CHAPTER - VIII
GENESIS OF PHOSPHORITE
INTRODUCTION:

The genesis or origin of phosphorites is a controversial problem. The complexity of the processes involved in the formation of marine phosphorite deposits has been the subject of study by a large number of investigators for a fairly long time. Several divergent views regarding the deposition and accumulation of phosphorites have earlier been put forward. However, from a general review of the work on the important phosphorite deposits of the world, it may be said that the formation of phosphorites was essentially controlled by certain interrelated geologic, biogenic and chemical factors.

As regards to their sources, the phosphorites were earlier supposed to have been derived from coprolites (see Sollas, 1873 and Penrose, 1888), Plentons (see Murray and Renward, 1891), fish remains following their catastrophic deaths (see Blackwelder, 1915, 1916) and residual accumulation at unconformities (see Grabau, 1919).

A departure from earlier thinking on the source and formation of phosphorites was first made by Mansfield (1920), who postulated that the phosphate of Phosphoria Formation of North America owed its origin to the progressive replacement of originally calcareous oolitic deposits by the phosphates present in sea water in a soluble state.
Mansfield (1940) made an attempt to correlate the periods of phosphate deposition within the geologic record with periods of widespread volcanism. He thought that unusual addition of fluorine to the ocean from hydrofluoric vapour emanated from volcanoes, might have lowered the solubility of apatite resulting in its chemical precipitation.

The modern theories of phosphorite formation are more or less modelled after Kazakov (1937, 1938 a), who first suggested a model of direct inorganic precipitation of marine phosphorites. He proposed that phosphate facies are encountered mainly in the border zone between shallow water platform sediments and the deep water geosynclinal accumulation. He also envisaged two types of phosphate deposits. The platform type phosphorites having low to moderate $P_2O_5$ content and being usually nodular are associated with glauconite and arenaceous materials. The geosynclinal phosphorites are usually bedded, platy, flagstone type, high in $P_2O_5$ and associated with limestones, blackshales and cherts.

According to Kazakov (1937, 1950) the $P_2O_5$ content of marine waters increases with depth from a minimum in the zone of photosynthesis to a maximum at about 500 metres depth as the pH and temperature decreases and the partial pressure of CO$_2$ increases. At greater depths, the $P_2O_5$ content decreases as slightly as the CO$_2$ content drops. The sea water at first gets saturated with calcium carbonate which is immediately precipitated, and later, with calcium phosphate.

According to Sant (1979), by and large the Kazakov-McKelvey concept of the role of the 'oceanic upwelling' in
the formation of marine phosphorite (which contributes a major share to the phosphate resources of the world) has been accepted, though there is considerable disagreement on the actual process of deposition, precipitation and fixation of phosphate in sea water. It has, however, been established that the formation of sedimentary phosphate is controlled by certain specific factors such as palaeogeography, palaeotectonics, sedimentary environment and lithoassociation. The right type of environment should also necessarily be prevalent for a long period to facilitate better and large scale deposition and formation of the phosphate. Existence of such environments in various parts of the world at different periods in its history is evidenced by the occurrence of several major marine phosphate deposits in geological formations ranging in age from Cambrian to Tertiary.

As evidenced by the known phosphate occurrence in India, such conditions prevailed, at least in past, during the Precambrian, Aravalli, Bijawar, Cuddapah times and also during the Jurassic and Cretaceous - Eocene Periods.

Ocean circulation gyres driven by the trade winds and westerly winds have strong divergent upwelling in the trade wind belt on the eastern sides of the oceans; these gyres have been suggested as the mechanism for marine phosphogenesis (see Kazakov, 1937 and 1950; McKelvey and others, 1953; McKelvey, 1967). However, the most effective circulation systems in so
far as phosphogenesis is concerned are equitorial upwelling during episodes of transition from high level, warm oceans to low land cold oceans. The effectiveness of the upwelling of either type depends on the interplay between deep-ocean richness of phosphorus and the intensity of upwelling (see Kazakov, 1937; Klemme, 1958; Kelvey, et al., 1959; Strakhov, 1962; Sheldon, 1964; Legeres, et al., 1967; Saffir and Rubin, 1970; Sheldon, 1980).

According to some authors, phosphorites may be formed by replacement of CaCO$_3$ by phosphate solutions. This assumption is based on the fact that the conversion of calcite into carbonate apatite may take place at PO$_4^{3-}$ and Ca$^{+2}$ concentrations considerably below those required for apatite precipitation. The formation of carbonate apatite by calcite replacement has been investigated in detail by Ames (1959) and followed by Pevear (1966, 1967).

Most economic phosphate sediments of marine origin, occurring typically as stratified deposits, constitute highly anomalous sediments deposited under very specific conditions, resulting in P$_2$O$_5$ concentrations which may be up to 100-125 times that of the crystal average of 0.23% P$_2$O$_5$. Theories on the formation of sedimentary phosphate deposits have been concerned chiefly with establishing how phosphate in solution in sea water could be concentrated sufficiently to produce very large quantities known to exist as phosphate deposits, some of which may extend over hundred or thousand of square kilometers. Most of the theories fall into one of 3 groups, according to whether emphasis is placed on physico-chemical,
biological or diagenetic processes as the controlling factors in concentrating phosphate in the sediments (see Gulbrandsen, 1969; Riley, 1968; Warin, 1968; Cook, 1976 a and Trudinger, 1979).

Studies of recent phosphate formation in the off-shore areas of Peru-Chile (see Baturin, et al., 1972; Veeh, et al., 1973; Manheim, et al., 1975; Burnett, 1977; Burnett and Veeh, 1977) and S.W. Africa (see Baturin, 1969, 1971; Senin, 1970; Calvert and Price, 1971; Roman Kevid and Baturin, 1972; Summerhayes, 1973; Price and Calvert, 1978), indicate that there are three main requirements for the formation of contemporary phosphorites, i) an oxygen minimum layer impinging on the sea floor; ii) a limited supply of terrigenous and carbonate detritus and iii) strong persistent upwelling. The oxygen minimum layer is usually between 100 and 500 metres of depth in the present oceans, and thereby encroach into shallower water during periods of slowed oceanic circulation (see Emdyanov and Senin, 1969 and Piper and Codispooti, 1975 and Fishcher and McArthur, 1977).

Bachra, et al. (1965) and Martenand Harris (1970), on the basis of their experimental studies, proposed that the presence of Mg$^{2+}$ ion in solution resembling sea water inhibit the precipitation of apatite. However, they suggested that there was probably a threshold of Ca/Mg ratio above which apatite could precipitate. The diagenetic mobilization of phosphorus and the formation of apatite concentration from interstitial waters in the model proposed by Bushinskii (1966) and favoured by Kolodny (1978) in a recent view of the genesis
of phosphorites. This is also the opinion of the Price and Calvert (1978) based on a geochemical study of phosphorites from the Namibian shelf. They concluded 'the origin of the phosphorites is believed to be the result of the diagenetic precipitation of the phosphorus within sediments'.

The central California margin phosphorites are the result of direct interstitial precipitation. This is supported by recent experimental data which have demonstrated for the first time. They precipitate from marine waters simply by increasing the phosphorus and fluoride content via degradation of organic material (see Gulbrandsen, 1966; Cristopher and others, 1970 and Gulbrandsen, et al., 1984).

Al-Bassam, et al. (1983) reported that most of the phosphate in the Campanian-Masstrichtian depositional basin in the part of Iraq was syngenetically precipitated as phosphate mud at the sediment water interface, mixed with fine quartz, clay minerals and carbonaceous matter. Further, they added that the intensity of phosphate precipitation was greatly increased in certain periods only giving rise to the phosphate bearing horizon, when physico-chemical condition favourable for apatite precipitation and preservation occurred.

According to Mauricce Slansky (1986) phosphate deposits are mainly supplied with phosphorus from deep oceanic reserves by means of upwelling currents. Phosphate minerals precipitate from the interstitial water near the water sediment interface and the margins, particularly the upper boundary of O₂ minimum layer. Oxidizing encourages stability of the humic compounds formed from planktonic organic matter; the humic acids seem to
play a direct role in the phosphate precipitation and in the formation of phosphatic particles.

According to Baturin (1989), sedimentation, diagenesis and subsequent transformation control the compositions of marine phosphorites. The role of the first two factors can be judged from the compositions of the phosphorites and the enclosing sediments. However, phosphorites are often redeposited, so the effects on their compositions from the original sediments must remain an open question. One of the few reliable ways of considering this is to examine recent (Holocene) phosphorites in the coastal part of the Namibia shelf, which were formed in recent diatom muds by diagenesis.

Hence, there are three main schools of thought regarding the genesis of phosphorites. Some propose an organic origin based on their association with true coprolites and skeletal materials (see Penrose, 1888). Others proposed a replacement from shells and sponges (see Fisher, 1873; Traask, 1939; Waggaman, 1952; Graham, et al., 1954; Gulick, 1955; Ames, 1959; LeGeros, 1965; Degens, 1965; Gulbrandsen, 1960, 1966; Krauskopf, 1967; Valdiya, 1972; Patwardhan and others, 1975; Verma, et al., 1975 and Srivastava, et al., 1978).

Another school of thought proposed an inorganic origin of phosphorites (see Kazakov, 1937; McKelvey, 1959, 1967; McKelvey and others, 1953; Cheney, 1955; Chenny, et al., 1959; Sheldon, 1964; Maughan, 1966; Yochelson, 1968; and Israel, 1976 a, b and 1978).

The area under study has also been investigated by several workers and various views regarding the origin have
been put forward. According Ravishankar (1955) the chert member of Nigalidhar, Korai, Mussoorie and part of Garhwal synclines which now occupy separate areas represent part of the same depositional basin. This basin might have been either a sealed, inland extension of a sea gulf or embayment from north or a sheltered depression in the shallow marine restricted circulation with undulatory floor topography. The cycles of deposition were presumably controlled by alternate marine transgression and regression, possibly due to an oscillating movement of the basin floor. The phosphate rock might have been formed by the biochemical process with the phosphate derived from decay of phytoplankton, algae, river and sea water.

Rao and Rao (1971) proposed that the chemical composition of the Mussoorie phosphorites falls within the range of carbonate hydroxyl-fluorapatite which usually occurs in the form of marine phosphorites. The composition is also in conformity with the carbonate, phosphorite gradation. Patwardhan and Ahluwalia (1973, 1974) suggested a biochemical mode of origin for the Mussoorie phosphorite deposit on the basis of some geological and petrographical criteria. They believed in an indirect role of organism whose productivity was supported during the oceanic upwelling for the deposition of Mussoorie phosphorites.

On the basis of rare metal studies, Sharma (1974) suggested that the Mussoorie phosphorites appear to be the direct chemical precipitates from phosphate rich upwelling currents.
Chaudhari (1978) discussed the origin, transportation and accumulation/precipitation of phosphate deposits in Mussoorie and other areas, invoking almost all types of mechanism postulated for phosphorite genesis. According to Patwardhan and Panchal (1984), it is felt by more and more previous workers that some kind of a trapping mechanism for the accumulation of the phosphorus carried up the continental margin by the upwelling currents of oceanic water is necessary for the formation of sedimentary phosphorite deposits. The mechanism should obviously be related to the regional basin topography and palaeogeographic and palaeotectonic conditions.

Recently, Ahluwalia (Abstract volume, 1989) proposed that the Tal phosphate of the Himalaya and many other phosphorites of the world cannot be exclusively categorized as organic or inorganic in origin and more often than not, result from a suitable combination of these two factors.

In the light of the foregoing views of phospho-genesis, an attempt has been made to discuss the geologic, biogenic and chemical controls on the formation of phosphorites of the study area.

Geologic Controls:

Cook and McElhinny (1979) suggested that the Cambrian phosphate deposits of Australia were laid down generally in the east-west sea way extending from Australia into Asia and perhaps into Europe. They proposed that the way these deposits were laid down on the southern side of the sea way was
analogous to the Mesozoic Tethyan situation. They believe that probably there would have been strong currents flowing through the sea way 'producing high productivity as a result of coastal entrainment and upwelling, and particularly as a result of intense dynamic upwelling associated with topographic highs'.

Riggs (1979) in a paper entitled 'Phosphorite sedimentation in Florida-A model Phosphogenic system' described that the formation and subsequent accumulation of phosphorite sediments sufficient to comprise a major stratigraphic unit with the potential of becoming an economic deposit requires a very highly specialized set of environmental conditions in a very specialized geologic setting. Only if all of a complex set of tectonic and environmental variables are just right will there be a significant precipitation and major accumulation of sedimentary phosphorites. Such stratigraphic occurrences represent sediment systems which are geologically quite abnormal.

Riggs (1979) pointed out that the structural framework which controlled the formation and deposition of phosphorites in Florida was a series of topographic highs. Extensive coastal, shallow near shore shelf, and platform environments occurring around the highs were the sites of major phosphorite sedimentation. Phosphorite precipitation took place as upwelling sea water moved across the shallow platforms and into coastal environments. Further, Riggs argued that phosphorite was deposited wherever phosphorus sources were adequate, the current and geochemical systems were appropriate, and shallow marine environments had the proper geometry.
The ultimate magnitude of phosphorite deposition depends on the size and extent of the structural system, the duration of the phosphogenic system through geologic time, and, of course, the volume of phosphorus provided from the sea or from other sources.

The experimental data available on inorganic precipitation of phosphorites (see Krumbein and Garrels, 1952 and Gulbrandsen, 1969), pertains in reality to the mineral apatite which is seldom the form in which marine phosphorites occur. However, presuming that an abiotic precipitation of phosphorites (apatite) should be possible under some geological control.

Most of the older phosphorites deposits show pronounced laminations on a time scale of probably a few years to a few hundred years with thin laminae of shale, mudstone, carbonate or chert. These alternations result from local changes, e.g. shifting of river mouths or of morphological features on the shallow sea-bottom, slight changes in the direction and strength of currents, small scale temporary oscillation, variations in the amount of rainfall on the nearby land and a variety of similar causes (Kazakov, 1937; McKelvey, 1963; Sheldon, 1964; Bentor, 1980 and Boyle, 1984). In the study area, the association of three rock types namely, limestone, chert and shale and preservation of primary bedding and laminations in the bedded phosphorites indicate a change of flow of direction of ancient rivers, shallow sea bottom and strength of low sea basinal currents during and after the deposition of the phosphorites.
According to Liang and Chang (1984), there are two models of deposition of phosphorite and its host rock in an appropriate medium, viz., 1) if the medium is slightly acidic to alkaline, the depositional order will be (from bottom to top): dolomite, phosphorite, limestone (calcite); and silica (quartzite and chert, etc.); and 2) if the medium happens to be alkaline to acidic, the depositional order will be (from bottom to top): silica, limestone, phosphorite and dolomite. The stratigraphic sequence of deposition (from bottom to top) in the study area is limestone, chert, phosphorite and shale. This sequence is somewhat similar to the second model of deposition proposed by Liang and Chang (1984) and indicates slightly alkaline to weakly acidic medium of the basin.

Some workers assumed that some pelletal and oolitic phosphorite deposits must have been rolled out by currents to give them their typical rounded/oval shape (see Folk, 1959; Sheldon, 1980; Bagti and Mundepi, 1984). The laminations indicated that the environment of phosphorite deposition had much less energy, leading to the inference that the size distribution of phosphorites is not due to mechanical sorting by currents but due to certain processes of accretionary growth (see Gebelien, 1960; Basu, 1984).

Feas and Riggs (1965, 1968), Baturin (1971) and Riggs (1979 a) proposed that the pellets of the Florida phosphorite deposits (USA) were formed by erosion of an apatite-mud or microsphorite and subsequent rounding and abrasion as the sediment was being reworked.
Tooms, et al. (1969); Reeves and Saadi (1971) and Calvert (1977) proposed that well developed apatite pellets are formed diagenetically in the muds.

In the study area the occurrence of ovulitic to oolitic shaped collophane indicates poor transportation, rounding and accretions of phosphatic minerals. The pelletal shape of collophane may be due to reworking, and diagenetic origin.

According to Bremner (1979), pelletal phosphorites show evidence of having originated by direct precipitation of apatite. He concluded that precipitation occurred in shallow warm lagoons which were periodically disturbed by storm generated waves. Pellets resulted from the disruption of semi-lithified collophane in upwelled water circulating into the lagoons.

Slightly deformed and semispherical shape of the pellets suggest that the excreted pellets remained soft during subsequent transport and became indurated only prior to their burial by subsequent sedimentation.

The presence of amorphous, crypto- to microcrystalline apatite phase in a few of the samples may be on account of direct inorganic precipitation of apatite. The thin laminations observed in the bedded phosphorites indicates their precipitation in a low energy shallow marine water basin.

At places some lenticles in lenticular phosphorites are aligned oblique to the bedding plane indicating that either some penecontemporaneous deformation occurred before compaction possibly due to agitation of the basin floor when the sediments were in plastic stage, or it may also be
due to effects of current action.

Sheldon (1964 a) was first to point out that the palaeolatitudinal distribution of ancient phosphorites matches the latitudinal distribution of young phosphorites, with both falling within 40° of the equator. Subsequently, Sheldon (1964 b) and later Freas and Eckstrom (1968), applied palaeolatitudes and palaeogeographic reconstructions to the search for new phosphate deposits. The palaeolatitudes of all deposits show a spread from about 0° to 70° but with a clear maximum within 20° of the palaeoequator. When only the major deposits are taken, the two latitude peaks are more clearly defined with peaks between 10° to 20° from the equator. This supports the view that phosphate deposition is most abundant at low latitude locations with a preference towards a sub-equatorial (10° to 20°) location rather than an equatorial one (0° to 10°) site (see Cook and McElhinny, 1979; Birch, 1980; Al-Bassam, et al., 1983).

According to Long Kang and Zhendong (1988), warm and dry palaeoclimate suggests a low latitude epicontinental sea along the ancient continental margins. Before the overlapping of the Liuping Formation on the Daxing Formation, there had been an uplift in the region. After that the crust became more stable, completing the transformation of geosyncline to platform and favouring the deposition of phosphorite (see Long Kang and Chendony, 1988).

The phosphorite deposits of Mussoorie lie between latitudes 30°25'N and 30°30'N which indicates warm and dry palaeoclimatic conditions with low latitudes, epicontinental
sea basin along the ancient continental margin. It may also be suggested that the basinal uplifting might have caused the initiation of the geosynclinal condition followed by platform structure on which the phosphatization processes took place. This is corroborated by the occurrence of bedded (geosynclinal type) and nodular (platform type) phosphorites in the study area.

The open shelf in turn faced deep water euxinic basin on which pyrite carbonaceous shales were deposited both under acidic and strongly reducing conditions, (see Gulbrandsen, and Pettijohn, 1957; Mason, 1966; Pettijohn, 1969; Beaelkes, 1984). There is a close link between phosphate occurrence and the complex clay minerals, both tending to occur at horizons of reduced sedimentation (see Fuller, 1979). A horizon of black shale associated with phosphorites suggests a gradual change in the basinal conditions from euxinic (black shale) to aerated intertidal environment at the time of deposition (see Kanwar and Ahluwalia, 1980; Liang and Chang, 1984; and Verma, 1984).

In the outer Lesser Himalayan region a long narrow linear basin was formed which accommodated Blaini-infra Krol-Krol-Tal sequence of the Krol Belt. Restricted nature of this basin with initial deposition of Boulder Bed suggests faster rate of erosion of the provenance on the north. As a consequence the terrigenous influx became minimum, allowing precipitation of carbonates of the Krol Formation followed by phosphate accumulation and deposition in Lower Tal times.
However, the nature of cover rocks of phosphorite beds/bands and the arenaceous upper Tal sequence suggests the upliftment of the provenance again to such heights that it became capable of supplying terrigenous material to the Krol-Tal basin due to faster rate of erosion and denudation. This process perhaps continued till the fossiliferous shell limestone of upper most Tals was deposited at the Subathu sea (Eocene) that invaded the entire the outer Lesser Himalaya and considerable parts of the Inner Lesser Himalaya depositing the Nummulitic rocks suggesting that this transgressive phase did not last long and the Krol Belt rocks were also uplifted due to early Tertiary orogenic impulse and a fore deep was formed in which molassic Siwaliks were laid down (see IGCP Project - 156, Phosphorite; ed. G.S.I. and P.P.C. Ltd.).

According to Radcliffe, et al. (1984), on the basis of lithology and the occurrence of primary sedimentary structures it is suggested that the sediments of the Lower Tal Formation were deposited in tidal flat environment. Two idealised facies viz., intertidal and shallow subtidal can be chiefly recognised in the Lower Tal Formation, whereas subtidal conditions prevailed during the deposition of Krol beds.

They further added that during Lower Tal sedimentation, some parts of the basin were deeper due to their restricted or sealed nature and this resulted in the deposition of chert and phosphate rock associated with carbonaceous and pyritiferous black shale.

The Mussoorie phosphorites are associated with a carbonaceous shale-chert-limestone succession which is
recognised as an ideal phosphatic suit of rocks or lithological setting for the deposition of marine phosphorites. From the nature of these associated rocks and their superposition it is evident that they are typically geosynclinal type of deposits. A detailed study of lithology and aerial distribution of the rock types of the chert member indicates that the surrounding ancient land masses, that were probably low lying areas, had very little drainage thus restricting the supply of detrital material which included fine quartz and mud during the deposition of the chert members. The general paucity of the terrigenous sediments also suggests that the depositional basin was bordered by tectonically stable, low land area with mature topography. This presumption leads to believe that climate was warm but arid and therefore, only few rivers flowed into the basin from the bordering land, bringing very little detrital material.

It appears plausible that due to marine upwelling the terrigenous phosphatic material, that had accumulated in marine environment got concentrated in a more or less restricted basin of deposition occupying the arms of a pre-existing sea that also probably extended over the shelf areas. Certain favourable physico-chemical conditions supported the growth of colonies of algae in this part of the ancient sea to maintain their metabolic activities. The various submarine highs divided the Tal phosphorite basin into sub-basins, and the sub-basinal topography further restricted the circulation of the bottom waters leading locally to stronger euxinic conditions even in an otherwise shallow marine basin.
The variable trend of concentration of phosphates in these deposits may be partly due to the removal of excess soluble silica and lime with subsequent minor structural disturbances, viz., brecciation, pulverization and fragmentation aided by collapsing action by meteoric water, which subsequently brought out natural upgradation of the phosphorites.

The granular and pelletal phosphorites might have been formed at the high energy region near the shoreline areas by the continuous working of soft heterogeneous (dirty) mud by waves and currents. Local transportation and redeposition of the granular phosphate ingredients were probably responsible for the roundness of these grains, their sharp and definite contact with cementing materials and the presence of broken pellets. On the other hand, the fine-grained phosphate mud settled out and accumulated as cementing material away from the shore in the deeper parts of the basin where wave action was less effective. Remnants of the original phosphate mud is retained in the host rocks as phosphate cement.

**Chemical Controls:**

According to Subramanian (1980), most of the world's phosphate production comes from marine phosphates. Hence any treatment to explain the mechanism of phosphate formation should take into account the physical chemistry of the sea water. Association with the carbonate minerals and the presence of black shale and pyrite can easily be explained in the light of various mineral equilibria in the system containing CO\(^{-2}_3\).
PO_4^{3-} and S^{-2}. The effect of P and T conditions on such equilibria can explain the occurrence of various deposits in the deeper part of the marine environment.

Selective precipitation, dissolution, exchange reaction with animal shells, sorption by organic and inorganic compounds in the marine environment, isomorphous substitution of a number of cations and also of some anions are the various mechanisms that can account for the compositional variability of the phosphate minerals. Fe^{2+} is an effective ion to remove the phosphates from water in reducing environments (see Subramanian, 1980).

According to him, some important features of phosphorites of interest to its chemistry of formation are:

1. Association with carbonate minerals.
2. Presence of black-shale, pyrite and other features of reducing environment.
3. The role of organic and inorganic processes in influencing the concentration and precipitation of phosphates.
4. Occurrence of sedimentary apatite involving extensive isomorphous substitution of both cations and anions.
5. The vast areal extent of phosphorites considering the low P content of the present and past sea water.

According to McArthur (1978) the fact that different types of phosphate, deposited in the same basin at the same time may show large differences in their chemistry, argues against the formational environment being important in producing the variations in the contents of Na, CO_3 and SO_4 in marine carbonate-fluorite. Furthermore, phosphorite genesis appears
to have taken place on an open shelf environments in contact with sea water (see Baturin, 1969, 1971; Manheim, et al., 1975). Fluctuations in the chemical composition of sea water did not occur either to a sufficient degree or with sufficient rapidity to account for the variations.

Thus, the chemical factors triggering the formation of phosphorites are reviewed and discussed. The following chemical factors are supposed to be effective in controlling the formation and deposition of the phosphorites of the study area:

1. Effect of pH
2. Effect of Eh
3. Effect of pressure and temperature
4. Effect of geochemical behaviour of significant major and trace elements.

1. Effect of pH:

The acidity or alkalinity of an environment is an important factor in determining whether or not certain minerals will precipitate (see Pettijohn, 1984). Krumbein and Garrels (1952) had a pH of 7.8 (about that of sea water) as 'limestone fence'. Calcite is freely precipitated at this or higher pH values. According to Kazakov (1937), the precipitation of phosphorite takes place at pH value of about 7.1 and that of calcium carbonate at pH values between 7.1 and 7.8. Simultaneous precipitation may also take place when pH is about 7.8, but the ratio of calcium carbonate would be
much higher in this case due to its high absolute solubility (see Krumbein and Garrels, 1952). According to Campbell (1962), phosphorite precipitates predominantly in the pH range 7.1 to 7.8 and calcium carbonate, when pH is above 7.8. McKelvey, et al., (1953) while discussing the genesis of phosphorites of the Phosphoria Formation of North America remarked that when cold phosphate-rich water upwelled into the larger shelving embayment from the ocean, phosphorite was deposited from these ascending waters as their pH increased along with the increase in temperature and decrease in partial pressure of CO₂. The carbonates were deposited from these waters when they reached more shallow depth at somewhat higher pH. Thus, it is reasonable to derive that chemical environment of phosphate precipitation is principally dependent upon pH conditions and controlled by variation in the partial pressure of CO₂.

Marten and Harris (1969) showed experimentally that Mg ions tend to inhibit apatite precipitation in the sea, and that at pH values of 7.5 - 8.0 this precipitation could take place with a Ca/Mg ionic ratio greater than or equal to 5.2, which is well above the value generally found in sea water, usually around 0.20.

Nathan and Lucas (1976) confirmed this lower limit of 5.2 for the Ca/Mg ratio for sea water with a pH value of 7.8-8.1.

Increase of pH causes coprecipitation of both calcite and apatite; the calcite/apatite ratio will be higher; since Ca⁺², PO₄⁻³ and CO₃⁻² all have single valence states, changes
in Eh cannot produce separation into carbonate rich and phosphate rich layers; hence the individual enrichment would have to take place within a narrow pH range. Relative to CO$_3^{-2}$, the Ca$_3$(PO$_4$)$_2$ is less soluble (the solubility product of CaCO$_3$ is $4 \times 10^{-9}$ as against $1.3 \times 10^{-30}$ for Ca$_3$(PO$_4$)$_2$). Hence, in the pH range 7 - 7.5 Ca$_3$(PO$_4$)$_2$ can first precipitate while CO$_3^{-2}$ remains in solution so long as the pH is buffered in that range. When pH increases to 8, CaCO$_3$ will precipitate (see Garrels and Christ, 1965).

In the study area, it has been observed that the phosphate, carbonate and silica have been occasionally found mutually replacing each other. This could be explained possibly by the physico-chemical conditions of the precipitation of the phosphate, carbonate and silica controlled by the pH of the marine environment. A little change in the pH of 7.8 might facilitate the formation of one or the other of these three sediments. Thus, pH in the study area presumably fluctuated around 7.8 as phosphate rock indicates pH values less than 7.8 but the associated dolomite and calcite indicate pH values greater than 7.8. The same pH range has also been reported by Sharma (1974).

2. Effect of Eh:

In a general way sediments are deposited under either oxidizing (aerobic) or reducing (anaerobic) conditions. The measure of the oxidizing capacity of an environment is the Eh or oxidation-reduction potential (see Mason, 1949; Zobell, 1946). According to Krumbein and Garrels (1952) and Teodorovich
(1955), the oxidation reduction surface, that is the plane separating the oxidizing from the reducing environment, may be above or coincide or below the sediment water interface. In more strongly reducing environments it is above the mud-water interface.

The primary precipitation or replacement $\text{Ca}_3(\text{PO}_4)_2$ need not be influenced by $\text{Eh}$, the state of oxygenation in a given environment indirectly plays a role by controlling the rate, extent and nature of release of $\text{P}$ from other sinks in the oceans. For example, it is observed that $\text{P}$ has a strong tendency to be associated with $\text{Fe}$ in many equatic environment. Bortleson and Fred Lee (1974) have indicated that $\text{Fe}$ and $\text{P}$ are positively correlated in lake sediments and that the oxidation conditions will control the rate of $\text{Fe}$ in either mobilizing or releasing $\text{P}$ to the water. Subramanian (1976) has suggested that $\text{Fe}$ and $\text{P}$ are cogenetic in fresh water as well as in estuarine environment, while Nariagu (1972) has experimentally verified the role of $\text{Fe}$ in $\text{P}$ mass transfer in the aquatic environment. In a very highly oxidising environment, $\text{Fe}^{+3}$ removes $\text{P}$ from water by the formation of sorbed complex on $\text{Fe(OH)}_3$ thereby making available only a small amount of $\text{PO}_4^{-3}$ for $\text{Ca}^{+2}$ to form apatite in the marine environment. Hence, for the continent-derived $\text{P}$ to reach the ocean for apatite precipitation the river should have positive but not extreme oxidising and acidic conditions. Changes in these parameters may trap the dissolved $\text{PO}_4^{-3}$ in the estuarine region where the $\text{P}$ could be sorbed by $\text{Fe(OH)}_3$ or clay minerals.
The narrow pH buffering required for the carbonate and phosphate separation can be generated by the tidal cycles whereby the continent derived fresh water (pH - 6.15, Livingstone, 1983) and the open ocean water (pH - 8.1, Turekian, 1968) can mix in changing ratios, first to give a more alkaline water to precipitate carbonate, and then to give a less alkaline water to precipitate the phosphate minerals. This perhaps is the geochemical process underlined by the term intertidal.

Usually conodonts, occasional fish remains, and spores and pollen are the fauna or flora of those shales formed in a highly reducing environment. A further indication of oxygen deficiency is an abnormally high (over 2 or 3 per cent) content of organic matter. Normal microbiological and scavenger action tend to destroy the organic residues which settle to the bottom. Inhibition of such action because of oxygen deficiency leads to an increase in these materials in the black shales and related deposits. Iron sulphides (pyrite or marcasite) signify a reducing and wholly oxygen deficient medium (see Krumbein and Garrels, 1952).

In the study area, the presence of conodonts (as reported by Azmi and his associates, 1980, 1981 and 1983), organic matter, low content of iron and association of pyrite and black shales with phosphorites suggest a reducing environment with negative Eh (see IGCP, Project - 156, Phosphorite, 1981) possibly due to restricted circulation.
3. Effect of pressure and temperature:

Since temperature affects the solubility of many minerals and gases, it has therefore, an important effect on chemical precipitation. At lower temperature the solubility of \( \text{CO}_2 \) is greatly enhanced. Hence the solution of calcium carbonate is promoted in cold waters and conversely precipitation of the same material is brought about by a rise in temperature. Temperature also affects the composition of mixed crystals or solid solutions. Shell carbonate is richer in MgO at the lower temperature (see Chave, 1954).

The data given by Berner (1971) indicates that the temperature ranges from 20°C at the surface to 2°C at the bottom of the oceans corresponding to a pressure change from 1 atmosphere to 500 atmospheres. Pressure and temperature have opposing effects on the phosphate solubility but the constant values for dissolved phosphate below 100 metres indicate that the pressure effect on the phosphate equilibria is negligible. On the other hand, because of the involvement of the gaseous phase of \( \text{CO}_2 \) in the carbonate equilibria, there may be quantitative changes in the carbonates that are associated with phosphate deposits formed at various depths; similar to the carbonates, phosphates dissolved at greater depth will be reprecipitated at the surface. The effect of temperature on these equilibria can be calculated from the standard chemical thermodynamic concepts (see Koltz, 1988), whereby solubility at any given temperature can be evaluated from known values at standard conditions.
Kramer (1964) calculated solubility products for carbonate fluorapatite, which shows small decrease in solubility of phosphate with increase in temperature over representative of natural conditions. The indirect effect of temperature is possibly due to the antipathetic relationship between temperature and CO$_2$ solubility, pH and temperature are naturally related. An increase in temperature is likely to cause an increase of pH and a decrease in solubility of phosphorite and vice-versa.

4. Effect of geochemical behaviour of significant major and trace elements:

According to Banerjee, et al. (1984), the availability of the elements in the formational environment and their ionic radii which determine the possibilities of inter element lattice accommodation control the percentage of an element in a rock and its distribution within various rock constituents. According to McConnell (1938), apatite represents a group of minerals containing Ca$^{+2}$ and PO$_4^{-3}$ as essential constituents with associated trace elements among which Mg, Mn, Sr, K, Na, Ba, Cr, Fe, Al, ASO$_4^{-3}$, VO$_4^{-3}$, SO$_4^{-3}$, SiO$_4^{-4}$, CO$_3^{-2}$, F$^{-1}$, Cl$^{-1}$ and OH$^{-1}$ are important.

It has been experimentally shown (see Bachra, et al., 1965; Marten and Harris, 1970) that Mg$^{2+}$ ions inhibit the precipitation of apatite probably because Mg$^{2+}$ compete with Ca$^{2+}$ in the apatite structure. Marten and Harris (1970) deduced some threshold values for the Ca/Mg ratio necessary
for apatite to precipitate from solution. The magnesium ions seem to retard the reaction (salinity) when Ca/Mg ratio approaches to 4.5 to 5.2. This ratio remains almost constant in normal sea water. Pore water is, however, known to vary greatly from the sea water values. Thus, it seems that diagenetic reaction occurring with anoxic sediment could raise the Ca/Mg ratio to the point (> 5.2) when phosphate may precipitate.

The experimental results suggest a path way for the genesis of apatite and indicate conditions for its formation, which could prevail within the sediments in very shallow water during the very early diagenetic stage (see Walter and Honov, 1978; Morse, 1979; Nathan and Lucas, 1981 and Lucas, 1984).

In the study area, the high Ca/Mg ratio may be due to preferential entrance of Ca\(^{+2}\) ions in carbonate apatite. The antipathetic relationship of MgO with CaO suggest that Mg\(^{+2}\) could be substituted by Ca\(^{+2}\) in the apatite structure and may also decrease the crystallite size of apatite by increasing the Mg ions as reported by Cruft, et al. (1965) and McConnell (1973). MgO has negative relationship with P\(_2\)O\(_5\). The chain of replacement between CaO-MgO-P\(_2\)O\(_5\) during phosphatization indicates that MgO acted as a catalyst in the process of replacement of CaO by P\(_2\)O\(_5\) (see Bachra, et al., 1965; Gullbrandsen, 1969; Marten and Harris, 1970, Atlas, 1975; and Burnett, 1977). The antipathetic relationship among these three oxides also indicates that surficial leaching had a leading role in increasing the P\(_2\)O\(_5\) content, predominantly
at the expanse of MgO. It, therefore, seems plausible that the replacement involving carbonates may be responsible for the increase of Ca/Mg ratio.

According to Slansky (1986) if the CaO/P_{2}O_{5} ratio is greater than 1.31, the increase may be either due to the substitution of PO_{4} by CO_{3} in the apatite, or to the presence of calcite or dolomite in the phosphorite. In the study area, most of the samples of phosphorites have CaO/P_{2}O_{5} ratio greater than 1.31, the most common substitution is that of PO_{4}^{3-} by CO_{3}^{2-}. Banerjee and McArthur (1991) have reported CaO/P_{2}O_{5} ratio in one sample of Mussoorie phosphorite as 1.20 well below the 1.32 for end member fluorite showing that there is a CaO deficiency in the sample which could be balanced by Al_{2}O_{3}.

The sympathetic relationship of H_{2}O^{+} with CaO/P_{2}O_{5} ratio suggests the possibility of reversible substitution in between PO_{4} \rightleftharpoons (OH)_{3}.

According to Subramanian (1980), the chemical affinity between apatite and fluoride is so considerable that apatite is often used as filters to remove fluoride from drinking water. Thus fluoride, in association with Ca^{2+} fixes phosphorus from sea water into the sediment. The source of fluoride may be submarine volcanism, spring water or even ground water. Mansfield (1940) speculated that unconformities associated with phosphorite deposits may locally represent periods of active volcanism, causing the fixation of both F and P into fluorapatite.
The $\text{CO}_3^{-2}$ and $\text{OH}^-$ are considered to be the principal substitution ions, and Si, Na and Mg are less but significant substitution ions for $(\text{PO}_4)^{3-}$.

**Biogenic Controls:**

Banerjee (1970) has suggested that the algal stromatolites might have played an important role in trapping and precipitating the dissolved inorganic phosphorus from the sea water. According to him the algal stromatolites in the phosphorites of Udaipur was responsible for the coprecipitation of carbonate and phosphate due to change in environmental condition.

The phosphorite limestone of Lower Tal at Chaiwapakumali in Tehri and near Mussoorie are found to be stromatolitic (Raha and Gururaj, 1979, and Raha, 1977). The Mussoorie stromatolites include what looks like, *Mala costroma* econertricum of Mississippian age (Raha, 1977), forms resembling diminutive *collenia parva* and small branching cylindrical columns.

According to Banerjee (1987), pyrite is intimately associated with the stromatolitic phosphorites of Mussoorie, particularly those of Maldeota and Durmala. Pyrite layers are generally concordant with the laminae of domal and stratified stromatolites. Pyrite is finely disseminated in the phosphatic matrix between stromatolite bands and also it is found in larger peloids in peloidal phosphorite. This intimate association of pyrite and apatite suggests that both were formed within anoxic muds possibly in embayments where water circulation was
restricted. The absence of non-pyritic ions suggests that pyrite formation was iron-limited (see Raiswell and Berner, 1985) and sulphate reduction was pronounced. According to Banerjee, et al. (1984), the variability in the concentration of the trapped trace elements was possibly a function of the quantity and nature of the organic matter present at the time of initial development of the Precambrian phosphatic stromatolites. Original concentration of the trace elements in biologically, controlled basinal waters, was possibly the prime controlling factor. The final redistribution of the trace elements within the sediments was exclusively a function of their chemistry.

In the central Wyoming, the organic matter associated with the phosphorites are so extensive that oil is commercially exploited there. McConnell (1965) has suggested that in the presence of carbonic anhydrase enzymes precipitation of phosphates takes place under low $\text{HCO}_3^-/\text{PO}_4^{3-}$ ratio whereas this ratio needs to be high as was shown by Ames (1959), for inorganic phosphate precipitation. In addition to extraction of phosphorus from sea water for their metabolism, certain organisms have a particular type of cells which may act as porous membranes. These membranes selectively diffuse phosphorus into the body which subsequently combine with the bones. After the death of the organisms $\text{Ca}_3(\text{PO}_4)_2$ in the form of bone, teeth, etc. accumulate which on reworking yield substantial amounts of $\text{Ca}_3(\text{PO}_4)_2$ in the form of francolite minerals.
H₂S and NH₃ are products of organic decay and may cause certain equilibrium reactions to proceed. For example, Berner (1971) experimentally decomposed fish in sea water and observed the presence of NH₃ and other species in the decay products. In reference to phosphatisation, NH₃ can be utilised as -

\[
\begin{align*}
\text{NH}_3 + 2\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{NH}_4^+ + 2\text{HCO}_3^- + \text{H}^+ \quad \ldots \quad (i) \\
\text{HCO}_3^- + \text{Ca}^{2+} & \rightarrow \text{CaCO}_3 + \text{H}^+ \quad \ldots \quad (ii)
\end{align*}
\]

and

\[
\begin{align*}
2\text{PO}_4^{3-} + 3\text{CaCO}_3 & \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 3\text{CO}_3^- \quad \ldots \quad (iii)
\end{align*}
\]

Also \( H_2S = S^{2-} + 2H^+ \) \ldots \ (iv)

\[
\begin{align*}
\text{FePO}_4 & = \text{PO}_4^{3-} + \text{Fe}^{3+} \quad \ldots \quad (v) \\
\text{Fe}^{3+} + \text{e} & \rightarrow \text{Fe}^{2+} \quad \ldots \quad (vi) \\
\text{Fe}^{2+}S^{2-} & = \text{FeS}_2 \text{ (pyrite)} \quad \ldots \quad (vii)
\end{align*}
\]

The above chemical reactions can account for the association of organic matter, carbonates, black shales and pyrite with the phosphate deposits. Reaction (vi) and (vii) would suggest a reducing and hence an Eh negative environment for pyrite associated phosphate deposits.

According to Ahluwalia (Abstract volume, 1989), the organisms being an important source of phosphate in the oceans where phosphate content is known to increase with phytoplankton and high organic productivity, a biogenic factor does seem to be relevant in Tal where evidences of organic activity are in plenty besides the ubiquitous presence of organic matter in the entire suit of sediments.
Thus, in the study area, the presence of organic matter, association of pyrite and black shales with the phosphorites, enrichment of vanadium and the presence of stromatolites as reported by some of the earlier workers, conclusively suggest that the formation of Mussoorie phosphorites was partially controlled by biogenic factor in shallow water under reducing conditions.

A PROPOSED GENETIC MODEL OF THE PHOSPHORITE DEPOSITS OF MUSSOORIE:

In the light of foregoing statements of facts and discussions, an attempt has been made to present cautiously a modest model for the formation of the phosphorites of Mussoorie, as stated below:

(1) Tal sediments were deposited in shallow marine conditions as evidenced by the presence of phosphorite associated with limestone - chert - shale succession, which is recognised as an ideal phosphatic suit of rocks for the deposition of phosphorite. The low manganese content in the analysed samples of these sediments can also be cited as one of the evidences of shallow water conditions of deposition.

(2) The phosphate deposits of Mussoorie were formed in warm and dry palaeoclimatic conditions as indicated by the low latitudes (30°25' N : 30°30'N) of the area. A high concentration of CaO and CO₂ in these phosphorites, which is due to the precipitation of CaCO₃ at pH greater than 7.8, also indicates
a warm and arid climate and therefore, only few rivers flowed into the basin bringing very little detrital materials.

(3) The basinal uplifting was probably initiated the development of a geosyncline followed by evolution of a platform structure on which the phosphatization process commenced. The occurrence of bedded phosphorites with thin laminations and association of chert and shale support their geosynclinal origin.

(4) The ingredients of phosphate are probably derived from three different sources viz. a) volcanic, b) phytoplankton and other micro-organisms and c) rivers. The phosphate-charged upwelling ocean currents coming from deep oceanic reservoirs of the pre-existing sea or an arm of it were the major contributors of phosphorite in the area. These upwelling currents, which were due to localized disturbances during deposition brought phosphatic material to the shallower parts of the basin where the increasing pH mostly due to the escape of CO$_2$ gave rise to the enrichment of $P_2O_5$.

(5) Assimilation of the dissolved phosphorus by certain marine organisms and their decay and concentration after their final burial on the sea bottom. The decay of organisms produces ammonia and ammonium salts, which are converted into phosphates and nitrates as follows:

\[ \text{NH}_3 + 2\text{CO}_2 + \text{H}_2\text{O} = \text{NH}_4^+ + 2\text{HCO}_3^- + \text{H}^+ \quad \ldots (i) \]
\[ \text{HCO}_3^- + \text{Ca}^{+2} = \text{CaCO}_3 + \text{H}^+ \quad \ldots (ii) \]

and
\[ 2\text{PO}_4^{-3} + 3\text{CaCO}_3 = \text{Ca}_3(\text{PO}_4)_2 + 3\text{CO}_3^{-2} \quad \ldots (iii) \]
The cycle continues for long till the amount of soluble phosphates in mud increases at the sea bottom. The restricted sea bottom circulations preserve the phosphate rich solutions.

(6) The precipitation of phosphorite is controlled by the pH changes. When cold phosphate-rich water upwelled from the ocean bottom, phosphorite is deposited from these ascending waters as their pH increased along with the increase in temperature and decrease in partial pressure of CO$_2$. The carbonates were deposited from these waters when they reached more shallow depth at a somewhat higher pH. Hence in the pH range 7 - 7.5, Ca$_3$(PO$_4$)$_2$ can first precipitate while CO$_3^{2-}$ remains in solution so long as the pH is buffered in that range. When pH increases to 8, CaCO$_3$ will precipitate.

(7) Apatite is the primary mineral which represents a group of minerals containing Ca$^{2+}$ and PO$_4^{3-}$ as the essential constituents. The crystal structure of apatite favours a number of minor substitutions. For example, VO$_4^{3-}$, SO$_4^{2-}$, CO$_3^{2-}$ and OH$^{-1}$ are usually substituted by equivalent amounts of PO$_4^{3-}$ and minor amounts of Mg, Mn, Sr. Abundance of V and Sr indicates such type of substitution which was influenced by the environment of phosphate mineralisation. The most common substitution in Mussoorie phosphorite is that of PO$_4^{3-}$ by CO$_3^{2-}$ which is corroborated a higher (1.31) by CaO/P$_2$O$_5$ ratio.

(8) The compositional variations with higher CaO/P$_2$O$_5$, CaO/MgO ratio indicate the formation of phosphorite by replacement processes. The antipathetic behaviour of MgO with respect to CaO and P$_2$O$_5$ indicates a chain replacement between
CaO-MgO-P\textsubscript{2}O\textsubscript{5} during phosphatization which further supports that MgO acted as a catalyst in the process of replacement of CaO by P\textsubscript{2}O\textsubscript{5}. The antipathetic relationship among the three oxides also indicates that surficial leaching had a leading role in increasing the P\textsubscript{2}O\textsubscript{5} content.

(9) The dispersion pattern and behaviour of trace elements detected in phosphate and other associated rocks suggest that the fixation of these elements was more or less geochemically controlled by adsorption on the surface of apatite or by the substitution in the apatite lattice or by some biogenic activity.

(10) The presence of organic matter, higher concentration of vanadium and also of Ni and Cu, and association of carbonates, blacksshales and pyrite with phosphorite suggest that the phosphorites were deposited in a reducing environment. The enrichment of Cr and V in the phosphorites suggest a slightly anaerobic to highly anaerobic facies.

(11) A greater concentration of the phosphates in the mud possibly led to the formation of phosphate pellets, lenticles, the ovules, etc. under some environmental vicissitudes.

(12) Later concentration of phosphates may have taken place during diagenetic processes and also a little supergene enrichment through lateritization as evidenced by some textural complexities in the phosphorites.