Section -B
Mineralogy, Petrography, Geochemistry, Factor Analysis, Summary and Conclusion
CHAPTER V

MINERALOGY AND PETROGRAPHY

Thin sections of various samples were prepared for mineralogical and petrographical studies under microscope. In addition stain test suggested by Rodgers (1940) was carried out for differentiating calcite and dolomite in thin sections. The uncovered thin sections were kept in copper nitrate solution for about half an hour which on fixing with ammonia, gives a deep blue colour on calcite, while dolomite remains uncoloured.

Mineralogy:

The common minerals present in all rocks are dealt herewith in order of decreasing abundance.

1. Calcite: It is one of the main constituents of dolomites and dolomitic limestones, frequently occurring in all the Members of Gangolihat Formation. Very fine grained, sometimes granular and platy in shape, colourless but sometimes cloudy. The coarse grains of it show rhombohedral cleavage, (Plate. III, Fig. 4). Polysynthetic twinning is occasionally seen. It occurs in the matrix and also in the form of granoblasts.

2. Dolomite: It forms one of the essential constituents of dolomitic limestones. It is colourless, fine grained, occasionally coarse and subhedral to subhedral in shape. Twinning and rhombohedral cleavages are characteristically present. It occurs in fine grained matrix of calcite.
3. **Magnesite:** The magnesite occurs in Chandaak Member. It is coarse grained, subhedral to euhedral and platy in shape. Perfect rhombohedral cleavage is the characteristic feature of this mineral. Twinning is absent, it forms bladed crystals and shows granoblastic texture in the rock. (Plate-IV, Fig. 1).

4. **Collophane:** It is massive, colourless in plane polarized light, but in crossed nicols it becomes dark. It occurs in the form of pellets ranging in size from 2 - 5 mm in width, and sometimes in microcrystalline cement in dolomites, as microsparite (Riggs and Freas terminology, 1965). (Plate-V, Fig. 3).

5. **Dahlrite:** It occurs as minute crystals in patches, streaks, and laminae of collophane, pale brown to grey in colour and becomes dark in between the crossed nicols. It has probably been formed by the gradual crystallization of collophane.

6. **Talc:** It frequently occurs associated with dolomites and magnesites, colourless in thin sections and shows cleavage. Sometimes it occurs in the form of shreds in intergranular spaces, and gives upper third order interference colours.

7. **Sericite:** It occurs in Purple Phyllites as minute shreds and thin laminations showing fissility planes in the rock.
8. **Garnet**: Massive and dark brown in colour, isotropic, occurs in fine to medium grain size and anhedral to subhedral in shape. It occurs in laminations present in dolomites (Plate V, Fig. 1).

9. **Zircon**: Pale brown in colour, very minute in size, cleavage absent, extinction parallel and gives pale tints of the fourth order interference colours. It occurs as detrital mineral in carbonate and non-carbonate rocks as well.

10. **Tourmaline**: It characteristically occurs in Purple Phyllites as an accessory mineral in the form of minute grains, showing pleochroism and buff colour. Cleavage is absent but it shows cross fractures.

11. **Quartz**: It occurs in veins and laminations, and shows an authigenic origin, in slates it forms leucocratic texture. (Plate V, Fig. 2). Sometimes it is cloudy. Silica in the form of chert is also present in dolomites, which is isotropic. In magnesite it is perhaps replaced by talc because it shows an inverse relation with the later.

12. **Uranium minerals**: Radioluxographic studies were performed to establish the uranium minerals in phosphorites because they are well known to occur in many phosphorite deposits of the world. About forty-five slides were studied.
by the R.L.X. method in which only three responded. The chemical analysis also revealed very negligible amount of $U_3O_8$ i.e. $< 0.002$ ppm. It is therefore inferred that uranium minerals in these rocks are of secondary origin, and include autunite ($CaO$ $UO_3$$_2$ ($PO_4$$_2$ $10 - 12$ $H_2O$) and pitchblende ($U_3O_8$), (Plate-II, Figs 1, 2, and 3)

Petrography:

1. **Purple Phyllites:** These are finely laminated rocks, showing compressional wrinkles. Sericite forming perfectly oriented fibrous mass containing blood-red iron oxide granules and detrital quartz grains showing nematoblastic texture. Among accessory minerals tourmaline and zircon are present (Plate-II, Fig. 4).

The interbedded quartzite is microcrystalline showing mosaic texture, in which sericite and chlorite are present variably (Plate-III, Fig. 1).

2. **Chhara Member:** This member consists of alternating bands of talcose-calc-phyllites and dolomites.

(1) **Talcose-Calc-Phyllite:** They are thinly laminated greasy in feel, show nematoblastic texture under microscope. Talc forms platy fibrous planes showing parallel arrangement. Among accessories, quartz of secondary origin is present in these rocks. (Plate-III, Fig. 2).
(ii) *Dolomite*: These are greyish in colour, and show microcrystalline texture, very fine grained, talc is present in interstitial patches.

3. *Hiumpaui Member*: They are white to cream and dark bluish grey in colour and can be grouped into two types on the basis of resistivity to cold dilute hydrochloric acid, namely, harder (5.5 hardness) which do not react with acid easily and, softer (3.5) those react spontaneously to acid treatment.

The thin section study reveals that they are microcrystalline or micritic in texture (Folk's classification 1959). Coarse to fine grained, alternating laminations ranging in thickness from 0.5 to 1.4 cm are characteristic features of these dolonites. Coarse grained granular subhedral to anhedral twinned crystals of calcite and dolomite present in patches and veins produce dismicritic character. Authigenic quartz and very fine opalline chert occurs in intergranular boundaries, it also contains cloudy inclusions of carbonates. Among the accessories pyrite and talc are important, the later occurs as intergranular flakes (Plate-III, Figs. 3 and 4).

4. *Chandaak Member*: The Chandaak Member is made up of magnesite, it is very coarse grained, sometimes grains are 1.5 mm thick and are platy in shape, one may gets
confused with granite when looking from a distance.

In thin section study, it gives a perfectly granoblastic texture, constituted of unoriented large, elongate and bladed crystals of magnesite. Talc developed in interstitial spaces varies from sample to sample and does not appear in the presence of silica and gives an inverse relationship with it (Plate-IV, Fig.1).

A specimen taken from Chandaak magnesite shows typical schistose texture and dark colour in hand specimen. Under microscope, it reveals a well developed schistosity to the extent that an augen texture is developed. The thin black carbonaceous matter wraps around the cherty silica grains that are about 0.5 mm in length. This supports the view that magnesite was formed due to metamorphism of the dolomite. (Plate-IV, Fig. 2). Opaque mineral probably pyrite occurs as an accessory mineral.

4. Dhari Member: The dark grey coloured having characteristically developed curved laminations varying in width from 1.0 to 1.6 mm is an orthochemical limestone. Microscopic study reveals no such laminations. These are microcrystalline and contain patches of coarse grained twinned calcite and dolomite. The authigenic quartz frequently occurs in contact planes and reflects that they have served as channels for migration of silica solution (Plate-IV, Figs. 3 and 4).
Along the lamination planes, veins and streaks of grey opalline silica are well developed which is an important characteristic of these dolomites. These veins are impregnated by dusty pyritic or carbonaceous matter (Plate V, Fig. 1).

Sor Slates: Sor slates are dark in colour and consist of indistinguishable paste of chlorite and sericite fibres, intermixed intimately with microcrystalline quartz, calcite and branched threads of black organic matter. These slates also show rhythmically alternate quartz rich leucocratic and dark carbonaceous laminae. As a whole the texture is nematoblastic.

Minute reddish needles of rutile, euhedral tourmaline, muscovite and detrital zircon are among the accessories (Plate V, Fig. 2).

Olive green and brown slates are similar in texture and mineral composition except they are lacking in carbonaceous material.

Phosphorite: Although no typical band of rock phosphate occurs in the area under study but it is found almost associated with columnar structures of stromatolites and in depressions between biohermal colonies in pelletal forms. Phosphorite frequently occurs in Dhari Member, but sporadic
occurrences have also been noticed in Chandaak and Hiunpani Member.

In thin sections, the phosphorite occurs as collophane pellets, greyish black or brown isotropic veins and streaks. Within the streaks of collophane dahllite occurs in small amount (Plate-V, Fig. 3).

The collophane occur in calcitic matrix, range in size between 0.19 and 1.30 mm. The collophane is impregnated with tiny inclusions of carbonates, dusty carbonaceous matter and authigenic quartz. The matrix of the rock is composed of sparry calcite.

Sometimes collophane occurs along the lamination planes and forms microphorite. Often fractured and filled up by authigenic quartz (Plate-V, Fig. 4 and Plate-VI, Fig. 1).

**Basic Intrusives:**

**Metadolerite:** The metadolerite dykes and sills, which are intruding into slates, are dark green in colour, medium grained, and demonstrate blastophitic relict texture. Calcic plagioclase and andesine are poikilitically enclosed within large crystals of light green feebly pleochroic hornblende (Plate-VI, Fig. 2).
CHAPTER-VI

GEOCHEMISTRY OF THE MAJOR ELEMENTS

All lithological units of the present investigated area were analysed for twelve major elements in order to determine elemental distribution and their bearings on genetic significance of phosphatic and associated sediments. For each lithological unit the plotting of various oxides is done indicating the range of a particular oxide by bar and its average content by a dot (Fig. 6), the data so obtained are presented in Table-III, whereas the complete results of 12 major elements are given in Table - IV.

The distribution of various oxides in all the rock types is given as follows with the average in parentheses.

1. Purple Phyllite: This rock unit is composed of alternating bands of phyllites, slates and quartzites in which $\text{SiO}_2$ varies from 51.51% to 54.68% (53.09%), $\text{Al}_2\text{O}_3$ between 1.20 and 2.2% (1.70%), $\text{CaO}$ from 18.40 to 19.60% (19.00%) and $\text{MgO}$ from 9.40% to 10.40% (9.80%). $\text{Na}_2\text{O}$ and $\text{Fe}_2\text{O}_3$ are in low amount and vary in between 0.10% and 0.20% (0.15%) while $\text{K}_2\text{O}$ is comparatively high and varies from 2.02% to 2.10% (2.06%), whereas $\text{MnO}$ and $\text{TiO}_2$ were not found in these rocks. Loss on ignition due to water vapours and volatiles varies from 13.00% to 15.05% (14.025%).

2. Chhara Member: This member is composed of alternating thin bedded dolomites and phyllites.
In these rocks SiO$_2$ varies from 20.15% to 42.91% (32.03%), Al$_2$O$_3$ from 0.81% to 16.60% (8.70%), P$_2$O$_5$ from 2.50% to 8.30%, whereas CaO found to be varying between 0.51% to 21.11%. MgO lies between 2.20% to 16.40%. As far as Fe$_2$O$_3$ and FeO is concerned no variation is noticed and both remain constant in phyllites as well as in dolomites i.e. 0.015%. MnO is very low and varies from 0.01 to 0.02%. Similarly Na$_2$O content is low in phyllites (0.20%) but slightly higher in dolomites (0.30%), while K$_2$O shows a remarkable variation between phyllites 0.02% and dolomites 0.02%. The loss on ignition due to volatiles and water vapours is low in phyllites 27.10% and exceedingly high in dolomites i.e. 33.10%.

3. Hiunpani Member: The Hiunpani Member which overlies Chhera Member is mainly composed of dolomites and is characterized by thin bands and nodules of chert ranging in length up to 2 inches.

Due to the presence of chert in these dolomites, SiO$_2$ content is high and ranges from 10.14% to as high as 38.11% (25.71%). Next in concentration comes CaO varying between 0.30% and 33.96% (25.13%), MgO concentration lies in between 4.30% and 32.14% with an average of 17.10%. P$_2$O$_5$ concentration is generally low (i.e. 2.73%) but varies from 0.07% to 20.20%. Al$_2$O$_3$ is also low and varies from 0.18% to 0.40% (0.89%). Fe$_2$O$_3$ and FeO both are very low. Fe$_2$O$_3$ found to be varying between 0.08% and 1.00% (0.24%), while FeO concentration
is 0.05% showing negligible variation. MnO is also low and varies from 0.01% to 0.12%, while Na₂O and K₂O vary from 0.02% to 0.50% and 0.01 to 1.2% respectively. The loss on ignition varies from 18.45% to 40.12% with an average of 28.98%.

4. Chandanak Member: This Member is highly magnesitic which displays very well preserved vestiges of the original stromatolitic structures. These relic structures are also enveloped along the curved vestigial laminae by black collophane.

In this Member SiO₂ is low in general and varies from 7.13% to 23.12% (15.18%). P₂O₅ is high as compared to Hmunpani Member (4.51%) varying between 0.03% and 34.30%. The CaO content is low and varies from 2.60% to 28.10% with an average of 18.5%, whereas MgO content is high and ranges in between 15.60% to 46.85% with an average of 28.46%. Al₂O₃ is very low varying between 0.16 and 1.00% with average content of 0.87%. Fe₂O₃ and FeO vary from 0.08% to 1.00% and 0.0% to 0.11% (0.20% and 0.04% ) respectively, like other Members. MnO and TiO₂ are very low, and vary from 0.10% to 0.51% (0.14%) and 0.10% and 0.19% (0.11%) respectively. Na₂O lies in between 0.02 and 0.05% (0.25%) while K₂O varies between 0.01 and 0.05% (0.02%). Loss on ignition varies between 12.45 and 40.85% with an average of 30.76%.
5. Dhari Member: The rocks of the Dhari Member are dolomitic limestone having stromatolites of *Collenia beicalica* group.

In Dhari Member the $SiO_2$ content varies from 8.95% to 30.59% (20.14%) and $CaO$ varies from 9.80% to 30.80% (25.69%); whereas $MgO$ content having an average of 18.69%, varies between 12.90% and 26.00% and $P_2O_5$ varies between 0.28% to 31.80% (4.65%). As far as $Al_2O_3$ is concerned it is low (i.e. 0.87%), ranging in between 0.10 and 1.80%. Iron determined as $Fe_2O_3$ and $FeO$ is also low in these dolimites like other older Members and vary between 0.05 - 0.95% (0.28%) and 0.01 and 0.21% (0.04%) respectively. $MnO$ and $TiO_2$ are also very low and vary from 0.01% to 00.5% (0.10%) and 0.01 and 0.21% (0.04%) respectively. Among the alkali metals $Na_2O$ and $K_2O$ were determined, both having an average content of 0.26% and 0.05% respectively. L.O.I. was obtained to be varying between 13.15% and 42.55% (29.50%).

6. Sor Slates: The Sor Slates overlying Gangolihat dolomite Formation consists mainly slates and shales.

Here $SiO_2$ is high and varies from 45.37% to 56.45% (49.32%). $Al_2O_3$ varies from 12.50 to 15.10% (13.47%). $CaO$ varies from 0.01% to 10.50% (5.16%). $MgO$ varies between 1.80% and 4.80% (3.68%). $Fe_2O_3$ ranges from as low
as 0.05% to 3.10% (0.90%), whereas FeO is also low
varying between 0.04% and 1.00% (0.18%). $P_2O_5$ content
is slightly higher as compared to other slates reported in
published literature so far and varies from 0.03% to 3.4%
(2.09%). Among alkalies $Na_2O$ and $K_2O$ both are high
(0.28% - 5.30%, 1.73%) and 0.60% to 5.30% (2.39%)
respectively. In these rocks $K_2O$ is somewhat richer than
$Na_2O$. Loss on ignition due to volatiles and water vapour
varies from 20.50% to 24.61% (22.69%).

7. Dolomites around Gangolihat town: The term Gangolihat
dolomites is taken from the type area Gangolihat where this
Formation was first studied.

In these dolomites $SiO_2$ content varies from 3.45%
to 20.21% (17.42%), $Al_2O_3$ from 0.55% to 1.20% (0.93%),
$CaO$ from 6.30% to 29.40% (25.61%), while $MgO$ varies from
3.80% to 26.00% (19.35%).

Iron determined as $Fe_2O_3$ and $FeO$ varies from 0.02%
to 0.70% (0.19%) and 0.01% to 0.05% (0.03%) respectively.
The $P_2O_5$ content in Gangolihat dolomites is also high but
lower than that of Pithoraghar. It varies from 0.05%
to 15.90% whereas the average $P_2O_5$ content in these limestones
is 03.31%. $MnO$ varies from 0.01 to 0.11% (0.04%), $TiO_2$
ranges in between 0.01% to 0.02% (0.015%). $Na_2O$ and $K_2O$
very from 0.02% to 0.40% (0.26%) and 0.01% to 1.70%
(0.19%) respectively. $LOI$, on the other hand lies in
between 26.55% to 39.00% with an average of 33.68%.
In order to ascertain the physico-chemical nature of the basin of deposition, it is desirable to find out the relationship between the various elements. In the present study an attempt has been made to find out the relationship of $P_2O_5$ with other elements on the one hand and the inter-relationship of various elements on the other.

### Relationship with $P_2O_5$:

The author has tried to find out the behaviour of various chemical components in phosphate rich and phosphate poor environment. The results so obtained are discussed below.

#### $P_2O_5$ vs. $SiO_2$:

The relationship between $SiO_2$ and $P_2O_5$ is represented by plotting $SiO_2$ against $P_2O_5$ in Fig. 7, for purple phyllites and Sor Slates, Chhera and Himpani Members, Chandaak and Dhari Members and for Gangolihat dolomites. It is observed that in all the rocks an antipathetic relationship exists between these two oxides, indicating thereby a gradual removal of $SiO_2$ by $P_2O_5$, because ionic radii of $Si^{4+}$ ($0.39\ \AA$) and $P^{5+}$ ($0.35\ \AA$) are very similar hence a diadochic relationship exists between the two. The present study further supports
the existence of this relationship between these two elements.

\[ P_{2}O_{5} \text{ vs. } CaO \]

The plotting of \( P_{2}O_{5} \) against \( CaO \) also shows a remarkable antipathetic relationship like \( SiO_{2} \) (Fig. 8).

The inverse relationship between \( P_{2}O_{5} \) and \( CaO \) indicates a gradual removal of one by another. Ames (1959) has suggested that carbonate fluorapatite is the end member product of diagenetic replacement in which dissolved phosphate ions substitute for carbonate in calcareous materials. Krauskopf (1967) on the other hand believed that the precipitation of \( CaCO_{3} \) is favoured where water is warm and \( CO_{2} \) is being lost by evaporation or photosynthesis. Krumbein and Garrels (1952) have proposed that pH of the water is most important factor in the precipitation of both \( CaCO_{3} \) and \( P_{2}O_{5} \). They have also suggested that an increase in pH causes precipitation of \( CaCO_{3} \), whereas phosphatic solubility decreases with increase in pH.

From the above discussion it is evident that a sediment high in calcium phosphate and low in calcium carbonate could be formed only when there are conditions for continuous removal of calcium as the phosphate and the activity product of carbonate is not exceeded, this can
FIG 8 PERCENT $P_2O_5$ PLOTTED AGAINST PERCENT $CO_2$
occur in a restricted basin with low pH i.e. 7.0 - 7.5.

It is therefore inferred that during the phosphatisation the sea became enriched in phosphate content by lowering in pH due to release of CO₂ in shallow marine environment which is subjected to continuous chemical changes with mixing of various types of material brought by the rivers etc.

\[ P_2O_5 \text{ vs. MgO} \]

Fig. 9 represents the relationship between \( P_2O_5 \) and MgO for Purple Phyllites, Slates, Chhera, Hiunpani, Chandaak and Dhari Members, and for Gangolihat dolomites. An inverse relationship is obtained in all these rock types which indicates a continuous replacement of MgO by \( P_2O_5 \) during the diagenesis.

Furthermore this inverse relationship is supported by the experiments carried out by Martens and Harris (1970) who concluded that \( Mg^{2+} \) ions inhibit the precipitation of apatite because \( Mg^{2+} \) competes with \( Ca^{2+} \) for sites in the apatite structure due to which a decrease in MgO content occurs during \( P_2O_5 \) enrichment.

\[ P_2O_5 \text{ vs. Na}_2O \]

When \( P_2O_5 \) plotted against \( Na_2O \) no significant conclusion could be drawn because no change is noticed in \( Na_2O \) content with the increase or decrease of \( P_2O_5 \) (Fig. 10).

\( Na_2O \) content in these rocks is very low and this very low concentration of \( Na_2O \) in these sediments might have been due to a decrease in the climatic sequence like glacial
Fig 10 PERCENT P₂O₅ PLOTTED AGAINST PERCENT MgO
arid-humid which enhanced the rate of weathering prior to deposition (Ronov, et al. 1965).

\[ \text{P}_2\text{O}_5 \text{ vs. } \text{K}_2\text{O} \] Plot of \( \text{P}_2\text{O}_5 \) against \( \text{K}_2\text{O} \) for purple phyllites and slates (Fig. 11) shows a sympathetic relationship between the two, whereas in Hiumpani, Chhera, Dhari and Chandask Members a gradual decrease in \( \text{K}_2\text{O} \) with the increase in \( \text{P}_2\text{O}_5 \) content is noticed, while in Gangolihat dolomites there is no effect on the concentration of \( \text{P}_2\text{O}_5 \) by \( \text{K}_2\text{O} \).

**Interrelationship Of Various Oxides:**

1. \( \text{SiO}_2 \) vs. \( \text{MgO} \) The relationship between \( \text{SiO}_2 \) and \( \text{MgO} \) is observed only for purple phyllites and Sor Slates (Fig. 12A). In both these rock types an inverse relationship is noted between the two oxides.

   The \( \text{MgO} \) content in phyllites and slates is rather high due to the presence of chlorite in these rocks. The concentration of magnesium is directly related to the increase or decrease of matrix in a rock. It is therefore inferred that high concentration of \( \text{MgO} \) in these Slates and Phyllites might be due to high amount of matrix present in these rock types.

2. \( \text{SiO}_2 \) vs. \( \text{Fe}_2\text{O}_3 \) For Purple Phyllites and Sor Slates the relationship between \( \text{SiO}_2 \) and \( \text{Fe}_2\text{O}_3 \) is shown in Fig. 12B.
which indicates no significant correlation between these two oxides. In majority of the samples \( \text{Fe}_2\text{O}_3 \) remains constant and \( \text{SiO}_2 \) is found to be varying due to its removal during weathering from the parent material.

Iron, during weathering is converted into ferric oxide and carried as stabilized colloids or as adsorbed coatings on detrital particles. The iron content which is absorbed on these colloidal particles is separated according to their settling velocities (Wedepohl, 1970). These rocks being very fine grained contain almost an equal amount of iron, hence no variation is observed except in a few samples where iron is little higher than the majority of the samples.

3. \( \text{SiO}_2 \) vs. \( \text{Al}_2\text{O}_3 \): Pettijohn (1957) noted that the abundance of \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) reflects the mineralogical maturity of sandstones and shales.

When \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) plotted on a graph (Fig. 12-C), the Purple Phyllites and Sor Slates show considerable scatter on \( \text{Al}_2\text{O}_3/\text{SiO}_2 \) diagram which is a reflection of the complex mineralogical variations of these rocks. The immature nature of these sediments is mainly due to their deposition immediately after erosion.

4. \( \text{Na}_2\text{O} \) vs. \( \text{K}_2\text{O} \): Fig. 12-D shows the graphical representation of \( \text{Na}_2\text{O} \) vs. \( \text{K}_2\text{O} \) in Sor Slates where it is
FIG 12. %SiO$_2$ plotted against (A) %MgO, (B) %Fe$_2$O$_3$, (C) %Al$_2$O$_3$ for slates and purple phyllites.

FIG 12. (D) %Na$_2$O plotted against %K$_2$O for slates and purple phyllites.

Symbols:
- Slates
- Purple phyllites
observed that in these slates Na$_2$O content is very low (1.00%) whereas K$_2$O is quite high (5.3%). The low concentration of Na$_2$O as against K$_2$O further supports humid climatic conditions at the time of deposition of these rocks.

5. $\text{SiO}_2$ vs. CaO: In Purple Phyllites a negative correlation is obtained in between $\text{SiO}_2$ and CaO, while in Sor Slates it is observed that $\text{SiO}_2$ remains constant during the increase in CaO (Fig. 13), whereas in Chhera Member a negative correlation is noticed and in Hiunpani Member no significant relation is noticed (Fig. 13). In Dhari and Chandak Members too CaO remain constant with the variation of $\text{SiO}_2$ (Fig. 13). In Gangolihat dolomites also no significant correlation exists (Fig. 13).

The negative correlation in between $\text{SiO}_2$ and CaO in Purple Phyllites indicates that there was some CaO present in interstitial water. The increasing CO$_2$ pressure in these waters led the deposition of CaCO$_3$ during diagenesis while silica was gradually removed with the increase in pH (Degens, 1965; Krauskopf, 1967; Avasthy, 1977, and Verma, 1978).

6. CaO vs. MgO: The CaO and MgO are important constituents of calcareous rocks, whereas they are also found in small quantities in Purple Phyllites and Sor Slates. A sympathetic
Fig 13 PERCENT CaO PLOTTED AGAINST PERCENT SiO₂
relationship between CaO and MgO is noticed in all these rock types (Fig. 14). It is observed that in Sor Slates no effect is noticed on MgO content due to increasing CaO, whereas in Chhara and Hiunpani Members, the plots are so scattered that no notable correlation exists. It is quite possible that both CaO and MgO were competing during diagenesis, for their survival in the presence of P$_2$O$_5$ (Israeli, 1978b), while an antipathetic relationship exists in Chandaak and Dhari Members. It is due to that Mg is known to substitute for Ca in apatite structure (Cruf et al. 1965, McConnell, 1973), or due to more liming of P$_2$O$_5$ for MgO rather than CaO (Israeli, 1978b). During phosphatization a chain of replacement between CaO-MgO-P$_2$O$_5$ is noticed. It was also observed that MgO acted as a catalyst in the process of replacement of CaO by P$_2$O$_5$ (Israeli, Loc. Cit.).

7. $\text{Al}_2\text{O}_3$ vs. $\text{Fe}_2\text{O}_3 + \text{FeO}$: Percentage alumina plotted against percentage of total iron on a graph is shown in Figs. 15 A, B, C, and D for all the rock types studied.

It is observed that for $\text{Al}_2\text{O}_3$ content below 0.8% iron is also low (i.e. 0.2%), whereas for $\text{Al}_2\text{O}_3$ in between 0.8% - 1.0%, the $\text{Fe}_2\text{O}_3$ concentration goes up to 1.00%, indicating a close affinity between the two oxides in these rocks. It is suggested that both total iron and alumina
Figure 15: Total iron (Fe₂O₃ + FeO) with Al₂O₃ for various lithological units.
behave similarly in a shallow marine environment which is subjected to rapid physico-chemical changes even at a short distance due to the mixing of the land derived material. Their concentration is affected only by hydroxyphosphates of Mg and other cations in slightly alkaline (calcareous) medium (wedepohl, 1970).

8. **MgO vs. MnO**: The relationship between MgO and MnO is shown for Chandaak and Dhari Members (Fig. 16-A), for Hiunpani and Chhera Members (Fig. 16-B), and for Purple Phyllites and Sor Slates (Fig. 16-C).

It is observed that in Dhari, Chandaak, Chhera and Hiunpani Members no definite correlation exists between the two oxides. In Purple Phyllites a sympathetic and in Sor Slates an antipathetic relationship is observed. The remobilization of MgO and MnO during greater metamorphism in slates and their concentration due to gravity might be the possible causes for such a relationship.

9. **Fe₂O₃ vs. MnO**: Figs. 17 A, B, and C represent graphically the relation between Fe₂O₃ and MnO for Chandaak and Dhari, for Chhera and Hiunpani and for Purple Phyllites and Sor Slates respectively. All the Formations of the area show an inverse relationship between these two oxides.

Though the manganese minerals form very close parallelism to the iron minerals in sediments, but in rocks under study a higher concentration of iron over manganese is noticed. It is possible that iron and manganese do not occur as siderite or rhodochrosite in these sediments but as solid solutions in carbonate minerals (Eriksson et al. 1975).
Figure 16: Percent MnO plotted against percent MgO and their variation in various rock formations of the area.
FIG. 16. Percent Mio plotted against percent MnO and their variation in various rock formations of the area.
FIG. 17 Percent MnO plotted against percent Fe₂O₃ +FeO and their variation in various formations of the area.
Table V reveals that the dolomites have high MgO/MnO and FeO/MnO ratios. It is presumed that the pH of the medium might have slightly been increased due to the mixing of various land derived materials giving rise to several chemical changes that resulted in more enrichment of Fe and Mg as oxides and depletion in the concentration of MnO.

10. Fe$_2$O$_3$ vs. MgO: The relationship between Fe$_2$O$_3$ and MgO is shown in Fig. 13 A, B, and C, for Purple Phyllites, Chhera and Hiunpani, Chandaak and Dhari Members respectively. It is observed that the Purple Phyllites (Fig. 13-C) indicate an inverse relationship whereas, Chhera and Hiunpani Members reflected a sympathetic relationship between these two oxides, whereas Dhari and Chandaak Members reveal an inverse relationship. In Purple Phyllites and Sor Slates also MgO decreases with the increase of Fe$_2$O$_3$.

The antipathetic relationship observed in these rocks may be due to the similarity of Mg$^{2+}$ ion with Fe$^{2+}$ which caused mutual substitution of one for another under similar physico-chemical conditions for their enrichment.

11. SiO$_2$/Al$_2$O$_3$ vs. P$_2$O$_5$: When SiO$_2$/Al$_2$O$_3$ ratio (Table V) was plotted against P$_2$O$_5$ (Fig. 19), it was observed that P$_2$O$_5$ increases with the decrease of SiO$_2$/Al$_2$O$_3$ ratio. The author thus is of the opinion that P$_2$O$_5$ may also be taken as maturity index and its abundance in rocks should be an indicator of their mineralogical maturity.
FIG. 18. Shows the variation between total iron (Fe$_2$O$_3$ + FeO) and MgO%.
FIG 19. %P₂O₅ PLOTTED AGAINST SiO₂/SiO₂ Ratio for Phosphatic Rocks of the Area.
Close affinity of \( P_{0.5} \) with limestones, dolomites and quartzites also favours the above observation.

12. CaO/SiO\(_2\) vs. \( P_{2.0.5} \)!: Fig. 20 represents that with the increase of CaO/SiO\(_2\) ratio (Table-V, ) there is a decrease in \( P_{2.0.5} \) content indicating thereby that concentration of \( P_{2.0.5} \) results in the depletion of CaO or SiO\(_2\).

13. CaO/MgO vs. \( P_{2.0.5} \)! The CaO/ MgO ratio (Table-V) plotted against \( P_{2.0.5} \) also indicates an inverse relationship (Fig. 21). It has already been stated earlier that in the processes of \( P_{2.0.5} \) enrichment there is a gradual removal of CaO and MgO upto a certain limit (upto 30-35% of \( P_{2.0.5} \) ) from where MgO remains stationary and only CaO is removed at the expense of MgO (Istaili, 1978 b).

14. \( SiO_2-Al_2O_3-K_2O \)!: The Principal group of constituents not related to apatite composition are those forming the quartz silicate group of minerals. Fig. 22 shows the relationship between \( SiO_2, Al_2O_3 \) and \( K_2O \) to one another for Dhari, Chandaak and Hiumpani Members. The plot reveals two main features one the constant \( Al_2O_3/K_2O \) proportion as is evidenced by the linear distribution of sample points and the other an increase in \( SiO_2 \) content at the expense of others. It could be due to the supply of free silica or chert to these sediments in different proportions along with other silicate minerals. Table VI represents the recalculated values to 100 weight percent of \( SiO_2, Al_2O_3 \) and \( K_2O \).
FIG 20 PERCENT $P_2O_5$ PLOTTED AGAINST $CaO/SiO_2$ RATIO FOR PHOSPHATIC ROCKS OF THE AREA.
Fig. 21: Percent P₂O₅ plotted against CaO/MgO ratio for phosphatic rocks of the area.
Petrochemical Fields And Trends:

The idea of this study was taken from Green and Poldervaart (1958). Though it is difficult to drive a general trend for sedimentary rocks due to the complex physico-chemical conditions which brought out these rocks, topography of source highlands and sea floor, an attempt is made here to suggest the fields and trends for the dolomitic limestones.

Firstly the sedimentary averages are plotted in Fig. 23, based on suggestions made by Mason (1966), in a $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{FeO} - \text{SiO}_2 - \text{CaO} + \text{MgO}$ triangular diagram. It is observed that $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{FeO})$ do not increase 5 percent of $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{FeO} + \text{CaO} + \text{MgO})$ in calcareous rocks, and only reaches up to 25 percent in slates with more than 50 percent SiO$_2$ i.e. only in Sor Slates. The recalculated values of $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{FeO}$, SiO$_2$ and CaO + MgO are given in Table-VII.

Fig. 24 shows variation in CaO-Na$_2$O-K$_2$O ternary diagram with strong scatter of points widening towards the Na$_2$O-K$_2$O side approximately at Na$_2$O : K$_2$O = 3 : 17, indicates high percent of K$_2$O. It might be due to an alkaline provenance which has also been inferred on the basis of yttrium content in these sediments. The recalculated values of these oxides are given in Table-VIII.
FIG. 24 CaO–Na₂O–K₂O diagram for various formations
Figs. 25 and 26 show the averages of various oxides plotted on a series of eleven triangular diagrams expressed as oxidic weight percent. The first figure is an SiO$_2$-Al$_2$O$_3$-MgO diagram which reveals that most of the points lie along MgO-SiO$_2$ line and Al$_2$O$_3$ does not increases beyond 5 percent. In pelitic rocks the case is just reverse where Al$_2$O$_3$ ranges between 20% - 30%, and MgO does not increases beyond 10 percent. (Tables IX to XIX represent recalculated values to 100 weight percent for each triangular diagram).

The CaO - Fe$_2$O$_3$ - Al$_2$O$_3$ diagram shows concentration of points on Ca corner and spreading towards Fe$_2$O$_3$ + FeO-Al$_2$O$_3$ side with a high concentration on the Al$_2$O$_3$ side, indicating a low matrix content.

The next two diagrams MgO -CaO-Al$_2$O$_3$ and MgO-CaO-Fe$_2$O$_3$+FeO also show a variation along CaO-MgO line for calcareous rocks whereas pelitic rocks are low in MgO content (i.e. upto 20%) and high in CaO-Al$_2$O$_3$ and CaO-Fe$_2$O$_3$+FeO (varying between 40% - 60%).

The next two diagrams CaO-Fe$_2$O$_3$-Na$_2$O+K$_2$O and MgO-CaO-Na$_2$O+K$_2$O also represent the same variation for calcareous and pelitic rocks i.e. high CaO-MgO and low Na$_2$O+K$_2$O and Fe$_2$O$_3$+FeO content.

In Fig. 26, the CaO-Al$_2$O$_3$-Na$_2$O+K$_2$O and MgO-Fe$_2$O$_3$+FeO-Al$_2$O$_3$ diagrams also represent the similar pattern.
FIG. 27. 'AD•Q'-Al'O•NdO Diagram and Quadrants with variables Ad0, Qd0, To0, T00, 0.5e0, 0.5e-0.5e

The diagram shows various quadrants and lines representing different variables. The axes are labeled with specific values, indicating the range and scale for each variable.
On the basis of these diagrams in which CaO or MgO lies on one of the corners of the triangle, it is noticed that in the carbonate rocks most of the points lie on the CaO-or MgO corner and their spread towards Al₂O₃ corner indicates a somewhat argillaceous content in these rocks.

The rest three diagrams of Fig. 2 show the variations in (i) Al₂O₃-Fe₂O₃-FeO-Na₂O+K₂O, (ii) MgO-Al₂O₃-Na₂O+K₂O, and (iii) MgO-Fe₂O₃-FeO-Na₂O+K₂O contents.

In Al₂O₃-Fe₂O₃-FeO-Na₂O+K₂O diagram the concentration of the points is nearer to Al₂O₃ corner and show a spread towards Na₂O+K₂O-Al₂O₃ line pointing towards a pegmatite like provenance.

In MgO-Al₂O₃-Na₂O+K₂O diagram, the calcareous rocks fall on MgO corner spreading slightly towards Al₂O₃, whereas pelitic rocks are rich in Al₂O₃+Na₂O+K₂O. On the other hand in MgO-Fe₂O₃-FeO-Na₂O+K₂O diagram the variation is towards Na₂O+K₂O corner.

**Classification Of Phosphorites:**

For the classification of the phosphorites and other phosphatic sediments the author has used the parameters suggested by Israeli (1978b), based on CaO/P₂O₃ or CaO/SiO₂ ratios for phosphorites associated with limestones or siliceous rocks respectively.
Due to well defined association of these phosphorites with dolomitic limestones in the area of study only $\text{CaO}/\text{P}_2\text{O}_5$ ratio (Table-XX) is used in the classification of these sediments.

On the basis of the above classification the rocks of the area could be grouped as under.

1. **Slightly phosphatized limestones** ($\text{CaO}/\text{P}_2\text{O}_5$ ratio 49.99:1 to 10:1): Most of the area is covered by this type of limestones, because the phosphatic concentration in these limestones is very low, and sporadic, such type of limestone is most common in Chhera, Hiunpani, and some sporadic occurrences are noticed in Dhari Member. In other words it can be said that the majority of the rocks of Gangolihat dolomite Formation belong to this category. It is therefore suggested that the term Gangolihat dolomites is rather inappropriate and it should be termed as Gangolihat phosphatized dolomites both for stratigraphic and lithologic convinience.

2. **Phosphatic limestone** ($\text{CaO}/\text{P}_2\text{O}_5$ ratio 9.99:1 to 2:1): This type of limestone is most common in all the Members of the area under present investigation.

3. **Calc-phosphorite** ($\text{CaO}/\text{P}_2\text{O}_5$ ratio 1.99:1 to 1:1): This type of phosphorite is occasionally found in Dhari and Chandaak Members and is rare in Hiunpani Member.
4. **Phosphorite** (CaO/P₂O₅ ratio 0.99:1 to 0.5:1):

   It is most common in Chandaak Member and is rarely found in Dhari Member.

   In the present study it is noticed that though various types of phosphatic sediments occur but they are so sporadic and low in concentration that their economic exploitation at present is impossible. It is possible that they might be used in future, with an advancement of techniques of mining and beneficiation.

**CONCLUSION:**

The thick succession of Calc Zone is composed of alternate calcareous, argillaceous, and again calcareous formations, which is underlain and overlain by quartzites of Berinag and saryu valley respectively. The Purple Phyllites of Berinag quartzites are rich in SiO₂ (53.09%), CaO (19.00%) and MgO (09.8%), and poor in alumina (1.70%), iron (0.15%) and alkalies (Na₂O and K₂O, 10.15% and 2.10% respectively).

The calcareous rocks vary in chemical composition and have been further divided into four Members i.e. Chhera, Hiumpani, Chandaak, and Dhari.
The Chhera Member is Phyllitic to dolomitic, varying in composition from a siliceous to calcareous nature. The Hiunpani Member is rich in silica content due to cherty nodules. Next comes the magnesitic horizon which is high in magnesium content (28.46%) and is overlain by Dhari Member having almost the same chemical composition with a rather low magnesium content. The calcareous rocks are overlain by Sor Slates having high SiO₂ and Al₂O₃ contents (49.32% and 13.47% respectively) and poor in CaO and MgO (5.16% and 3.18% respectively).

In a nutshell, the Gangolihat sea represents a variation in the environmental conditions of basin and also in the supply of material from the provenance. The change in basin varies from dolomitic phyllites through cherty stromatolitic dolomite, magnesitic horizon to stromatolitic dolomite horizon and finally into Sor Slates which indicates deep water conditions of deposition. It is also noticed that the younger calcareous rocks become enriched in P₂O₅ content indicating a shallowing in the basin of deposition that brought about a lowering in pH and a luxuriant growth of bioherms, mostly the blue green algae—the precursor of stromatolites. The same Gangolihat Formation when studied around Gangolihat town revealed a low SiO₂ (12.42) and high CaO (25.61%) content.

It has been observed that in all rock types when P₂O₅ plotted against SiO₂, CaO, MgO an inverse relationship exists, which indicates a gradual replacement of these
oxides by $P_2O_5$ during diagenesis.

Furthermore the precipitation of $CaCO_3$ indicates a warm climate and loss in $CO_2$ which resulted in the lowering of pH around 7 to 7.5 and led to the precipitation of phosphorites.

It is suggested that dolomitization took place after the phosphatization but not during diagenesis because $MgO$ is found to be replacing phosphorus. Alkali metals like $Na_2O$ and $K_2O$ do not show any effect on phosphorite enrichment but remain constant.

The purple phyllites show that $Al_2O_3$ and $SiO_2$ constituents remain constant in which some $CaO$ was present in interstitial water that during diagenesis replaced the alumina. The high concentration of $MgO$ in purple phyllites and sor slates indicates a large amount of matrix in these rocks.

The petrochemical fields and trends reveal that probably the provenance of these rocks was from pegmatitic and similar other sources. It is therefore suggested that the rocks of the Pithoragarh region were deposited in a geosynclinal basin where phyllites and sandstones were deposited, followed by the calcareous material resulted in the deposition of dolomites under shallow water conditions as is supported by low FeO/MnO ratio and luxuriant growth of
blue green algae—the precursor of stromatolitic colonies. Gradually the basin became deeper in which the slates were laid down. Further shallowing in the basin resulted in the deposition of stromatolitic limestones of Thalkedar Formation.

On the basis of CaO/P₂O₅ ratio, the dolomitic rocks have been classified into four types viz. (1) Slightly Phosphatized dolomites (2) Phosphatic dolomites (3) Calc-phosphorites, and (4) Phosphorites. Due to the consistency of CaO/P₂O₅ ratio between 49.99:1 to 10:1 in all these rocks, it is suggested that the Gangolihat dolomites, should be termed as slightly phosphatized dolomites.
CHAPTER VII

GEOCHEMISTRY OF THE TRACE ELEMENTS

General Statement:

The general recognition of trace elements is not of recent origin. Earlier workers, particularly in the beginning of the 20th century have emphasized the significance and distribution of trace elements in geological materials. Washington (1913) while discussing the distribution of the elements in the earth's crust described that the minor elements were not only related to the rock types but also to the major elements constituting the rocks. Vogt (1918) and Buddington (1933) pointed out certain complications in the distribution of trace elements. According to Goldschmidt's (1954) concept of trace elements geochemistry, there is a tendency for certain minor elements to follow major elements that are similar to them in radius and bond type. Graf (1960) noticed the following forms in which minor and trace elements occur in carbonates vis, (i) solid solubility in the individual minerals (ii) in detritial minerals (iii) as authigenic precipitates (iv) as by-products of recrystallisation and (v) Elements, or their compounds adsorbed on the various minerals.

Strakhov and his co-workers (1956) mentioned that Fe, Mn, P, and number of minor elements such as V, Cr, Ni,
Co, Cu, Pb, Zn, Ga and others remain mainly in suspension during transportation by river waters and enter true solution only to a minor extent. Also within the size range of a suspension, some elements may occur in coarser portions, whereas, others may constitute part of the finer components. These differences in mode of element migration in streams are partly responsible for the differentiation of elements during sedimentation.

Elements adsorbed in colloidal matter tend to accumulate in the clay zone, whereas detrital minerals and elements present in their lattices are deposited both in silts and sands.

In case where an element migrates both in a lattice of coarser particles and adsorbed on colloidal matter the curve may have two maxima, one for sand, and the other for clay deposits.

In addition to the suspension/solution ratio and distribution of elements in the different size grades, geographic factors of element availability are important. Thus the ultimate element distribution is affected by the type and intensity of weathering in the source area and degree of sorting during transportation and deposition.

Intense chemical weathering of the source rock breaks down the complex silicates, aluminosilicates, and sulfides of igneous and metamorphic rocks. The elements thus obtained (Fe, Mn, P, V, Cr, Co, Cu, Pb, Zn, Be, etc.) migrate partly in
suspension as clay minerals, consequently there will be a higher concentration of the elements in fine grained argillaceous and calcareous deep water sediments. Although there are well established methods dealing with data in igneous geochemistry, there is no general recognized procedure for interpreting the chemical variations in a closely related series of sedimentary rocks. Krynin (1949) pointed out that sedimentary rocks may be regarded as a mixture of material carried into the basin of deposition in the solid state and in solution, and this concept has been applied in sedimentary geochemistry by Hirst and Nicholls (1953) and Nicholls and Loring (1962).

For comparing the relative abundances of various trace elements in the different rocks, the following arbitrary scale of concentration of elements has been adopted:

<table>
<thead>
<tr>
<th>Values (ppm)</th>
<th>Scale symbol</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>EH</td>
<td>Exceptionally high</td>
</tr>
<tr>
<td>200–300</td>
<td>VH</td>
<td>Very high</td>
</tr>
<tr>
<td>100–200</td>
<td>H</td>
<td>High</td>
</tr>
<tr>
<td>50–100</td>
<td>M</td>
<td>Moderate</td>
</tr>
<tr>
<td>10–50</td>
<td>L</td>
<td>Low</td>
</tr>
<tr>
<td>2–10</td>
<td>VL</td>
<td>Very Low</td>
</tr>
<tr>
<td>p–2</td>
<td>T</td>
<td>Traces</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>Not detectable</td>
</tr>
</tbody>
</table>
The distribution of trace elements in various lithological units is represented in Table-XXI, whereas the average concentration of trace elements in phosphorites given by Krauskopf (1955) and trace elements threshold values for phosphoria Formation given by Gulbrandsen (1966) are compared with the average trace elements content of the phosphorites of the area under study and are given in Table-XXII.

Figs. 27-31 represent the modal distribution of trace elements with respect to P₂O₅ content in the order of decreasing abundance for Hiunpani, Chandaak, and Dhari Members; Sor Slates, and Dolomites from Gangolihat town respectively.

Table-XXII-Comparison of Trace-elements content in Pithoragarh phosphorites with other areas (in ppm)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Phosphorites of Pithoragarh (average)</th>
<th>Phosphorites (Krauskopf 1955) average</th>
<th>Phosphorites of Phosphoria Formation (Gulbrandsen 1966) Threshold values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>32</td>
<td>30-300</td>
<td>100</td>
</tr>
<tr>
<td>Ce</td>
<td>&lt;2</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>20</td>
<td>30-400</td>
<td>1000</td>
</tr>
<tr>
<td>Cu</td>
<td>11</td>
<td>4-40</td>
<td>100</td>
</tr>
<tr>
<td>Ga</td>
<td>03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>La</td>
<td>&lt;2</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>Ni</td>
<td>06</td>
<td>4-200</td>
<td>100</td>
</tr>
<tr>
<td>Pb</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rb</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sr</td>
<td>&lt;2</td>
<td>-</td>
<td>10⁰</td>
</tr>
<tr>
<td>V</td>
<td>35</td>
<td>50-1000</td>
<td>1000</td>
</tr>
<tr>
<td>Y</td>
<td>20</td>
<td>30-200</td>
<td>300</td>
</tr>
<tr>
<td>Zn</td>
<td>18</td>
<td>10-200</td>
<td>300</td>
</tr>
<tr>
<td>Zr</td>
<td>10</td>
<td>10-100</td>
<td>30</td>
</tr>
</tbody>
</table>

BARITHMATIC AVERAGE: THE MEAN VALUE OF GEOCHEMICAL ANALYSES.
Fig. 27 The distribution of trace elements in order of increasing concentration is shown in different modes with respect to $P_{755}$ concentration for Humfan Member.
FIG 2.8 THE DISTRIBUTION OF TRACE ELEMENTS IN THE RESTAURANT S SHOWN IN DIFFERENT MODES WITH PERCENTAGE. SAMPLES 31, 32, 40, 93, 147.
FIG 29 THE DISTRIBUTION OF TRACE ELEMENTS IN ORDER OF DECREASE IN ABUNDANCE IS SHOWN IN DIFFERENT MODES WITH RESPECT TO FeO CONTRACTIONS FOR DHARI MEMPIS.
FIG. 30 THE DISTRIBUTION OF TRACE ELEMENTS IN ORDER OF DECREASING ABUNDANCE IS SHOWN IN DIFFERENT MODES WITH RESPECT TO $P_2O_5$ CONCENTRATION FOR SOR SLATES.

N.D.—Not detected
DOLOMITES FROM GANGOLIHAT TOWN

Fig 31: The distribution of trace elements in order of decreasing abundance is shown in different modes with respect to $\text{P}_2\text{O}_5$ concentration of dolomites around Gangolihat Town.

ND: Not detected.
The geochemistry and distribution of individual elements have been discussed in the foregoing pages.

**Strontium:** In nature, it behaves as a lithophile element and occurs in oaksalts in residual sediments like sandstones. It becomes concentrated by secondary infiltration into the porous materials. In hydrolysate sediments and in the clay minerals of soils, strontium may be fixed on a very moderate scale by base exchange. In carbonates, the strontium content varies widely as reported by various workers like Rankama and Sahama (1950), 425 - 765 ppm, Krauskopf (1955), 400 - 300 ppm, Runnels and Schleicher (1956), 470 ppm; Ostrom (1957), 490 ppm and Graf (1960) 420 ppm.

Katchenkov (1959) observed that argillaceous carbonate rocks generally contain more strontium than pure carbonates. Vinogradov et al. (1952) showed that both the SrO content and SrO/CaO ratio for carbonate rocks regularly increased during the evolution of the earth.

In the present area of investigation the strontium content is highly variable. The maximum concentration of strontium recorded in these sediments is 378 ppm, which is slightly lower than previously given concentrations.

It varies between moderate to exceptionally high in all the Members except for or Slates. It is also noticed that phosphorus rich samples have high Sr concentration, it is
therefore, inferred that strontium concentration
follows the $P_2O_5$ concentration as is demonstrated in
Figs. (27 - 31). In slates strontium content varies
from moderate to high.

The increasing content of Sr with $P_2O_5$ could be due
to the isomorphous replacement of Ca by Sr in the phosphate
minerals and also possibly to the formation of supergene
strontium phosphates. The tendency of Sr to replace Ca
in mineral structures is furthermore shown by its presence
in apatite and in calcium bearing amphiboles and pyroxenes.
It has been demonstrated (Khudolozhkin et al., 1972)
that strontium ions occupy mainly sites Ca II (in the
polyhedra with seven Vortices) in the apatite structure and
that the degree of ordering decreases almost linearly
with increase of belovite, (Sr-apatite end member)
$\text{Sr}_{10} (\text{PO}_4)_6 (\text{OH})_2$, content in apatite.

Kulp et al. (1952) and Turekian (1955) stated
that the Sr/Ca ratio in carbonate shells, and sediments
is a function of several variables namely (1) The Sr/Ca
ratio in the liquid phase, (2) The particular polymorph
calcite or aragonite into which Sr is incorporated,
(3) The effects of the organisms (4) The temperature and
(5) The salinity of the liquid phase. In the present
study it is felt that organisms were the important source for strontium concentration.

The relationship between Sr/Ca and percentage of Ca as demonstrated in Fig. 32, reveals a slightly negative correlation reflecting thereby that there is a considerable proportion of Sr associated with Ca and in many cases the Sr content is independent of calcium content.

The Sor Slates have a high Sr/Ca ratio (Table XXIII), i.e. $67.85 \times 10^{-3}$ indicating that the absorption sites on clay particles prefer strontium relative to calcium. It seems possible that Sr is left behind as a weathering product of igneous rocks relative to calcium, since the clay minerals are prominent residues of weathering.

**Vanadium:** Vanadium is a lithophile element. In igneous rocks it occurs in three stable oxidation states, viz, as trivalent, quadri-, and quinquivalent vanadium. In sediments and sedimentary rocks vanadium occurs in quinquivalent state. It replaces aluminium preferably in clay minerals.

In apatite $V^{5+}$ may replace $P^{5+}$, which explains the concentration of vanadium in the apatite rich iron ores as observed by Landergrgen (1949). Like phosphorus and arsenic the quinquivalent vanadium has a pronounced tendency to form $(VO_4)$ tetrahedra in mineral structures.
FIG. 22. VARIATION IN THE RATIO OF Sr/Ca WITH % Ca
Vanadium is highly variable in carbonate rocks. It is found to be varying from traces (Ostrom, 1952) and up to 3000 ppm (Runnals and Schiecher, 1956). Graf (1960) has given a range of 10-150 ppm with 12±3 ppm as an average. In the marine phosphorites of Idaho, Jacob et al. (1933) have reported 1300 ppm of vanadium.

In the Gangolihat Formation vanadium varies between 20-310 ppm, but it is high in phosphorus rich rocks. It has been noticed that rock phosphates having 20% P₂O₅ show above 300 ppm of vanadium, otherwise in rocks in which P₂O₅ is less than 20%, it is low. On the other hand in Sora Slates it varies between 32 and 92 ppm. In the dolomites around Gangolihat it does not increases more than 40 ppm.

Table-XXIII shows the V/P ratio. The plotting of this ratio against P content (Fig. 33), two trends have been observed. The low phosphate content samples give a negative correlation with V/P ratio, whereas the phosphate rich samples show a constant V/P ratio. It indicates that V was supplied to the basin along with phosphorus and was enriched in sediments with high phosphorus content implying thereby that the physico-chemical conditions for the enrichment of both are similar or nearly so.

The enrichment of V with P is supported by Nicholls and Loring (1962) who found the high vanadium content in coal cyclothemes in Great Britain, due to absorption of V by clay and organic matter. Further Tourtelot (1964)
suggests that in organic matter of marine origin absorption and biogenic concentrations are more effective. It is therefore inferred that in Pithoragarh phosphorites the vanadium concentration is mostly due to the absorption and biogenic concentrations because of their close association with the marine algae.

The V/Al, V/Fe and V/Mg ratios (Table XXIII) were also calculated and on the bases of their high variations in calcareous rocks (i.e., 0.41 to 59.61 x 10^{-2}, 0.47 to 42.35 x 10^{-2} and 0.01 to 1.66 x 10^{-2} respectively). It is inferred that vanadium is neither associated to clays nor to dolomites, but with phosphorus as is shown by their almost constant V/P ratio (i.e., V/P 3 x 10^{-3}) with the increase of P content (Fig. 33).

Rubidium: It is a lithophile element, its geochemistry is very closely related to that of potassium.

Of all the alkali metals, rubidium has the highest tendency to interstitial capture and is readily absorbed, even more readily than potassium (Goldschmidt, 1937). As a result of this tendency of quick absorption and particle inclusion of rubidium in the crystal lattices of clays, the bulk of this element is released during the weathering of igneous and metamorphic rocks, it is bound to be more in clay minerals.
According to Wadepohl (1970) the abundance of Rb in dolomites vary from 6-370 ppm, in silty limestones 6-167 ppm, in sands and sandstones 9-100 ppm, in shales 20-663 ppm, and in argillaceous sediments 23-220 ppm.

Table XXII, represents the rubidium concentration in these sediments. In Hiumpani Member it is low to high (22-134 ppm), in Chandasad low to very high (30-225 ppm) in Dhari low to very high (40-235 ppm), in Gor Slates low to moderate (23-35 ppm), whereas in samples around Gagolihat town, it varies between low to moderate (i.e., 20-63 ppm).

Potassium when plotted against rubidium shows a sympathetic relationship between the two in slates, because of the fact that rubidium has higher absorption energy and hence is absorbed by clay minerals in the catchment area and is firmly retained by them (Goldschmidt, 1930), while in calcareous rocks a negative correlation is observed (Fig. 34).

In the calcareous rocks it is found that Rb increases with the increase in P₂O₅ content (Figs. 27-31).

Barium: Geochemistry of barium in igneous rocks is characterized to a large extent by its relationship to potassium. The ionic radii of divalent Ba (1.43 Å) and
FIG. 34 VARIATION IN BETWEEN %K AND Rb (ppm)
and univalent K (1.33 Na) are sufficiently similar to allow barium to be captured by K-minerals. Due to decomposition it is dissolved and brought into circulation in aqueous bicarbonate solutions.

The barium content determined by various authors in carbonates is reported to be 120 ppm (Runkama and Sahama, 1950), 20-200 ppm (Krauskopf, 1955), 390 ppm (Runnells and Schleicher, 1956), 260 ppm (Ostrom, 1957) and 220 ppm (Graf 1960). On the other hand Von Engelhardt (1936) has reported 270-900 ppm Ba in phosphorites, whereas in phosphoria Formation its content is low i.e. 100 ppm (Gulbranssen, 1966).

In the present area of investigation Ba varies from low to very high in calcareous rocks (i.e. 22-224 ppm), whereas the Slates show low content of barium (i.e. 25-40 ppm), as compared to calcareous sediments.

It is found to be increasing with phosphorus content (Figs. 27-31). The curve relating Ba/K to percentage K (Fig. 35) shows high tendency towards inverse relationship. The high variation in Ba/K (0.04-10.58x10^2) and Ba/Mg+K (0.019-1.97x10^2) ratios (Table XXIV) in calcareous rocks, suggest that barium was transported into the basin independently. Barium rather associated with
phosphorus, as it shows a positive correlation with the later. (Figs. 27-31). In slates, clay minerals control the barium content as is evidenced by their increase in Ba/K ratio with increasing K-content (Fig. 35) because of their concentration in hydrolysate sediments (Rankam and Sahama, 1950).

**Chromium:** As chromium very much resembles to iron and aluminium in its chemical properties, ionic size, and ionic charge, it follows them during exogenic cycle and is therefore concentrated in resistates and hydrolysates.

Rankama and Sahama (1950) have reported 2 ppm Cr in carbonate rocks, whereas others give as 5 ppm, (Krauskopf, 1955); 13 ppm (Runnels and Schleicher, 1956); 11 ppm (Ostrom 1957) and 13 ppm (Gref 1960). In phosphorites, chromium concentration has been reported to be quite high. Krauskopf (1955) has reported 30-400 ppm and Gulbrandsen (1966) up to 1000 ppm of chromium in Phosphoria Formation.

Chromium concentration in the Gangolihat Formation is low and varies from not detectable to 72.00 ppm but in phosphorites it is high and goes up to 165 ppm.

The high concentration of Cr in phosphorites might be due to the presence of organic matter (Vinogradov, 1953). Later studies by Krauskopf (1956) also confirm Vinogradov's observations.

As proposed by Frolich (1960) on the other hand, that chromium in sediments is concentrated in micas and
FIG. 35 Variation in the ratio of Barium to Potassium with percentage Potassium in Pithoragarh formations.
phosphorus, as it shows a positive correlation with the later. (Figs. 27-31). In slates, clay minerals control the barium content as is evidenced by their increase in Ba/K ratio with increasing K-content (Fig. 35) because of their concentration in hydrolysate sediments (Rankama and Sahama, 1950).

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As proposed by Frohlich (1960) on the other hand that chromium in sediments is concentrated in micas and
clay minerals, Hirst (1962), and Nicholls and Loring (1962) have also determined the relationship between Cr content and aluminium in sediments. The author in the present study has also analysed the data and calculated Cr/Al and Cr/Fe ratios (Table-XXIV) which vary from 3.30 to 31.13x10^{-3} and 0.35-15.71x10^{-2} respectively. The plotting of Cr/Al against percent Al further indicates that even on the variation of Cr/Al ratio (Fig. 36) percentage alumina remains constant (i.e. 0.04 to 0.06%), which confirms that Cr is not associated with clay minerals in these sediments.

Fig. 37 represents a sympathetic relationship between Ni and Cr which may be expected owing to their similar chemistries and petrogenetic affinities. It may also be due to the provenance that might be rich in basic rocks (Angino, 1966).

**Nickel:** Geochemically Ni is very pronouncedly siderophile and its bulk is found in metallic iron. In acid igneous rocks Ni is less enriched than basic and ultrabasic rocks.

During the weathering of ultrabasic rocks it forms a number of hydrosilicates with complicated chemical composition. In sea water nickel most probably prevails as dissolved species mainly as nickelous ions, as either aquato or chloro-complexes.
FIG. 36 Variation in ratio of Cr to Al with percent Aluminium
The nickel content in carbonate rocks has been reported by various workers and there is great divergence in their data. Krauskopf (1955) has reported 3-10 ppm of Ni whereas Runnels and Schleicher (1956) and Graf (1960) have reported 10 and 15 ppm of Ni in carbonate sediments respectively.

In the Gangolihat Formation, it varies from 4-40 ppm, generally low but high in phosphorus rich sediments. In Sor Slates, it varies from 12-25 ppm, which is comparatively lower than calcareous rocks.

The Ni/Al and Ni/Fe ratios (Table-XXV) are found to be varying in calcareous rocks (i.e. $13 \times 10^{-3}$ to $71.15 \times 10^{-3}$ and $1.14 \times 10^{-2}$ to $55.7 \times 10^{-2}$ respectively), while fairly constant Ni/Al ratios exist in slates ($0.34 \times 10^{-3}$ to $0.59 \times 10^{-3}$). The plotting of Ni/Al against percentage Al (Fig. 38), it is observed that in calcareous rocks and Sor Slates no significant correlation exists between the two and the alumina percentage remains constant (0-3-0.5%), while Ni/Al ratio varies from 0.2 to $18 \times 10^{-3}$, indicating that Al is independent of Ni. On the other hand Ni/Mg ratios (Table-XXV) are fairly constant and vary between narrow limits (i.e. $0.02 \times 10^{-3}$ to $0.66 \times 10^{-3}$), indicate that most probably nickel is associated with Mg, whereas on examining Figs. 27-31, it is observed that nickel increases with $P_2O_5$, hence it supports the view of Israeli (1978 b) that MgO acts as a catalyst.
**FIG. 37** Ni plotted against Cr (in ppm) for all rocks of the area.

**FIG. 38** Variation in ratio of Nickel to Aluminium with percentage Aluminium.
**Zinc:** Though zinc is predominantly a chalcophile element but in upper lithosphere, it is classified among oxyphile elements. During weathering Zn goes readily into solution as sulphate or chloride, which later on transported in surface or ground waters. It is consequently very mobile, according to Wickman (1944) it lies on the border between the soluble cations and the elements of hydrolyzates.

P.H. Lundegardh (1949) reports an average value of 100 ppm zinc for Archaean and paleozoic slates. Rankama and Sahama (1950), Krauskopf (1955), Runnels and Schleicher (1956), Ostrom (1957), Graf (1960) have reported 50 ppm, 4-20 ppm, 35 ppm, 40 ppm, 16±3 ppm, Zn content respectively in the calcareous rocks.

Table XXI represents the Zn concentration in these sediments. Generally it is low and varies between traces to 65 ppm, its concentration increases with increasing P<sub>2</sub>O<sub>5</sub> (Fig. 27-31), whereas with iron it shows a perfect inverse relationship (Fig. 39).

**Copper:** It is a chalcophile element but with siderophile tendency, it shows high affinity with sulphur. Due to the similarity of radii of Cu<sup>2+</sup> (0.33 K x) and Fe<sup>2+</sup> (0.33 K x) Carobbi and Pieruccini (1947) have suggested that Cu replaces Fe<sup>2+</sup> and Mg<sup>2+</sup> for instance in tourmaline.

Krauskopf (1956) has shown that Cu is effectively absorbed by Fe (OH)<sub>3</sub>, Mn (OH)<sub>3</sub> and clay minerals. In
FIG. 39 Zn PLOTTED AGAINST IRON

FIG. 40 VARIATION IN RATIO OF COPPER TO PHOSPHORUS WITH % PHOSPHORUS.
Carbonate rocks average concentration of Cu is 20 ppm. In the rocks of Pithoragarh Cu content is low and varies between 7 and 33 ppm.

Cu/Al and Cu/Mg ratios (Table-XXV) of these sediments are highly varying (i.e. from $1.15 \times 10^{-3}$ to $28.84 \times 10^{-3}$ and $0.010 \times 10^{-2}$ to $1.12 \times 10^{-2}$ respectively) suggest a noncoherence of Cu with both these elements. Whereas Cu/P ratio (Table-XXVI) plotted against percentage phosphorus (Fig. 40), the curve shows that Cu/P ratio becomes constant at Cu/P $0.024 \times 10^{-2}$, while phosphorus varies (0.0 to 15%). It is mainly due to the ionic substitution of Cu in the phosphate lattice at the site of deposition. The ratios above this are probably due to additional Cu contributed by some other sources or mechanisms. According to Krauskopf (1955) the concentration of Cu in phosphate is due to algal matter, such a possibility has also been reported by Verma (1978) Raha (1978), whereas Israeli (1978c) on the other hand believes that the high concentration of Cu in sediments associated with blue green algae possibly be due to similar physico-chemical conditions ($E_n - pH$) at the time of their concentration.

**Gallium**: Geochemistry of Ga is very closely related to aluminium, the size of the trivalent cations of Ga 0.62 Å and Al 0.57 Å are so nearly alike that most of the Ga is hidden away or camouflaged in aluminium minerals.
It is typically a dispersed element, whose abundance in minerals is determined by its isomorphism with other elements, mainly with Al, Zn and Fe. Its content decreases with increasing basicity of the rock.

The average Ga content in calcareous rocks is 3 ppm. In the Gengolihat Formation the Ga content varies between 2 and 6 ppm whereas in Sor slates it is comparatively high and varies between 16 and 36 ppm.

According to Burton et al. (1959) the reluctance of Ga to enter carbonate minerals is probably due to the fact that it does not form carbonates but instead either goes into solution as the gallate ion, or precipitates as hydroxides. The Ga/Al and Ga/Na + K ratios are highly variable in calcareous rocks (i.e., 3.6 x 10^{-4} - 60.0 x 10^{-4}, and 0.66 x 10^{-3} - 4.39 x 10^{-3} respectively) and indicate that it is not associated with clay minerals (Table XXVI). But in the present study it is observed that Ga increases with P_2O_5 content in calcareous rocks while in slates it decreases (Figs. 27 - 31). Which reveals that the gallium and P_2O_5 are concentrated in an alike geochemical environment.

Lead: It is occurring in the upper lithosphere both as a chalcophile and a lithophile element. The ionic radius of Pb
(1.32 Å), makes it possible to replace Sr (1.27 Å) and Ba (1.43 Å). Accordingly, divalent lead commonly occurs in the K-minerals and also in apatite. It is present in silicate and phosphate minerals as Pb$^{2+}$ ions and particularly replaces Ca (1.06 Å) diadochically and is found in such calcium minerals as apatite (upto 50g/ton Pb, Goldschmidt 1937 b). However, it may replace Ca$^{2+}$ in minerals formed at lower temperatures.

In the carbonates its concentration is highly variable as evidenced by 5-10 ppm (Rankama and Sahama, 1955); 16 ppm (Runnels and Schleicher, 1956); 26 ppm (Ostrom, 1957) and 7.2 ± 4.2 (Graf, 1960).

In the Gangolihat Formation Pb is low (18-50 ppm) whereas in phosphorites it is high and goes up to 144 ppm (Figs. 27 - 131). Horowitz (1974 a) found that carbonates can act as a host for Pb that is why it becomes enriched in phosphorites.

**Selenium:** Geochemically selenium is close to sulphur but less active. It forms primary metal compounds with heavy elements like Pb, Hg, Bi, Ag, Cu, Co, Fe, Tl, Ni, Zn and Cd.

During supergene processes it is characteristically associated paragenetically with uranium, vanadium, silver, molybdenum and copper. It precipitates in a reducing.
environment.

In the present area of investigation the selenium content is very low and in most of the samples it is below the detectable limits. In slates no selenium is recorded.

**Zirconium:** Zirconium is a lithophile element which occurs in silicate form. During weathering it remains largely in the resistates in form of zircon. It becomes concentrated in resistates than hydrolysates. Some zirconium also goes into solution and it is removed from solution by hydrolysis and does not form secondary minerals.

In the present area of investigation zirconium content is low and varies from 10 to 40 ppm in carbonate rocks, whereas in slates its concentration does not increases more than 12 ppm.

Figs. 27 to 31 represent that zirconium content increases with P2O5 content in all the lithologic units. This increase in zirconium content with P2O5 also supports the view that phosphate material was derived from igneous source, because of the reason that in sedimentary rocks zirconium is derived mostly from igneous rocks.
Rare Earths: Among the rare earths, the major elements determined include cerium, lanthanum and yttrium. Although these elements exhibit a marked degree of coherence therefore anomalous assemblages are found in minerals.

Average Y content in earth's crust according to Goldschmidt (Lot. Cit.) is 0.0020%. Of all the lanthanides, cerium is the only rare earth with a higher abundance. Among the phosphates, xenotime (YPO$_4$) and churchite (YPO$_4$.2H$_2$O) are rich in yttrium content having 26% and 26% Y respectively.

Heterovalent isomorphism is pronounced between Y and Ca, Zr, U, Pb, Mn, Fe such as

\[
\begin{align*}
Y^{3+} + Al^{3+} & \quad (Mn Fe)^{2+} Si^{4+} \quad \text{Spessartite} \\
Y^{3+} & \quad U^{4+} O^{2-} \quad \text{Uraninite} \\
Y^{3+} + B^{3+} & \quad Ca^{2+} C^{4+} \quad \text{Calcite} \\
Y^{3+} S^{2-}_{0.5} & \quad Pb^{2+} \quad \text{Galena}
\end{align*}
\]

Most of the yttrium fluorides and silicates (Gagarinite, gaddolinite, thalenite, etc.) undergo
substantial chemical weathering, their alteration products are hydrous carbonates and phosphates of yttrium, e.g. churchite, Y-bastnasite, tengerite etc.

The abundance of yttrium in various rocks is as follows

<table>
<thead>
<tr>
<th>Mineral/Rock</th>
<th>Locality</th>
<th>$Y_{2}O_{3}^{%}$</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schists</td>
<td>Average for</td>
<td>0.0026</td>
<td>Turekian and Wedepohl (1961)</td>
</tr>
<tr>
<td></td>
<td>the Earth's</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>crust</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argillaceous</td>
<td>Japan</td>
<td>0.0030</td>
<td>Minami (1935)</td>
</tr>
<tr>
<td>Shale</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandstone</td>
<td>Average for</td>
<td>0.0040</td>
<td>Turekian &amp; Wedepohl (1961)</td>
</tr>
<tr>
<td></td>
<td>the Earth's</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>crust</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonates</td>
<td>Average for</td>
<td>0.0030</td>
<td></td>
</tr>
<tr>
<td></td>
<td>the Earth's</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>crust</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limestone</td>
<td>New Mexico</td>
<td>0.016</td>
<td>Cr.H (1960)</td>
</tr>
<tr>
<td>Phosphorites</td>
<td>U.S.S.R.</td>
<td>0.016</td>
<td>Smernov et al. (1962)</td>
</tr>
<tr>
<td>Pelagic marine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sediments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonates</td>
<td>Average for</td>
<td>0.0042</td>
<td>Turekian &amp; Wedepohl (1961)</td>
</tr>
<tr>
<td></td>
<td>Earth Crust</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>Southern</td>
<td>0.005</td>
<td>Sahama (1952)</td>
</tr>
<tr>
<td></td>
<td>Lapland</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lanthanides include elements having atomic numbers 57-71 and 39, among which lanthanum 57 and cerium - 58 are important, and have been determined in these sediments.
They can isomorphously replace a large number of elements having radii from 1.39 Å (Ba) to 0.7 Å (Sn). They exhibit isomorphism with Ca, Sr, Ba, Mn, Fe, Th, U, Zr, Hf, K, and Na.

The average content of La and Ce as given by Semenov et al. (1962) is 15.9% and 32.5% respectively.

Elwakael and Riley (1961) have found that in pelagic sediments the rare earths content is ten times higher than igneous rocks. Goldberg and Arrhenius (1953) have recorded 0.21% \( \text{La}_2\text{O}_3 \) in apatite and phillipsite concretions formed in Pacific Ocean.

Of all the sedimentary rocks, placers and phosphorites show the greatest enrichment in rare earths. Graf (1960) has reported 14 ± 11 ppm Y and 13 ± 8 ppm Ce in carbonate rocks.

The rare earth concentration in Gangolihat Formation and Sor Slates is as follows:

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Y (ppm)</th>
<th>Ce (ppm)</th>
<th>La (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hitpani Member</td>
<td>18-164</td>
<td>Tr-28</td>
<td>11 - 45</td>
</tr>
<tr>
<td>Chandaak</td>
<td>14-175</td>
<td>Tr-42</td>
<td>Tr-34</td>
</tr>
<tr>
<td>Dhari</td>
<td>18-194</td>
<td>Tr-30</td>
<td>Tr-45</td>
</tr>
<tr>
<td>Sor Slates</td>
<td>15-52</td>
<td>Tr-24</td>
<td>Tr-12</td>
</tr>
</tbody>
</table>

After carefully observing the whole succession of Gangolihat Formation it is noted that there is a progressive enrichment of Y in younger rocks than older (i.e., Hitpani member), this increase in yttrium content is due to
due to enrichment of $P_2O_5$ in younger Members.

Fleischer (1965) has recently shown that a positive relation exists between lanthanide abundances in apatite from igneous rocks and mineral paragenesis.

Cruft (1966) has plotted ratios of Ce:Y:La in ternary coordinates and has marked a fairly constant ratio of three elements in apatite from igneous intrusions, metamorphic apatites and hydrothermal apatites, whereas pegmatitic apatites are rich in Y content.

The author while plotting the Ce:Y:La ratios (Table-XXVII) in ternary coordinates (Fig. 41) noticed that Y is more enriched in these phosphorites. This high concentration of Y relative to other rare earths suggests that there was a pegmatitic like source in the provenance which supplied high concentration of Y to these sedimentary phosphate deposits.

Khalodov (1972) observed a constant $RE_2O_3/P_2O_5$ ratio in catchment and discharge area during weathering of Karatau phosphorites, and suggested that when the phosphatic and carbonate materials are separated by ground waters the rare earth follow phosphatic material being strongly bound in it and accumulate in the same area as the high quality phosphorite.

The author while plotting La:Ce/P ratios (Table-XXVI)
against percentage P noticed a constant ratio while P increases indicating a coherence between P and La+Ce (Fig. 42).

Moreover Bliskovskiy et al. (1969 a, b) favour that RE₂O₃ enters isomorphously into the crystal structure of fluorapatite, hence the ratios between RE₂O₃ and P₂O₅ remain constant (Fig. 43).

Further Volkov and Fomina (1973) have found that RE increase with P₂O₅ content in Pacific sediments. Nathan (1976) found that rare earth elements are held mainly in fine grained accessory phosphate minerals such as apatite and monazite. Ronov, et al. (1972) observed that the rare earths were absorbed by clay and carbonate particles or else enclosed in authigenic phosphates.

**Interpretation and conclusion:**

Generally the trace element concentration in these sediments is highly variable, and corresponds to the earlier published values of dolomites and limestones, except the rare earths which are comparatively high.

On the bases of trace element contents, an attempt has been made to find out the provenance and environmental conditions at the site of deposition.
FIG 42 VARIATION IN RATIO OF La+Ce to P WITH PERCENTAGE PHOSPHORUS

FIG 43 VARIATION BETWEEN $P_2O_5$ AND $Y+La+Ce$
The low gallium content (i.e., 4 ppm average) suggests a marine environment, which is supported by Degens, et al. (1967), Hirst (1962) and Potter et al. (1963), that the marine sediments have low Ga than freshwater sediments, but the Sdr Slates have slightly higher Ga content (i.e., 24 ppm) indicating a change in basin from marine to brackish water environment.

High Ga/Al ratio of these sediments as compared to average igneous rocks (2.36×10^-4, Shaw, 1957) seems likely that it can be explained by weathering of an igneous source rock which was responsible for such a high Ga/Al ratio.

According to Horstman (1957) Rb in carbonates is very low (i.e., below detection limit), while, Weber (1964) has given 23 ppm in secondary dolostone. In sediments of the study area it is comparatively high (158 ppm), and shows strong positive correlation with P O\textsubscript{5}. If we assume that apatite was supplied by pegmatites on the basis of yttrium then this high rubidium content could also be due to those pegmatites.

The strontium content in these dolomites ranges from 3 to 90 ppm, whereas in phosphorites upto 378 ppm. In ancient dolomites, Shimochawandi and Shearman (1966), Graf (1960) and Awasthi (1970) found a strontium content one-half to two-thirds lower than in undolomitised portions of the same rock unit. Data of Katz et al. (1972) indicates that dolomite with a Sr content as low as 250 ppm could be
formed by direct precipitation or by replacement in sea-
water pore fluid. The strontium content of the dolomites
around Pithoragarh is too low to be explained by diagenesis
in a sea-water pore fluid which is further supported by
If this possibility is true then the question of low Sr
content in these dolomites is also satisfied by this conclusion.

Keith and Degens (1959) have applied chromium
also as an indicator of environmental conditions, whereas
Nicholls and Loring (1962) are of the opinion that it is
not a good indicator, however on the basis of low Cr content
it is concluded that a shallow marine environment was prevailing.

Beside this, it is observed that almost all the traces
are increasing with increasing phosphatic content, while
some of them (Y, Co, La, Cr, Zr,) are very low and below
detection limit in phosphate poor carbonates.

Many earlier workers like Van Ingen, (1915),
Van Ingen and Phillips (1915), Phillips (1917, 1922),
Noddeck and Noddeck (1939), Bowen and Lutton (1951),
Black and Mitchell (1952), La Riche (1959), Nicholls
and Loring (1962), Tourtelot (1964), Verma (1973) and
Raha (1973) are of the opinion that V, Cr, Ni, Cu and
Zn can be accumulated in sediments by organic metabolism.
Israelí (1973 c) on the other hand refuted the above observations on the ground that even a slight concentration of many of these elements in solution is toxic to algal and other organisms, hence the question of their concentration by the biothermal and other organisms does not arise.

The concentration of trace metals by organisms is well documented and it has been shown that the metals are retained by fairly strong chemical bonds are not readily eluted and therefore may remain in the sedimentary rocks if organic material has been incorporated.

Furthermore both these processes are operative and the absorption mechanism supplemented by organic reactions appears to furnish a qualitative explanation for the distribution of zinc in marine sedimentary rocks (Krauskupf, 1956).

The author is of the opinion that the high concentration of these elements (V, Cu, Ni, Cr) in the phosphorite rich samples is mainly due to similar physico-chemical conditions i.e. low Kh-pH, salinity and shallow water conditions at the time of their deposition. It is the same zone where the mixing of land derived material brings chemical changes even at shorter distances. It is also the region where blue green algae thrive most. The association thus with the phosphorites and other metallic deposits is mainly due to similar conditions of deposition.
Factor analysis is a branch of multivariate statistics that has been used and developed largely by psychologists. The principal aim of this analysis is to reduce the complex pattern of correlation amongst many variables to simpler sets of relationship amongst fewer variables. The principal contributors to the theory include Pearson (1901), Spearman (1904), Thurstone (1931), and Holzinger (1944), while a comprehensive modern account can be found in Harman (1960). In recent years geologists have begun to use factor analysis as an aid in the interpretation of complicated problems.

Imbrie and Purdy (1962), and Krumbein and Imbrie (1963) have applied the technique to sedimentary problems, while Reeves and Saadi (1971) have used it for deposition of phosphate bearing strata.

The factor analysis may proceed by examining the relationship between variables (R-mode of analysis) or between samples (U-mode of analysis), but here only the relationship between variables are examined. Furthermore it should be mentioned that this analysis in no way replaces interpretation, it merely assembles the data in more readily interpreted form.
Factor analysis involving a large number of variables is only valid with the aid of a high speed electronic computer. For this study the program used was an I.B.M. package program, listing of which is given in appendix and was provided by computer centre A.M.U. Aligarh.

Assume a \( p \)-variate system \( X_1, X_2, \ldots, X_p \), each observed on 'n' individuals. If \( X_{ij} \) is the \( j \)th observation on the \( i \)th individual, the variables can be arranged in a matrix of dimension \( n \times p \) and can easily be manipulated using the rules of matrix algebra.

If it is possible to define the system with less than \( p \) variables it means that some of the variables must be linear combinations of some of the others. However in general, it is not possible to effect a reduction of this sort, partly because of the error factor involved.

Factor analysis assumes that each variable \( X_i \) can be expressed in the form

\[
X_i = a_{i1}f_1 + a_{i2}f_2 + \ldots + a_{im}f_m + u_{i1}
\]

where the \( f_j \) are common factors and the \( a_{ij} \) indicates the relative importance of the common factor \( f_j \). A common factor is a factor that is present in each variable. The \( u_{i1} \) is a factor that is unique to the particular variable in question.
Most problems are concerned only with the common factors. Because the readings are arranged so that the variance of each variable is unity, the sum of squares of the coefficients of the common factors account for the variance of that variable and is known as the communality.

The dimensional reduction is carried out in an approximate way by choosing the first factor so that it accounts for as much of the variance as possible and then choosing each succeeding factor so that it also accounts for as much of the variance as possible and is uncorrelated with all preceding factors. If the first few factors account for a large proportion of the variation it may be possible to ignore the rest.

The R-mode of analysis proceeds from an analysis of correlation matrix where the product-moment correlation coefficient between \( x_j \) and \( x_k \) is given by

\[
\tau_{jk} = \frac{\sum (x_{ji} - \bar{x}_j) (x_{ki} - \bar{x}_k)}{\sqrt{\sum (x_{ji} - \bar{x}_j)^2 \sum (x_{ki} - \bar{x}_k)^2}}
\]

The correlation coefficient is a measure of the linear relationship between two variables and its value lies between \(+1\) and \(-1\), depending on whether the variables are related sympathetically or antipathetically.
After the variables corresponding most closely to the factor axes have been determined, they must be interpreted geologically.

However, because the number of possible solutions of the factor analysis model is usually infinite, care must be taken to substantiate all conclusions arrived at solely as a result of study of this sort.

**RESULTS:**

**Means, standard deviations and coefficient of variation:**

Means were calculated in the usual way and standard deviations were obtained using the formula

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{N - 1}}$$

The coefficient of variation is a measure of the relative dispersion of a variable and enables direct comparisons to be made between distributions having different units of measurement. It was computed using the formula

$$v = \frac{s}{\bar{x}}$$

The values of means, standard deviations, and coefficient of variation for the determined major and trace elements are given in Table XXVIII.

**Correlation Matrix:**

The correlation matrix is given in Table XXIX. The
values are product-moment correlation coefficients (as previously defined).

**Rotated Factor Matrix:**

The rotated factor matrix is shown in Table XXX. Seven factors explaining approximately 78.90 percent of the total variation in the data have been extracted from the correlation matrix and the system has been rotated so that the seven independent factor axes correspond with groupings present in the data. The grouped variables that correspond most closely to any particular factor axis may be obtained by scanning each column of the matrix for the highest values. It can be seen that factor-1 may be represented by $P_2O_5$, $SiO_2$, $V$, $Rb$, $Sr$, $Ba$, $Y$, $La$, $Ce$, $Cr$, $Zn$, $Rb$, $Ni$, and $L.O.I.$ (loss on ignition). Factor-2, by $MnO$, $Al_2O_3$, $Ga$, and $Ni$; Factor-3, by $CaO$, $MgO$ and $SiO_2$; Factor-4, by $Fe_2O_3$, $Al_2O_3$, $L.O.I.$, $K_2O$, $Zn$, and $Ni$; Factor-5, by $Cu$, $Zn$, $Ni$, and $SiO_2$; Factor-6, by $Na_2O$, $K_2O$, $SiO_2$ and $Al_2O_3$ and Factor-7, by $Rb$, $MnO$, $Ga$, $Rb$, $Ce$ and $L.O.I.$.

The column headed by communality indicates what proportion of the variability of any particular variable has been explained by the seven factors shown. It is obtained by squaring the absolute values in each row (e.g. a communality of 0.78154 for $SiO_2$ is obtained by adding ($0.60852)^2 + (0.33999)^2 + (0.22860)^2 + (0.1413)^2 + (0.31457)^2 + (0.33983)^2 + (0.16948)^2$).
Discussion:

As can be seen from the means (Table-XXVIII), CaO, MgO, SiO₂, and L.O.I. are determined in significant amounts while P₂O₅ is also present but less significant. The high significance of earlier three elements is due to the reason that host rocks in which phosphatization took place are dolomitic limestones.

The coefficient of variation (V), indicates clearly the wide dispersion of K₂O, MnO, La, Ce, V and the much smaller dispersion of CaO, MgO, Al₂O₃, SiO₂, L.O.I., Ga, Na₂O, Zn, Fe₂O₃, Cu, and Ba. This demonstrates that sample estimates of the population means of the later group of elements is likely to be better approximation than those of the former. On the other hand Y, Sr, P₂O₅, Ni, Eu, Pb, and Cr take up a somewhat intermediate position.

The correlation coefficient matrix (Table-XXIX) shows high to moderate positive linearity between P₂O₅ and traces such as Sr, Ba, Y, Ce, La, Zn, Cr, V, Ni, and Pb, while CaO shows slight positive correlation, whereas MgO has very low negative correlation with the traces. Further high correlations have been obtained between V/Le, V/Y, Sr/La, Sr/Ba, and V/Sr, which are an indication towards the
association of all these elements with one another.

Interpretation of Factors:

Seven factors representing about 72.90 percent of the total variance of the data were extracted. It is evident that the bulk of the variance (38.60%) is explained in factor one.

Factor-1 - Supply of phosphate in solution:

This factor shows high positive loadings for \( P_2O_5 \), \( Sr, V, Y, Ba, Rb, La, Ce, Cr, Zn, \) and \( Ni \), while moderate negative loading for \( SiO_2 \). It is therefore essentially a homopolar factor.

Supply of phosphate would promote algal activity and controls the amount of stromatolites produced. The stromatolites are mainly phosphatic, and the \( Sr, Y, Ba, V, La, \) etc., loadings are suggested as an indicator of replacement of \( Ca \) by these traces in the phosphate lattice. For high concentration of phosphate a fall in pH in the basin with adequate supply of phosphatic material is necessary. This factor thus represents oxygen free, slightly acidic, phosphatic, siliceous, upwelling and shallow oceanic water.

Factor-2 - Detrital clay supply:

Factor two has high positive loadings for \( Al_2O_3 \), \( MnO, Ga, \) and low positive for \( SiO_2 \) and \( Ni \). On the basis
of high positive loadings for Ca and Al this factor is inferred for clay supply. This factor has negative correlation with factor one, and it is therefore inferred that detrital clay supply inhibits the phosphate precipitation.

**Factor-3 - Carbonate precipitation**

Factor three is a bipolar factor having high positive loading for MgO and high negative loading for CaO and SiO$_2$ (slightly low). This factor has no correlation with any other factor and hence is to be said as independent factor. This factor is thought to represent normal shelf sea water of slightly oxidizing and alkaline character from which sedimentation of limestone can occur, further negative loading for MgO is suggestive of a contemporaneous dolomitization. In such an environment phosphate deposition will be inhibited and carbonate deposition takes place. The loading of SiO$_2$ thus may be assumed as a function of pH, because SiO$_2$ is less soluble at low pH, hence its presence indicates a variation in pH condition, which favoured the precipitation of carbonate and authigenic silica simultaneously.

**Factor-4 - Oxidizing conditions**

This factor has high positive loading for Fe$_2$O$_3$ and low positive loading for Al$_2$O$_3$ and Zn, while K$_2$O, Ni and L.O.I. show low negative loadings. On the basis of Fe$_2$O$_3$ loading this factor is therefore named for oxidizing conditions of the basin, because of the rule that oxidizing
conditions promote the iron precipitation, furthermore the high pH is also responsible for iron precipitation.

Factor four is an independent factor and does not show any correlation. It could therefore be inferred that pH of the system became high in the later stage, which abandoned the complete phosphatization.

**Factor-5—Organic activity**

This factor has high positive loadings for Cu and Zn, and slightly low for Ni, while SiO₂ shows a low negative loading. Copper and zinc have been found associated with organisms (Cannon, 1955, Van Ingen, 1915; Black and Mitchel, 1952; etc.), Willey (1976) has recorded their association with organic carbon in Placentia Bay, this factor is therefore thought to act for organic supply in the basin.

This factor has a negative correlation with factor one and two, hence it is inferred that phosphate precipitation is independent of organic activity. Though the loading of Zn is present in factor one but Cu is nil, this Zn loading in factor one may therefore be due to similar physico-chemical conditions.

**Factor-6—Silica precipitation**

Factor six has only one positive loading (0.339) for SiO₂, while Al₂O₃, Na₂O and K₂O show negative loadings.
This factor has been interpreted as silica precipitation factor. The factor six shows very low positive correlation with factor—seven—the residual pore water factor, indicating that silica was supplied in solution and was precipitated authigenically as is revealed from thin section study.

Another important point to be noted here is that, this factor has no correlation with the factor two, i.e. detrital clay supply, but in both these factors the silica loading is positive (0.339), indicating that most probably both factors behaved sympathetically. Two interpretations of this correlation may be possible.

1. The silica is partially detrital hence its loading is observed on both factors.

2. The deposition of silica took place in shallow marine environment near shore line, which permitted the incorporation of silica with detritus.

On the bases of authigenic silica, distribution of major and minor elements, and presence of algal bioclasts it could be inferred that these dolomites have been deposited in shallow marine environment. The second possibility of the incorporation of silica with detritus appears to be more plausible.
Factor 7 - Residual pore water:

The factor seven shows high positive loadings for Pb, MnO, and Ce, and negative for L.O.I. and Ga. The MnO loading is thought to be insignificant because of its high coefficient of variance (1.20), and it is therefore treated as dismissed. Having dismissed the MnO loading, all the other loadings are for elements commonly found in sea water, and pore water. Factor seven is therefore interpreted as a function of trapped pore water.

This factor has got positive correlation with factor one, the supply of phosphate in solution, and factor six, the silica precipitation. It is therefore concluded that both the phosphate and silica were supplied in solution.

Conclusion

Seven factors were deduced by factor analysis to account for the variation of twenty-one chemical variables in forty-one phosphate bearing rock samples.

1. Supply of phosphate in solution - One of the most important factor controlling much of the variance of P₂O₅, Sr, V, Y, Ba, Pb, La, Ca, Cr, Zn, and Ni.
2. Detrital clay supply - Second important factor influencing Al₂O₃, MnO, Ga, SiO₂ and Ni.
3. Carbonate precipitation - Another important factor accounts for the variance of CaO, MgO, and SiO₂.
4. Oxidizing condition - This factor explains most of the variance of \( Fe_2O_3 \), \( Al_2O_3 \), Zn, Ni and \( K_2O \).

5. Organic Activity - This factor influences for Cu, Zn, and Ni.

6. Silica precipitation - It is an important factor, much of the variance of \( SiO_2 \), \( Al_2O_3 \), \( Na_2O \) and \( K_2O \) is explained.

7. Residual pore water - This factor shows the variation of Pb, Rb, MnO and Co.

The study of factor analysis high-lights various important clues and the puzzle of the genesis of these phosphorites could be solved by utilizing this aspect of statistical study.

(1) The phosphate material was supplied in solution which was originally rich in yttrium, cerium, and lanthanum, suggesting a pegmatitic like source, to the basin.

(2) The precipitation of the phosphorite is independent of any organic activity, as is marked by the fact that factors one and five show no correlation.

(3) The pH - Eh conditions of the system were highly varying, as is evidenced by the precipitation of phosphorite and carbonate, and most probably silica acted as a buffer solution in the basin which did not allow the pH
to increase or decrease beyond the limits of phosphate and carbonate precipitation.

(4) The presence of high concentration of phosphorite with stromatolites poses a problem, which can be solved by assuming that stromatolites were flourishing in the same environment that formed barriers for the supply of phosphate solution which was concentrated along these stromatolites, and if the stromatolites were the prime source for phosphate liberation (Valdiya 1972) then what can be said about the unphosphatic stromatolites in Humpani Member was it possible that they didn’t die or did not liberated phosphorus after their death?

The lack of phosphorites in lower Members could be explained by the direct precipitation of phosphorus (Gulbrandsen 1966; D'Anglejan, 1968; Ames, 1950) which was supplied to the basin and was precipitated in the later stages when the conditions were favourable for its precipitation.
SUMMARY AND CONCLUSION

The Calc Zone of Pithoragarh comprising of three formations, viz, Gangolihat dolomites, Sor Slates, and Thalkedar limestones, covers a vast area of the southern part of Pithoragarh district. The Gangolihat dolomite Formation is of prime importance and was studied in detail due to the abundance of stromatolitic phosphorites. This Formation is lithologically further subdivided into four Members i.e. Chhera, Hiunpani, Chandaak and Dhari Members.

Six types of stromatolites have been recognised in these Members, viz *Collenia columnaris*, *C. baikalica*, *Jurusania*, *C. buristica*, and *C. Kusiensis*, which led to conclude the author an age of these rocks between 1650 m.y. and 950 m.y.

According to their mode of occurrence the phosphorites of the area under investigation could be grouped into three categories namely a) Pelletal Phosphorites b) Algal phosphorites and c) Brecciated phosphorites. On the basis of their relationship with stromatolites, they may be divided as, a) Collenial phosphorites b) Oncolitic phosphorites, and c) Fragmentary stromatolitic phosphorites.

Texturally and petrographically the collophane occurs as interstitial to rounded, or in the form of pellets,
compacted and cemented by sparry calcite. The collophane pellets are greyish to black or brown, and are isotropic. Phosphorites also occur in the form of very fine grained matrix, showing micritic texture, for which the term microphorite is used.

The major elements geochemistry reveals that the purple Phyllites are rich in SiO$_2$ (53.09%), CaO (19.00%), MgO (9.80%), and poor in alumina (1.7pp%) while alkalies are rather high (Na$_2$O and K$_2$O, 10.15 and 2.10% respectively). The Chhema Member is phyllitic to dolomitic which varies in composition from siliceous to calcareous in nature. Hiumpani Member is rich in silica content due to cherty nodules. Chandaak Member while being magnesitic is high in MgO content (20.46%) and is overlain by Dhari Member having almost the same chemical composition except low magnesium content. The Sor Slates overlying calcareous rocks are rich in SiO$_2$ and Al$_2$O$_3$ (5.16% and 3.18% respectively).

This variation in chemical composition represents on one hand the changes in the supply of material while on the other a variation in physico-chemical nature of the basin of deposition. There was shallowing in the basin in later stages of Gangolihat Formation which led in the lowering of pH, mixing of various land derived materials, flourishing of algal and other bioherms and enrichment of P$_2$O$_5$ in these rocks. The antipathetic relationship of P$_2$O$_5$ with SiO$_2$. 
CaO, Mn and MgO, indicate a gradual replacement of these oxides by $P_2O_5$ during diagenesis.  

As far as the trace elements are concerned they vary from as low as below the detection limit to exceedingly high. In Ganges Delta lead varies from 10-144 ppm, copper from 5-29 ppm, nickel from 7-43 ppm, gallium varies between 2-6 ppm, vanadium between 20-365 ppm, rubidium between 22-225 ppm, strontium between 15-378 ppm, barium 20-230 ppm, yttrium between 22-165 ppm, cerium between traces to 42 ppm, lanthanum varies from below the detection limit to 45 ppm, whereas zinc and chromium also vary from below the detection limit to 75 and 84 ppm respectively.  

The rare earths study particularly of yttrium, cerium and lanthanum reveals a pegmatitic source in the provenance.  

The R-mode factor analysis was also applied to study the variation of the twenty-one chemical variables (like $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $P_2O_5$, CaO, MgO, MnO, Na$_2$O, K$_2$O, L.O.I., Cu, Pb, Ni, Ga, Ve, Rb, Sr, Ba, Y, La, Ce, and Zn) which were assembled into seven coherent groups or factors, on the basis of their elemental assemblages such as (a) supply of phosphate in solution, (b) detrital clay supply, (c) carbonate precipitation, (d) oxidizing conditions, (e) organic activity (f) silica precipitation and (g) residual pore water.
On the bases of major and trace elements geochemistry and factor analysis, an attempt has been made to find out the provenance, environmental conditions of the basin of deposition and genesis of these phosphatic dolomites. An attempt has also been made to classify the phosphate bearing sediments on the basis of CaO/P₂O₅ ratio.

**Provenance:**

The following observations conclude towards a pegmatitic like source in the provenance, which supplied the phosphatic material.

1. The CaO-Na₂O-K₂O ternary diagram shows strong scatter of points widening towards the Na₂O-K₂O side approximately at Na₂O : K₂O = 3:17, indicate high percentage of K₂O, which might be due to pegmatite like source.

2. In Al₂O₃-Fe₂O₃-FeO-Na₂O+K₂O diagram the concentration of points is near to Al₂O₃ corner, and shows a spread towards Na₂O+K₂O-Al₂O₃ line, again reflecting a pegmatitic like source.

3. The Y;Ce;La diagram shows high concentration of Y in these rocks also points towards a pegmatitic provenance.
Paleoenvironment

Reviewing the literature on the depositional environments of these sediments, Valdiya (1965) has established shallow warm water conditions on the basis of stromatolites and other lithological parameters. According to him these sediments are a product of protected shallow lagoons.

In recent years the geochemical methods have received increasing emphasis for reconstructing paleoenvironments. The author therefore has applied the geochemical techniques in this regard and also reached at the conclusion of a shallow marine environment at the time of deposition of these dolomites on the following bases:

1. According to McKelvey et al. (1953) and Sheldon (1964) the shallow water conditions are necessary for phosphate precipitation. Furthermore the presence of algae which give rise to phosphate deposition (Cloud 1942) is attributed to photosynthesis - a process which takes place in clear water, shallow enough to be penetrated by sunlight. Ginsburg (1955) has observed that the modern equivalents of Paleozoic and Pre-cambrian stromatolites occur in the shallow protected marine environments. On the bases of the presence of phosphorite and like sediments and algal
bioherms, it becomes evident that the basin was shallow and warm water conditions were prevailing at that time which further support Kazakov’s (1937, 1938) theory that phosphatization occurs below the zone of photosynthesis, in a depth range of 50 – 200 m.

2. The low manganese content in these sediments can also be cited as one of the evidences of shallow water conditions of deposition.

3. The low gallium and chromium content also point out towards marine conditions.

4. The presence of pyritic minerals in carbonate sediments is an indication of anaerobic conditions. Valdiya (1965) on the basis of carbonaceous material also reached on the same conclusion, which is further supported by restricted circulation due to algal bioherms.

From the study of above mentioned observations it is inferred that a shallow marine environment was prevailing at that time.

**Genesis Of Phosphorites:**

The genesis or origin of phosphorites is a controversial problem. Some propose an organic origin based on their association with true caprolites and other skeletal materials (Penrose, 1888). Others proposed a replacement

But another school of thought proposed an inorganic origin of phosphorites (Kazakov, 1937; McKelvey 1959, 1967; McKelvey and others, 1953, Cheney, 1955; Cheney et al. 1959; Sheldon 1964; Maughan, 1966, Yochelson, 1969, and Israeli 1976 a,b and 1978 b).

In the present area of investigation it is noticed that both types of stromatolites are present i.e. phosphate poor (Hiunpani Member) and phosphate rich (Dhari Member) and in most of the cases it is noticed that the $P_2O_5$ content is more in the matrix than in the stromatolitic colonies, indicate a more proximity with the propounders of an inorganic theory for the origin of phosphorites.

Firstly, it is presumed that such depositions in the basin were followed by local disturbances resulted in the development of upwelling currents that brought the phosphatic material to the shallower part of the basin where the lowering of pH mostly due to the escape of $CO_2$ gave rise to the enrichment of $P_2O_5$.

Secondly, the mixing of land derived material in this
part of the basin (Shallow) brings about various chemical changes even at shorter distances where algal and other bioherms thrived most. It is the same zone where the enrichment of most of base metals, oxides of iron and manganese and uranium is reported to occur due to these chemical changes. The mere coincidence of occurrence of the algal bioherms with these deposits thus could not be cited as a proof of their contribution in the genesis of these deposits.

Classification:

An attempt has also been made to classify the dolomites into four major groups on the basis of \( \text{CaO} / \text{P}_2\text{O}_5 \) ratio vis. a) slightly phosphatized limestones, b) phosphatic limestones, c) Calc-phosphorites, and d) phosphorites. Due to the consistancy in \( \text{CaO} / \text{P}_2\text{O}_5 \) ratio between 49.99 : 1 to 10:1 in all the calcareous rocks, it is suggested that the Gangolihat dolomites instead be termed as slightly phosphatized dolomites.