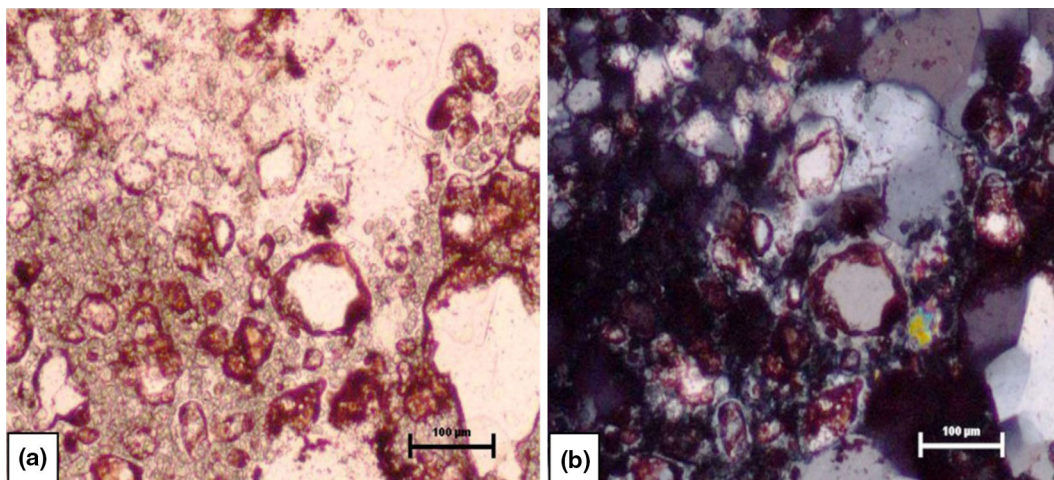


**Figure 2.** Photomicrographs of thin sections of phosphorites of the Sonrai basin showing pseudo-ooliths and pellets of collophane **a** in plane polarized light and **b** between crossed nicols ( $\times 10$ ).

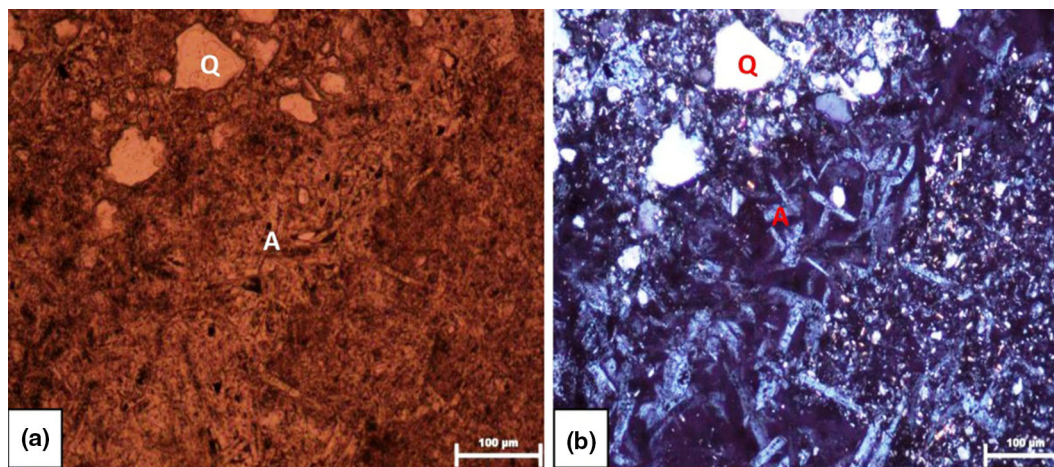
**Table 2.** The Stratigraphy of Sonrai Basin, Lalitpur District, Uttar Pradesh, India (After Pant et al. 1989; Khan et al. 2012a, b; Dar 2013)

Vindhyan Super Group	Sandstone, conglomerates and shale
Unconformity	
Bijawar Group	
Solda Formation	
Hadda Member	Quartzite shale intercalations
Dhauri Sagar Member	Tuffaceous shale
Sonrai Formation	
Bandai Member	Tuffaceous shale, sandstone and grit
Rohini Member	Sandy, shaly and dolomitic carbonate
Kurrat Lava	Rocks basic volcanics and pillow lava
Tori Member	Massive quartzite with <i>phosphorite</i>
Brecciated Quartzite Member	<i>Brecciated quartzite with lenticoid bodies of phosphorite</i>
Shale Member	Grey, green and red shales with carbonate and phosphorites bands
Berwar Formation	Banded haematite quartzite, chloritic shale, quartzite and conglomerate
Unconformity	
Bundelkhand Group	Bundelkhand Granitoids complex with pegmatite and quartz veins etc





**Figure 3.** Photomicrographs of thin sections of phosphorites of the Sonrai basin showing replacement of phosphate material by silica **a** in plane polarized light and **b** between crossed nicols ( $\times 20$ ).



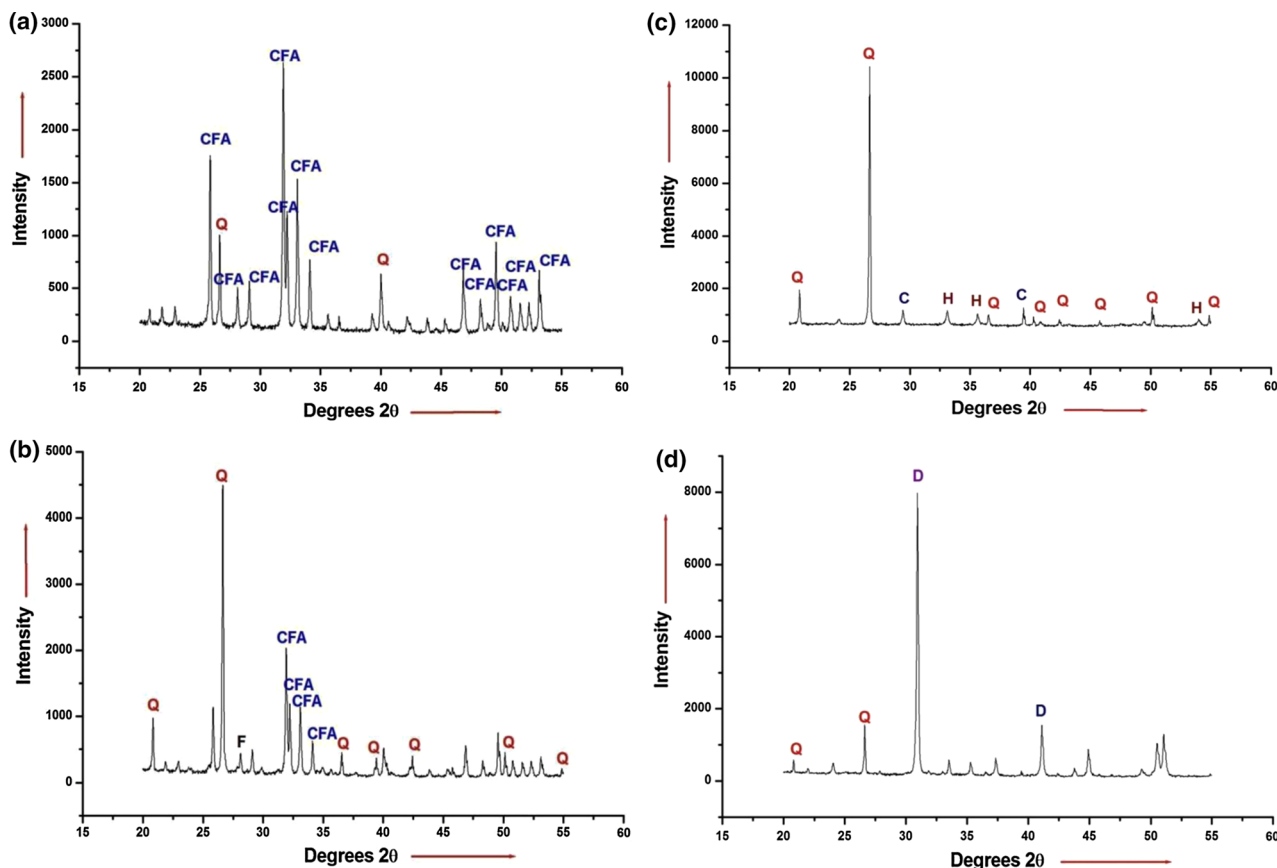
**Figure 4.** Photomicrographs of thin sections of phosphorites of the Sonrai basin showing colophane groundmass of fibrous apatite needles with radiating arrangement as 'microspherulitic texture' **a** in plane polarized light and **b** between crossed nicols ( $\times 10$ ).

three bands. The second horizon occurs at the base of the brecciated quartzite member, overlying the black shales and consists of brecciated phosphorite containing lensoid bodies with phosphorite cement. The phosphorite could be the basal part of the brecciated quartzite. The third horizon consists of massive to brecciated phosphorite and occurs within the brecciated quartzite. This horizon contains angular to subangular fragments of quartzite cemented by high-grade phosphorite. It is widespread and amenable to beneficiation. The fourth uppermost horizon overlies the brecciated quartzite and is the most important phosphorite in the Sonrai basin

as it consists of lensoid bodies of phosphorites (Pant et al. 1979, 1989; Dar 2013).

## MATERIALS AND METHODOLOGY

With the help of the geological map of the area, systematic and careful sampling was carried out and 40 fresh representative samples from different lithological units and horizons were collected at regular intervals during fieldwork. Microscopic study was done for optical mineralogical characters of the phosphorites.



**Figure 5.** XRD patterns of the Sonrai basin indicating: **a, b** carbonate-fluorapatite (*CFA*), quartz (*Q*) and feldspar (*F*) minerals in the phosphorites; and **c, d** quartz (*Q*), haematite (*h*), calcite (*c*) and dolomite (*d*) minerals in the associated rocks.

As the intensity of diffracted light very much depends upon the state and grain size of the sample, the preparation of sample is very important. In order to obtain a good diffraction pattern of a mineral, the sample was powdered to approximately  $-200$  mesh size and sample powder was taken and put into the glass slide holder and loaded on the sample of the machine. The diffraction data were obtained with a Rigaku-Ultima IV X-ray diffractometer using nickel filtered  $\text{Cu K}\alpha$  radiation at National Institute of Oceanography (NIO), Goa. This incorporated a focusing monochromator from a tube separated at 40 kV and 20 mA. The divergence and scatter slits were  $1^\circ$  wide and the receiving slit 0.3 mm wide.

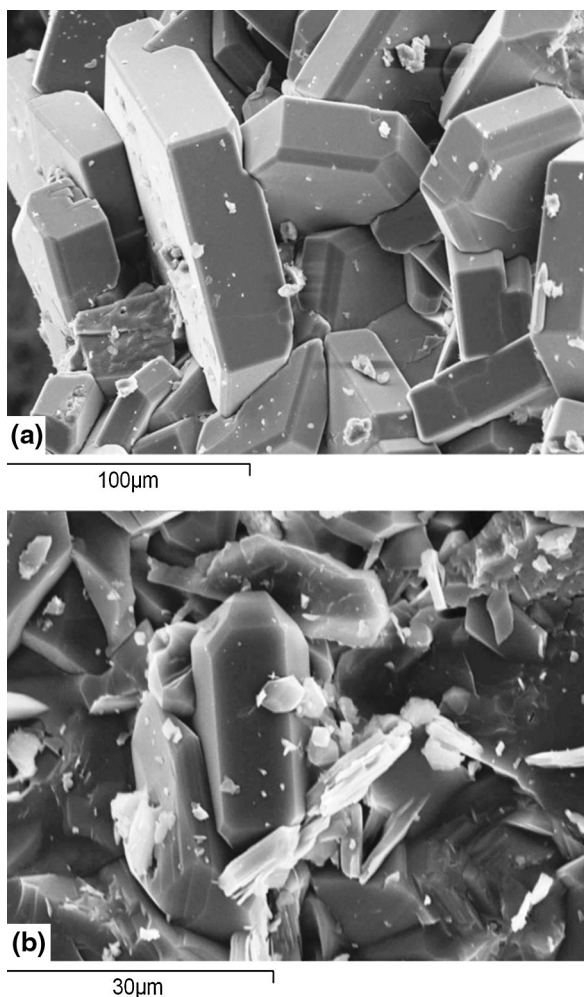
Samples were run at  $25^\circ\text{C}$  and the line profiles were recorded at scanning rate of  $0.02^\circ 2\theta/\text{s}$ . The scan was made over an angular range of  $8^\circ$  to  $70^\circ 2\theta$  and the chart speed was 10 mm per minute. The range conditions chosen were  $1 \times 10^3$  CPS and  $4 \times 10^2$  CPS to permit maximum resolution of the peaks for

accurate measurements. Diffractograms so obtained were used for mineralogical interpretation.

The X-ray reflection (peaks) was carefully measured and the minerals were identified by conversion of  $2\theta$  to 'd' values using the table of National Bureau of Standards, series 10 of US Department of Commerce. The mineralogical identification was done by measuring the intensity of each reflection against their respective 'd' values. The maximum reflection was taken as 100 and each reflection was converted to nearest whole number with respect to this 100 percentile maximum reflection. This was done to obtain a definite intensity ratio. The mineral identification was subsequently done following the X-ray identification charts of JCPDS cards.

For SEM studies, a rock sample was broken into small pieces and the freshly broken surfaces of some phosphorite samples were taken and kept on a carbon tape which was pasted on a metallic stub without touching the hand. A sample was coated



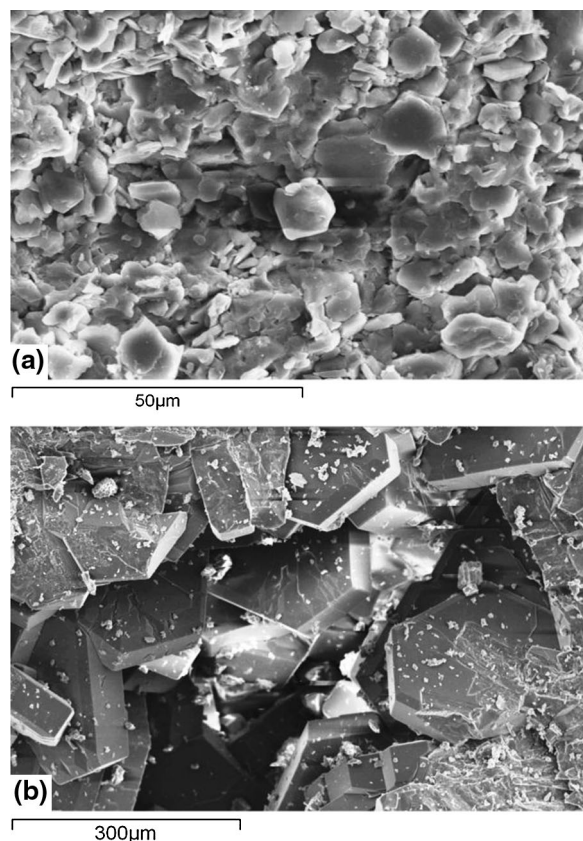


**Figure 6.** SEM photomicrographs showing crystalline hexagonal apatite of phosphorites of the Sonrai basin.

with a thin coating of gold sputter cotter. A sample was then observed under JEOL 5800LV SEM attached with EDS analyser at various magnifications to observe the shape, size and nature of the grains of phosphate minerals. The micrographs were obtained with maximum resolution at an acceleration voltage 20 kV facility at National Institute of Oceanography (NIO) Goa.

## RESULTS AND DISCUSSION

The thin section studies indicate that the phosphate minerals are found in the form of concretion pellets, nodules and oolites composed mainly of the mineral francolite ( $\text{Ca}_{10}(\text{PO}_4\text{CO}_3)\text{F}_{2-3}$ ) or fluorapatite typically found in cryptocrystalline nature (grain



**Figure 7.** SEM photomicrographs of phosphorites of the Sonrai basin showing **a** crystalline apatite and **b** euhedral apatite crystals, which exhibit carbonate-fluorapatite (CFA) recrystallization.

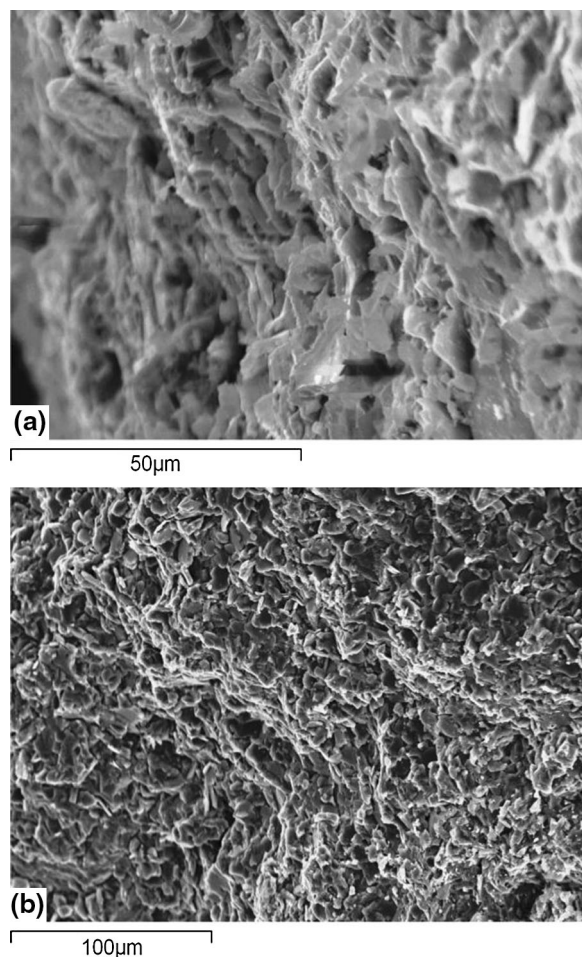
sizes  $<1\ \mu\text{m}$ ) generally referred as “collophane”, which is a dominant phosphate mineral in the Sonrai phosphorite deposits. The colour of collophane ranges from greyish yellow to greenish black. It is isotropic to weakly anisotropic. The form of the collophane is mostly oolitic. Since they generally lack concentric structures, they are often called as ‘pseudo-ooliths’ or more commonly ‘pellets’ (Fig. 2). Few thin sections show replacement of phosphate by silica (Fig. 3). Under high magnification, the collophane groundmass appears as fibrous mass of fine apatite needles which at places are randomly oriented or show radiating arrangement giving the rock a ‘microspherulitic texture’ (Fig. 4).

The XRD studies indicate that carbonate-fluorapatite (CFA) is the major apatite phase (Fig. 5a, b), which is responsible for  $\text{P}_2\text{O}_5$  content in these rocks. Other minerals available in minor quantities are mica and haematite (Fig. 5c, d). Similar findings have been reported in the phosphorite deposits of

Gafsa Basin of Tunisia, where the XRD patterns show narrow peaks indicating large crystallites and well crystallized materials (Ounis et al. 2008).

The SEM studies of fresh broken phosphorites show unaltered micro-crystalline hexagonal apatite crystals (Fig. 6). The occurrence of crystalline apatites (Fig. 7a) in these phosphorites are in accordance with the findings of Van Cappellan and Berner (1991), Rao et al. (2008) and (Dar 2013) that phosphates precipitated initially as amorphous or poorly-crystalline meta-stable phase, which transformed into crystalline apatite depending on the degree of supersaturation of fluorapatite content. Scanning electron micrographs of some of the phosphorites showing euhedral crystals of apatite also support this recrystallization process of CFA (Fig. 7b). These findings are also in accordance with those of Imamoglu et al. (2009) that microbial phosphate laminae resemble the bundles of submicron-size filaments wrapping nuclei of nodules as parallelly aligned phosphate micro-laminae (Fig. 8). The laminations laterally blur into structureless mass of phosphate. Elsewhere several submicron-size tubules form laminae and detrital particles interspersed between the laminae. It may, therefore, be presumed that microbial activities may have been involved in their formation. Similar findings have also been reported by Rao et al. (2007, 2008) and Dar (2013).

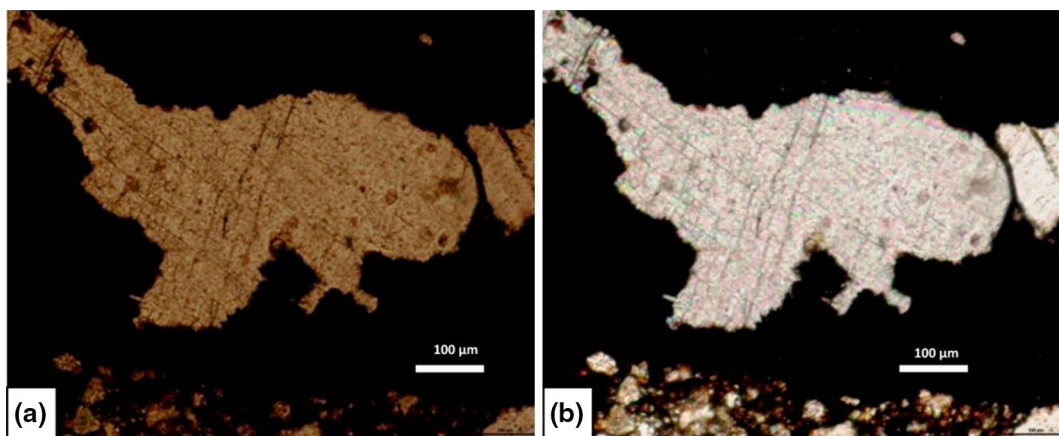
Calcite ( $\text{CaCO}_3$ ) is the main carbonate gangue mineral. It is usually colourless to light grey and occurs as coarse-grained subhedral to euhedral crystals with rhombohedral cleavage. They are equidimensional with polysynthetic twinning and are tightly packed with slight sutured margins, apparently an effect of solution pressure. The calcite crystals show very high birefringence and marked change in relief (twinkling) and pearly to white interference colours of higher order. The extinction angle is symmetrical to the cleavage traces. The calcite grains are embedded in iron ore groundmass (Fig. 9). They also show the effect of chemical corrosion. At places calcite veins are also seen in the thin sections (Fig. 10). Rounded to subrounded detrital grains of quartz are also seen in a fine-grained dolomitic mosaic (Fig. 11). Occasionally silica and iron oxides constitute the cementing material. The presence of calcite and dolomite as gangue minerals and their differentiation in these phosphorites has also been inferred from the XRD results (Fig. 5c, d). Quartz is associated as dominant gangue mineral in the entire mass of these phos-



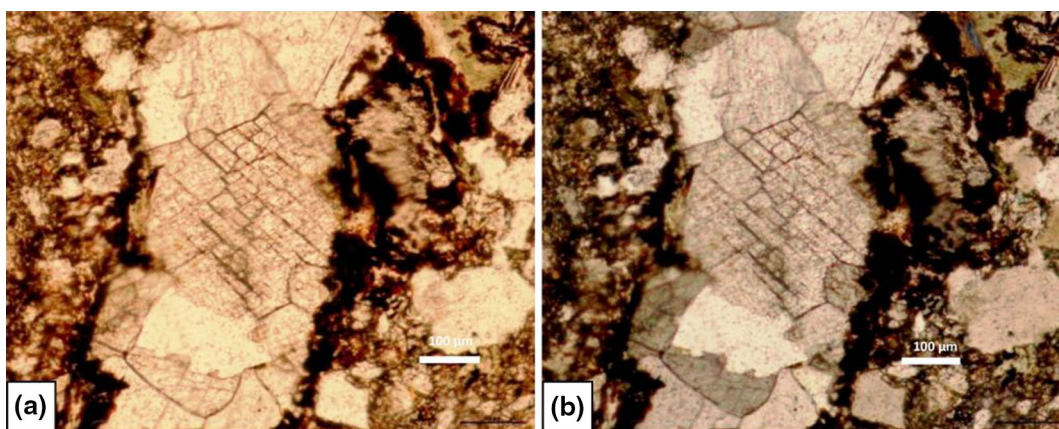
**Figure 8.** SEM photomicrographs of freshly broken surface of phosphorites of the Sonrai basin showing the microbial phosphate laminae resembling bundles of micro filaments.

phorites. The anhedral grains of quartz, having no cleavage, show low birefringence and first-order grey, white or yellow interference colours (Fig. 12). The XRD studies also support the presence of quartz as gangue (Fig. 5). The strongly pleochroic mica flakes showing perfect one set cleavage, medium birefringence, parallel extinction and yellowish green to pinkish interference colours are seen under microscopic studies. At places thin laminae of clay minerals are seen to be embedded in fine ground mass of quartz (Fig. 12). Along with the fine-grained granular mass of iron bearing minerals, brownish coloured anhedral to subhedral grains of haematite are seen in ferruginous chert being partially replaced by iron oxides (Fig. 12). This is also evident from the XRD results (Fig. 5). At places iron oxide veins are found across the ground mass of apatite (Fig. 13).

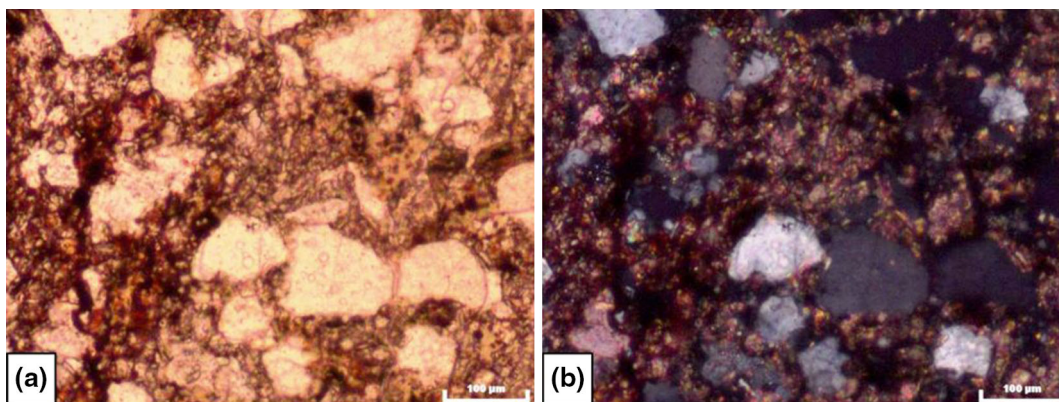




**Figure 9.** Photomicrographs of thin section of dolomitic limestone showing calcite embedded in iron rich groundmass indicating the effect of chemical corrosion **a** in plane polarized light and **b** between crossed nicols ( $\times 10$ ).

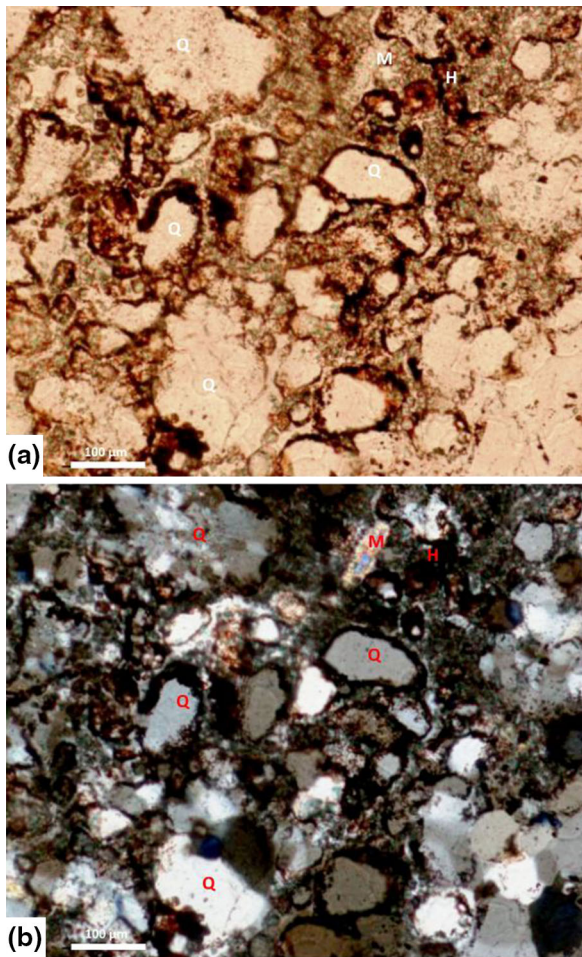


**Figure 10.** Photomicrographs of thin sections of dolomitic limestone of the Sonrai basin showing calcite vein in ground mass of iron **a** in plane polarized light and **b** between crossed nicols ( $\times 10$ ).



**Figure 11.** Photomicrographs of thin sections of dolomitic limestone of the Sonrai basin showing subrounded detrital quartz grains in fine-grained, laminated dolomitic mosaic **a** in plane polarized light and **b** between crossed nicols ( $\times 10$ ).



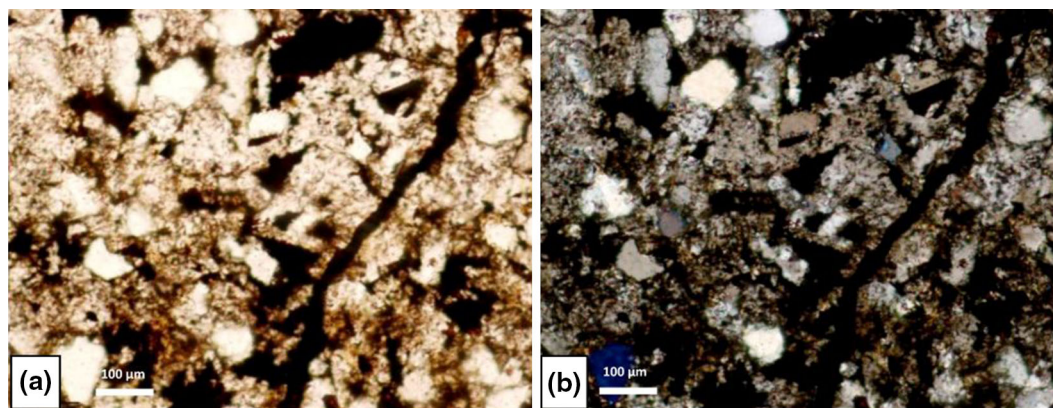


**Figure 12.** Photomicrographs of thin sections of phosphorites of the Sonrai basin showing quartz (*Q*), haematite (*H*) and mica flakes (*M*) **a** in plane polarized light and **b** between crossed nicols ( $\times 10$ ).

All the present findings about these phosphorites indicate that their formation may have taken place in fairly oxidizing environmental conditions to very weakly reducing conditions in a shallow marine basin of deposition. The varieties of phosphorites may be due to different environmental vicissitudes followed by some replacement processes and biogenic activities.

**CONCLUSION**

The phosphorite deposits in the Sonrai basin of Lalitpur district of Uttar Pradesh are associated with ferruginous shale, ironstone, limestone and quartz breccia. The XRD and SEM studies reveal that carbonate-fluorapatite is the dominant phosphate mineral of apatite family while calcite, dolomite, quartz, mica and haematite are the dominant gangue constituents. The presence of iron mineral (haematite) in the groundmass of iron oxides in most of the thin sections may be an indication of the prevailing oxidizing conditions during the formation of the deposits. The collophane is found to occur in oolitic pseudo-liths and petal form showing mutual replacement of phosphate by carbonate, silica and iron oxides. SEM studies show meagre evidence of filaments of microbial phosphate laminae in these phosphorites indicating little role of micro organisms in the formation of the deposits. On the basis of XRD and SEM studies present here, it may be concluded that the mineral constituents of these phosphorites may have been formed in a shallow marine basin having oxidizing to very weakly



**Figure 13.** Photomicrographs of thin sections of phosphorites of Sonrai basin showing iron oxides forming a vein cutting across the ground mass of apatite **a** in plane polarized light and **b** between crossed nicols ( $\times 20$ ).

reducing conditions and different environmental vicissitudes followed by some replacement processes and biogenic activities.

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