CHAPTER - IX
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Mussoorie, which occupies an elongated E-W Hill is situated about 31 kms. north of Dehradun town and is located between 1600 m. and 2600 m. above m.s.l. in the Doon valley of the Uttar Pradesh state. The study area in Mussoorie lies between north latitudes, 30°25' N ; 30°30' and east longitudes, 78°00'48" ; 78°10'57". The phosphorite deposits of Mussoorie are the only well known and old phosphorite deposits of U.P. The deposits are quarried from several opencast mines on the top as well as on the slopes of the Mussoorie hill - a popular summer hill resort of Uttar Pradesh.

The only exploitable phosphorite deposit of Mussoorie, being intimately associated with a variety of shale-chert-carbonate rocks of sedimentary origin with some pyrites, constitutes a part of the lowermost sequence of the Tal Formation of the Lesser Himalayan region of north-western India.

In Mussoorie area, the syncline made up of Blaini, Infra-Krol and Tal rocks, is in direct contact with Nagthat Formation on the northeast. The Tal Formation, which conformably overlies the Krol Formation, constitutes the upper most lithostratigraphic unit of the thick sedimentary sequence of the Krol Nappe and is divided into two formations, viz., Lower Tal Formation and Upper Tal Formation. The Lower Tal Formation, that varies in thickness from 75 m. to 880 m., is divisible
into four members viz., chert, pelitic, psammitic and calcareous on the basis of their difference in lithology and the dominance of one type of sediments over the others. The Upper Tal Formation, which is less in thickness than the Lower Tal (70 m. to 160 m. in thickness) is sub-divided into a lower quartzite member and an upper limestone member.

The phosphorite horizon being largely restricted to the upper part of chert member, varies in thickness from a few mm. to about 10 metres. The main phosphorite horizon occurs between the chert and black shales but thin phosphatic bands are also found intercalated with the underlying chert as well as the overlying black shales. The phosphorite horizon extends for about a total strike length of over 120 kms. along both the limbs of the Mussoorie syncline.

The Krol and Tal Formations, which have a thrust contact with Jaunsars, form a syncline that appears to have been tilted to the south. The strike of these formations varies from N10°W to N55°W. At certain places a few reversals indicate refolding of the formations resulting in the generation of local synforms and antiforms. The principal streams in the area generally follow old fault alignments. Faulting, which resulted in the development of steep scarps, often display shearing, shattering and drag folds of the formations.

Presently, the age of the Mussoorie phosphorite belonging to the Tal Formation which was hitherto believed to have been formed either in the Permian or in the Jurassic-Cretaceous period has been redefined to be Late Precambrian to Cambrian.
The phosphorites of Mussoorie may be classified into five distinct varieties on the basis of their megascopic characters as - platy and laminated, granular, lenticular, nodular and pelletal. The phosphorite deposits located at Maldeota and Durmala blocks are of economic values.

Petromineralogical studies have revealed that carbonate hydroxyl fluorapatite (collophane) is a dominant phosphate mineral and some dahlite at places. Calcite, dolomite and minor and variable amounts of quartz are the dominant gangue constituents. Quartz occurs as microcrystalline silica, cryptocrystalline, fibrous and detrital quartz. Ferruginous minerals like pyrite and limonite occur sporadically. The other associated gangue constituents are feldspars, muscovite, sericite, carbonaceous matter and opaques of iron oxides. Phosphate minerals are found in the form of pellets, nodules, ovules and oolites mutually replaced by carbonate and silica.

Representative samples of phosphorites from Maldeota and Durmala were chemically analysed in order to determine quantitatively their major oxides viz., $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{FeO}$, $\text{TiO}_2$, $\text{MnO}$, $\text{CaO}$, $\text{MgO}$, $\text{P}_2\text{O}_5$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{H}_2\text{O}^+$ and $\text{CO}_2$ in terms of weight per cent. The distribution of various chemical constituents show a wide variation from rock to rock, in various lithological units of the area. The concentration trends of certain major oxides indicate that limestone, is more enriched in $\text{CaO}$, $\text{CO}_2$ and $\text{SiO}_2$ than alumina, iron and alkalies. The chert is having higher concentration of $\text{SiO}_2$ and $\text{CaO}$ than the other constituents. Black shales are relatively
richer in SiO₂, CaO, and CO₂ than other major oxides. Most common types of phosphorite in the study area contain higher concentration of P₂O₅, CaO, SiO₂, MgO and CO₂.

The dispersion pattern, correlation coefficient and mutual relationship of significant major oxides represented by plotted diagrams, indicate that SiO₂, CaO and MgO are antipathetically related with P₂O₅. The relationship suggests a gradual replacement among these oxides during diagenesis. The presence of magnesium inhibits the growth of apatite crystallites. The sympathetic relationship of H₂O⁺ with CaO/P₂O₅ ratio and presence of considerable amount of water suggest the possibility of reversible substitution in between PO₄ ⃗️ (OH)₄. The CO₂ exhibits sympathetic relationship with MgO in Durmala phosphorites while CaO and P₂O₅ are antipathetically related with CO₂. It is, therefore, suggested that with the entry of CO₂ in the apatite lattice Ca and P were partially replaced.

Since majority of the samples have CaO/P₂O₅ ratio greater than 1.31, the most common substitution is that of PO₄³⁻ by CO₃⁻. The higher CaO/P₂O₅, CO₂/P₂O₅ ratios in the phosphorites are also primarily indicative of the presence of carbonate fluorapatite and the formation of phosphorite by replacement processes of these constituents. The principal oxides like SiO₂, Al₂O₃, TiO₂, K₂O, etc., which are not related to apatite may have association with the silicate group.

The variation trends in the chemical composition of the phosphorites and the host rocks may perhaps be due to certain marked changes in the supply of the material, variation in
composition of waters and physico-chemical conditions of the basin of deposition. The low manganese content confined with low FeO/MnO ratio, enrichment of $P_2O_5$ in the younger sediments, low content of alkalies as well as their inter-relationship and distribution pattern in the petrochemical fields indicate that most probably these phosphatic rocks were deposited in a shallow water geosynclinal basin favoured by slightly alkaline medium often approaching a very weakly acidic medium in an euxinic milieu.

The trace elements such as Cu, Pb, Ni, Co, Zn, Cr, Sr, Ba, Rb, V, Li and Cd have been determined quantitatively in the phosphorites and country rocks during the present investigation. The concentration trends of trace elements reveal that the phosphorites are more enriched in Ba, V, Sr, Cr, Ni, Cu and Pb than in Li, Cd, Co and Rb. Similarly, the black shales are relatively richer in Ba, V, Sr, Cr and Ni than in Li, Cd, Co and Rb.

Sr and Pb are the elements which are susceptible to adsorption by phosphate minerals and the elements which are possibly adsorbed by organic matter include Ni, Zn, Cr, V, Cu and Cd. Elements adsorbed by clay minerals include Li and Rb.

The pattern of trace element distribution in the phosphorites and the geochemical behaviour of individual elements suggests that most of the trace elements, that found their way into the ancient sediments, appear to have invaded the lattices of the phosphates, carbonates, silicates and clay minerals and combined with them structurally.
Variable concentration of trace elements in the phosphates have been influenced by various physico-chemical processes involved during weathering and leaching of the pre-existing rocks, and subsequently many of them were assimilated to the sediments. The adsorption of some trace elements was mainly influenced by the principal absorbants like the phosphate minerals, some organic matter in addition to clay, iron and silicate minerals.

Correlation coefficient and plotted diagrams of significant trace elements indicate that the presence of these elements may be due to their inter-elemental affinities. However, adsorption on the surface of the apatite, substitution in the apatite lattice and biogenic activity are supposed to be chiefly responsible for the distribution, abundance and fixation of significant trace elements. Thus higher concentration of certain trace elements in the phosphate rich ores is mainly due to certain favourable physico-chemical conditions such as low Eh-pH, moderate salinity, slightly anaerobic to highly anaerobic shallow water reducing environmental conditions, etc. at the time of their deposition.

A statistical method (Factor-Vector analysis) was followed to explain the complex relations among several geochemical variables in terms of simpler and more meaningful relations with the help of varimax-R-mode factor analysis. The major and trace elements variability of Maldeota and Durmala phosphorites were computed in terms of various admixture of factor and vector scores. Based on the nature of loadings the factors have been specified as follows :-
1. Silica precipitation  
2. Phosphate precipitation  
3. Carbonate precipitation  
4. Organic activity  
5. Detrital clay supply  
6. Residual pore water  
7. Oxidising to reducing condition  

The results of the factor-vector analyses indicate that phosphatic material, supplied in a soluble state, was originally rich in calcium and strontium and the precipitation of phosphorite was accompanied by the co-precipitation of calcium carbonate and calcium phosphate. The formation of these sediments suggests variation in pH conditions. The variation of Eh conditions suggest reducing to slightly oxidizing shallow marine environment. The concentration of trace elements viz., Cu, Co, Cr, Pb, Zn and V in phosphorite may be attributed to their association with organic matter.

The ingredients of phosphates are probably derived from three different sources, viz., a) volcanic, b) phytoplankton and other micro-organisms and c) some pre-existing rivers. The phosphate charged upwelling ocean currents coming from the deep oceanic reservoirs of the pre-existing sea or an arm of it were the major contributors of phosphorites in the basin. It is suggested that the deposition of phosphate might have occurred in an euxinic shallow marine environment aided by slightly alkaline to very weakly acidic medium with restricted circulation in warm and dry palaeoclimatic conditions. Additionally, the deposition is controlled by some geological and biogenic factors.
such as excess charge of phosphate in certain zones of phosphogenic basin, lithological facies variations, sub-basinal topographic restrictions, some structural disturbances and concentration of dissolved phosphorus by certain micro-organisms. Negative Eh, pH with around 7.8, influence of the pressure and temperature, relative proportions of CaO/MgO and CaO/P₂O₅, the chain of replacement among CaO-MgO-P₂O₅ as well as easy ionic substitution of certain elements are the other factors favourable for the deposition of the ores. Penecontemporaneous and post-deposition also played some role in controlling the concentration of the deposits.

A genetic model of the phosphorite deposits of Mussoorie has also been proposed. It suggests that the role of geochemical environment in the deposition of phosphorites as well as the accompanying activity of micro-organisms mutually interacted under a set of shallow intertidal and subtidal environmental conditions, leads one to believe that precipitation of phosphate was essentially dependent upon pH and Eh conditions, partial pressure of CO₂, temperature, replacement processes and ionic substitution. The presence of appreciable quantity of organic matter, higher concentration of vanadium and chromium, association of carbonates, black shales and pyrite, suggest deposition of phosphorite in a more or less reducing environment. The various forms in which phosphorite occurs appear to be related to some environmental vicissitudes at the time of deposition followed by some later structural disturbances related to the uplift of Himalaya. Later enrichment of phosphates may have taken place during the period of diagenetic processes as also a little supergene enrichment through lateritization.