CHAPTER- IX

SUMMARY AND CONCLUSION

Masrana and Kimo blocks are part of Mussoorie Syncline, which forms the outer hill ranges of the Himalaya in Uttrakhand. It occupies about 30 km$^2$ and covers about 20 km strike length of Krol-Tal contact. It is located between 1600 m. and 2600 m. above msl in the Doon valley of the Uttrakhand state. The study area lies between latitudes; 30°27′0″N and 30°28′0″N and longitudes; 78°9′0″E and 78°8′30″E. The phosphorite deposits of Himalayan terrain of Uttrakhand especially those of Mussoorie Syncline are the well known phosphorite deposits of the country. In the Masrana block the thickness of the phosphorite horizon varies from 01 metre to 07 metres with 15% to 33% P$_2$O$_5$ content and phosphatic horizon is traceable over a strike length of about 1.5 km. In the Kimo block the most prominent phosphorite zone occurs over a strike length of about 1.2 km and the thickness of the phosphatic horizon varies between 0.5 to 03 meters and P$_2$O$_5$ content ranges from 15% to 33%.

The exploitable phosphorite deposit of Uttrakhand, occurring at Masrana and Kimo blocks and intimately associated with a variety of shale-chert-carbonate rocks, an ideal phosphatic suit of sedimentary origin with some pyrites, constitutes a part of the lowermost sequence of the Tal Group of the Lesser Himalayan region of north-western India.

The Krol and Tal Groups, which have a thrust contact with the Jaunsars, form a syncline that appear to have been tilted to the south. In Mussoorie area, the syncline made up of Blaini, Infra-Krol and Tal rocks, is in direct contact with Nagthat Group on the northeast. The Tal Group, which conformably overlies the Krol Group, constitutes the uppermost lithostratigraphic unit of the thick sedimentary sequence of the Krol Nappe and is divided into two groups, viz., Lower Tal Group and Upper Tal Group. The thickness of the Lower Tal varies in different sections from 75m to 880m. The group is further divisible into four members on the basis of their difference in lithology and the dominance of one type of sediments over the other, viz., cherty, argillaceous, arenaceous and calcareous. The Upper Tal Group, which is less in thickness than the Lower Tal (70 to 160 m) is sub-divided into a lower quartzite member and an upper limestone member.
The phosphorite horizon, being largely restricted to the upper part of the 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 individual phosphorite bands are not continuous though the phosphorite horizon extends for about a total strike length of over 120 kms along both the limb of the Mussoorie Syncline.

The strike of Krol and Tal Groups varies from N10°W to N55°W. At certain places a few reversals indicate refolding of the groups resulting in the generation of local synforms and antiforms. The principal streams in the area generally follow old faults alignments. Faulting, which resulted in the development of steep scarps, often display shearing, shattering and drag folds of the groups.

Presently the age of the phosphorite deposits of the study area belonging to the Tal group which was hitherto believed to have been formed either in the Permian, Jurassic-Cretaceous or Precambrian has been redefined to be of Early Cambrian and are not contemporaneous with their counterparts on the Indian shield.

Petromineralogical studies have revealed that carbonate hydroxyl fluorapatite (collophane) is a dominant phosphate mineral and some dahllite at places. Calcite, dolomite and variable amounts of quartz are the dominant gangue constituents. Quartz occurs as microcrystalline silica, crystallophane, fibrous and detrital quartz. Quartz veins are also found cutting across the pellets of collophane. Ferruginous minerals like pyrite and hematite occur sporadically. The other associated gangue constituents are muscovite, sericite and carbonaceous matter. Phosphate minerals are found in the form of fragments, pellets, nodules, plates, lenticles and oolites occasionally replaced by carbonates.

The nature of the pelletal structure of the phosphate minerals, association of phosphatic sediments with black shales, and presence of pyrite indicate that the environment of precipitation may be fairly reducing to slightly oxidizing. The presence of oxidized rim, sponge spicules and stromatolitic structure also suggest shallow marine conditions of environment of deposition leading to the formation of phosphorite layers as primary biogenic precipitates by bacterial or algal activities.
Fresh representative samples of phosphorites from Masrana and Kimoi were chemically analysed in order to determine quantitatively their major oxides viz., SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MnO, MgO, CaO, K$_2$O, TiO$_2$, P$_2$O$_5$ in terms of weight percent. The distribution of various chemical constituents show a distinct variation due to changes brought during and after the deposition.

The distribution pattern, correlation coefficient and mutual relationship of significant major oxides represented by plotted diagrams, indicate that SiO$_2$, CaO and MgO are sympathetically or weak antipathetically related with P$_2$O$_5$ which suggests a slight replacement among these oxides during diagenesis. The presence of magnesium inhibits the growth of apatite crystallites.

The average CaO/P$_2$O$_5$ ratios are very close to 1.31, suggesting substitution of PO$_4^{3-}$ by CO$_3^{2-}$ which is the most common substitution in the apatite. This CaO/P$_2$O$_5$ ratio in the phosphorites is a primarily indicative of the presence of carbonate fluorapatite, calcite or dolomite in these rocks. The principal oxides like SiO$_2$, Al$_2$O$_3$, TiO$_2$, K$_2$O, etc, which are not related to apatite may have association with the minerals of silicate group.

The variation trends in the chemical composition of the phosphorites may perhaps be due to variation in composition of waters and physico-chemical conditions of the basin of deposition. The low Mn content confined with low FeO/MnO ratio, enrichment of P$_2$O$_5$, low content of alkalies, inter-relationship of elements and distribution pattern in the petrochemical fields indicate that most probably the phosphorites were deposited in a shallow water geosynclinal basin favoured by slightly alkaline medium often approaching a very weakly acidic medium in an strongly euxinic to weakly pontic 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 during the present investigation. The concentration trends of trace elements reveal that the phosphorites are more enriched in Ba, V, Cu, Pb, Ni, Cr, Zn and Sr than in Co, Rb and U. 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, and Cu and those adsorbed by clay minerals are Li and Rb.
The pattern of trace element distribution in the phosphorites and the geochemical behaviour of individual element suggest 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. The adsorption of some trace elements was mainly influenced by the principal adsorbants like the phosphate minerals, 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, shallow water highly reducing to slightly oxidising environmental conditions, etc at the time of their deposition.

PAAS normalised REE distribution patterns display normal sea water patterns exhibiting LREE depletion, negative Ce and positive Eu anomaly. Relationship of Ce with other elements suggests that Ce anomaly work as a depositional sea water signature. There are very limited diagenetic effects on REE patterns and depositional conditions of the phosphorite deposits. Negative Ce and positive Eu anomalies result from upwelling and mixing of sea water during or prior to the Early Cambrian. PAAS-normalized REE distribution preserved the primary signatures of seawater. Later diagenesis and weathering processes have only minimal effects on the phosphorites of the study area.

The ingredients of the phosphates are probably derived from three different sources, viz., a) volcanic (hydrothermal solution), b) phytoplankton and other micro-organisms and c) little bit through 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 may also be the contributors of phosphorites in the basin. It is suggested that the deposition of the phosphate might have occurred in an strongly euxinic to weakly pontic shallow marine environment aided by slightly alkaline to
very weakly acidic medium with restricted circulation in warm and dry palaeo-climatic 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 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 the area has also been proposed. It suggests that the role of geochemical environment in the deposition of the 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 the 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, negative Ce and positive Eu anomaly suggest deposition of phosphorites in a more or less fairly reducing to slightly oxidising environment. The various forms in which phosphorite occurs appear to be related to some environmental vicissitudes at the time of deposition followed by some lateral structural disturbances related to the uplift of Himalaya. Later enrichment of phosphates may have taken place during the period of diagenetic processes and also a little bit of supergene enrichment through lateritization.