Petro-Mineralogical Studies of Phosphorite Deposit of Sallopat Block of Banswara District, Rajasthan, India

K. F. Khan, Samsuddin Khan

Abstract—The Paleoproterozoic phosphorite deposit of Sallopat block of Banswara district of Rajasthan belongs to kalinjara formation of lunavada group of Aravalli Super Group. The phosphorites are found to occur as massive, brecciated, laminated and stromatolitic associated with calcareous quartzite, interbedded dolomite and multi coloured chert. The phosphorites are showing alternate brown and grey coloured concentric rims which are composed of phosphate, calcite and quartz minerals. Petromineralogical studies of phosphorite samples using petrological microscope, XRD, FEG- SEM and EDX reveal that apatite-(CaF) and apatite-(CaOH) are phosphate minerals which are intermixed with minor amount of carbonate materials. Sporadic findings of the uniform tiny granules of partially anisotropic apatite-(CaF) along with dolomite, calcite, quartz, muscovite, zeolite and other gangue minerals have been observed with the replacement of phosphate material by quartz and carbonate. The presence of microbial filaments of organic matter and alternate concentric rims of stromatolitic structure may suggest that the deposition of the phosphate took place in shallow marine oxidizing environmental conditions leading to the formation of phosphorite layers as primary biogenic precipitates by bacterial or algal activities. Different forms and texture of phosphate minerals may be due to environmental vicissitudes at the time of deposition followed by some replacement processes and biogenic activities.

Keywords—Petro-mineralogy, phosphorites, sallopat, apatite.

I. INTRODUCTION

PHOSPHORITE is a non-detrital sedimentary rock bearing high amount of phosphate minerals [1]. Phosphorites or rock phosphate is used as a raw material for the manufacture of fertilizers in the form of mono-ammonium phosphate, diammonium-phosphate, superphosphate and triple phosphate. For enhancement in agricultural production, prospecting of phosphorite or rock phosphate had been in great demand. This is due to adequate concentration of element P (phosphorus) which in turn is a critical and non- renewable element for fertilizer production upon which global fertility depends [2]-[4]. Apatite mineral is an important host of phosphorus element with other constituents as calcium, fluorine and chlorine. Therefore, the important mineral species of phosphorite belong to apatite family.

Sallopat phosphorites deposit in India was discovered by Geological Survey of India in 1969 [5]. Due to scarcity and high demand of phosphorite, Sallopat and its surrounding areas have been subjected to prospecting from time to time.

Kunwar Farahim Khan is with the Department of Geology, Aligarh Muslim University Aligarh, India (e-mail: farahimamu@gmail.com).

The previous investigators have carried out their findings on various aspects of the area as phosphorite prospecting [5], stromatolites [6], geological mapping [7] and deformation pattern [8] etc. However, petro-mineralogical aspects of the deposit by modern techniques have not been studied in detail.

Present study is an attempt to observe and describe, with the help of modern techniques, the mineralogical characteristics, nature, distribution pattern, optical behavior and texture of phosphate minerals and associated gangue in order to delineate their formation in the depositional basin of the area. Moreover, the findings in this paper may be helpful in the interpretation of environmental conditions prevailing at the time of deposition of these phosophorites in the study area. Further, these may be used as a guiding tool for researchers in order to formulate a genetic model for such type of deposits of similar geological setting in the world.

II. GEOLOGICAL SETTING

The regional geology of Banswara district of Rajasthan is represented by the sequence in Table I. In this sequence, the phosphorite deposit is hosted by the Aravalli Super Group which is considered to be a host of a unique assemblage of Precambrian Stromatolitic phosphorites [8]. Sallopat phosphorites lie at $23^{0}10'35''$ latitude and $74^{0}10'00''$ longitude. The rocks of the study area constitute the youngest Lunavada Group [9] comprising a variety of metasediments that form shelf sequence of the Aravalli Super Group. The Aravalli Super Group (2500 to 3300 Ma) is overlying the Archaean basement of gneisses and granites (Banded Gneissic Complex) with an intense unconformity [10]. The maximum Pb/Pb isochron age of Aravalli Super Group is 2200Ma as suggested by [11] and [12].

The Kalinjara formation of Lunavada Group (Table II) in descending order is composed of phyllite-subgreywacke, dolomitic limestone, orthoquatzite, stromatolitic phosphorite, arkosic dolomitic limestone, meta-conglomerate and manganiferous phyllites [13]. The eastern and western parts are covered by high flat hills of deccan traps. The exposed metasediments of Sallopat area are folded, sheared and represented by meta-arkose, conglomerate, schist, quartzite, dolomite, calc-schist and predominant phyllites, Fig. 1. The Sallopat phosphorite deposit is associated with interbedded dolomite, variegated chert and calcareous quartzite [14]. Exposures of phyllites and mica-schist are confined to lowlying areas.

Stromatolitic dolomite is the host rock for phosphorites and

occurs as lenses within phyllites and schists. The best exposures are seen from the south of Sallopat to Khunta Galia in the NW with a maximum surface width of 1.5 km. There are numerous chert intercalations of varying dimensions in dolomite. These interclations range from 1 to 250 m in length and few centimeters to 5 m in width. Sallopat phosphorites are found to occur in five different forms viz. stromatolitic, banded, massive and brecciated.

Stromatolitic phosphorite is composed mainly of phosphatic stromatolites occurring in bioherms. They are bluish white and light pink colored set in a dolomitic matrix. At places they are pressed due to folding. Banded phosphorite shows thin bands of phosphate-calcite, muscovite and quartz. Banded type contains thick regular veins and stringers of bluish grey color within the dolomite. Massive phosphorite is similar to grey or pinkish cherty quartzite and, at places, thinly laminated. Brecciated phosphorites are blue grey to light grey in color in the form of fragments embedded in a dolomitic/siliceous matrix [14]. The phosphorite laminae in the stromatolite represent organic-rich layer of the algae whereas the nonphosphatic layers represent precipitation of calcium carbonate.

TABLE I Regional Stratigraphy [15], [16]		
Succession	Lithology	
Deccan Trap Volcanics (upper Cretaceous~ 100 Ma)	Basalt, Related Dykes,	
Godhra Granite (Neo- proterozoic ~1000 Ma)	Granitic intrusions	
Sediments of, Delhi Super Group (Meso- Proterozoic ~1700-1400 Ma)	Quartzite, conglomerate, arkoses, phyllites, Green schist to granulite facies	
Volcano-sedimentary, Aravalli Super Group (Paleo Proterozoic ~2300-1800 Ma)	Carbonate- arenite, argillite, metavolcanic assemblages	
Banded Gneissic Complex		

TABLE II			
STRATIGRAPHY OF ARAVALLI SUPER GROUP [13]			
Group	Formation	Lithology	
Champaner Group	Lambia Formation	Metasubgraywacke, meta-conglomerate, gneiss	
	~~~~UNCO	NFORMITY	
	Wagidora Formation	Metasubgraywacke, mica schist, pebble and quartzite	
Lunavada group		Phyllite Felspathised-mica schist	
	Kalinjara Formation	Quartzite	
		Dolomite	
		Stromatolitic dolomite (Phosphorites)	
		Petromict-meta-conglomerate	
		Manganiferous phyllite	
	~~~~UNCO	NFORMITY	
Synorogenic granite & gneiss			

III. MATERIAL AND METHODOLOGY

Sampling was carried out with the help of the geological map of the area and 50 fresh representative samples of regional lithological strata were collected from the field at determined intervals. Microscopic study was done for optical behavior and mineralogical characters of the phosphorites.

In order to generate better diffraction pattern of a mineral, the phosphorite samples were powdered to around -200 mesh size. This powder was kept into glass slide holder and loaded on the sample of XRD instrument. The relevant diffraction data were generated by Panalytical-Empyrean X- ray diffractometer using nickel filtered K α radiation at Indian Institute of Technology (IIT), Bombay. The Instrument was run at 45kV generator voltage, 40 Ma tube current with fixed 0.5 divergent slit. The scan carried out over a range of 40 to 890 20 with a scan rate of 0.01° 20/s.

Resultant diffractograms were used for mineralogical interpretation. The peaks obtained from diffractograms were cautiously measured and the minerals were recognized by the conversion of 2θ to 'd' values with help of table of National Bureau of Standard series 10 of US Department of Commerce. The mineral identification was done with measuring intensity of each reflection against their respective d values. Highest value of reflection or peak was considered as 100 and each reflection was converted to nearest whole number with respect

to 100 percentile maximum reflection. Such process was done to get a definite intensity ratio.

The obtained mineral reflection data were matched with mineral identification charts of (JCPDS) cards and also with X'pert HighScore plus® software.

Rock samples were broken into small pieces for SEM studies. One part of these pieces was used to prepare thin sections for the SEM studies and other part was fixed with carbon tape on a brass stub without touching. These stub fixed samples were coated with a thin coating of Platinum by platinum sputter cotter.

Prepared samples were examined under JEOL JSM- 7600F FEG-SEM attached with EDS analyzer at diverse magnifications to observe shape, size and nature of grains of phosphorite minerals. Photomicrographs of thin sections of phosphorites were taken with help of Nikon SMZ800 camera assembled with optical petrological microscope at National Geophysical Research Institute (NGRI), Hyderabad.

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Fig. 1 Geological map of Sallopat area of Banswara district, Rajasthan, India [8]-[14]

IV. RESULTS AND DISCUSSION

Petro-mineralogical study of phosphorite samples reveal that there are light to dark grey cryptocystalline to microcrystalline phosphate laminae which contain more than one mineral species of apatite family named as apatite-(CaF) previously known as fluorapatite and apatite-(CaOH), Fig. 2 (C). Between crossed nicols, the color of phosphate mineral is light grey occurring in lenticular and pelletal form, Fig. 2 (B). The mineral is anisotropic having gradational boundaries with adjacent laminae of fine grained calcite. At places the grains of phosphate minerals are intermixed with calcite grains indicating the replacement of carbonate material by phosphate, Fig. 2 (C). Stromatolitic phosphorite shows alternate dark and light colored concentric rims in crossed nicols. The dark colored rim is composed of phosphate material and organic matter whereas the light colored rim shows quartz, calcite and dolomite minerals, Fig. 2 (D). Dolomite and calcite are dominant carbonate gangue minerals. Dolomite is colorless to vellowish showing perfect rhombs. Calcite is colorless to light grey in plane polarized light showing bright interference colors between crossed nicols. It is cryptocrystalline to coarse grained showing subhedral to euhedral crystal forms with rhombohedral cleavage. Polysynthetic twinning parallel to short and long diagonals of rhomb is observed. Calcite shows high birefringence, twinkling and the effect of chemical corrosion, Fig. 2 (F). Quartz is found to be distributed in the entire rock mass forming major part of the matrix. The grains are anhedral showing grey of first order interference color and wavy extinction. Quartz is found to occur as microcrystalline silica and at places detrital quartz associated with phosphate material, Fig. 2 (F). The elongated laths of muscovite embedded in dolomite and phosphate are seen. Muscovite is showing bright pinkish interference color, Fig. 2 (E).



Fig. 2 Photomicrographs of Sallopat Phosphorites; (A) Perfect hexagonal apatite crystal (A=Apatite, O= Organic matter), (B) Phosphate pellets, (C) Phosphate laminae (Pl) and alternate concentric rims of (C=Calcite, Q=Quartz, D=Dolomite), (D) Stromatolitic Phosphorite showing alternate rims of calcite-quartz (Cq) and organic matter (O), (E) Muscovite (M) embedded in phosphate (P) and Dolomite (D), (F) Mutual replacement of carbonate silica and phosphate material

Mutual replacement of carbonate, silica and phosphate material has been observed in thin section of phosphorite samples, Fig. 2 (F). At places organic matter is partially replaced by phosphate material forming a perfect hexagonal apatite crystal, Fig. 2 (A).

X-ray diffractometry reveal that Apatite-(CaF) is the dominant apatite phase having chemical composition $Ca_5F_1O_{12}P_3$ which is accountable for P_2O_5 concentration in Sallopat phosphorites. Apatite-(CaOH) having chemical composition $H_{1.84}Ca_{10}O_{25.92}P_6$. Fig. 3 (b).

Dolomite(D), Quartz(Q), Muscovite(M), Calcite(C) and Zeolite(Z) minerals are found in minor amount as represented by their peaks, Figs. 3 (a)-(c). These findings are correlated with Gafsa Basin of Tunisia and Sonrai Basin of India where

X-ray diffraction patterns show narrow peaks indicating great crystallites and well crystallized materials [17], [18].

As shown by XRD data, the concentration of Apatite-(CaF) varies from 41% to 71% whereas that of Apatite-(CaOH) is about 2.4%. The percentage wise descending sequence of minerals in Sallopat phosphorite suite is apatite-(CaF), dolomite, ankerite, quartz, muscovite, calcite, and zeolite.

The associated rock is composed of dolomite, quartz, fluorphlogopite (a variety of mica) and plagioclase minerals as shown by the peaks in Fig. 3 (d).

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Fig. 3 XRD patterns of the Sallopat block showing (a)-(c) Fluorapatite (FA), or Apatite-(CaF) quartz (Q), dolomite (D), zeolite (Z), ankerite (A), hydroxyapatite (HA) or apatite-(CaOH) and calcite (C) minerals in the phosphorites; (d) fluor-phlogopite (FP), quartz (Q), plagioclase (P) and dolomite (D) minerals in the associated rock

The SEM studies of broken piece of phosphorite show hexagonal, partially impregnated apatite crystals in cryptocrystalline carbonate material, Fig. 4 (b). The presence of crystalline apatite in phosphorites, which is resembled with the findings of [18], [19] indicates that phosphate was initially precipitated as amorphous or least-crystalline metastable phase which was later on transformed into crystalline apatite depending upon degree of super saturation of apatite-(CaOH) content. Equants or euhedral crystals of apatite in SEM image, Fig. 5 (b), support the recrystallization of apatite-(CaOH).

In some phosphorites, independent rod shape detrital apatite grains are available which might be a part of prior formed phosphorites Fig. 6 (b). The EDX pattern of SEM images of the samples is giving an elemental pattern for P, Ca and O of phosphate minerals in the form of peaks which is an essential part and proof for the members of apatite family, Figs. 4 (c), 5 (c), 6 (c). Mutual replacement of carbonate and phosphate minerals is commonly shown by SEM image in Sallopat phosphorites Fig. 7 (b).

Presences of bundles of microbial filaments are shown in Fig. 8 (b). These phosphorites may be due to microbial activities involved in their formation. These findings are corroborated with those of [20]. The microbial filaments of organic matter may suggest that the deposition of phosphate may have taken place in shallow marine oxidizing environmental conditions.

Alternate concentric rims of stromatolitic structure of phosphorites and presence of microbial filaments of organic matter may suggest that the deposition of these phosphorites might have taken place in shallow marine oxidizing environmental conditions. The precipitation was controlled by the biogenic activities. The occurrence of phosphate minerals in different forms and texture indicate a change in the energy conditions and environmental vicissitude at the time of deposition followed by some replacement and diagenetic processes.



Fig. 4 SEM image showing crystalline hexagonal crystals of apatite embedded in carbonate material



Fig. 5 Recrystallisation of apatite



Fig. 6 SEM image of rod shaped detrital apatite grain



Fig. 7 SEM image showing replacement of carbonate by phosphatic material



Fig. 8 SEM image showing microbial filaments

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