Chapter VII

GEOCHEMISTRY AND DISTRIBUTION OF TRACE ELEMENTS

General Statement

The general recognition of trace elements is not of recent origin. Earlier workers, particularly in the beginning of the twentieth century, have emphasized the significance and distribution of trace elements in geological bodies. Washington, H.S. (1913), while discussing the distribution of the elements in the earth's crust stated that the minor elements were related not only to the rock types but also to the major elements constituting the rocks. Vogt, J.H.L. (1918) and Buddington, A.F. (1933) pointed out certain problems in the distribution of trace elements. However, in recent years our knowledge regarding the geochemistry of trace elements has vastly increased.

Goldschmidt, V.M. (1937) has made certain useful observation regarding element distribution in rocks and minerals and proposed a geochemical classification on the basis of their chemical affinity. He observed that the elements indicate their presence into an iron phase, sulphide phase and a silicate phase and classified them as siderophile, chalcophile and lithophile elements respectively. Goldschmidt (1937) found that the distribution of the elements in these phases depends upon the electronic configuration of their atoms. He also explains certain interesting relationships on the basis of ionic radii. 

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and charge. The concept of ionic radius was first introduced by Bragg, W.L. (1937).

Recent advances in geochemistry revealed that Goldschmidt's rules (first rule is based on his own observation regarding distribution of elements in rocks while the rest two were derived from inverse square law of electrostatic attraction applied to ionic lattice) need some modification. According to Fyfe, W.S. (1951) partial covalent bond in zinc compound shows certain departure from the laws governing isomorphism. Shaw, D.M. (1953) and Ahrens, L.H. (1953) were of the opinion that the chemical bonding could explain for most of the geochemical relationship of elements during recrystallization.

Ringwood, A.E. (1955a) used electronegativity as an indicator of bond type in rocks. The concept of electronegativity was first advanced by Pauling, L. (1948, 1960) and defined it as "the power of an atom is a molecule to attract an electron into itself". Ringwood (1955a) applied electronegativity to the distribution of trace elements and proposed the following rules:

"Whenever mutual replacement between two elements in a crystal is possible, possessing appreciably different electronegativity, the element with the lower electronegativity will be preferentially incorporated because it forms a stronger and more ionic bond than the other". The rule satisfactorily applies to such causes in which the difference in electronegativity is more than one. Ringwood (1955a) also favoured the use of ionization potential as suggested earlier by Ahrens (1953) and Goldschmidt
as a possible replacement of electronegativity criteria.

Graf, D.L. (1960) suggested the following five forms in which minor and trace elements occur in the carbonates: i) Solid solubility in the individual mineral; ii) in detrital mineral; iii) as authigenic precipitates; iv) as by products of recrystallization and v) elements or their compound adsorbed by the various minerals.

Strakhov, N.M. et al. (1959) suggest that Fe, Mn, P and various other minor elements, viz., Cu, Ni, Co, V, Pb, Zn, Cr and Ga remain mainly in suspension during transportation by river water and enter solution only to a minor extent. The differences in mode of element migration in river is partly responsible for the differentiation of elements during sedimentation.

An attempt has been made/present and discuss the geochemical abundance and distribution of the significant trace elements associated with the phosphorites and associated rocks individually in the light of the work done as cited above. The concentration trend of the various trace elements occurring in the phosphorites of the study areas have been compared with the average values of trace elements in phosphorites as determined by Krauskopf (1955) and Gulbrandsen (1966) and also with the average trace element values computed by Tooms et al. (1969) who used the data compiled by Swami (1962) on world phosphorite deposits (Table XLIV).

The trace elements of the various rock types including phosphorites of the two areas of study along with their ranges of
concentration is presented in Tables XLI, XLII and XLIII. Their relative distribution has been shown in Figs. 15, 16, 17 and 18. Fig. 19 represents the variation range of the trace elements found in the phosphorite horizons.

**Copper**

Copper is a strong chalcophile element in its geochemical behaviour. It occurs mainly in sulphide state though small amounts of copper have also been reported from silicate and carbonate phases. The similarities among the ionic radii of Cu\(^{2+}\) (0.71 Å), Fe\(^{2+}\) (0.75 Å) and Mg\(^{2+}\) (0.66 Å) make it possible for Cu\(^{2+}\) to replace Fe\(^{2+}\) as well as Mg\(^{2+}\), as for example in tourmaline (Carobbi, G. and Pieruccini, R., 1947).

It has been experimentally shown that Cu is effectively absorbed by Fe\(\text{(OH)}_3\), Mn\(\text{(OH)}_4\) and the clay minerals (Kauskopf, 1956). Mitchell, R.L. (1951) and Synder, J.L. (1959) suggested the replacement of sodium and divalent iron in silicate and oxides by copper in the formation of independent sulphide minerals.

The Cu content in phosphorites as reported by Krauskopf (1955) and Gulbrandsen (1966) is 4 to 40 and 100 ppm respectively. The concentration of Cu in Matoon phosphorite varies from N.D. to 80 ppm whereas in Dakan Kotra phosphorite it ranges from 7 to 94 ppm. The copper content in quartzites associated with phosphorite is quite high and ranges from 78 to 600 ppm. The result of the analytical data and their variation from rock to rock clearly indicate preferential association of copper in silicate phase as compared to carbonate and phosphate. The graph showing Cu/P ratio
FIG. 15 HISTOGRAMS SHOWING THE RELATIVE DISTRIBUTION OF CERTAIN TRACE ELEMENTS IN MATOON PHOSPHORITES
FIG. 16 HISTOGRAMS SHOWING THE RELATIVE DISTRIBUTION OF CERTAIN TRACE ELEMENTS IN DAKANKOTRA PHOSPHORITES
FIG. 17 HISTOGRAMS SHOWING THE RELATIVE DISTRIBUTION OF CERTAIN TRACE ELEMENTS IN QUARTZITIC ROCKS OF MAATON PHOSPHORITE DEPOSIT.
FIG. 18 HISTOGRAMS SHOWING THE RELATIVE DISTRIBUTION OF CERTAIN TRACE ELEMENTS IN HOST ROCKS OF DAKANKOTRA PHOSPHORITE DEPOSIT.
FIG. 19 TRACE ELEMENT VARIATIONS OF PHOSPHORITE SAMPLES OF MATOON (●) AND DAKANKOTRA (○)
(Tables XLV and XLVIII) plotted against P$_2$O$_5$ per cent (Fig. 20A) indicates an inverse relation with negative correlation coefficient (-0.53) between Cu and P$_2$O$_5$. It is suggestive of the ionic substitution of copper in apatite lattice during diagenesis. The negative correlation of copper with alumina and variable Cu/Al ratios further suggest the non-coherence of Cu with Al$_2$O$_3$. The strong negative correlation of Cu with Ca (C.C. = -0.78) may be due to replacement of Ca$^{2+}$ by Cu$^+$ in apatite lattice. Copper seems to be geochemically related with magnesium and iron oxides as indicated by sympathetic relationship of Cu/Mg values with MgO per cent (Fig. 20B) and strong positive correlation coefficient with iron oxides.

It is known that under deduced physico-chemical condition the algae was responsible for the removal of copper from stromatolites (toxin) and its concentration in the rocks adjacent to the algal matter (Raha, P.K., 1978 and Verma, K.K., 1978). It is therefore suggested that the distribution of copper in the carbonate, silicate and phosphate rocks has been largely influenced by the presence of stromatolites forming algae.

**Nickel**

The distribution of nickel in rocks was first studied by Vogt (1923). Geochemically, nickel is a siderophile element and the bulk of it is always associated with metallic iron. The ionic radius of Ni$^{2+}$ (0.69 Å) where it is close to those of Mg$^{2+}$ (0.66 Å) Fe$^{2+}$ (0.75 Å), suggests that nickel could substitute one or both
FIG. 20 Cu/P-P2O5, Cu/Mg-MgO, Ni/Al-Al2O3, Ni/Fe-Fe2O3, Ni/Mg-MgO, Zn/Ca-CaO, Cr/Al-Al2O3, Sr-P2O5, Sr-CaO, V-P2O5, V/Al-Al2O3 AND Li-MgO PLOTS FOR MATOON (○) AND DAKANKOTRA (○) PHOSPHORITES
the elements. According to Goldschmidt (1944), nickel is likely to be enriched in magnesium bearing minerals because Ni-O bond is stronger than Mg-O bond and more covalent in nature. Ringwood (1955, 1956) suggested the relationship among Mg-Ni-Fe phase on the basis of their electronegativity values. According to him, Fe-O bond is weaker than Ni-O bond and Fe$^{2+}$ is more mobile than Ni$^{2+}$. Therefore, Fe$^{2+}$ is easily replaceable by Ni$^{2+}$.

The trace concentration of nickel in carbonate rocks has been reported by many earlier workers, e.g., 3 to 10 ppm by Karauskopf (1956), 10 ppm by Runnels and Schlicher (1956) and 15 ppm by Graf (1960). The studies carried out by Krauskopf (1955) and Gulbransen (1966) indicate that in phosphorites the concentration of Ni ranges from 4 to 200 ppm and 100 ppm respectively. The present study indicates that the abundance of Ni ranges from 143 ppm to near absence in Matoon phosphorites whereas it ranges between 14 and 32 ppm in Dakan Kotra phosphorites. Nickel does not show any significant relationship with P$_2$O$_5$. The Ni/Al, Ni/Fe and Ni/Mg ratios are found to be variable in these phosphorites (Tables XLV and XLVIII). When Ni/Al, Ni/Fe and Ni/Mg ratios examined in more details by plotting against Al$_2$O$_3$, Fe$_2$O$_3$ and MgO percentage (Fig. 20C and D) they show a tendency towards an inverse relation suggesting the replacement of Al and Fe by Ni in Dakan Kotra phosphorites, whereas it (Ni) shows close coherence with the similar elements of Matoon Phosphorites. The sympathetic relationship of Ni/Mg values with MgO per cent (Fig. 20E) suggests Ni was retained along with Mg in sediments under the favourable physico-
chemical condition. Furthermore, adsorption of nickel by organic matter during their life activities is also possible (Nicholls, G.D. and Loring, D.H., 1962).

Cobalt

Cobalt is a siderophile element and member of iron family (Goldschmidt, 1929) or ferrides (Landergren, S., 1943). Geochemically, cobalt is closely related to nickel. The ionic radius of Co$^{2+}$ (0.72 Å) is found very near to those of Ni$^{2+}$ (0.69 Å), Fe$^{2+}$ (0.74 Å) and Mg$^{2+}$ (0.66 Å). The larger size of Co$^{2+}$ ion possibly restricts the entry of cobalt in the magnesium position to a greater degree than nickel. There is possibly a preponderance of cobalt over nickel in soluble products of weathering. The Ni$^{2+}$ ion seems to more stable in solution than that of Co$^{2+}$ ion. It has been suggested by Butler, J.R., (1953) that the loss/Co in the weathered product of igneous rocks is greater than Ni.

The concentration of cobalt in Dakan Kotra phosphorite ranges from 8 ppm to absent, whereas, only four phosphorite samples of Matoon show 5 to 13 ppm of Ni. The result of the analytical data indicates that cobalt does not show any significant relation with P$_2$O$_5$. However, Co shows close coherence with Ni, Fe and Mg. Most probably the traces of Co found in these phosphorites were drawn from the weathering product of the adjacent older gneisses. The positive correlation coefficient of Co with CO$_2$ suggest their adsorption by organic matter.
Lead

Lead is a chalcophile element and an element of ore complexes. In phosphate and silicate minerals it occurs mainly as $\text{Pb}^{2+}$. Lead ($\text{Pb}^{2+}$) appears intermediate in ionic size between $\text{Ca}^{2+}$ and $\text{K}^+$ and thus it is expected to occur in the carbonates, K-feldspars and micas substituting potassium. The ionic radius of $\text{Pb}^{2+}$ (1.20 Å) makes it possible to replace $\text{Sr}^{2+}$ (1.18 Å). The Sr-O bond is more ionic than that of the Ca-O bond, but $\text{Sr}^{2+}$ is much larger and enter the $\text{K}^+$ position as readily as $\text{Ca}^{2+}$ lattice sites (Heir and Taylor, 1959b). The $\text{Pb}^{2+}$ ion shields $\text{PO}_4^{3-}$ ion more effectively than $\text{Ca}^{2+}$ ions in apatite, where calcium occurs in nine-fold coordination with oxygen thus acts as a host for Pb.

The Pb concentration in the carbonate rocks has been reported to be fairly variable, e.g., 5 to 10 ppm by Rankama, K. and Sahama, T.G., (1950) and Krauskopf (1956), 16 ppm by Runnels, R.T., and Schleicher, J.A. (1956) and 26 ppm by Ostrom, M.E. (1957).

In the present study concentration of Pb in phosphorites has been found to be highly variable. In Maton phosphorite Pb ranges from 310 ppm to absent whereas in Dakan Kotra phosphorite, it ranges from 24 to 56 ppm. The concentration of lead in the adjacent quartzites varies from 11 to 800 ppm. The positive relationship of Pb with the elements related to apatite from both the areas suggests that under favourable physico-chemical condition, Pb was rather separated from its original host mineral during weathering and transported in the form of soluble stable
compound in association with carbonate minerals. It is, therefore, probable that lead in the carbonate and phosphate rocks is mainly influenced by the presence of stromatolites forming algae.

**Zinc**

Zinc is predominantly a chalcophile element. Clarke, F.W. and Washington, H.S. (1924) reported 40 ppm Zn in the upper lithosphere. The crystallochemical parameters of Zn\(^{2+}\) (\(r = 0.74\); \(e = 1.50;\) \(i = 2.70\)) are closely similar to that of Fe\(^{2+}\) (\(r = 0.75;\) \(e = 1.60;\) \(i = 2.67\)). Data relating to the ionic radii (\(r\)), electronegativity (\(e\)) and ionic potential (\(i\)) are taken from Taylor, S.R. (1965). The virtually identical ionic radii of these two ions suggest that Zn\(^{2+}\) should be camouflaged in Fe\(^{2+}\) following the classical principles (Goldschmidt, 1937). However, Zn-O bond is more covalent than Fe-O bond as indicated by electronegativity and ionization potential data. Zn\(^{2+}\) also shows geochemical relationship with Mg\(^{2+}\), Mn\(^{2+}\) and Ca\(^{2+}\). It has been suggested that Zn\(^{2+}\) should be able to replace Mg\(^{2+}\) (0.66 Å), Mn\(^{2+}\) (0.80 Å) and Ca\(^{2+}\) (0.99 Å) in calcite, but not to as great extent as Mn\(^{2+}\) (Berry, L.G. and Mason, B., 1959).

The concentration of Zn in Matoon phosphorite ranges from 20 to 203 ppm, while in Dakan Kotra phosphorites it ranges from 6 to 148 ppm. The concentration of Zn in adjacent quartzites varies from 5 to 112 ppm, whereas in the phyllites it is 114 ppm. The present study reveals that Zn is related to the elements present in apatite. From the sympathetic relationship indicated by Zn/Ca ratios plotted against CaO per cent (Fig. 20F) it appears that
zinc is present in the crystal lattice of calcite. The higher variability of Zn/Pb ratio and lower of Zn/Fe ratio indicate non-coherence of Zn with respect to Pb and Fe (Tables XLVI and XLIX). The negative correlation coefficient values of Zn with Mg in the phosphorites of the two areas suggest replacement of Mg$^{2+}$ by Zn$^{2+}$, possibly in the calcium phosphate lattice. The higher concentration of Zn in phyllites is possibly due to their preferential entrance in biotite (Tauson, L.V. and Kravchenko, L.A., 1956).

**Chromium**

Chromium in phosphate and silicate rocks preferably occurs in pentavalent state, and rarely in trivalent or hexavalent state. In silicate minerals it occurs as a cation outside the complex silicon-oxygen framework. Because of the identical chemical properties, i.e., ionic size and ionic charge, Cr replace ferric iron and alumina didochically in silicate rocks.

The concentration of chromium in carbonate rocks, as reported by Rankama and Sahama (1950) is 2 ppm, Krauskopf (1956), 5 ppm, Runnels and Schleicher (1956), 13 ppm, Ostrom (1957), 11 ppm and Graf (1960), 13 ppm. In the phosphate rocks the concentration of Cr was reported to be higher by Krauskopf (1955), 30 to 400 ppm and Gulbrandsen (1966), 1000 ppm. The concentration of Cr in Matoon phosphorite ranges from 270 ppm to absent whereas, in Dakan Kotra phosphorite it ranges from 30 to 147 ppm. In the adjacent quartzites Cr ranges from 62 to 450 ppm, which is quite high as compared to the phosphorites. In Matoon phosphorite Cr
shows close coherence with the elements related to silicate minerals as it is evident by its positive correlation coefficient with SiO$_2$, Fe$_2$O$_3$ and K$_2$O etc. Hirst, D.M. (1962) and Nicholls, G.D. and Loring, D.H. (1962) determined the relationship of Cr with Al. The variable Cr/Al ratios plotted against Al$_2$O$_3$ per cent (Fig. 20G) shows an inverse relation suggesting non-coherence of Cr with alumina. According to Frohlich, F. (1960) the bulk of Cr present in sediment is found to be associated with mica and clay mineral, mainly illite. X-ray diffraction analyses of the phosphorites shows the presence of illite, that might be responsible for the retention of chromium (Cr$^{3+}$). The Dakan Kotra phosphorite indicates the coherence of chromium with elements related to apatite, suggesting its concentration mainly due to presence of stromatolites forming algae. Vinogradov, A.P. (1953) also suggested the association of Cr with organic matter.

Strontium

Strontium is a lithophile element and occurs as oxysalts in residual sediment. The crystallo-chemical parameters of Sr$^{2+}$ ($r = 1.18, \ e = 1.0, \ i = 1.69$) are closely similar to those of Ca$^{2+}$ ($r = 0.99, \ e = 1.0, \ i = 2.02$) and Pb$^{2+}$ ($r = 1.18, \ e = 1.6, \ i = 1.67$). The virtually identical ionic radii of Pb and Sr suggest the replacement of the former by the latter in some lead minerals.

In carbonate sediments Sr content varies widely as reported by Rankama and Sahama (1952), 425 to 765 ppm; Krauskopf (1956)
400 to 800 ppm; Runnels and Schleicher (1956) 470 ppm, Ostrom (1956) 490 ppm, and Graf (1960) 420 ppm. Strontium in phosphorites ranges from 50 to 1000 ppm as reported by Krauskopf (1955). Strontium in Maton Phosphorite ranges from 49 to 517 ppm, whereas in Dakan Kotra phosphorite it varies from 104 to 251 ppm. Sr in adjacent quartzites ranges from 65 to 300 ppm and in phyllites, it is 104 ppm.

The concentration plot of Sr with CaO and P$_2$O$_5$ (Fig. 20H and I) indicates a strong positive relationship from which it may be inferred that Sr was incorporated in the carbonate apatite structure at the time of its formation and remained fixed during the postdepositional alteration. The strong positive correlation coefficient between Sr and P$_2$O$_5$ (0.62) in Maton phosphorites favours the possibilities of formation of supergene strontium phosphate. The low Sr/Ca values (Tables XLVI and XLIX) in these phosphorites relative to any admixed CaCO$_3$ implies that Sr content was also derived from another source in addition to that present in calcium carbonate mineral.

**Rubidium**

Rubidium has been included in the group of lithophile elements. It is very similar in its chemical character to potassium with which it has close association. Rubidium apparently penetrates into the lattice of clay minerals where it replaces potassium (Horstman, E.L., 1959). Of all the alkali metals Rb possesses the highest tendency of interstitial capture and more readily
adsorbed in clays than potassium (Goldschmidt, 1938). The bulk of Rb, that is released during weathering of igneous and metamorphic rocks, enter partially into the crystal lattice of clays as a result of adsorption.

According to Wedepohl, K.H. (1970) the mean concentration of Rb is 6.37 ppm in dolomite, 6.67 ppm in silt, 9 to 100 ppm in sand and sandstone, 20 to 663 ppm in shale and 28 to 220 ppm in argillaceous sediment. Smirnov, A.I. (1959) reported the highest concentration of Rb in phosphorites is 0.00077 per cent. In Matoon phosphorites Rb ranges from 4 to 14 ppm, whereas in Dakan Kotra phosphorites it varies from one to 14 ppm. The range of Rb in quartzites is from 6 to 34 ppm and in phyllites it is 166 ppm.

Rubidium shows strong positive relationship with potassium in phyllites, because of its high adsorption energy. Rb in Matoon phosphorites show noncoherence with the elements related to apatite whereas in Dakan Kotra it is found associated with the phosphate minerals. The relatively constant Rb/Al and Rb/K values (Tables XLVI, XLVII and L) suggest their close coherence with potassium and alumina. The bulk of Rb in Matoon phosphorite seem to have been derived from the alumino-silicate minerals of adjacent older gneisses.

Vanadium

Vanadium is pronouncedly a lithophile element. It occurs in three stable oxidation states in igneous surrounding, viz., trivalent, quadrivalent and quinquevalent state. In sedimentary
rocks it occur in quinquevalent state. Vanadium seem to have been released in course of weathering of igneous rocks and subsequently incorporated in clay minerals due to low solubility and immobility of \( \text{V(OH)}_3 \). The close affinity of \( \text{V}^{3+} \) towards \( \text{Fe}^{3+} \) and \( \text{Al}^{3+} \) in micas possibly suggest the replacement of \( \text{Fe}^{3+} \) and \( \text{Al}^{3+} \) by \( \text{V}^{3+} \) (Wager, L.R. and Mitchell, R.L., 1951).

In carbonate rocks the concentration of vanadium was reported to be widely variable by Runnels and Schleicher (1956) 300 ppm and by Graf (1960) 10 to 150 ppm. According to Jacob et al. (1933) the maximum concentration of V was found to be 1300 ppm in marine phosphorites of Idaho. Krauskopf (1955) quoted a range of 20 to 200 ppm of V in phosphorites. The threshold value of vanadium in phosphoria Formation (phosphorites) of Montana, Wyoming and Utah (U.S.A.) was found to be 300 ppm (Gulbrandsen, 1966). The concentration of vanadium in Matoon phosphorite ranges from 144 ppm to absent, whereas in Dakan Kotra phosphorite it ranges from 36 to 121 ppm. Vanadium in adjacent quartzites of Matoon phosphorites ranges from 8 to 127 ppm, whereas in phyllites its concentration is 154 ppm.

Vanadium shows close coherence with the elements related to the phosphate as well as aluminosilicate minerals. The slightly variable V/P values (Tables XLVII, L) and sympathetic relationship of V with \( \text{P}_2\text{O}_5 \) per cent (Fig. 20J) in Dakan Kotra phosphorite suggest that vanadium was supplied to the basin along with phosphate mineral. In Matoon phosphorite vanadium shows negative correlation with \( \text{P}_2\text{O}_5 \), which possibly suggests replacement of
P^{5+} by V^{5+}. The variable V/Al ratio plotted against Al_2O_3 percent (Fig. 20K) indicates a sympathetic relationship suggesting the coherence of V with clays. This relationship coupled with positive correlation coefficient values of V with silica, iron, titanium and sodium suggest the association of V with aluminosilicate minerals.

Lithium

Lithium is an alkali metal and strongly lithophile in its geochemical character. In many respects it follows magnesium. Due to high abundance magnesium acts as a protective element for lithium. Strock, L.W. (1936) suggested that the replacement of Li by Mg possible only when electrical balance of the structure is maintained by the introduction of a trivalent six coordinated cation. Li^+ (r = 0.68, e = 0.95) forms more ionic bond with oxygen than either Mg^{2+} (r = 0.66, e = 1.20) or Fe^{2+} (r = 0.74, e = 1.70).

The concentration of lithium in various rocks were reported by many earlier workers. Rankama and Sahama (1950) reported 46 ppm of Li in shale, whereas Strock (1936) reported 26 g/ton of Li in limestone. Solodov, N.A. (1961) quoted upto 0.015 percent of Li in apatite.

The concentration of lithium in Matoon phosphorite ranges from one to 18 ppm, whereas in Dakan Kotra phosphorite it ranges from one to 9 ppm. Li in quartzite ranges from one to 24 ppm and in phyllites it is 34 ppm.
Lithium in both the phosphorites seems to be not related with the elements of apatite. The slightly variable Li/Mg ratio plotted against MgO per cent (Fig. 20L) indicates a sympathetic relationship. It is suggestive of the close coherence of Li with Mg-mineral. It is, therefore, believed that during the process of weathering and sedimentation lithium followed the course of magnesium.

**Cadmium**

Cadmium is predominantly a chalcophile element in its geochemical character. The electronegativity of cadmium \( (e = 1.5) \) is found close to that of zinc \( (e = 1.5) \) and Fe\(^{2+} \) \( (e = 1.6) \). The close similarities of the ionic radii of Cd\(^{2+} \) \( (0.97 \text{ Å}) \) and Ca\(^{2+} \) \( (0.99 \text{ Å}) \), suggest that these elements are found closely associated with each other in nature (Sandell, E.B. and Goldich, S.S., 1943 and Rankama and Sahama, 1950).

The geochemistry of cadmium during sedimentation processes has not yet been studied in details by any previous workers. Hence no reliable data is available for the distribution of Cd in sedimentary formations. Cadmium was determined in marine phosphorites by Rankama and Sahama (1950), Haberland, H. (1947), Malinovskii, F.M. (1955) and Kholodov, V.N. (1959). A range from 0.000015 to 0.003 per cent Cd in apatite was quoted by Noddack, I. (1935).

The concentration of Cd in Matoon phosphorites is less than 5 ppm, whereas in Dakan Kotra it ranges from 5 to 8 ppm. The
almost constant Cd concentration show sympathetic relationship 
with the elements related to apatite.

**Silver**

Silver is typically a chalcophile element in its geochemical 
character and manner of occurrence. The similarities between 
ionic radii of Ag$^{+}$ (1.26 Å) and Cu$^{+}$ (0.96 Å) suggest a close 
coherence of the elements mainly in sulphide.

Wagoner (quoted by Clarke, 1924) reported concentration of 
Ag 0.44 g/ton in sandstone and 0.2 g/ton in limestone. Mitchell 
(1944) reported Ag 0.2 g/ton from soil.

The concentration of silver in Matoon phosphorite ranges 
from 5 to 15 ppm, whereas in Dakan Kotra it occurs below 5 ppm. 
Matoon phosphatic rocks show close coherence of Ag with elements 
related to the alumino silicate minerals. The positive correlation 
coefficient of Ag with iron oxides suggests the association of 
silver with limonitic concretions present in phosphatic pellets.

**Gallium**

The geochemistry of gallium is mainly influenced by the 
similarity in its ionic radii of Ga$^{3+}$ (0.6 Å) with Al$^{3+}$ (0.51 Å) 
and anion affinity index (1.08) approaching unity (Ahrens, 1953). 
Gallium is commonly camouflaged with aluminium and trivalent 
iron. The electronegativity values of Ga and Fe indicates that 
Ga-O bond is more ionic than Fe-O bond. The ionization potential 
indicates an equal degree of ionic character of both Ga$^{3+}$ and
Fe$^{3+}$. Gallium possibly enters Fe$^{3+}$ position more readily than Al$^{3+}$ position and therefore, exhibits close coherence with Fe$^{3+}$.

The geochemistry of gallium indicates that it is a typically dispersed element whose abundance in minerals is determined by its isomorphism with Al$^{3+}$, Fe$^{3+}$ and Zn$^{2+}$.

Only two samples of Matoon phosphate rocks show the presence of 6 and 20 ppm gallium content. In quartzite gallium concentration ranges from 6 to 17 ppm. The absence of Ga in phosphate rocks clearly indicates its non-coherence with apatite. The bulk of Ga is found associated with alumino silicate minerals. The fairly constant Ga/Al ratio suggests that Ga entered the basin and structurally combined with clay minerals. The variable Ga/Na + K values in comparison to Ga/Al ratio suggest a better coherence of Ga with one clay mineral, possibly illite.

Uranium and Thorium

Uranium and thorium being radioactive elements, are strongly lithophile in geochemical character. The geochemistry of these two elements has been reviewed by Adams et al. (1959). The electronegativity of U$^{4+}$ (e = 1.4) is found equal to that of Th$^{4+}$ (e = 1.4). But the Th$^{4+}$-O bond appear to be more stronger than U$^{4+}$-O bond as indicated by their melting point 3050°C and 2175°C respectively.

The enrichment of uranium in phosphorites in comparison to sediment and sedimentary rocks is well documented by Altschuler et al. (1958) and Tooms et al. (1969). The association of

The geochemistry of thorium is characterised by the uranium-thorium didochy. Tooms et al. reported 5 to 100 ppm Th concentration in phosphorites and suggested the replacement of Ca by Th in apatite owing to close similarity of their ionic sizes.

The concentration of uranium and thorium in Matoon and Dakan Kotra phosphorites ranges from 0.005 to 0.008 per cent and 0.001 to 0.003 per cent respectively. The variable $U/P_2O_5$ values (Tables XLVII and L) and negative correlation with $P_2O_5$ in both the phosphorites possibly suggest the entrance of uranium in apatite lattice and substitution of $Ca^{2+}$ as well as $P^{5+}$. Thorium seems to be related to elements of apatite to some extent in Matoon phosphorite. On the other hand, its negative correlation with $P_2O_5$ in Dakan Kotra...
phosphorite suggests replacement of Ca by Th. The strong positive correlation coefficient between U and Th (C.C. = 0.55 for Matoon and 0.73 for Dakan Kotra) suggests close coherence of U with Th. The high and low values of Th/U ratio (Adams et al., 1959 and Goldberg, E.D. and Parker, R.H., 1960) suggest the oxidizing and reducing environments respectively.

General Discussion

Geochemical methods have received increasing emphasis in recent years as a means of reconstructing the ancient environment. An attempt has been made here to find out the provenance and environmental condition of phosphorite deposits based on the geochemical association, behaviour and distribution pattern of various trace elements determined.

From the preceding discussion of individual elements it appears that considerable amounts of trace elements entered the basin of deposition, adsorbed and structurally entered the lattice of various minerals. The variable concentration of trace elements in Matoon and Dakan Kotra phosphorites have been influenced by various physico-chemical processes involved during weathering and leaching of the pre-existing rocks, and subsequently they were added to the sediments in traces. The adsorption of some trace elements was mainly influenced by the principal absorbents like phosphate mineral, organic matter, clays, iron and silicate minerals.
Sr, V, Cr, Pb, Zn and Th are the elements which are susceptible to adsorption by phosphate minerals. The elements which were possibly adsorbed by the organic matter include Ag, Cu, Ni, Co, Cr, Cd, Pb and Zn along with perhaps Rb and U. Elements adsorbed by clay mineral include Ga, Li and Rb. Possibly Cu, Co and V have been incorporated by cation exchange and appear to have been taken into the lattice of iron and the silicates. Trace element dispersion in the phosphorite associated with fossil algae possibly suggests that fixation of Ag, Cd, Cu, Cr, Co, Pb, Th and Zn was geochemically controlled by biogenic activity (Rao, 1981) under shallow marine environmental condition. The closer association of trace elements, viz., Cu, Ni, Co, Pb and Zn with organic metabolism was suggested by many of the earlier workers namely Van Ingen, G. (1915), Van Ingen G. and Phillips, A.H. (1915), Phillips, A.H. (1917, 1922), Noddack, I. and Noddack, W. (1939), Bowen, V.T. and Sutton, D. (1951), Krauskopf (1956), LeRiche, H.E. (1959), Nicholls and Loring (1962), Tourtelot, H.A. (1964), Raha (1978) and Verma (1978).

A closer examination of the correlation coefficient of Sr, Pb, Zn, Cr and V with respect to $P_2O_5$ of the phosphorites generally indicates higher positive values, whereas the correlation coefficient values of Rb and Cd with $P_2O_5$ in Dakan Kotra and of Th in Matoon phosphorites are on the lower side (Tables LIII and LIV).

The Ga/Al ratios in all the rocks analysed were found to be closer to the average ratio of the elements in the igneous rocks
as reported by Shaw (1957) who explained it as due to insignificant separation of Ga from Al even in the weathering product of igneous rocks. The general trend of concentration of the majority of trace elements found in phosphorites and associated rocks of the two areas of investigation appear to be similar to those of marine sediments (Keith, M.L. and Degens, E.T., 1959). In a general way it may, therefore, be suggested that the environmental condition for the deposition of these phosphorites was controlled by the shallow marine waters. Moreover, the Th/U ratio in the phosphorites which is very near to 0.2 suggests that at the site of deposition fairly oxidizing condition prevailed.