Chapter X

SUMMARY AND CONCLUSION

The phosphorite deposits of Matoon and Dakan Kotra, Udaipur district, Rajasthan State, occur within the area located between latitudes 24°31' : 24°33' and longitudes 73°44' : 73°47'. Stratigraphically, these deposits are included within a thick succession of Precambrian rocks belonging to Matoon Formation of the Aravalli Super Group. The Aravalli Super Group in the Udaipur region are divisible into three Formations namely, Debari (lower), Matoon (middle) and Udaipur (upper) Formations. The phosphorites are found stratified with the dolomitic limestone/marble, phyllites, quartzites belonging to the Matoon Formation.

The rocks encountered from east to west of Matoon comprise mainly of dolomitic limestone/marble, calcareous grit, ortho-quartzite, cherty brecciated quartzite, and phyllites of Matoon Formation. The important rock types of Matoon Formation occurring at Dakan Kotra are cherty brecciated quartzite, dolomitic marble, calcareous quartzite, and phyllites in addition to the post-Arvalli intrusive granite.

The calcareous facies of Matoon Formation is represented by dolomitic limestone/marble, which is essentially composed of calcite, dolomite, quartz and minor amounts of ferruginous material.
The rocks show varying degrees of recrystallisation that may be traceable in the northern and eastern parts of Matoon and western part of Dakan Kotra. The phosphorites are generally associated with the dolomitic limestone of Dakan Kotra which is also stromatolitic.

The quartzites which are differentiated as orthoquartzite, cherty brecciated quartzite, jaspery quartzite, usually form the higher ridges at Matoon. The cherty brecciated quartzite is predominantly exposed in the central and southern parts of Matoon and south-eastern part of Dakan Kotra. They are highly ferruginous in nature and consist of fragmentary phosphorites. The younger calcareous quartzite occurs in the western part of Dakan Kotra. Beside quartz, which is the major mineral constituent of the rock, small amounts of calcite, dolomite, muscovite and feldspar also occur in the rock.

The phyllites, which are made up of carbonaceous phyllites, sandy phyllites and chloritic phyllites and exposed in the valley areas west of Matoon and north-west of Dakan Kotra, constitute the youngest member of Matoon Formation. In the southern part of Matoon, phosphorite occurs in association with phyllites which show grey to greenish-brown colour. They are essentially composed of quartz, muscovite, sericite, chlorite, biotite, feldspar with minor amounts of calcite, dolomite and graphite.

The Aravalli sequence of the area strikes from N-S to
NNE-SSW and dips at high to moderate angles, dominantly towards the west. In general, the rocks of Matoon and Udaipur Formations show mesoscopic open fold, plunging $10^\circ - 15^\circ$ towards NNE while the rocks of Debari Formation form an anticline in the west and a syncline in the east of Udaipur district. The rocks in the Matoon area form a syncline plunging towards the north-west. The phosphorite deposits of Matoon are located in the eastern limb of this syncline while those of Karbaria-ka-Gurha appear to be occupying the western limb of the syncline upto which the Matoon phosphorites extend. The phosphorite deposits of Dakan Kotra form an antiformal structure, whose fold axis strikes NNW-SSE and plunges steeply towards north or NNE.

Most of the rocks of the study area comprising mainly of quartzites, dolomitic marble, phosphorites, phyllites and graywackes are the products of low grade regional metamorphism and comparable the chlorite-schist facies.

The phosphorites of Matoon and Dakan Kotra may be classified as follows:

i) Columnar algal stromatolitic phosphorites
ii) Laminated algal stromatolitic phosphorite
iii) Fragmental stromatolitic phosphorite
iv) Massive bedded phosphorite
v) Nodular phosphorite
vi) Pelletal phosphorite

The phosphorite deposit of Matoon, which occurs as a single horizon, is traceable over a strike length of about 3 kms. Its thickness varies from 0.5 to 20.0 metres. The richest portion
of the deposit (>30 per cent P₂O₅) is confined to the central part of the Matoon. Also, in the Dakan Kotra area only one horizon of phosphorite has been encountered over a strike length of about 750 metres in the north-western part. Its P₂O₅ content varies from west to east and the richest portion (>20 per cent P₂O₅) is confined to the central and western part of the area.

The phosphorites of the Udaipur region inclusive of Matoon and Dakan Kotra are found intimately associated with algal stromatolites. The various species of stromatolites from Matoon and Dakan Kotra have been identified and described on the basis of their general shape and structure, mode and kind of branching, arrangement of basic geometric units, nature of lateral surfaces and boundaries, the degree of convexity of the elementary laminae, width of intercolumnar space and character and nature of the layer. The identified species resemble those of Collenia columnaris Fenton and Fenton, Collenia baicalica Maslov, Collenia kusienis Maslov, Collenia symmetrica Fenton and Fenton, Baicalica prima Semikhatov, Minjaria calceolata Korolyuk and Weedia Walcott. A geometric classification of these stromatolite species is proposed as follows:

i) LLH-S ... LLH-C
ii) LLH-S ... SH-V
iii) SH-V ... LLH (C and S)

Out of these species, the Collenia columnaris is non-phosphatic whereas, the rest of the species are highly phosphatic
in nature. However, all the species suggest that the environmental condition of the basin in which they flourished was shallow subtidal to shallow intertidal.

An attempt has been made to propose the age of the Aravalli Super Group and the Matoon Formation on the basis of the species of stromatolites identified and their importance in stratigraphic correlation. The assemblage of stromatolite species indicates that the age of the Aravallis may fall between 1,000 and 1,500 million of years and that of Matoon between the middle and upper Riphean.

The phosphate rocks have collophane, francolite and dahllite as the dominant phosphate minerals. Quartz is the dominant gangue constituent of fragmental phosphorite and occurs as i) fine-grained inclusions in collophane, and ii) coarsely crystalline grains with chert composing the matrix of phosphate minerals. Calcite and dolomite are the chief gangue mineral constituents of stromatolite bearing phosphorite. The other associated gangue minerals include chert, feldspar, muscovite, tourmaline, goethite, zircon, anatase, illite and kaolinite. There are also some instances of replacement of calcite by collophane.

The infra-red spectral analyses of these phosphorites reveal the presence of structural $CO_3^{2-}$ and $OH^-$ ions in apatite structure. The discrete phase of $CO_3^{2-}$ in Dakan Kotra phosphorites is indicated by the presence of $V_4$ vibration in 710 cm$^{-1}$ frequency region. The presence of a band in 650 cm$^{-1}$ frequency region
indicates the presence of hydroxyl apatite.

Representative samples of phosphorites from Matoon and Dakan Kotra were chemically analysed in order to determine quantitatively their major oxides, viz., SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, FeO, MnO, TiO$_2$, CaO, MgO, P$_2$O$_5$, Na$_2$O, K$_2$O, H$_2$O$^+$, CO$_2$ as well as F in terms of weight per cent. The main departure in the abundance of major oxides between Matoon and Dakan Kotra phosphorites is that in the former the concentration of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, FeO, TiO$_2$, MnO, Na$_2$O, K$_2$O, F and P$_2$O$_5$ is higher and that of CaO, MgO, H$_2$O$^+$ and CO$_2$ is lower than in the latter. The ionic composition (based on 10 cations) of Matoon phosphorite corresponds to the theoretical carbonate fluorapatite having the formula: $\text{Ca}_{10.10} \text{(PO}_{4}\text{)}_{4.7} \text{(CO}_{3}\text{)}_{1.42} \text{(F}_{1.14}\text{, OH}_{1.75})$. The higher concentration of CO$_2$ and H$_2$O$^+$ in the phosphorites of Dakan Kotra than that found normally in carbonate fluorapatite is rather unusual. Contrastingly, the phosphorites have unusually lower concentration of fluorine. Accordingly, such a compositional abnormality may be explained as due to deficiency of PO$_4$ and excess of CO$_3$ and OH components in the carbonate fluorapatite associated with the Dakan Kotra phosphorite. The chemical formula $\text{Ca}_{9.58} \text{(PO}_{4}\text{)}_{2.22} \text{(CO}_{3}\text{)}_{5.89} \text{(OH}_{4.83}\text{, F}_{0.54})$ that was computed on the basis of 10 different cations warrants the nomenclature of the phosphate mineral as carbonate hydroxyl fluorapatite.

The sympathetic relationship between CaO and P$_2$O$_5$ indicates the formation of stable calcium phosphate. The presence of Mg$^{2+}$ rather inhibits the growth of apatite crystallites. The strong
negative relationship of MgO with CaO and P₂O₅ suggests the replacement of magnesian calcite by calcium phosphate. The excess water and sympathetic relationship of H₂O⁺ with CaO/P₂O₅ ratio explicitly suggest the possibility of PO₄ →(OH)₄ substitution. The CO₂ exhibits sympathetic relationship with MgO and H₂O⁺ while CaO and P₂O₅ are antipathetically related with CO₂. It is, therefore, suggested that CO₂ in these phosphorite is a function of water forming stable magnesian carbonate. Moreover, with the entry of CO₂ in the apatite lattice Ca and P were partially replaced. Furthermore, the sympathetic relationship of CO₂ with F as well as OH suggests the possibility of substitution of CO₃F and/or CO₃OH by PO₄. Fluorine is believed to have remained fixed in apatite structure in an early stage and possibly occupied the vacant oxygen site when CO₃⁻ substituted for PO₄⁻³. The discrepancy of F in Dakan Kotra phosphorite is possibly due to the excess of OH, where F was replaced by OH.

The higher CaO/P₂O₅, CO₂/P₂O₅ and F/P₂O₅ ratios in the phosphorites are primarily indicative of the presence of carbonate fluorapatite and the formation of phosphorite by replacement processes.

The principal oxides like SiO₂, Al₂O₃, TiO₂, K₂O, etc., which are not related to apatite may have association with the silicate group. The high SiO₂/Al₂O₃ and low K₂O/Al₂O₃ ratios signify the presence of quartz and alumino-silicate minerals in
these phosphorites. The excessively high $\text{SiO}_2$ content might have possibly caused one of the dilution of $\text{P}_2\text{O}_5$.

The trace elements such as Ag, Cd, Co, Cr, Cu, Ga, Li, Ni, Pb, Rb, Sr, Th, U, V and Zn in the phosphorites and country rocks have been determined quantitatively. Most of the trace elements that found their way into the basin of deposition appear to have invaded the lattice of phosphate, carbonate, silicate and clay minerals and combined with them structurally. The elements like Sr, V and to a lesser extent, Cr and Th seem to be related to apatite. Pb and Zn are probably associated with the carbonate minerals. Ag, Cu, Ni, Co and U are found in the silicate minerals while, Ga, Li and Rb are closely associated with the clay minerals.

Biogenic activity is supposed to be chiefly responsible for the distribution, abundance and fixation of Ag, Cd, Cr, Co, Cu, Ni, Pb and Zn in the phosphate rocks. The Th/U ratio (about 0.2) suggests a slightly reducing to fairly oxidizing environmental condition.

A statistical method (Factor-Vector analyses) 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 element variability of Matoon and Jakan Kotra phosphorites were computed in terms of various admixture of eight factor and vector scores. Based on the nature of loadings the eight factors
have been specified as follows:

i) Silica precipitation
ii) Phosphate precipitation
iii) Carbonate precipitation and dolomitization
iv) Organic activity
v) Detrital clay supply
vi) Residual pore water factor
vii) Oxidizing condition

The results of the factor-vector analyses indicate coprecipitation of calcium carbonate and calcium phosphate and simultaneous replacement of early formed calcium carbonate by calcium phosphate. The formation of carbonate, phosphate and silicate group of minerals suggests variation in pH conditions. Detrital supply seems to be very limited and indicates the formation of leucophosphate. The Eh conditions suggest slightly reducing to fairly oxidizing shallow marine environment. The concentration of the trace elements like Cu, Co, Cr, Pb, Zn, Ag and Th in the stromatolite bearing phosphates may be attributed to their association with the stromatolites.

The initial phosphorus seems to be derived from the pre-existing Banded Gneissic Complex as a result of their chemical decay followed by release of phosphorus to the shallow marine water and sediments. Marine upwelling caused the concentration of the phosphatic minerals over the shelf areas of a more or less restricted basin of deposition occupying some arms of the pre-existing sea. The role of geochemical environment in the
deposition of phosphorites as well as the accompanying activity of algal matter, that mutually interacted under a set of shallow intertidal and shallow subtidal environmental condition leads one to conclude that precipitation of calcium phosphate was essentially dependent upon the pH and Eh conditions, partial pressure of CO$_2$, photosynthesis, temperature and replacement processes. The various forms in which phosphorite occurs appear to be related to some environmental vicissitudes at the time of deposition followed by structural disturbances.