Chapter - V

GEOCHEMISTRY AND DISTRIBUTION OF TRACE ELEMENTS IN ROCKS, MINERALS AND SOILS

General statement

The general recognition of the trace elements is not of recent origin. Earlier workers particularly, in the beginning of the 20th century, have emphasized the significance and the 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 rock. Vogt (1918) and Buddington (1933) pointed out certain complications in the distribution of the trace elements.

In recent years, vast knowledge has accumulated regarding the geochemistry of the trace elements. Colossal work is being done on the distribution of trace elements in igneous rocks and their geochemical behaviour during the fractional crystallization of magma. Goldschmidt (1937), one of the pioneer workers in the field of geochemistry, has made certain useful observations regarding element distribution in rocks and minerals and proposed a geochemical classification of the elements based on their chemical affinity. He observed that the elements indicated preference to enter into an iron phase, sulphide phase and a silicate phase, and classified them as siderophile, chalcophile and lithophile elements respectively. Shand (1947) proposed the term thiophile
substituting the term chalcophile. Goldschmidt (1937) found that the distribution of the chemical elements in these phases depended on the electronic configuration of their atoms. Further, he assumed that mutual replacement (diadochy) of ions in magmatic minerals was purely ionic. He explained certain interesting interionic relationships on the basis of ionic radii and charge. In fact, the concept of ionic radius was first given by Bragg (1937), who found that when two ions come closer to each other, a repulsive force is generated and which prevents them to come closer than a certain limiting value of interatomic distance. He defined this effective distance as a characteristic radius of each ion.

A comprehensive study led Goldschmidt to propose three basic rules governing the distribution of elements in rocks and minerals. The first rule is based on his own observation while the rest two were derived from inverse square law of electrostatic attraction applied to ionic lattices.

Recent advances in geochemistry revealed that the Goldschmidt’s rules needed modification. Greater emphasis has now been given on the significance and the nature of chemical bonding. According to Fyfe (1951), partial covalent bond in zinc compounds brings certain departures from the laws governing isomorphism. Ramberg (1925), Shaw (1953) and Ahrens (1953) were of the opinion that chemical bonding could explain for most of the geochemical relationship of elements during crystallization.

Ringwood (1955a) used electronegativity as "an indicator of bond type in minerals and rocks". The concept of electronegativity was originally given by Pauling (1955), who defined it as "The power of an atom
in a molecule to attract an electron unto itself". Pauling (1940) stated
that when two atoms of similar electronegativity are joined by a bond, it
would be a covalent bond. But when there is a difference in electronega-
tivity in the two atoms, the shared electron will be pulled closer by the
atom having a higher electronegativity. This results in creating an ionic
component into the bond. When the difference in electronegativity is
greater, the bond will be more ionic.

Ringwood (1955a), following Fyfe (1951), applied electronegativity
to the distribution of trace elements and proposed the following rule:

"Whenever diadochy in a crystal is possible between two elements
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 cases in which the difference
in the electronegativity is more than 0.1.

Ringwood (1955a) also favoured the use of ionization potential,
suggested earlier by Ahrens (1953) and Goldschmidt (1954), as a possible
replacement of electronegativity criteria.

Ringwood's (1955a) modifications to Goldschmidt's rules was
criticised by Curtis (1963) and others because they found it difficult to
explain the behaviour of elements when ionic radius and/or charge and
electronegativity act in opposition. Nockolds (1966) also felt this
difficulty and pointed out that "bond length to oxygen may play an equally
important part and need consideration also".
Further, the distribution of elements in a crystal structure during the fractional crystallization is also governed by the geometric arrangement of atoms (see Krauskopf, 1967).

The geochemistry and distribution of individual elements has been discussed in the foregoing description in the light of the above cited work.

**Copper in rocks and minerals**

Copper is a strongly chalcophile element. It occurs chiefly as sulphides. Small amounts of copper have also been reported from the silicate phase. Buddington (1927) reported that traces of Cu were commonly associated with diorites. Sandell and Goldich (1943) observed that Cu has a greater tendency to be enriched in the basic igneous rocks. According to them acid igneous rocks have about 1/10 of Cu content as compared to the basic igneous rocks. Rankamae and Sahama (1950) stated that Cu largely occurred as sulphide in most igneous rocks. Wager and Mitchell (1951) have experimentally shown that during the earlier stages of crystallization of a basic magma, copper being free, would be incorporated in the silicate minerals. Wager et al. (1957) found chalcopyrite in the lower layered rocks at Skaergaard.

The granites and granitic rocks of the Khetri Copper Belt have Cu content varying from 10 to 48 ppm (20 ppm, Vinogradov, 1962). The higher concentration is generally in the gneissic variety. The quartzites, schists and phyllites in general show anomalous values particularly those near the mineralized zone. The dolerites also have indications of copper mineralization.
and show values varying from 10 to 445 ppm (87 ppm, Turekian and Wedepohl, 1961). The separated ferromagnesian minerals show preferable concentration of Cu as compared to felsic minerals.

Copper is the chief element of ore complexes. The chemistry of its being accommodated in the silicate phase, and later concentrating in the residual magma is discussed below.

It is well known that copper has a strong tendency to concentrate in residual magmas and precipitate as chalcopyrite. The reason being that during the crystallization of a magma Na⁺ (0.96Å) in the plagioclases comouflages Cu⁺ (0.96Å). Similarly in the ferromagnesian minerals, Fe⁺⁺ (0.74Å) camouflages Cu⁺⁺ (0.72Å) although both the univalent and divalent copper have ionic radii less than the respective elements, Na⁺ and Fe⁺⁺. Goldschmidt's rules fail to explain such a behaviour.

Ringwood (1955a) explained this anomaly on the basis of electronegativity. He compared the electronegativity of Cu⁺ (1.8) and Na⁺ (0.9) and pointed out that Cu⁺⁻ O bond would be weaker as compared to the Na⁺⁻ O bond. Similarly in the case of Cu⁺⁺ (2.00) and Fe⁺⁺ (1.65), the Cu⁻ O bond would be weaker as compared to the Fe⁺⁺⁻ O bond. Therefore, as a rule the elements forming stronger bonds with oxygen will be preferably incorporated.

**Copper in residual soils**

The geochemical behaviour of copper during the formation of residual soils is not well worked out. Generally the copper contents in the residual soils are less than the parent rock.
It is also known that among the ferromagnesian minerals which are the chief host for Cu, biotite is usually more resistant to chemical weathering than hornblende (see Goldschmidt, 1954). It also indicates that the ferromagnesian minerals formed at a higher temperature are more susceptible to chemical weathering than those formed at a lower temperature (see Krauskopf, 1967).

Residual soil samples of Khetri in case of granites and granitic rocks and schists and phyllites generally show higher content of metal than the parent rock while in case of quartzites the case is reverse. This anomaly has been discussed in the foregoing pages where a comparative study of the primary and secondary dispersion patterns has been made.

**Lead in rocks and minerals**

Lead was found to concentrate mostly in the acid igneous rocks. Sandell and Goldich (1943) found that the acid rocks have twice as much lead as the basic rocks. Hevesy (1931) reported that the lead content in normal granitic rocks is six times greater than that of gabbros and similar rocks. Goldschmidt found 5-50 ppm of Pb concentrating in normal granites. According to Wedepohl (1956) and other workers, among feldspars, microcline in pegmatites often shows maximum lead concentration. The enrichment of lead in the late syenite differentiates has also been reported by some workers. Apatite is a good host and generally has up to 50 ppm of Pb. The radiogenic Pb usually remains associated with its parent elements.

Lead has a controlled dispersion in all the samples of the belt and
the values range from 10-126 ppm. Among igneous rocks in general, pink granites and pink granite gneisses gave values up to 85 ppm (20 ppm, Vinogradov, 1962) while dolerites record up to 69 ppm of Pb (8 ppm, Vinogradov, 1962). Quartzites, schists and phyllites both from and away the mineralisation zone show a limited range of dispersion of Pb. Even the sulphide ores do not record abnormal values. Ferromagnesian minerals show enrichment in Pb. The felsic group (quartz + feldspars) also gave higher values.

Pb is a chalcophile element and an element of ore complexes. The factors governing its capability to crystallize as sulphide or enter into the silicate phase are discussed below.

Generally it is the belief that Pb$^{++}$ preferably occurs in the potash feldspars (5-50 ppm) of silicate rocks. Goldschmidt (1937) was of the opinion that lead could possibly replace K$^+$, Sr$^{++}$, Ba$^{++}$ and to some extent Ca$^{++}$ also. Since the ionic radius of Pb (1.20Å) is smaller and the charge is higher than K (1.33Å), obviously Pb can replace K$^+$ from early formed potash-minerals (see Goldschmidt, 1954). But other workers, viz., Bankhama and Sahama, 1949; Nockolds and Mitchell, 1948 suggested that Pb could not enter potash lattice as efficiently as K$^+$ but could concentrate in the residual magma.

Ringwood (1955a) qualified these observations by explaining them on the basis of their electronegativity as follows:

The electronegativity of Pb is 1.8 while that of K$^+$ is 0.8. The Pb-O bond is therefore, more covalent and thus weak as compared to K-O bond.
in potash-minerals. Therefore $K^+$ enters with relatively greater ease into potash-minerals while Pb concentrates in the residual magma.

It is therefore evident that primary lead exists mostly in the sulphide state on account of its great affinity towards sulphur. Either it may occur as a primary sulphide mineral, viz., galena or formed by the interaction between the Pb present in the silicate lattice of feldspars and the available sulphur compounds.

**Lead in the residual soils** - Not much is known about the geochemical behaviour of lead during the process of weathering of silicate rocks. Whatever information is available about the behaviour of the metal, it is largely from its association with the sulphide ores. It is, however, known that lead sulphide in the zone of oxidation changes to Pb SO$_4$. Frequently Pb CO$_3$ is also formed by its reaction with available CO$_2$.

The soil samples of the area under study, in general, show low values of dispersion of Pb than the rock samples. Its geochemical behaviour during chemical weathering has been discussed in the foregoing chapter of dispersion patterns.

**Zinc in rocks and minerals**

The occurrences of zinc in rocks and minerals in the form of sulphide and silicate have been reported by several earlier workers. Clarke and Washington (1924) reported a value of 40 ppm of Zn in the upper lithosphere. Newhouse (1936) did not find any sphalerite in the igneous rocks. Sandell and Goldich (1943) found that the concentration of zinc in a basic rock was twice as much as in an acid rock. Lundegaordh’s (1948)
investigations show that zinc concentrates in granodiorites in preference to gabbros and granites. He also found out that zinc was closely associated with the amount of biotite in granitic rocks.

Zinc in the granites and granitic rocks of this area has dispersion values up to 82 ppm (60 ppm, Vinogradov, 1967) except in a few cases. Quartzites have less Zn content than the schists and phyllites. The various rock samples from the Khetri copper mines show normal values for Zn while the sulphide ores have higher content. Dolerites in general record values up to 340 ppm (130 ppm, Vinogradov, 1962). Among mineral fractions, ferromagnesians are found to be the chief hosts of Zn.

Zinc is a chalcophile element and an element of ore complexes. It forms sulphides and also shows a tendency to enter into the silicate lattice. Its geochemical behaviour in both the cases is discussed as follows:

The ionic radius of zinc (0.74Å) is very much similar to those of the elements in the iron-magnesian group. It is, therefore, expected that zinc should be able to replace Mg\(^{++}\) (0.66Å) and Fe\(^{++}\) (0.74Å) contents of all such mafic minerals. Investigations have shown that olivine and pyroxene have distinct traces of zinc, while higher concentrations were recorded in amphiboles (200 to 2,000 ppm) and biotites.

It is now known that high co-ordination exists when zinc is bonded to fluorine (see Ahrens, 1964). Further it was observed that amphiboles and biotites have some water and fluorine. Ahrens (1964) pointed out that it might be due to the presence of fluorine in these minerals that zinc co-ordination tended to be octahedral and it replaced Mg\(^{++}\) and Fe\(^{++}\) easily,
resulting thereby concentration of zinc.

The concentration of zinc in the residual magma was explained by Ringwood (1955a) on the basis of electronegativity. The electronegativity of Zn is 1.7 while of Fe$^{++}$ is 1.65. Obviously more of zinc than Fe$^{++}$ will be concentrated in the residual magma. Zinc sulphide has also a marked capacity of capturing traces of other metals.

Zinc in the residual soils - Little is known about geochemistry of zinc in the process of chemical weathering. The present knowledge is, however, largely based on the weathering of primary rocks in the oxidation zones of zinc ore deposits. The products formed are usually sulphates and to a certain extent, carbonate of zinc.

The geochemical behaviour of zinc in the residual soils of the area, under study, shows that during chemical weathering it is generally more affected than Cu. Its details have been discussed in the foregoing chapter of dispersion patterns.

Nickel and cobalt in rocks and minerals

The distribution of nickel in rocks and minerals was first studied by Vogt (1923). According to Clarke and Washington (1924) the igneous rocks were found to have 0.001 per cent of Co and 0.02 per cent of Ni. Newhouse (1936) found that femic rocks have more sulphide minerals than salic rocks. Later Sandell and Goldich (1943) determined Co:Ni ratio as 3:10 for upper lithosphere, while Goldschmidt (1958) gave a ratio of 4:10. Wager and Mitchell (1951) investigated ferromagnesian minerals of early crystallisation to be enriched in Ni. Nockolds and Mitchell (1948) while working on some
Caledonian plutonic rocks, confirmed the observation of Vogt (1943) that Ni has a tendency to concentrate in the early magmatic differentiates. Turekian and Carr (1960) found that Cr and Ni were generally higher in early-formed pyroxene crystals than in the later ones in a particular extrusive or intrusive cycle.

Cobalt was reported to be usually concentrating in the ultrabasic rocks. Sandell and Goldich (1943) generally found the granites to have less than 1 ppm cobalt. Their observations were largely based on the granites from Minnesota. Nockolds and Mitchell (1948) found the value of Co to be below 15 ppm in granites and granodiorites. Lundegaordh (1945) and Du Rietz (1955) found the values of Co to be varying from 50 to 200 ppm in some ultrabasic rocks of Sweden. Turekian and Carr (1960) on the basis of their investigations on Stillwater complex, found Co to be following very closely only Mg in granitic rocks.

The sulphide minerals generally accommodate an appreciable amount of Co and it enters with greater ease in pyrite and pyrrhotite than chalcopyrite (see Gavelin and Gabrielson, 1947). An interesting observation was made by Hegemann (1943) who observed that the amount of Co in the sulphides was directly proportional to the degree of metamorphism of the sulphide deposits.

The granites and granitic rocks of the area show a maximum dispersion of 60 ppm of Ni (6 ppm, Vinogradov, 1962) and 8 ppm of Co (5 ppm, Vinogradov, 1962). The granite gneisses in general give higher values for
both the elements. Dolerites have values ranging from 18 to 140 ppm (130 ppm, Turekian and Wedepohl, 1961).

In the separated mineral fractions of granites and granitic rocks and host rocks of copper ores, both Ni and Co show concentration in the ferromagnesian phase. The separated sulphide ores have anomalously higher values for the Ni and Co contents. Ni was found to be essentially concentrated (upto 621 ppm) in the pyrrhotite. The Ni/Co ratio in the separated chalcopyrite and pyrrhotite fractions is 1.23 to 1.49 and 1.5 to 1.70 respectively.

Both the elements show a consistency in their dispersion and are generally associated with the copper ores. Thus they may be used as indicator elements of the regional geochemical background in the area under study.

In igneous rocks, the Co and Ni are usually present in the silicate structure. In the absence of any sulphide mineral, the silicates usually host all the Co and Ni contents of a rock and Co content in the granitic rocks increases at the expense of Ni (see Goldschmidt, 1958).

Generally, it is believed that the ionic radius of Ni$^{2+}$ (0.69Å) and Co$^{2+}$ (0.72Å) being very near to those of Mg$^{2+}$ (0.66Å) and Fe$^{2+}$ (0.74Å), either Ni or Co or both should be able to replace one or both of the latter metals. Goldschmidt (1944) suggested that Ni is likely to be enriched in the Mg-bearing minerals because Ni-O bond is stronger than Mg-O bond on account of its more covalent nature. But the idea did not sustain the criticism of Ringwood (1955a) who stated "that the effect of increased
covalent bonding is to weaken the bond". He (1955a) pointed out that since the radius of \( \text{Ni}^{2+} \) is smaller than \( \text{Fe}^{2+} \), the former could substitute the latter and further \( \text{Fe}-\text{O} \) bonding is weaker than \( \text{Ni}-\text{O} \) bonding and \( \text{Fe}^{2+} \) is more mobile than \( \text{Ni} \). This may render \( \text{Fe}^{2+} \) to be easily substituted by \( \text{Ni}^{2+} \).

Earlier Ahrens (1953) attempted to explain it on the basis of his field function concept. He suggested that "when competing for a site in a growing crystal \( \text{Ni}^{2+} \) is likely to arrive and perhaps enter before \( \text{Fe}^{2+} \) and \( \text{Mg}^{2+} \) because the positive field about \( \text{Ni}^{2+} \) is greater than that associated with the other two ions".

Co has generally been found to be concentrated in the mafic minerals. The ionic radii of \( \text{Co}^{2+} (0.72\text{Å}) \) and \( \text{Fe}^{2+} (0.74\text{Å}) \) have such a small difference that a close relationship between these two elements should exist. But there is a little variation in \( \text{Co}/\text{Mg} \) ratio as compared to \( \text{Co}/\text{Fe} \) ratio as one passes from basic to acid rocks (see Carr et al., 1961). Thus a linear relationship between \( \text{Co} \) and \( \text{Mg} \) was envisaged. The same authors also reported that the \( \text{Co} \) content in high-calcium granites was generally high (6.6 ppm) and low in low-calcium granites (0.88 ppm).

**Chromium in rocks and minerals**

Usually the ultrabasic rocks have a high concentration of chromium. Wager and Mitchell (1945) found 1,000 gms/ton \( \text{Cr} \) in olivine from a gabbro-picrite. Lundegaardh's (1946) investigations show that \( \text{Cr} \) has a tendency to be enriched in forsterite-rich olivine. The fayalite-rich olivines were found to be deficient in \( \text{Cr} \). Nockolds and Mitchell (1948) while working on some Caledonian plutonic rocks, found \( \text{Cr} \) to be concentrated in the early
differentiates of the magma. Carr and Turekian (1961) found that the biotites in granitic rocks were good hosts for Cr (190 ppm). They also found that the magnetites separated from high-grade metamorphic rocks from the Adirondacks as well as phyllites have less than 3 ppm Cr.

Chromium generally has a low dispersion in the granites and granitic rocks of the belt except in a few cases where the value is as high as 90 ppm (22 ppm, Carr et al., 1961). Dolerites give anomalous values up to 580 ppm (170 ppm, Turekian and Wedepohl, 1961). Quartzites record lower values as compared to the schists and phyllites (upto 245 ppm). The rock and ore samples from mines and the separated mineral fractions do not have unusual dispersion. Ferromagnesians show relatively higher concentrations.

Chromium has been taken as an element of the regional geochemical background because of its chalcophile character and regularity of dispersion in the area. The chemistry of its ionic replacement is discussed below.

It has been generally observed that Cr is preferably incorporated in the silicate phase. Its chalcophile character comes into play only when oxygen is either low or absent (see Goldschmidt, 1958). It occurs as an oxide as well as silicate in igneous rocks.

According to Goldschmidt (1958), Cr$^{3+}$ may replace Fe$^{3+}$ and Al$^{3+}$ diadochally. Wager and Mitchell (1951) found that Cr$^{3+}$ (0.63Å$^0$) was camouflaged by Fe$^{3+}$ (1.80) during fractionation of magma. Therefore, high concentration of Cr in the ferromagnesian minerals cannot be explained on the basis of simple ionic radius. Ringwood (1955a) observed that the smaller electronegativity of Cr$^{3+}$ (1.6) than that of Fe$^{3+}$ (1.8) might be responsible
for such a behaviour. Carr and Turekian (1962) observed a good correlation between Cr and Mg contents in a granitic rock. Further, they found that Cr contents in high-calcium granitic rocks were 12 to 22 ppm, while in low-calcium granitic rocks were 3 to 4 ppm.

Cadmium, lithium and silver in rocks and minerals

These elements do not show any significant dispersion quantitatively in the samples of the Khetri copper belt. Their geochemical behaviour has been briefly described here.

Cadmium - The geochemistry of cadmium is not studied much by the research workers. It has a strong chemical affinity for sulphur. Sandell and Goldich (1943) found that absolute amount of Cd is higher in gabbroid rocks than in granites. Cadmium is usually present in sphalerite crystals. It has been investigated that in the early magmatic sulphides the amount of Zn and Cd are low. These two elements go to the late differentiates and form substantial constituents of late crystallizing ore fluids which intrude the neighbouring rocks in the form of apophyses. Cadmium could not be estimated in the rocks of the Khetri copper belt because of its low traces.

Lithium - Lithium is an alkali metal but in many respects it follows Mg. The Li:Mg ratio shows a steady increase in the late crystallizing rocks and minerals. Strock (1936) who made a careful study of this ratio for various igneous rocks suggested that this element could be used as an index to the stage of differentiation reached by a rock. During fractional crystallization the concentration of Li ions increases in the liquid phase while that of Mg ions decreases and thus favourable conditions for
Li to enter into early crystallizing ferromagnesian minerals. The element is more enriched in the granitic rocks than syenites and nepheline syenites. Generally the granite gneisses of the Khetri copper belt show little content of Li. Schists and phyllites also have limited dispersion while in quartzites it is not detectable. Dolerites and the mine samples also have insignificant traces of Li.

Silver - The geochemistry of silver is known considerably. It is found to be more connected with the gabbroid magmas than with granites and highly siliceous rocks. In the case of hydrothermal sulphide deposits Ag, preferably concentrates in chalcopyrite than pyrrhotite. Its presence and qualitative assessment indicates the chemical history of the deposit particularly as regards the temperature of crystallization. It is therefore used in the present study as an element indicating stage of mineralization.

All the samples of the Khetri copper belt have low traces of silver which could not be estimated by the Atomic Absorption Spectrophotometer.
Interpretation of Analytical Data

Rocks and ores

The work is based on the analyses of granites and granitic rocks (25 samples), quartzites (31 samples), schists and phyllites (27 samples), rocks and ore samples from the Madhan-Kudhan and Kolihan mines (23 samples), dolerites (8 samples), amphibolites (4 samples), pegmatites (3 samples) carbonate rocks (3 samples), etc. for trace elements viz., Cu, Pb, Zn, Ni, Cd, Cr, Li and Ag by Atomic Absorption Spectrophotometer (Perkin-Elmer, Model 303). Additional determination for Co was done from the samples of granites and granitic rocks and also those from the Madhan-Kudhan and Kolihan mines.

Residual soil samples

Eighty-two residual soil samples of various groups of rocks, viz., granites and granitic rocks (21 samples), quartzites (20 samples), schists and phyllites (25 samples) and a miscellaneous group (16 samples) consisting of dolerites, pegmatites, amphibolites, carbonate rocks, were analysed for determining the traces of Cu, Pb and Zn, by Atomic Absorption Spectrophotometer (Jarrell and Ash).

The analytical results are plotted on histograms on ppm ranges for rock as well as residual soil samples. The pattern of arrangement of the samples in the figures, the epithets used and the points observed to arrive at certain generalizations are the same in both the cases.

The background values for granites and granitic rocks have been taken from other workers. For metamorphic rocks and the copper mine samples
the values have been calculated from the determined analytical data as has been discussed in Chapter VI.

The sample numbers in the figure are arranged according to their location in the Khetri copper belt. The first sample was taken from the extreme north while the last sample from the extreme south of the belt.

The epithets used in the interpretation are listed below. They connote the following order of relative abundance of elements. The same terminology has been used in Chapter VI:

1. "Insignificant" Below the limit of sensitivity of the instrument.
2. "Poor /Low/Depleted" Much lower than the background value
3. "Marginal" Within a close range of background value.
4. "High/abundant/enriched" Much above the background value.
5. "Anomalous" Distinctly above the threshold value.
6. "Highly anomalous" Many times higher than the background value.

Rocks and ores (see Text Figs. 4 & 5).

Granites and granitic rocks:

1. There is a general depletion in the Cu, Cr, and Li content and enrichment in Pb, Zn, Ni, while Co, Cd and Ag have insignificant values.

2. Cu is rarely high (38 ppm). Dispersion of Cu in the granite gneisses of the southern part of the belt is relatively higher than in the granites of the northern part of the same belt.

3. Ni, Zn and Pb show abundance as compared to their respective background values. Their concentrations are relatively high in the granite gneisses of the southern part of the area.
4. The values for Co in granites vary from 3 ppm to 8 ppm which are quite significant as very little of Co content was reported from the granites of other places.

5. The samples having high Cu content have ordinarily higher values for the other trace elements as well.

6. Pb and Zn show antipathic relationship with each other. Frequently, where Pb records a high value (70 ppm), the value of Zn becomes correspondingly low (26 ppm), and where the value of Pb is comparatively low (15 to 25 ppm) the value of Zn is usually high (95 to 200 ppm).

7. Ni and Co also have antipathic relationship. Where the values of Ni are 10 ppm, the values for Co are as high as 8 ppm. Similarly where the value of Ni is high (42 ppm) the value of Co goes down (3 ppm).

8. Cr gives anomalous values in the case of two samples of the northern part of the belt. Samples having higher Cr contents show enrichment in Zn and Ni but rarely in Cu.

9. Li is confined to a few samples of the granite gneisses only.

There was no distinct inter-relationship among these trace-elements. Generally Ni and Co show antipathic relationship, Cu to some extent has sympathetic relationship with Zn. Pb and Zn also show antipathy in some cases.

Quartzites

1. There is a general enrichment in Cu, Pb, Ni and Cr, and depletion in Zn, while Cd, Li and Ag have insignificant values. All the above trace elements show scattered dispersion all over the belt.
2. Cu gives very high values (770 to 1160 ppm) but only in a few exceptional cases. Where Cu shows anomalous values, Pb is also high (36 to 44 ppm) while Zn remains low (20 to 21 ppm). Ni and Cr are either low (except in one case) or absent.

Where Cu is low or insignificant, Pb and Zn are usually low while Ni and Cr show appreciable enrichment.

3. The samples of the northern part of the belt, particularly the amphibole quartzites, show enrichment in Cu and Pb contents and depletion in Zn, Ni and Cr. On the other hand the samples of the southern part of the belt (mostly felspathic and massive quartzites) show comparatively low dispersion of Cu and Pb and enrichment in Cr, Zn and Ni (in order of increasing abundance). There are, of course, a few exceptions to this generalisation.

4. Commonly Pb and Zn have antipathic relationship, and the value of Pb concentration is anomalous (74 ppm), Zn is either low (20 ppm) or insignificant (< 5 ppm) and where Zn content is high (89 ppm) the value for Pb becomes low (12 ppm).

5. A sample of amphibole quartzite collected from the quartzite ridge of Singhana recorded anomalous values for Cu, Pb, Zn, Ni and Cr. It, however, appears to be an exception.

6. Ni and Cr showed sympathetic relationship in a number of cases.

7. Li in general is insignificant. Only two samples recorded a value of 12 ppm.

8. Sericite quartzite (peak quartzite) was found to be barren of any mineralization.
It is evident from the above observations that the trace elements concerned hardly have any inter-relationship among each other. In some cases in which Pb and Zn have antipathy Ni and Cr have sympathetic relationship.

**Schists and phyllites**

1. Generally, Cu, Cr, Pb, Ni, Zn and Li show a general enrichment (in order of decreasing abundances), Cd and Ag occur in insignificant amounts.

2. There is a greater abundance of Cu in the schistose rocks than in the phyllitic rocks. In both cases where Cu is high (125 to 750 ppm) the value for Zn is low (30 to 57 ppm), Pb is appreciably constant (30 to 46 ppm) because the fluctuation in values is little. In some cases where Cu is low (15 ppm) Cr is exceptionally high (245 ppm) and so is the case with Ni (90 ppm).

3. Generally Cu occurs in greater abundance in the rocks of the northern part of the belt than those occurring in the southern part barring only one sample in which Cu is high (750 ppm).

4. Chlorite-schists and mica-schists show exceptionally high concentrations. Andalusite-schist also records higher values of Cu (55 ppm), Pb, Ni and Cr.

5. To some extent Zn and Ni and distinctly Ni and Cr show sympathetic relationship.

6. Except Cu (to some extent Zn also) none of the trace elements show selective enrichment in a particular part of the belt. Zn has appreciable enrichment in the samples NW of Saladipura (90 to 160 ppm).
7. Ni and Cr are more concentrated in the schists and phyllites than in the quartzites and granites or granitic rocks.


Zn gives higher values NW of Saladipura. Cr show enrichment in the northern portion of the belt. Ni and Pb have a distinct dispersion all over the belt.

Khetri copper mines samples

The samples include several types of schists and quartzites (host rocks), amphibolites, dolerites, etc. Some of the ore samples and separated chalcopyrite and pyrrhotite samples have also been analysed for elements other than Cu. Copper being exceptionally high in certain cases has been shown along the full length of the histograms.

1. There is a general enrichment in Cu, Co, Ni, Pb and Cr in the decreasing order of abundance. Zn occurs in appreciable amounts while Cd and Ag have insignificant values.

2. Schists have significantly abundant of Cu content (3^0 ppm). Co, Ni and Cr are also present in abundance in these rocks.

3. The quartzites have poor concentrations of Cu as compared to schists. Quartzites have high Co content particularly, the amphibole-quartzite (Co, 216 ppm).

4. Phyllites are generally low in Cu (75 ppm) but relatively enriched in Pb, Ni, Cr and Co. Zn is appreciably low (25 ppm).
5. The amphibolites have very low dispersion of Cu (20 ppm) but indicate higher concentration of Ni (55 ppm) and Pb (45 ppm).

6. Dolerites are relatively high in Cu (45 ppm) and so is the case with other trace elements as well.

7. The copper ore samples generally have higher concentration of Zn (250 ppm), Ni (235 ppm) and Co (360 ppm). Cr and Li give poor dispersion values (15 ppm and <10 ppm, respectively).

8. Commonly, the samples of host rocks with Cu are having higher contents of Cu give higher values for Ni and Co and low for Zn.

No assessment could be made of the inter-relationship of elements because of a wide variety of rock types obtained in this section.

**Dolerite**

1. The samples show general enrichment in Cu, Zn, Ni and Cr content while Pb and Li are marginally higher.

2. The values for Cu vary from 10 to 445 ppm showing its higher dispersion in the northern part of the belt.

3. Zn does not show any sector of preferential concentration and the values range from 48 to 340 ppm.

4. Ni contents do not show wide variation (18 to 140 ppm) while Cr contents have values varying from 10-580 ppm.

5. Both Cd and Ag lie below the sensitivity limit of the instrument except in one sample.
Pegmatites

1. Pegmatites do not show any abnormal concentration of Cu. The lowest value obtained is 10 ppm from pegmatites near Papurna and the highest value is recorded from the pegmatites SW of Chappoli (90 ppm). A sample from pegmatite vein NW of Madhan-Kudhan mines gave a value of 29 ppm.

2. Lead content appear to show direct relationship with copper because the samples having high copper values also show higher dispersion of lead.

3. Zn, Ni and Cr appear to be inversely proportional to Cu and Pb content.

4. Cd, Li and Ag show values < 5 ppm.

Amphibolites

1. Amphibolites show low dispersion of Cu except in one case in which the value is 45 ppm.

2. Pb has a consistent dispersion in almost all the samples.

3. Zn values range from 40 to 175 ppm showing a general enrichment.

4. Ni has values almost directly proportional to zinc. The values range from 30 to 130 ppm.

5. Cr shows poor dispersion except in one case (190 ppm). The values range from 10 ppm to 190 ppm.

6. Cd, Li and Ag have values < 5 ppm.

Carbonate rocks

1. The values for Cu vary from 10 to 65 ppm. There is no significant concentration.
TEXT FIG. NO. 6
2. Pb and Zn values appear to be dependent on each other and show general enrichment.

3. Ni shows variation from 32 to 66 ppm.

4. Cr has dispersion values ranging from 70 to 100 ppm.

Residual Soils (See Text Fig. 6)

Granites and granitic rocks - In general, Cu, Pb and Zn show a low dispersion. Rarely, the Cu content is high and touches a maximum value of 168 ppm. Samples having higher Cu content usually show depletion in the content of Pb and Zn. Similarly where Cu gives low values (16 ppm), Zn is usually high (45 to 77 ppm) and Pb is usually low (6 to 13 ppm).

Frequently Pb is more affected by the change in the Cu content and has a closer antipathic relationship with Cu than with Zn. The relationship is between Pb and Zn/rather uncertain and, therefore, it does not lead to any firm generalization.

Sometimes where Pb is high (38 ppm), Zn also records high value (63 ppm) and on the other hand, where Pb is low (9 ppm), Zn gives high values (76 ppm). Similarly, where Zn falls to a low value (21 ppm), Pb is either absent or records a low value (9 ppm). Such departures from any definite pattern lead to generalise that Pb and Zn relationship is antipathic in some cases and sympathetic in others.

The figure clearly shows that the samples on the left hand side (i.e., northern part of the belt) give relatively higher values for Cu than the samples on the right hand side (i.e., southern part of the belt). Further it was observed that the samples collected from the western margin of an outcrop had relatively higher values.
Quartzites - The samples show marked enrichment particularly in the Cu content.

There is a general enrichment of Zn while Pb has a low dispersion except in one sample of the southern part of the belt (44 ppm).

There is a wide variation in Cu-content. The values ranged from 12 to 610 ppm. Commonly the samples having higher Cu-content (377 to 610 ppm) give relatively low values for Pb (9 to 20 ppm) and Zn (50 to 53 ppm). Where the value for Cu is low (16 ppm) the value for Zn is usually high (82 ppm).

Pb and Zn do not show a clear relationship. The values of Pb came down to as low as 5 ppm while Zn shows appreciable and almost uniform dispersion all over the belt. Cu show antipathic relationship with Zn.

It was found that Cu is anomalously high in the samples of the northern part of the belt.

Schists and phyllites - Schists have higher dispersion in the northern part of the belt. Phyllites also show appreciable concentration of Cu.

There is a general improvement in the concentration of all the three elements. Cu shows anomalously high values to a maximum of 1436 ppm where the values for Cu are higher (364 to 1436 ppm), Pb and Zn have relatively low values. But such a relationship was not frequent. It was also true that some samples having a fairly high Cu content (106 ppm) give high value for Pb (53 ppm) and moderately high value for Zn (45 ppm). Further the samples having a low Cu content (18 ppm) have higher values for Zn and Pb (59 and 77 ppm respectively).
An antipathic relation exists between Pb and Zn in the samples recording low Pb content. But in some other cases where the value for Pb is high (46 ppm) Zn is generally high (71 ppm).

The samples distinctly show a higher concentration of Cu in the northern part but it gradually decreases in the schists and phyllites of the southern part of the belt. The values of Pb are comparatively high but it has not concentrated in any particular part of the belt.

**Residual soils of other rock types**

The residual soil samples of other rock types include soils of dolerites, pegmatites, amphibolite and carbonate rocks. A general quantitative assessment is made in the following way.

There is an appreciable concentration of all the three elements in the samples. Cu gives appreciably high values sometimes as high as 702 ppm. Where Cu gives high value (702 ppm) usually the value of Pb is low (9 ppm), where Cu is low (13 ppm), both Pb and Zn have higher values (63 and 65 ppm. respectively).

The dolerites have exceptionally high Cu value (702 ppm). Pegmatites do not show any enrichment. The amphibolites have comparable Cu content (30 ppm) though rarely the values of Zn are high (73 ppm). Carbonate rocks clearly show enrichment in the Zn content (106 to 142 ppm).

Based on a comparative study of the residual soil samples of granites and granitic rocks, quartzites, schists and phyllites and the other rock types, an overall picture of the trace element distribution is presented as follows:
1. There is a gradual increase in the Cu traces from granites to quartzites and from quartzites to schists and phyllites.

2. The variation is distinct in the samples of the northern part of the belt. The granites have low dispersion of copper. Felspathic quartzites occurring in contact with granites are also poor in Cu, while amphibole quartzites and phyllites occurring in contact of the schists show appreciable increase of Cu-traces. Schists in turn give highly anomalous values, for Cu. Other rock types in exceptional cases have high content of Cu.

3. Pb has a low dispersion in granites and granitic rocks and poor in quartzites. Schistose rocks and phyllites indicate appreciable abundance of lead. The other rock types also show some enrichment in Pb contents. There is no such area in the belt which can be said to have any sort of preferential concentration of Pb.

4. Zn records a marginal fluctuation (as compared to the background value) in all the samples. In most cases it shows an antipathic relationship with Cu. In general Zn shows a controlled dispersion.
DISTRIBUTION OF SOME TRACE ELEMENTS IN THE SEPARATED MINERAL FRACTIONS OF GRANITES AND GRANITIC ROCKS AND HOST ROCKS OF COPPER ORES

Granites and granitic rocks (see Text Fig. 7)

Ten samples were selected from the different outcrops of granites and granitic rocks of the area. Their ferromagnesian and felsic mineral fractions were separated and analysed for traces of Cu, Pb, Zn, Ni, Co and Cr and the results were plotted in histograms.

The ferromagnesian minerals viz., epidote, hornblende and biotite were separated as more or less pure monomineralic fractions (about 95 per cent pure). Only in two samples (No. 1 and 2) in which hornblende and epidote coexist, they had to be separated from one another. The results of analyses are plotted separately. Quartz and feldspars have been collected together as a felsic group for analyses.

All plotting has been done on ppm values. The serial number of the samples in the figure is with reference to their location in the belt. For example Sample No. 1 belongs to the extreme northern part while Sample No. 10 to the extreme southern part of the belt where such rocks are exposed.

A quantitative assessment is made in two ways. Firstly, a general trend of elements in the ferromagnesian and felsic group is considered and their order and preference of concentration are discussed. Secondly, the behaviour of these trace elements in each rock sample and their variation in the belt is considered.
General assessment

Cu, Pb, Zn, Ni, Co and Cr are preferably concentrated in the ferromagnesian phase.

Cu entered both hornblende (58 ppm) and biotite (62 ppm) with almost equal ease. This was particularly observed in the samples of hornblende-granite gneiss and biotite-granite gneiss from the southern part of the belt. In general Cu has a greater concentration in hornblende than biotite and relatively more in biotite than epidote (38 ppm).

Cu in all the samples of the felsic group reads insignificant values.

Pb, Zn, Ni and Cr are concentrated in hornblende, biotite and epidote in order of decreasing abundance.

Zn is exceptionally high in hornblende (415 ppm) and biotite (295 ppm) in the southern part of the belt.

Pb (10 to 29 ppm) and Zn (3 to 47 ppm) value are quite low in all samples of the felsic group.

Ni and Cr to some extent show a consistency in being accumulated in the ferromagnesian fractions. They preferably concentrate more in hornblende than in biotite and least in epidote.

Co behaves differently. It has slightly greater concentration in biotite (69 ppm) than hornblende (60 ppm) and least concentration in epidote (20 ppm).

Ni has a very low accumulation (6 to 13 ppm) in the felsic group.

Co and Cr are characteristically absent in all samples of felsic group.

Northern part

1. Hornblende - Where Cu is high, the values of Pb, Zn and Ni are low and where Cu is low, the values of Pb, Zn and Ni are high. Co and Cr remain low in both the cases.

2. Epidote - Where Cu is high, the values of Pb, Zn and Cr are high, while Ni and Co are low. Where Cu is low, the values of Pb and Cr are low while
SEPARATED MINERAL FRACTIONS OF HOST ROCKS OF COPPER ORES

TEXT FIG. NO. 8
Zn, Ni and Co are high.

3. **Biotite** - Where Cu is high, the values of Pb, Zn, and Co are low, while those of Ni and Cr are moderate. Where Cu is low the value of Pb, Zn and Co are high while Ni and Cr continue to record intermediate values.

**Southern part**

1. **Hornblende** - Where Cu is high, the value of Pb is low. Zn shows an exceptionally high value while Cr, Ni and Co are appreciably high.

2. **Biotite** - Where Cu is high, the value of Zn is intermediate. Pb and Cr give low values while Ni and Co are relatively low. Where Cu is low, the values of Pb, Ni and Co and Cr are high, while Zn continues to read intermediate values.

**Felsic group**

The felsic group does not show any specific pattern. The values of Cu, Pb, Zn and Ni are almost insignificant and do not indicate any relationship with one another.

**Host Rocks** (see Text Fig. 8)

Six samples were selected from the host rocks of copper ores. Three samples were collected from Madhan-Kudhan copper mines and three samples from Kolihan copper mine. The separated mineral fractions (95 per cent purity) include garnet, amphibole, biotite and quartz plus feldspars (felsic group). They were analysed for traces of Cu, Pb, Zn, Ni, Co and Cr. The analytical results were plotted in histogram.
General Assessment. - The following assessment has been made considering the points as stated in the case of granites and granitic rocks.

Cu, Pb, Zn and Co show preferable enrichment in amphibole. Ni and Cr are relatively higher in biotite. Garnet have comparable concentration of all the above trace elements. Felsic group has the least metallic content.

Copper is predominantly concentrated in amphibole (363 ppm) than garnet (330 ppm) and biotite (313 ppm). The garnets of garnetiferous biotite-schist (Kolihan copper mine) have low Cu content (85 ppm) while garnets of the garnetiferous quartz-chlorite schist of Madhan-Kudhan mine give higher content of Cu (330 ppm). The amphibole from amphibole quartzite of the Kolihan mine contain 295 ppm of Cu while that of Madhan-Kudhan mine records 363 ppm of Cu.

The felsic group does not have any Cu content in all the samples.

Lead and zinc are generally concentrated more in amphibole than biotite and least in garnet.

Nickel is high in biotite (68 to 80 ppm) than in amphibole (58 ppm, amphibole and chlorite) and marginally low in garnet (48 to 55 ppm). Amphibole from amphibole quartzite show values varying from 28 to 36 ppm of Ni.

Cobalt has a higher concentration in amphibole (115 ppm, amphibole + chlorite from garnetiferous quartz chloride schist) than in garnet (72 to 94 ppm) and biotite (59 to 78 ppm). The garnet from garnetiferous quartz-chlorite-schist have relatively more Co content (94 ppm) than in garnet from the garnetiferous biotite-schist (45 ppm).
Chromium is markedly higher in biotite (165 to 250 ppm) than in rest of the separated mineral fractions. Amphibole (amphibole + chlorite) are more enriched in Cr content (132 ppm) than in garnet (68 to 121 ppm). The garnet from garnetiferous biotite-schist gives higher values (121 ppm) of Cr than the garnet of garnetiferous quartz-chlorite-schist (96 ppm).

Generally Pb, Zn, Cr, Co and Ni are present in low concentrations in the felsic group and they occur in decreasing order of abundance.

**Relationship of other trace elements with copper in individual minerals**

1. **Amphibole** - (sometimes with chlorite). Where Cu is high Pb, Ni, Co and Cr are low, while Zn is high. Where Cu is low Pb, Ni, Co and Cr are generally high, while Zn is low.

2. **Garnet** -
   a) **Garnet from garnetiferous quartz-chlorite schist** - Where Cu is high Pb and Zn are low, while the values of Ni, Co and Cr are high. Where Cu is low, the values of Pb and Zn are high, while Ni, Co and Cr generally show low concentrations.
   b) **Garnet from garnetiferous biotite-schist** - Where Cu is high generally all the other trace elements are high and vice versa.

3. **Biotite** - Where Cu is high, generally all the other trace elements are high. Where Cu is low the other elements have marginally lower values.
VARIATION DIAGRAM SHOWING RELATIONSHIP BETWEEN Cu, Pb, Zn, Ni, Co & Cr CONTENT OF THE BULK ROCK & THEIR SEPARATED MINERAL FRACTIONS IN GRANITE & GRANITIC ROCKS

TEXT FIG.NO. 9
RELATIONSHIP BETWEEN Cu, Pb, Zn, Ni, Co, AND Cr CONTENTS OF THE BULK ROCKS AND THEIR SEPARATED MINERAL FRACTIONS IN GRANITES AND GRANITIC ROCKS

A comparative study of the distribution and relationship of some trace elements in granites and granitic rocks and its ferromagnesian fractions is done and the observations made are summarized below (see Text Fig. 9).

The concentration of Cu, Pb, Zn, Ni, Co and Cr are low in the bulk rocks while the ferromagnesians in them show enrichment of these elements.

Investigations carried out by Putnam and Burnham (1963) show that the Cu content of many bulk rock samples of granites are somewhat higher than the amount contributed by the ferromagnesian phase. They attributed this observation to the presence of small amounts of chalcopyrite in granites. The same authors also pointed out the possibility of the presence of small amounts of Cu in feldspars. Earlier Newhouse (1936) and Ramdohr (1940) also reported the presence of small amounts of chalcopyrite in granites.

In the present case the ferromagnesian minerals always give higher values for Cu as compared to the bulk rock. This indicates that no copper ore is associated with these granites and granitic rocks. Further the Cu in these rocks appears to have preferably concentrated in the mafic minerals.

Putnam and Burnham (1963) also found that the Cu contents of biotite coexisting with chalcopyrite in the granites are higher as compared to the coexisting hornblende. Shrivastava and Proctor (1962) found more Cu in the augite-hornblende-chlorite group than in the biotites in quartz-monzonite
which was supposed to be source rock of copper ores. They also reported small amounts of Cu in the feldspars.

In the rocks under study perhaps Cu entered into biotite and hornblende with almost equal ease. Biotites show a marginal edge over hornblende. This indicates that the ferromagnesian minerals of the granites may have some primary copper in them and that they have not been affected by later percolations or permeations. Further, Cu may have entered some of the ferromagnesian minerals by replacing Fe. Little occurrence of Cu in the felsic group may be attributed to the feldspars rather than quartz.

Similar to copper, Pb also shows enrichment in the ferromagnesian minerals. It was also found in appreciable amounts in the felsic group.

It is generally believed that Pb enters into granites diadochally with K⁺ and thereby potash-felspars may contain appreciable amounts of Pb (Goldschmidt, 1958; Wedepohl, 1956). Shrivastava and Proctor (1962) found that although Pb was preferably concentrated in the mafic minerals yet they (mafic minerals) constituted a small fraction of the bulk rock. They further considered feldspars as good hosts for Pb.

Lead in the present case reads higher values in the mafic minerals than the bulk rock. Further, the felsic group, which forms the major part of the bulk rock, has also appreciable amounts of Pb. Obviously Pb has also a significant concentration in the felspars of the felsic group. It was also observed that the pink granite-gneisses rich in potash-felspars have higher concentration of Pb than other rock samples.
Concentrations of zinc have been reported in basic igneous rocks (Sandell and Goldish, 1943) as well as biotites (Lundegaardh, see Wilson 1953). Wedepohl (see Putnam and Burnham, 1963) found occasional presence of Zn in feldspars.

The present analytical data show that the ferromagnesians are enriched in Zn as compared to the bulk rock. Further the felsic group also shows significant amounts of Zn. This indicates that Zn is possibly present in the silicate phase of the mafic minerals and feldspars of the felsic group and not as a sulphide. It might have been accommodated by replacing Fe$^{2+}$ and Mg$^{2+}$ of the mafic minerals (see Ahren, 1964).

Ni and Co are fellow travellers. Both these elements are found preferably concentrated in the ferromagnesians as compared to the bulk rock. The concentration of Ni is more than Co in general. The observations made are as follows:

i) Co and Ni are solely present in the silicate structure (Goldschmidt, 1958).

ii) Co and Ni have antipathic relationship.

iii) Co and Ni may/enriched in mafic minerals possibly substituting Fe$^{2+}$ (see Ringwood, 1955a) and Mg$^{2+}$ (see Carr and Turekian, 1961) respectfully.

Cr is reported to be preferably incorporated in the silicate structure and biotites are considered to be good hosts for Cr (see Carr and Turekian, 1961).

The ferromagnesians are significantly enriched in Cr contents as
compared to the bulk rock. The higher concentration of the metal in hornblende and biotite suggests that Cr is present in the silicate structure. It might have entered the lattice possibly substituting Fe$^{3+}$ (see Ringwood, 1955a).