Chapter VII

WALL-ROCK ALTERATION AND PROBABLE SOURCE AND NATURE OF MINERALISATION

Wall-rock alteration

It is very well known that the study of hydrothermal alteration of the wall-rocks of ore deposits has a great significance in metallogenesis. When hydrothermal solutions bring about some mineralogical, chemical and physical changes in the wall-rocks around an ore body, it becomes necessary to study the extent and nature of alteration, which is often a complex process. When properly interpreted, the study may give an idea regarding the source and nature of ore solution, in addition to the chemical process involved in the formation of the ore as well as the associated new minerals. Moreover, it may also serve as a guide to locate ore deposits of hydrothermal origin. There are many instances in which wall-rock alteration has proved to be a valuable tool in mineral exploration because the altered zones are usually more conspicuous than the ore bodies. It may be of interest to note here that in course of the present investigation, the author has been able to locate a number of new occurrences of sulphide ores in the Eastern Himalayas applying the knowledge of wall-rock alteration as a very useful guide. Several eminent workers such as Hewett (1928), Lindgren (1933), Lovering (1949), McKinstry (1946), Sales and Mayer (1949, 1950), Anderson (1949), Ohle (1951),
Schwartz (1955, 1959), Bateman (1959), Gawad and Ker (1959), Park Jr. and MacDiarmid (1964) and many others have dealt adequately with the wall-rock alteration and its importance in ore geology. According to Levering (1949) the hydrothermal alteration associated with ore deposits is contemporaneous with ore deposition and that the different mineralogical zones in the ore bodies and the surrounding country rocks are just like the reaction rims representing the diminishing activity of the powerful solutions that deposited the ore.

None of the earlier workers, who reported and described several occurrences of sulphide ore deposits from the study area or from any other region in the Eastern Himalayas, have stated anything about the pattern or nature of wall-rock alteration. An attempt has, therefore, been made to study carefully the wall-rock zones in the vicinity of some sulphide ore deposits in the Eastern Himalayas.

I. Alteration associated with the lead-zinc ore bodies in carbonate host rocks:

The silicified dolomitic limestones are the wall-rocks of lead-zinc deposits of Rishi area. The unaltered portions of the country rocks are represented by massive limestones.

The nature and sequence of alteration of the wall-rocks and their paragenetic relation with the ores have been determined from their petrological studies. They are presented as below:
Dolomitization
Silicification
Lead-Zinc Mineralization

The mineralisation is strictly confined to the dolomitized zones. The areas of alteration are sporadic. Generally, the change from limestone to dolomitic limestones appears to be abrupt. As a result of hydrothermal activity the limestones have undergone distinct and well-marked changes, as given below:

A. Physical changes due to alteration

1. Dolomitization

Changes in colour and texture of limestone due to dolomitization are easily discernible. Increase in porosity and permeability of the rock is distinct. Fracturing of mineral grains is a common feature.

Colour

The unaltered limestones of the study area are dark grey in colour while the altered dolomitic limestones show invariably cream or dirty white colour. Generally, the change of colour is gradational with a transitional zone of light grey coloured limestones having clusters of dolomite. Sometimes, however, the contacts between the unaltered and altered rocks are sharp. Hewett (1928), Watson (1905), Lovering (1949) and Park Jr. and MacDiarmid (1964) have recognised such a change from darker to lighter shades of grey colour during
hydrothermal activity on limestones. It is believed that the dark-coloured carbonate rocks undergoing hydrothermal alteration develop a tendency to expel impurities such as carbon and due to which the altered rocks become white or light grey in colour.

**Texture**

The alteration of fine-grained or micritic limestone of the area is always accompanied by a notable increase in grain size, producing thereby the medium grained varieties of dolomitic limestones. Presence of some unusually large sized isolated dolomite crystals within the smaller calcite grains is a striking feature of these dolomitic limestone. Some of the dolomite grains have grown upto a size of 5 or 6 mm in diameter. The grains are characteristically idiotopic in texture. Such changes in texture and grain size of the rocks in the altered zones as compared to those in the unaltered zone are remarkable. The contact between the fine-grained or micritic unaltered limestones and the altered dolomitic limestones is generally sharp. Sometimes a transitional zone comprised of a fine-grained dolomitic limestone was also encountered. In the field it is rather difficult to distinguish between them by their textural characters. One has to depend much on their petrographic characters, which are much more diagnostic. To some extent, however, the grey and light grey colour is defined, but that alone cannot be taken as a reliable criterion. Porphyrotopic texture is a common feature of the altered rock. The porphyrotopes of fresh and clear dolomite euhedra occur in a groundmass of fine-grained calcite which is always dusty, dull and
clouded. The normal size of the dolomite porphyrotopes varies from 1.6 mm to 2.0 mm in diameter.

The alteration of limestones to dolomitic limestones is thus a case of progressive change. The increase in grain size of dolomite is proportional to the increase in the content of dolomite, and thus it reflects the intensity of dolomitization to which the rocks were subjected. Such textural peculiarities have been reported from many parts of the world. Ohle (1951) stated "As recrystallisation proceeds, the average grain size increases and also the percentage of the total carbonate that is dolomite". He defined the hydrothermal dolomites as recrystalline. Rasul and Ali (1968) have recorded an increase in grain size as well as a change of colour of dolomites hosting the sulphide ore deposits from Bageshwar area in Almora district of Kumaon Himalayas. Similarly, Lovering (1949) and Schwartz (1959) have also observed increase in the grain size of carbonate rocks through dolomitization. As reported by Tarr (1936) and Ridge (1936) the hydrothermally affected dolomites are always found to be more coarsely textured than the unaltered dolomitic limestones. Hewett (1928) in his classic work reported similar variation in texture around the hydrothermal ore deposits of North America and Europe. Jicha Jr. (1951) reported abnormally large-sized crystals of hydrothermal dolomite increasing up to 1 cm in diameter from the lead-zinc deposits of Cave di Pradoe, in the Alps.
Porosity, permeability and fracturing

It is now believed that an increase in porosity is related to the dolomitization of the rock. Pinckney and Rye (1972) studied the alteration pattern around the Mississippian limestone wallrocks, and have found an increase in the porosity of rocks in the dolomitized zone. A comparative study of the petrographic and textural characters of the altered and unaltered carbonate rocks of the study area was made in order to determine the nature of physical and mineralogical changes in the altered rocks. Fracturing and jointing are the characteristics of most of the altered carbonate rocks within which there are innumerable vugs. Such features are typically absent from the unaltered rocks. The dolomitized carbonate rocks have porphyrotopes of dolomite that occur in clusters and are highly fractured. All such features like micro-vugs, fractures, etc., are rarely found in the unaltered rocks. The porous and vuggy dolomites thus became favourable receptacles for the ore deposits. Martin (1958) has supported the view of Currier (1935), and has suggested a relation between alteration and the loss of competency. Landes (1946) stated that "an increase in porosity is related to dolomitization." He interpreted this increase as a result of leaching (decalcification or dolomitization) and recrystallization during the process of replacement. Further, Landes (op.cit) stated that the conversion of calcite to dolomite occurs molecule by molecule by the substitution of magnesium carbonate for part of the calcium carbonate, causing thereby reduction in volume and increase in
porosity. However, Hewett (1928) has a different opinion and observes no increase in volume. Hewett (op. cit.) in his classic work on the alteration of carbonate rocks further put forward that dolomitized limestones near ore deposits are commonly slightly porous but the porosity is rarely more than 5 per cent.

An increase in porosity and permeability of the carbonate rocks through dolomitization was also supported by Tarr (1936), who believed that the hydrothermal dolomites are more porous than their unaltered counterparts. Ohle (1951) suggested that the high percentage and coarse granularity of dolomite may be responsible for an intense increase of the permeability of limestones. He calculated the increase in permeability of over 18,000 per cent in the carbonate rocks due to dolomitization. In his important paper on the origin of porosity in the carbonate rocks, Murray (1960) has given petrographic evidence for the relationship between porosity and dolomitization.

2. Silicification

The minor openings such as vugs and micro-fractures of the dolomitie limestones were later invaded by silica in the form of jasperoid which has also partly replaced both calcite and dolomite. This resulted in the silicification of some dolomites. Relics of calcite and dolomite crystals have occasionally been found in the silicified zones of the rocks. The rugged and irregular contact between calcite and jasperoid or dolomite and jasperoid, also show the eating away phenomena.
Rhomboideal pseudomorphs of jasperoid after dolomite are of common occurrence. The textural relation between the ore minerals and jasperoid indicates that the invasion of ore solutions followed the silicification. Two varieties of silica are commonly found, (1) grey fine-grained jasperoid replacing the carbonates, (2) white, semi-vitreous and coarse grained quartz occurring in vugs, voids and micro-veins. The deposition of ore is associated with the first type of silica. These two varieties of silica possibly belong to two different generations. According to Parks Jr. and MacDiamid (1964), silicification is abundant in the hydrothermal deposits, and the silica may be introduced by hydrothermal fluids. They believe that one of the prevalent features of the epigenetic silica deposits of hydrothermal origin is jasperoid. According to them (op.cit.), "This is process of silicification is one form of ground preparation, whereby soft, impermeable and unfavourable rocks are made more competent and more receptive to the introduction of fluids and the deposition of ores".

Pinckney and Rye (1972) reported that, "Mississippian limestone wall-rocks surrounding a low-temperature ore body in the Hicks dome area of southern Illinois were dolomitized, recrystallised and silicified." They believe that the hydrothermal activity produced these alteration effects at low temperatures.

The silicified wall-rocks in the work area are very hard and competent, and at places even the interbedded thin intercalations of shales clearly show the effects of silicification. /shales, which are
ordinarily impermeable and not very receptive to ore-bearing fluids had been rendered hard and somewhat brittle through silicification.

B. Mineralogical changes due to alteration

The mineralogical changes in the altered carbonate rocks are very distinct. Dolomite, calcite and talc are the chief minerals involved in this change (Fig. 26).

The following changes in the mineralogical composition of the rocks have been observed (Table 18).

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Unaltered rocks (Limestones)</th>
<th>Altered rocks (Dolomitic limestones)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average of 12 samples</td>
<td>Average of 10 samples</td>
</tr>
<tr>
<td>Dolomite</td>
<td>1 - 10 %</td>
<td>80 - 90 %</td>
</tr>
<tr>
<td>Calcite</td>
<td>80 - 90 %</td>
<td>5 - 10 %</td>
</tr>
<tr>
<td>Talc</td>
<td>NIL</td>
<td>Restricted to the mineralized zones with an average of 0 - 4%</td>
</tr>
</tbody>
</table>

The altered rocks with a large percentage of dolomite are characteristically idiotopic and coarsely crystalline. Talc, being associated only with the altered rocks, has been considered to be a mineral of hydrothermal origin (Lindgren, 1933; Park Jr. and MacDiarmid, 1964). The contrasting percentage of dolomite and calcite is rather very characteristic. It may be noted here that in the altered rocks (dolomitic limestones) dolomite is the most predominating mineral (80-90%), and calcite, which has been replaced by dolomite, is reduced to about 5 to 10% in the altered rocks (Table 18). On the other hand the order of percentage composition of dolomite and calcite is almost reversed in the unaltered limestones (Table 18).
Fig. 26

Fig. 27
C. Chemical changes due to alteration

In the area under investigation, major chemical constituents of the country rocks increase or decrease quantitatively from the highly altered zone through partly altered to the unaltered zone. The proportions in which Ca/Mg, SiO₂ and CO₂ occur and vary from one locality to the other have been shown in the variation diagram (Fig. 27).

<table>
<thead>
<tr>
<th>Major chemical constituents</th>
<th>Altered rocks (quantity in per cent)</th>
<th>Unaltered rocks (quantity in per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>26.55</td>
<td>47.45</td>
</tr>
<tr>
<td>MgO</td>
<td>16.24</td>
<td>1.25</td>
</tr>
<tr>
<td>CaO/MgO</td>
<td>1.40</td>
<td>36.36</td>
</tr>
<tr>
<td>Ca</td>
<td>15.1</td>
<td>21.76</td>
</tr>
<tr>
<td>Mg</td>
<td>14.2</td>
<td>11.94</td>
</tr>
<tr>
<td>Ca/Mg</td>
<td>1.08</td>
<td>1.62</td>
</tr>
<tr>
<td>CO₂</td>
<td>46.27</td>
<td>34.25</td>
</tr>
<tr>
<td>SiO₂</td>
<td>12.30</td>
<td>31.30</td>
</tr>
<tr>
<td>R₂O₃</td>
<td>1.77</td>
<td>2.64</td>
</tr>
<tr>
<td>Ins.</td>
<td>9.70</td>
<td>22.54</td>
</tr>
</tbody>
</table>

v Average of 40 samples

Ca/Mg distribution

It is clear from the variation diagram (Fig. 27) that the Ca/Mg ratio varies from 1.60 to 1.70 as shown at station Nos. 8-9, 20-21 and 36-37. The progressive decrease in the values of Ca/Mg ratio obviously indicates an increase in the dolomite content of the wall-rock:
towards the ore body.

$SiO_2$ distribution

The variation diagram (Fig. 27) shows an interesting pattern of $SiO_2$ distribution. A progressive decrease in the value of $SiO_2$ content towards the ore bodies is marked by a progressive decrease of $CaO/MgO$ content. The $SiO_2$ in the ore zones varies between 2.5 and 12.5 with a maximum of 52.5 in the unaltered limestones.

$CO_2$ distribution

The $CO_2$ content (Fig. 27) has an important quantitative relation with that of $SiO_2$. The increase in $CO_2$ is marked with a corresponding decrease in $SiO_2$ and vice versa. The $CO_2$ content in the ore bodies varies from 43 per cent to 50 per cent.

Indication of zoning

The mineralogical and chemical variations in the altered and unaltered rocks clearly indicate the presence of a well-marked zoning in the carbonate rocks around the lead-zinc deposits of Rishi area.

II. Alteration associated with the copper ore bodies in metamorphic host rocks

The low grade metamorphic rocks such as phyllites, schists, slates and quartzites of the Daling and Baxa Series have hosted the copper ores. The wall rocks of copper have been intensively chloritized and sericitised. Auden (1935) who took long traverses in the Eastern Himalayas upto Tibet, reported about the high order of chloritisation these and sericitisation of rocks.
Alteration zones adjacent to massive sulphide deposits in metamorphic rocks are commonly difficult to distinguish from regionally metamorphosed country rock, particularly in the greenschist facies (Anderson, 1949). According to Hemley and Jones (1964) "the pressure-temperature conditions controlling the origin of mineral assemblages developed in hydrothermal alteration probably range from typical hot-spring conditions to the upper pressure-temperature limits of greenschist grade metamorphism". Sericite and/or chlorite are the minerals common in both the greenschist facies and alteration zones adjacent to the massive sulphide deposits. According to Anderson (1949), "If this mineral assemblage is limited in extent, is envelope like and transects original lithologic units or is conformable to these units, alteration zones are indicated". Anderson (1949) believes that chlorite is present in appreciable volumes in the rocks adjacent to some massive sulphide deposits, and Fe and Mg metasomatism related to ore deposition is usually accepted as the reason for its presence. In the Rouyn-Noranda area in Quebec, chlorite-rich rocks associated with some sericite and secondary quartz form pipe-like alteration zones in rhyolite, is as much as 300 feet in diameter (Dugas, 1966). Widespread chloritisation is common on the foot wall of the United Verde massive sulphide pipe (Jerome, Arizona), and quartz porphyry was converted partly or wholly into chlorite, indicating large-scale Fe and Mg metasomatism (Anderson and Creasey, 1960).

The Coeur d'Alene district in northern Idaho, one of the largest lead-zinc-silver deposits in the world, is an excellent example of development of sericite as one of the few persistently stable minerals in the alteration zone.
hale, representing the conditions of hydrothermal mineralisation
(Park Jr. and MacDismid, 1964). Wall-rock alteration with sericitisation
and silification accompanied the deposition of base metal ores in
the Magma Mine, Arizona. It was most intensely developed in the diabase
sills, but has also affected schists and clastic sediments (Short et al.,
1943).

A. Physical changes due to alteration

The following are the physical changes that have been recorded
in the metamorphic rocks of the work area due to hydrothermal alteration:

Colour

The bleaching effect due to the hydrothermal alteration is most
conspicuous in these rocks which often show a change in colour from
dark grey to light grey or white. According to Wilson (1941) such
changes are related to hydrothermal alteration and the altered rocks
are commonly bleached; and light coloured minerals like sericite, quartz
carbonates, etc. appear. The change in colour due to bleaching has
been noticed in most of the disseminated copper deposits throughout
the world. For example, at Cananea, Mexico, where the rocks have been
bleached to a very light grey or white colour during intense
sericitisation. Anderson (1947), while describing the epithermal minerali-
zation at Last Chance and Hornsilver Mines, Lava Creek district, Butte
county, Idaho, has furnished an excellent example of bleaching of dark
coloured igneous rocks, forming a broad zone of light grey sericitic rock.
According to Howie (1924) the granodiorites and diabase at Grass valley,
California, have been bleached to such an extent that they have almost
lost their identity. Exceptions to such colour changes where dark coloured rocks are produced have also been reported by Knopf (1931), Park and Cannon (1943), James (1949) and Schwartz (1959). But such exceptions are very rare.

In the study area the wall rocks adjacent to ore bodies show a distinct change in colour. The altered rocks show various shades of green colour due to the formation of chlorite and biotite. The progressive change in colour from dark grey to green is due to development of chlorite and then it becomes greyish white as chlorite has been gradually replaced by sericite. Silicification may also be partly held responsible for adding some light coloured areas in the altered zones.

Texture

The alteration has also brought about a change in texture of the wall rocks in which an increase in the grain size of almost all the minerals constituents is a common feature. The altered rocks are characteristically coarse grained and roughly schistose. Even the accessory minerals such as quartz, chlorite, biotite, muscovite, etc. have grown in size. Quartz has become distinctly coarser with an average grain size of 0.24 mm in diameter. The grain size of muscovite varies between 0.015 and greater than 0.75 mm in diameter. The well-developed needles of muscovite sometimes occur like encrusted quartz. Porphyroblasts of chlorite are common. The original texture of the country rock was never disturbed in the early phase of alteration and recrystallisation. Textural obliteration is more conspicuous in the later stage of
alteration or sometimes adjacent to the ore bodies.

**Permeability and porosity**

Permeability of a host rock is an important factor that controls epigenetic mineralisation. The wall-rocks have generally become more or incompetent due to the effects of alteration.

The earlier phase of dolomitization was mainly responsible for a slight increase in porosity without any increase in the volume.

**B. Mineralogical changes due to alteration**

Significant mineralogical changes have been recorded from the rocks surrounding the ore zones. Chlorite and biotite occur persistently in the ore zone as well as outside although their proportions vary. These minerals also show a progressive change and variations in their quantities towards the ore bodies which is a significant feature and most characteristic of the hydrothermal deposits (Lindgren, 1913; Schwartz, 1959 and Parks Jr. and MacDarmid, 1964). Schwartz (1959) compiled a list of 65 minerals formed by hydrothermal alteration and considered biotite, chlorite, sericite and quartz as the important hydrothermal minerals.

The minerals constituting the country rocks in the area under investigation, show a variety of alteration products. The chemical changes show that there exists a relationship between the composition of the primary mineral and the related alteration products. Biotite in these rocks was commonly altered first.

Spurer (1808) was the first person who introduced a variety of fine-grained chalcedonic quartz as jasperoid and Irving (1804, 1811) was
one of those early workers to describe jasperoid silicification in the Black Hills, S. Dakota, U.S.A. Silica played an important role during the hydrothermal alteration and the silicification, like biotitization, chloritization and sericitization, was also intense. Hydrothermally altered rocks in the work area were later silicified by jasperoid.

The general nature and sequence of wall-rock alteration is as follows:

1. Dolomitization
2. Silicification
3. Biotitization
4. Chloritization and
5. Sericitization

Biotite, which is supposed to be one of the important minerals in hydrothermally altered rocks, shows the incipient stages of alteration into green to light brown biotite and chlorite. According to Schwartz (1958), the alteration of biotite by hydrothermal solutions at moderate temperature and pressures is very much effective.

In the course of recrystallisation, biotite formed an aggregate of lighter brown coloured crystals. The alteration of biotite seems to be closely related to the associated clusters of rutile needles (Deer, et al., 1961). The concentration of rutile grains in the altered zones was found to be an indication of the zone of biotite alteration. The progressive alteration further affected the chlorite
and resulted in the formation of sericite, another characteristic alteration product. However, such alteration of biotite or chlorite is generally partial. The equilibrium is rarely reached in the hydrothermal alteration of biotites. Schwartz (1959) pointed out that "recrystallised biotite is always earliest when present, and that this is commonly followed by chlorite". The chlorite is an important mineral of the hydrothermal sequence of the wall-rocks of the area. Where the alteration is more advanced, chlorite becomes an important hydrothermal mineral and is found associated with talc (Park Jr. and MacDiarmid, 1964). This is very evident in Peku and Rangpo mine areas, where chlorite-talc assemblage is conspicuous. Chlorite is therefore a diagnostic hydrothermal mineral of these deposits. Deer et al. (1961) believed that many low temperature hydrothermal veins of Alpine type in low grade metamorphosed sediments carry chlorite in addition to quartz, etc.

According to the foregoing discussions, chlorite, sericite, biotite, talc and quartz are the common minerals in the ore zones although their relative proportions vary.

A comparative study of biotite and chlorite in the rocks occurring around mineralized and non-mineralized zones was also made in order to record their quantitative and qualitative variations that may have some bearing on rock alteration.

**Chlorite and biotite content**

It is very clear from the variation diagram (Fig. 28) that the chlorite and biotite content increases towards the ore zone suggesting
Fig. 28

Fig. 29
their leaching of iron contents towards the lode. The value of index of refraction of biotite varies from a minimum of 1.630 in the ore zone to a maximum of 1.670 in the non-mineralised rocks (Fig. 29). The changes in the optical properties of chlorite are also very diagnostic and characteristic. The intermediate index of refraction (N\text{y}) of chlorites is found to be of the order of a minimum of 1.601 in the non-mineralised rocks and a maximum of 1.640 in the mineralized zones (Fig. 29). There is also a well marked change in their optic sign to negative nearer to the lode (Fig. 29). This indicates a decrease in Al and an increase in Fe of these chlorites towards the lode. This is also clearly evident from the results of chemical analysis of chlorites from the altered/mineralised and unaltered/non-mineralized zones (Fig. 34a). Conspicuously, the percentage of chlorite and biotite record high values in the ore zones (Fig. 28). On the contrary, generally in the non-mineralized zone, they record lower values except in two cases (Fig. 28a, and e), which may be due to local abnormalities. It is, therefore, evident that chlorite and biotite are preferentially concentrated in mineralized zones as a result of later hydrothermal activity. The chlorite/biotite ratio also significantly varies from a minimum of 0.25 in the non-mineralized zones to a maximum of 21 in the mineralised zones (Fig. 28).
Refractive index ($N_y$) of biotite and chlorite (with optic sign)

The variation diagram (Fig. 29) shows that the values of intermediate index of refraction ($N_Y$) of biotite steadily decrease. But sometimes reversed relations are also present and show the presence of two different compositional varieties of chlorite. Under such circumstances, the compositional variation of the coexisting biotites shows a remarkable regular pattern. No doubt, the variation of their optical sign is found to be always regular (Fig. 29), but there is a characteristic and well-marked change in their pleochroic scheme. The replacement of biotite to chlorites along the basal cleavage is a regular feature. In most of the cases there is a well-marked sequence of this replacement, starting from the normal brown biotite to faded brown and thence to a green biotite, which in turn alters to green chlorite. The presence of secondary biotite formed during the hydrothermal activity is very common. Sometimes its accumulation in the wall-rocks is very high and the rocks become biotitic as found at Kalimpong and Rangpo mines. A well-marked and noteworthy feature observed in this replacement is the absence of iron ore inclusions within the replacing chlorites. Schwartz (1959) stated, "During the replacement of biotite to chlorite, equilibrium is usually not achieved, and the original composition of biotite plays a strong influence on the composition of the replacing chlorite". This partly explains the observed irregularity in the compositional variation of these chlorites as indicated by the anomalous variation of their optical characters in the zone of wall-rock alteration (Fig. 29).
Pleochroism of biotite

In the country rocks or in the non-mineralised zones the biotites show usual and normal pleochroic schemes. For example, in the non-mineralized schists, near Rangoon mine, the pleochroic scheme was found to be normal as \( X = \) light yellow, \( Y = \) brown, and \( Z = \) deep brown with absorption \( Z > Y > X \). But in the mineralised parts of the schists which are highly chloritic and biotitic near Rangoon mines, an unusual colour and abnormal pleochroic scheme as \( X = \) almost colourless, \( Y = \) green and \( Z = \) deep greenish black was noted. The absorption being \( X < Y < Z \). Similar variations in the pleochroic scheme of biotites have been invariably noted in the non-mineralised and mineralised rocks from other parts of the area. The biotite from the mineralised zone at Kalimpong recorded an abnormal pleochroic scheme as \( X = \) pale brownish yellow, \( Y = \) brown and \( Z = \) very deep brown, where the absorption is \( X < Y < Z \). These marked variations in the pleochroic scheme of biotite indicate the well-marked zones of wall-rock alteration, where the biotite has been affected chemically as well as physically.
C. Chemical changes due to alteration

An attempt has been made to investigate the complex chemical changes suffered by the various wall-rocks of the hydrothermal copper ore deposits of Darjeeling Himalayas. Chemical analysis of carefully selected samples from the altered and unaltered country rocks and minerals of the various deposits permitted a general assessment of the results.

Chemical characteristics of wall-rocks

Generally, the wall-rocks have been so much affected and altered by the invading hydrotherms that often it is a problem to determine the nature of chemical change. However, proper care has been taken to interpret the analytical results (Tables 37 to 40) of the samples which are presented in the form of variation diagrams (Figs. 30, 31, 32 & 33).

It is revealed that the chemical changes are complex, while some of the elements are added to rocks by the action of hydrothermal solutions, still there are others which are removed from the rocks (Figs. 30, 31, 32 and 33).

Prominent chemical changes also occurred due to addition of some compounds and to removal of some others. Silica, magnesia, potassium, carbon dioxide, iron, sulphur and water are the important additions and lime, soda, alumina and phosphorous pentoxide are those which are removed from the system.

Mineralisation of copper is restricted mainly to four kinds of country rocks in the area, viz., slates, phyllites, schists and
quartzites. Not only the altered but also the unaltered rocks are taken into consideration for this study.

Silica

The $SiO_2$ contents in the unaltered phyllites, schists, slates and quartzites (Tables 5, 30, 32) are found to be 40.20, 44.72, 38.60 and 60.90 per cent respectively. The $SiO_2$ content increases gradually from the altered rocks to the copper ore zones where the same rocks recorded 52.35, 65.00, 41.00 and 62.35 per cent respectively. It is, therefore, evident that the schists are much more silicified than the slates and quartzites in the highly altered ore zone.

Alumina and Titania

Alumina and titania show a general decrease in their contents from unaltered to altered zones. $Al_2O_3$ contents in the unaltered phyllites, schists, slates and quartzites are found to be 26.20, 24.40, 28.65 and 24.60 per cent respectively. There is a marked depletion of $Al_2O_3$ in the schists, slates and quartzites from the altered rocks to the ore zone where the values of alumina with respect to the rocks concerned are 2.10, 2.00 and 1.01 per cent. In the phyllites, however, alumina indicates a different concentration trend altogether. Alumina has a tendency to decrease in the altered phyllites adjacent to ore zones (15.45 per cent) and to increase sharply in the ore zone itself (27.12 per cent). The general decrease in alumina from unaltered to altered zones is found to vary from 11 to 25 per cent. All the four rock types show a general decrease in $TiO_2$ contents from the unaltered through altered to ore zone. About 50 per cent of $TiO_2$ in the unaltered
zone was depleted in the altered ore-zone.

**Ferric oxide and ferrous oxide**

All the four types of unaltered rocks are comparatively poor in iron oxides than the corresponding altered rocks. The ferrous oxide exceeds ferric oxide in all the unaltered rocks. However, the same FeO-Fe₂O₃ relationship is not always maintained in altered rocks near the ore zones. For example, in the altered slates ferrous oxide slightly exceeds ferric oxide (Fe₂O₃, 5.60; FeO, 5.80) and this ratio continues upto near the ore zones. But a reversal in their relative proportion is indicated in the ore zone proper where ferric oxide (10.00 per cent) exceeds ferrous oxide (6.00 per cent). A progressive increase in both the oxides of iron in all the types of rocks the unaltered through altered to ore zones, has been recorded. In general, the ferric and ferrous oxides increase in the altered zones.

**Lime and magnesia**

Lime and magnesia show different trends in the altered wall-rocks as well as in ore zones. Lime content records a progressive decrease from the unaltered zones through altered to ore zones where it has minimum content. But unlike CaO, MgO shows a progressive increase from the unaltered through altered rocks to the ore zones.

**Potash and soda**

These two constituents have opposite relation with respect to their contents in the wall-rocks as well as in the ore zones. While the potash content shows a sharp increase, the soda content shows a
sharp decrease in all the rocks collected from the unaltered through altered to ore zones.

Water

The total water ($H_2O$) content of the unaltered rocks is much lower than that of the altered rocks. The water content records a sharp increase towards the ore zone. The maximum amount of water is concentrated in and around the ore zones which are supposed to be the centres of intense hydrothermal activity. All the rock types, viz., phyllites, schists, slates and quartzites, indicate a significant rise in total water content from the unaltered through altered to the ore zone.

Manganese and carbon dioxide

Like water, manganese and carbon dioxide are typically associated with altered wall-rocks. In the unaltered phyllites both MnO and CO$_2$ are practically absent. But the phyllites in the altered zone, about 10 ft. away from the ore zone, have 0.76 and 1.32 per cent of MnO and CO$_2$ respectively. In the ore zone the amount of MnO and CO$_2$ in the phyllites reached up to 2.01 and 3.20 per cent respectively. Other unaltered rock types, viz., the schists, slates and quartzites, however, recorded 0.03, 0.10 and 0.10 per cent of MnO, and 0.01, 0.08 and 0.20 percent of CO$_2$ respectively. Therefore, in phyllites, the proportions of MnO and CO$_2$ progressively increase from the unaltered through the altered to the ore zones.
Ferrous sulphide and sulphur

Ferrous sulphide and sulphur are found to be important constituents of the altered rocks as well as of the ore zone. The unaltered rocks are almost free from these two constituents. They do not, however, have any regularity in their concentration trends in the different rocks. Phyllites belonging to the altered and ore zones have more or less the same value of FeS₂.

Phosphorous pentoxide

The P₂O₅ content shows a sharp decline from the unaltered through altered rocks to the ore zone, recording a minimum value of the constituent. The P₂O₅ contents in the unaltered phyllites, schists, slates and quartzites are 2.08, 1.13, 2.92 and 2.15 per cent respectively, whereas the corresponding rocks in the ore zone have negligible amounts of P₂O₅. The P₂O₅ content is, therefore, mainly limited to the unaltered zones.

Oxide ratios

The oxide ratios of some major constituents of the rocks in all the three zones have been calculated and plotted in the variation diagrams (Figs. 30, 31, 32 and 33). SiO₂/Al₂O₃, Fe₂O₃/Al₂O₃, CaO/(Na₂O + K₂O) and Na₂O/K₂O ratios from the unaltered through altered rocks to the ore zone have been plotted.

From the pattern of the distribution of various major elements already described, it is, therefore, revealed that the wall-rocks have suffered changes in chemical composition during this process leading to the ore deposition.
Chemical alteration of the wall-rocks prior to ore deposition

Adequate lithological and petrological evidence is available to conclude that the alteration of the wall-rocks prior to deposition of copper ore, started with dolomitisation and ended with sericitisation, the sequence of alteration being dolomitisation-silicification-biotitisation-chloritisation-sericitisation.

It may be noted that the primary biotite, which was already present in the rock as an important constituent, underwent reconstitution.

The further action of hydrotherms resulted in the formation of chlorite and uniaxial muscovite. The variation of chlorite/biotite ratio in the ore zone is a function of both the $H^+$ ion concentration in the hydrotherms and the biotite content in the earlier rocks.

Chemical characteristics of chlorite and biotite in the phyllites of unaltered and altered zones

The variations in the chemical composition of biotite and chlorite derived from the phyllites of the ore-zones and the barren country rocks have been plotted (Fig. 34 (a,b), Tables 41 and 42). They are also later compared with the biotites derived from the granitic rocks of the area under investigation.

Chlorites (Fig. 34a)

The limited chemical study that was made on chlorites occurring as mineral constituents of phyllites, suggests that their composition in the altered and copper ore zones is different from that in the unaltered zones. Thus the difference in composition of chlorites within and away
from the ore zone is obviously due to the effect of hydrothermal solutions. This has enriched chlorites in some chemical compounds and impoverished in some others. The results of chemical analyses of chlorites (Table 41), plotted in the form of variation diagrams, are self-explanatory.

Silica

The SiO₂ content in the chlorites derived from the phyllites in unaltered zones around the Sikhip copper deposits is considerably higher than that occurring in the chlorites, derived from the same rocks in the altered as well as in the ore zones.

Alumina and titania

The Al₂O₃ and TiO₂ contents in the altered zone close to the ore deposit record higher values than those in the unaltered zones.

Ferric oxide and ferrous oxide

The amounts of ferric oxide in the unaltered and altered rocks do not indicate much variation. But the chlorites in the altered rocks contain ferrous oxide more than double of its amount present in unaltered rocks.

Lime and magnesia

Chlorites in the altered zones are considerably enriched in MgO and impoverished in CaO in comparison to the unaltered zones.

Potash and soda

Potash records a slight increase and soda a marked decrease in the altered zone.
Nannosese
Chlorites in the altered zone record a marked rise in its MnO content as compared to those in the unaltered zone.

Water
The chlorites of the altered zone have a total water content about three times more than that occurring in the chlorites of the unaltered zone.

Oxide ratios
All the oxide ratios, except CaO/Na₂O, viz., SiO₂/MgO, FeO/MgO, CaO/Na₂O + K₂O are considerably higher in the chlorites of unaltered rocks than those in the chlorites of altered zone. CaO/Na₂O ratio, however, increases in the altered zone.

The variations in the major chemical constituents and their oxide ratios in the chlorites, separated from the unaltered and altered country rocks of Sikhip copper deposits, are so conspicuous that they can happen only when there is a profound change in the chemical environment leading to rock alteration but to a limited extent.

Biotite
The analytical results of the biotites derived from the phyllites in the unaltered as well as in altered parts of the country rocks adjacent to Peku copper deposit have been studied. The tables as well as the corresponding histograms (Fig. 34 b) of the chemical compositions of biotites indicate that their compositions have been largely influenced by their geological environments.
The major chemical constituents in the biotites from the altered and mineralized wall-rocks and in those from unaltered rocks have some regularity in their distribution trends.

The biotites derived in the mineralized zone show an increase in the proportions of FeO, MgO and K₂O contents and a decrease in Al₂O₃, Fe₂O₃ and Na₂O contents (Table 42). As far as TiO₂, MnO, SiO₂ and CaO are concerned, the difference in their percentage compositions are rather insignificant. The biotites derived from the unaltered rocks show a complete absence of fluorine which is characteristically present in the biotites found in the altered rocks. The variations in oxide ratios are also very significant, e.g., SiO₂/MgO, CaO/Na₂O + K₂O are found to be slightly lower, and FeO/Na₂O, and FeO/Fe₂O₃ + TiO₂ are appreciably higher in the biotites associated with the mineralised wall-rocks, than in those occurring in the unaltered rocks. A comparative chemical study of biotites derived from the younger granites and those from the altered wall-rocks shows that some of these oxides have similar trend of distribution (Table 42).

III. Isotope variation in the country rocks and ore deposits

Isotopic studies dealing with the natural variations of the abundances of certain elements are of current interest and importance in geology, geochemistry and geochronology. An attempt has been made to solve certain problems pertaining to the mineralization and age of the base metal deposits of the area. Isotopic values of natural non-radiogenic oxygen, carbon and sulphur and also of radiogenic lead isotopes were determined.
A. Distribution of $\delta^{18}O$ and $\delta^{13}C$ values

1) Lead-zinc deposit

Engel and others (1959) made a detailed study of the oxygen and carbon isotopes of a hydrothermal alteration zone around the lead-zinc-silver ore bodies at Leadville and Gilman, Colorado. More recently, Pinckney and Rye (1972) have studied the variation of $O^{18}/O^{16}$, $C^{13}/C^{12}$ ratios in altered limestones in Hill Mine, Cave-In district, Illinois. It may be regarded as the first attempt to study the variation in the isotopic composition of the ore-bearing rocks in the Eastern Himalayas.

The highest values in the unaltered rocks are 26.5% $\delta^{18}O$ (SMOW) and 2.5% $\delta^{13}C$ (PDB) (Table 22, Fig. 35a). The isotopic values in the altered rocks are found to be as low as 0.0% $\delta^{18}O$ (SMOW) and -4.0% $\delta^{13}C$. It is also of interest to note here that the low values of $\delta^{18}O$ and $\delta^{13}C$ are dependent on the grain size (Table 20).

<table>
<thead>
<tr>
<th>$\delta^{18}O$</th>
<th>$\delta^{13}C$</th>
<th>Average size of minerals</th>
<th>Rock type</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.5</td>
<td>2.5</td>
<td>1.5</td>
<td>Limestone (unaltered)</td>
</tr>
</tbody>
</table>

The grain-size relation between calcite and dolomite has been adequately stated earlier while discussing the petrographic characters of the limestones. The lithological and other physical changes were
brought about in the limestones as alteration became more pronounced with the intensity of dolomitisation leading to the reduction in the size of calcite grains and their partial replacement by dolomite. The $\delta^{18}O$ and $\delta^{13}C$ values show a tendency to decrease at the contact of the unaltered and altered limestones and finally they record lowest values near the ore zones (Table 22; Fig.35a,b). In the unaltered limestone the range of oxygen and carbon isotopes is similar to most of the marine limestones throughout the world (Taylor, 1967).

It is obvious that because the limestones in the altered zones were recrystallised, dolomitized and continued to remain sufficiently porous to allow fluids to pass through them, their isotopic values became quite different from those rocks which remained unaffected during alteration. $\delta^{18}O$ variations in the altered rocks, therefore, reflect a thermal gradient.

The variation of $\delta^{13}C$ values in the altered dolomitic limestones indicate that a large amount of carbon was involved during alteration. According to Pinchney and Rye (1972), "The amount of carbon required for the amount of exchange means that a large volume of water passed through the rocks during recrystallisation. A large volume of water is consistent also with the amount of water required for the transportation of silica deposited in the wall rock, and the amount required by partial exchange of oxygen isotopes".

Therefore, a large volume of water is required for the introduction of quartz and with the amount of carbon needed to change $\delta^{13}C$ values of the rock. The main source of such a large amount of water
could be the hydrotherms. According to Pinckney and Rye (1972),

"... for a simple system in which carbon-bearing aqueous fluid passes
through a porous limestone and continuously exchanges isotopes of
carbon and oxygen at equilibrium along its course, the isotopic
ratios of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in both the fluid and the rock should
vary systematically".

The $\delta^{18}O$ values of calcite, quartz and dolomite crystals and
$\delta^{13}C$ values of calcite from altered and unaltered zones have also been
plotted in the variation diagrams. All of these variation diagrams
show a systematic decrease in isotopic values of $\delta^{18}O$ and $\delta^{13}C$ from
the unaltered rocks towards the ore-zone (Fig. 35c,d).

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Mineral</th>
<th>Altered dolomitic limestones</th>
<th>Unaltered limestones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\delta^{18}O$ (SMOW)</td>
<td>$\delta^{13}C$ (PDB)</td>
</tr>
<tr>
<td>1</td>
<td>Quartz</td>
<td>+15.3</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Quartz</td>
<td>+8.0</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Quartz</td>
<td>+16.5</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Quartz</td>
<td>+17.3</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Quartz</td>
<td>+10.0</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Calcite</td>
<td>+22.5</td>
<td>-0.10</td>
</tr>
<tr>
<td>7</td>
<td>Calcite</td>
<td>+16.9</td>
<td>-0.20</td>
</tr>
<tr>
<td>8</td>
<td>Calcite</td>
<td>+13.8</td>
<td>-0.20</td>
</tr>
<tr>
<td>9</td>
<td>Calcite</td>
<td>+11.0</td>
<td>-0.64</td>
</tr>
<tr>
<td>10</td>
<td>Calcite</td>
<td>+8.9</td>
<td>-0.80</td>
</tr>
<tr>
<td>11</td>
<td>Dolomite</td>
<td>+9.6</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Dolomite</td>
<td>+10.0</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Dolomite</td>
<td>+12.0</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>Dolomite</td>
<td>+13.0</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>Dolomite</td>
<td>+16.0</td>
<td>-</td>
</tr>
<tr>
<td>Serial No.</td>
<td>Altered dolomitic limestones</td>
<td>Unaltered limestones</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------------</td>
<td>----------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{18}O$ (%)</td>
<td>$^{13}C$ (%)</td>
<td>$^{18}O$ (%)</td>
</tr>
<tr>
<td>1</td>
<td>+23.0</td>
<td>+1.6</td>
<td>+26.5</td>
</tr>
<tr>
<td>2</td>
<td>+20.0</td>
<td>+1.5</td>
<td>+25.5</td>
</tr>
<tr>
<td>3</td>
<td>+18.0</td>
<td>+1.3</td>
<td>+25.5</td>
</tr>
<tr>
<td>4</td>
<td>+14.0</td>
<td>+0.9</td>
<td>+26.5</td>
</tr>
<tr>
<td>5</td>
<td>+12.0</td>
<td>+0.5</td>
<td>+26.2</td>
</tr>
<tr>
<td>6</td>
<td>+11.0</td>
<td>0.0</td>
<td>+26.0</td>
</tr>
<tr>
<td>7</td>
<td>+10.0</td>
<td>-1.6</td>
<td>+24.0</td>
</tr>
<tr>
<td>8</td>
<td>+8.5</td>
<td>-3.0</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>+8.0</td>
<td>-4.0</td>
<td>-</td>
</tr>
</tbody>
</table>

2) **Copper deposits**

According to the earlier statement, the phyllites around the copper deposits of Sikhip developed distinct zones of silicification, biotitization, chloritization and sericitisation. An attempt has been made to study the oxygen and carbon exchange between the altered rocks and invading hydrotherms by collecting the relevant data on the oxygen and carbon isotopic variations from the unaltered parent rocks unto the altered rocks in the ore zones. Also, the isotopic values $^{18}O$ of quartz and muscovite belonging to altered and unaltered rocks have been plotted (Figs. 36a, b, c; Tables 23 & 24).

The $^{18}O$ and $^{13}C$ values of altered rocks progressively decrease towards the ore body (Figs. 36a, b, c; Table 23). For example, in the unaltered rocks, $^{18}O$ and $^{13}C$ values range from 20 to 28 (SHLM), and 1 to 3 (PDB) respectively. Whereas in the altered rocks, $^{18}O$
### TABLE -23 Variations of $\delta^{18}O$ and $\delta^{13}C$ values in altered and unaltered rocks, Sikkim area.

<table>
<thead>
<tr>
<th>ALTERED ROCKS (Phyllites)</th>
<th>UNALTERED ROCKS (Phyllites)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{18}O$ (SMOW)</td>
<td>$\delta^{13}C$ (PDB)</td>
</tr>
<tr>
<td>+ 19.4</td>
<td>+ 0.5</td>
</tr>
<tr>
<td>+ 18.3</td>
<td>0.0</td>
</tr>
<tr>
<td>+ 17.2</td>
<td>- 1.7</td>
</tr>
<tr>
<td>+ 16.0</td>
<td>- 1.4</td>
</tr>
<tr>
<td>+ 14.0</td>
<td>- 1.0</td>
</tr>
<tr>
<td>+ 10.5</td>
<td>- 2.5</td>
</tr>
<tr>
<td>+ 7.0</td>
<td>- 2.0</td>
</tr>
<tr>
<td>+ 5.0</td>
<td>- 4.0</td>
</tr>
<tr>
<td>+ 4.0</td>
<td>- 5.0</td>
</tr>
</tbody>
</table>

### TABLE -24 $\delta^{18}O$ variation in quartz and muscovite collected from the altered and unaltered zones, Sikkim area.

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of mineral</th>
<th>ALTERED ROCKS (Phyllites)</th>
<th>UNALTERED ROCKS (Phyllites)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Quartz</td>
<td>+ 14.0</td>
<td>+ 17.0</td>
</tr>
<tr>
<td>2</td>
<td>Quartz</td>
<td>+ 13.0</td>
<td>+ 17.0</td>
</tr>
<tr>
<td>3</td>
<td>Quartz</td>
<td>+ 12.6</td>
<td>+ 17.0</td>
</tr>
<tr>
<td>4</td>
<td>Quartz</td>
<td>+ 11.0</td>
<td>+ 17.0</td>
</tr>
<tr>
<td>5</td>
<td>Quartz</td>
<td>+ 10.5</td>
<td>+ 15.0</td>
</tr>
<tr>
<td>6</td>
<td>Quartz</td>
<td>+ 10.4</td>
<td>+ 14.5</td>
</tr>
<tr>
<td>7</td>
<td>Quartz</td>
<td>+ 10.0</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Quartz</td>
<td>+ 8.9</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>Muscovite</td>
<td>+ 11.2</td>
<td>+ 14.0</td>
</tr>
<tr>
<td>2</td>
<td>Muscovite</td>
<td>+ 11.0</td>
<td>+ 14.0</td>
</tr>
<tr>
<td>3</td>
<td>Muscovite</td>
<td>+ 10.2</td>
<td>+ 14.0</td>
</tr>
<tr>
<td>4</td>
<td>Muscovite</td>
<td>+ 9.3</td>
<td>+ 13.0</td>
</tr>
<tr>
<td>5</td>
<td>Muscovite</td>
<td>+ 9.0</td>
<td>+ 12.0</td>
</tr>
<tr>
<td>6</td>
<td>Muscovite</td>
<td>+ 8.6</td>
<td>+ 11.4</td>
</tr>
<tr>
<td>7</td>
<td>Muscovite</td>
<td>+ 7.6</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Muscovite</td>
<td>+ 6.3</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 38

Fig. 39

Fig. 40
isotope in quartz and muscovite decreases from 14.5 to 8.0 (SMOW) and from 14.8 to 6.4 (SMOW) respectively, as the ore zone is approached. The same isotopes in the quartz and muscovite of unaltered rocks vary from 15.0 to 17.0 (SMOW) and from 11.8 to 14.8 (SMOW) respectively. It is, therefore, evident that the isotope ratios are higher in the unaltered rocks in comparison to the altered ones.

8. Distribution of $S^{32}/S^{34}$

Ore samples for this study were selected from the various Cu and Pb-Zn deposits falling within the area. They were analysed to determine the isotopic composition of sulphur and the results are presented in Table 25. The values are plotted as $S^{32}/S^{34}$, and as $S^{34}$ relative to standard Canyon Diablo Troilite (Figs. 30 and 39). The results are compared with the standard $S^{32}/S^{34}$ ratios and permil deviations of various other sulphide minerals of the world compiled by Jensen (1959) after the work of Kulp et al. (1956), Jensen (1957), and Jensen and Anstutz (1959). Smirnov (1968) also summarized the results of the variations of sulphur isotope composition in sulphides (Fig. 40a, b) determined by Russian geologists.

The $S^{32}/S^{34}$ ratios in the lead-zinc deposits of Rishi area show that they have more or less a common variation range in the altered as also in the ore zone. For example, the sulphur ratios of pyrite, sphalerite and galena vary from 22.10 to 22.25 in the altered rocks and 22.18 to 22.25 in the ore zone. Somewhat similar ranges of isotopes in the pyrite in the altered rocks (dolomitic limestones) adjacent to ore-zone have been found (Fig. 39). The isotopic range in the pyrites in unaltered rocks is different and the $S^{32}/S^{34}$ ratios vary from
<table>
<thead>
<tr>
<th>No.</th>
<th>Description and location of sulphide minerals</th>
<th>$^{32}\text{S}/^{34}\text{S}$</th>
<th>% $^{34}\text{S}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><strong>Chalcopyrite</strong> occurrence with pyrite, phyllite wall-rock; Sikhip area</td>
<td>+ 22.18</td>
<td>+ 1.9</td>
</tr>
<tr>
<td>2</td>
<td><strong>Chalcopyrite</strong> occurrence with pyrrhotite, phyllite wall-rock; Pekku area</td>
<td>+ 22.30</td>
<td>- 4.2</td>
</tr>
<tr>
<td>3</td>
<td><strong>Sphalerite</strong> dark brown, dolomitic limestone wall-rock; Rishi area</td>
<td>+ 22.28</td>
<td>- 3.7</td>
</tr>
<tr>
<td>4</td>
<td><strong>Chalcopyrite</strong> occurrence with pyrite quartzite wall-rock; Kalimpong area</td>
<td>+ 22.27</td>
<td>- 3.6</td>
</tr>
<tr>
<td>5</td>
<td><strong>Pyrite</strong> occurrence with sphalerite and galena, dolomitic limestone wall-rock; Rishi area</td>
<td>+ 22.27</td>
<td>- 3.6</td>
</tr>
<tr>
<td>6</td>
<td><strong>Pyrite</strong> occurrence with chalcopyrite, phyllite wall-rock; Sikhip area</td>
<td>+ 22.23</td>
<td>- 2.4</td>
</tr>
<tr>
<td>7</td>
<td><strong>Pyrite</strong> occurrence with sphalerite, dolomitic limestone wall-rock; Rishi area</td>
<td>+ 22.21</td>
<td>- 0.5</td>
</tr>
<tr>
<td>8</td>
<td><strong>Pyrite</strong> fine-grained, dolomitic limestone wall-rock; Rishi area</td>
<td>+ 22.29</td>
<td>- 4.0</td>
</tr>
<tr>
<td>9</td>
<td><strong>Pyrite</strong> coarse-grained, occurs with chalcopyrite and pyrrhotite, schist wall-rock; Bangpo area</td>
<td>+ 22.36</td>
<td>- 7.5</td>
</tr>
<tr>
<td>10</td>
<td><strong>Pyrite</strong> fine-grained variety, associated with chalcopyrite and pyrrhotite, slate wall-rock; Pachikhanli area</td>
<td>+ 22.20</td>
<td>0.0</td>
</tr>
<tr>
<td>11</td>
<td><strong>Pyrite</strong> associated with pyrrhotite and chalcopyrite; slate wall-rock; Pachikhanli area</td>
<td>+ 22.22</td>
<td>- 1.9</td>
</tr>
<tr>
<td>12</td>
<td><strong>Galena</strong> coarse grained crystal, dolomitic limestone wall-rock; Rishi area</td>
<td>+ 22.28</td>
<td>- 3.2</td>
</tr>
</tbody>
</table>

(Contd.)
<table>
<thead>
<tr>
<th></th>
<th>Mineral</th>
<th>Notes</th>
<th>Assay Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>Galena</td>
<td>Coarse grained crystal; dolomite limestone wall-rock; Rishi area</td>
<td>+ 22.26</td>
</tr>
<tr>
<td>14</td>
<td>Chalcopyrite</td>
<td>Associated with pyrite; phyllite wall-rock; Sikhip area</td>
<td>+ 22.30</td>
</tr>
<tr>
<td>15</td>
<td>Pyrite</td>
<td>Taken from schists (unaltered country rocks); Rangpo area</td>
<td>+ 21.80</td>
</tr>
<tr>
<td>16</td>
<td>Pyrite</td>
<td>Taken from phyllites (unaltered country rocks); Sikhip area</td>
<td>+ 21.60</td>
</tr>
<tr>
<td>17</td>
<td>Pyrite</td>
<td>Taken from phyllites (unaltered country rocks); Pekw area</td>
<td>+ 21.40</td>
</tr>
<tr>
<td>18</td>
<td>Pyrite</td>
<td>Taken from slates (unaltered country rocks); Pachikhani area</td>
<td>+ 21.60</td>
</tr>
<tr>
<td>19</td>
<td>Pyrite</td>
<td>Taken from limestones (unaltered country rocks); Rishi area</td>
<td>+ 21.70</td>
</tr>
<tr>
<td>20</td>
<td>Pyrite</td>
<td>Taken from limestones (unaltered country rocks); Rishi area</td>
<td>+ 22.00</td>
</tr>
</tbody>
</table>
21.69 to 22.19. This range is wide and it bears no relation with
that found in the altered rocks adjacent to ore zone, or in the
ore-zone proper. Therefore, pyrite, sphalerite and galena in the ore-
zone and the pyrite in the altered rocks adjacent to ore-zone may be
the
genetically correlated. But/range of sulphur isotope in the pyrite
found in the unaltered limestones indicates that it is definitely of a
sedimentary origin.

The variations of $^{32}/^{34}$ ratios in some of the copper deposits
have been shown in Fig. 38. In the ore zones chalcopyrite and
pyrite were analysed while in the adjacent altered wall rocks and
the unaltered country rocks, pyrite was analysed. The $^{32}/^{34}$ ratios in
the ore zones and the adjacent altered country rocks show a narrow
range in comparison to the wide variation $^{32}/^{34}$ ratio in the unaltered
country rocks. Sulphur isotope ratios of chalcopyrite in the ore zone
at Rampo and Sikhip mines and the altered wall rocks show a range of
22.16 to 22.22. At Pachikani, Peku and Kalimpeng they have ranges of
22.22 to 22.25, 22.25 to 22.35 and 22.10 to 22.25 respectively. The
variations in sulphur isotope ratios in these deposits are very narrow.

**Probable source and nature of mineralisation**

The question of the source of the base metal deposits occurring
not only in this part of the Himalayas but also elsewhere in western
Himalayas has been an enigma for a long time. It is, therefore, intended
to throw some valuable light on their probable source. As stated earlier
that there are two different suites of granitic rocks in the study area,
one of which is of older than the other belonging to the tertiary age. Further, since the younger granites and the ore deposits have close age relations as determined by their lead isotope ratios, the investigations are chiefly confined to these two geologic bodies. An attempt has been made to compare them with respect to their chemical composition of certain rock forming minerals, trace element contents of their mineral fractions and isotope abundances.

I. Chemical composition of biotites of host rocks and the younger granites.

The biotites, derived from the mineralized zones in the altered wall rocks and also those from the younger granitic rocks have been chemically analysed. The biotites from the mineralized zone have significant amounts of FeO, MgO and K₂O, but are depleted in Al₂O₃ and Na₂O contents. They (Fig. 41b; Table 42) show some similarity with the biotites of younger granitic rocks as far as their chemical composition is concerned.

The analytical results of the biotites derived from the mineralized wall rocks, unaltered rocks and the younger and older granitic rocks from the area are more or less comparable with the results obtained by Henrich (1946). (Fig. 41a).

The biotite in the younger granites contains 16.31% FeO, 7.07% Fe₂O₃ + TiO₂ and 7.91% MgO; whereas the respective values of these constituents in the biotites obtained from the wall rocks are 16.40%, 5.63% and 8.95%. These values fall well within the range given for the constituents in the diagram for granites (Henrich, 1946). According to Deer et al. (1961), who summarized the principal results obtained by
Fig. 41

**Variation of Chemical Composition of Phlogopites and Biotites with Rock Type:** Compiled from diagrams of Henriot, 1961.

**Fig.** Variation of chemical composition of biotites derived from the country rocks and graniitic rocks around Darjeeling Himalayas.
Henrich (1946), biotites in granites should have FeO content varying from 12 to 25%, Fe₂O₃ + TiO₂ generally less than 10% and MgO content up to 12%. The composition ranges of these three important constituents of biotites from the wall rocks adjacent to mineralised zones are well within those found in the biotites associated with granite. The biotites in these two different rock types may therefore have some genetic relation. Such a relation is possible only when the biotites in the granites as well as in the copper ore zone have a common source.

The biotites derived from the unaltered country rocks have 6.95%, 11.21% and 7.46% of FeO, Fe₂O₃ + TiO₂ and MgO respectively. It may be noted that FeO content is much lower and Fe₂O₃ + TiO₂ content higher than in the altered rocks. The discrepancies in the chemical composition of biotite from the unaltered rocks show that it cannot be correlated with the biotite derived from either the altered wall rocks or the younger granites.

The FeO and MgO contents in the biotites, derived from the older granitic rocks, are 12.30% and 13.23% respectively. The values are well within the range as recorded in these compounds in Precambrian granites (Deer et al., 1961). These values differ greatly from those obtained for the biotites derived from the mineralized rocks. This difference in composition may be considered as an evidence in support of the fact that the older granites have no relation with the wall rock alteration or ore deposition.

II. Distribution of copper, lead and zinc in biotite, hornblende, quartz and feldspars.

Biotite, hornblende, quartz and feldspar were separated from the younger as well as the older granites. Separated mineral fractions from
the copper ore deposits are biotite, quartz and feldspar. Quartz was the only mineral separated from the lead-zinc ores.

A. Abundances of copper in biotite and hornblende (Figs. 43a & b).

1) Biotite

The copper contents of the biotites derived from the altered phyllites of Sikhip copper deposit adjacent to ore zone and from the unaltered rocks vary from 40-1500 ppm and 4-14 ppm respectively. The copper contents of the biotite derived from the altered slate wall rocks in Kalimpong area vary from 30-500 ppm, and from 3-9 ppm in the unaltered host rocks.

The biotite derived from the younger intrusive granites have a very high content of copper which ranges from 45-1500 ppm. But the biotites from older granites have a very low concentration of Cu in the range from 2-40 ppm.

2) Hornblende

The analyses of hornblende show that the copper contents in the younger granites are higher than in the older granites and vary from 25-500 ppm. In the older granites it was found to vary from 2-20 ppm.

B. Abundance of lead in biotite, hornblende, feldspar and quartz (Figs. 43a, b).

1) Biotite

Lead content of biotites from the altered wall-rocks at Sikhip, Peku and Kalimpong copper deposits vary from 4-20 ppm, 4-10 ppm and
5-18 ppm respectively. The concentration of lead in the biotites of unaltered rocks from the same localities is appreciably higher and varies from 14-100 ppm, 12-90 ppm and 25-75 ppm, respectively.

Biotite in the older granites has 4-40 ppm of lead whereas the biotite in younger granite has a greater concentration of lead (35-500 ppm).

2) **Hornblende**

In the hornblende separated from older granites lead concentration is low (2-15 ppm) while in the younger granites hornblende has a higher concentration of Pb (20-225 ppm).

3) **Feldspar and quartz**

Generally, concentration of lead is higher in the feldspars and quartz derived from the altered wall-rocks than those from the unaltered rocks. For example, the lead content in the quartz and feldspars obtained from the altered wall-rocks and the unaltered rocks which hosted the Pb-Zn deposits at Rishi varies from 30-400 ppm, and 2-7 ppm respectively. Lead contents in quartz and feldspars from the altered wall-rocks around the copper deposits at Sikhip, Peku and Kalimpong areas vary from 10-40 ppm, 11-45 ppm and 12-40 ppm respectively. On the other hand, lead concentrations in the feldspathic minerals from the unaltered rocks in these deposits vary from 3-9 ppm, 2-8 ppm and 4-10 ppm respectively. The same minerals from the older granites have 2-35 ppm of Pb, whereas those from younger granites show a very high concentration of Pb (40-900 ppm).
C. Abundance of zinc in biotite, hornblende, feldspar and quartz (Figs. 44a,b & e).

1) Biotite

Zn content like Pb records comparatively lower values in the biotites derived from the wall-rocks of the copper deposits at Sikhip, Peku and Kalimpong. Biotites from the altered host rocks of these copper deposits contain 3-30 ppm, 2-16 ppm and 12-20 ppm of Zn respectively. But Zn concentration in the unaltered host rocks was found to vary appreciably at Sikhip, Peku and Kalimpong from 20-90 ppm, 10-60 ppm and 30-100 ppm respectively. The zinc values in the biotites, derived from the older granitic rocks, vary from 2-40 ppm whereas its value in the biotites from the younger granites varies from 40-200 ppm.

2) Hornblende

Zn content in the hornblende from the older granites ranges from 2-20 ppm and in the younger granites, it varies from 25-500 ppm.

3) Feldspars and quartz

Generally zinc content like that of copper was found to be higher in feldspar and quartz derived from the altered wall-rocks as compared to its abundance in the same minerals from the unaltered rocks. In the quartz-feldspars derived from the altered wall-rocks of the copper deposits at Sikhip, Peku and Kalimpong it varies from 30-75 ppm, 30-50 ppm and 12-40 ppm respectively. Zn values recorded in feldspars and quartz from unaltered country rocks around these deposits vary from 2-15 ppm, 5-10 ppm and 5-12 ppm respectively.

The zinc content in the quartz and feldspars derived from older granites varies from 4-38 ppm and in those derived from the younger
granites, it shows higher values ranging from 50-225 ppm.

Discussion

According to Pauling (1960) the structure of biotite provides a number of sites where diadochic substitution may take place. Goldschmidt (1954) provided the rules for such substitution. De Vore (1955) stated that the minor elements in biotite may occupy lattice position in addition to other sites in the mineral such as admixed solid and liquid inclusions and as exsolution product. Further, according to him, "copper, like cobalt, nickel or chromium, does not logically follow the distribution trends", and "... important amounts of trace elements do not occupy regular lattice sites but, through the mechanism of absorption, occur on growth surfaces, imperfections, dislocations and various interfaces within the crystal".

Biotite derived from the altered wall-rocks, adjacent to ore zones, have a greater concentration of Cu than in those derived from the unaltered country rocks. Biotites from the younger intrusives granites show a more or less similar trend of copper concentration to those derived from the altered wall-rocks. The biotites derived from the older granitic rocks, however, show lower values of copper. Sandell and Goldich (1943), who studied the rare metallic constituents of some North American igneous rocks, observed that the average copper content of biotites in acid, basic and intermediate igneous rocks, varies from 140 ppm, 16 ppm to 38 ppm respectively. Biotites derived from the different source rocks may therefore show variation in their copper content.
The analytical results definitely show that the distribution trends of Cu, Pb and Zn in the biotites derived from the older and younger granites of the study area are different. The higher concentration trend of Cu, Pb and Zn in the biotites derived from the various lithologically different altered wall-rocks and the younger intrusive granites indicates a genetic relation between the younger granitic bodies and the wall-rocks alteration. It was further supported by the fact that copper, lead and zinc contents have relatively higher concentrations in quartz and feldspar, derived from the same altered wall-rocks and the younger granites. However, the concentration trends of lead and zinc in the biotites derived from the altered wall-rocks of copper deposits are somewhat different from that of copper. In these rocks the lead and zinc contents in biotites are very poor although the metals have higher concentrations in the unaltered country rocks.

III. Isotope abundance in rocks and minerals

A comparison of the variation ranges of isotopes in the altered host rocks, the granitic rocks and some of their associated minerals has been found to be a useful guide to the source of the ore-forming fluids. It is well known that the isotopic compositions of the hydrothermal solutions differ in relation to their source and such differences can easily be used as a guide to the source of fluids from which mineral deposits are formed (Taylor, 1967). The $^{18}O$ isotopic values in the altered rocks as well as in minerals like quartz and muscovite, around the lead-zinc as well as the copper deposits have narrow ranges like those found in quartz and muscovite derived from the younger granites.
This is considered as a significant evidence supporting further the genetic association of the younger granites with the wall-rock alteration in both the deposits and the two silicate minerals associated with them. Such narrow isotopic ranges for the intrusive granitic rocks have been reported by various workers from many parts of the world (Figs. 37a, b). For example, Garlick (1964) has isotopically analyzed quartz from Boulde Batholith, Butte Copper deposit, for $^{18}O/^{16}O$ ratios and found that the values are typical of magmatic hydrothermal bodies.

Isotopic ranges of $^{32}S/^{34}S$ in ore minerals have been considered by various workers in different parts of the world as indications for close genetic relation between ore fluids and their probable source. According to Thode, MacNamara and Collins (1949) the isotopic compositions of pyrite bring to light the source of mineralisation. MacNamara et al. (1952) studied the isotopic ranges of sulphur from the sulphide minerals contained in igneous rocks of admittedly magmatic origin. The isotopic ranges of $^{32}S/^{34}S$ in the ores or rocks of magmatic origin have always indicated narrow range (Jensen, 1950; 1962; Smirnov, 1968).

This is the first attempt to apply the sulphur isotope ratio of some sulphide minerals of the area for determining their range of values and the consequent source of mineralisation. The narrow spreads of $^{32}S/^{34}S$ ratios in ore minerals like galena, sphalerite, chalcopyrite in some ore minerals, and also in pyrite from the ore zone and the adjacent wall rocks very much resemble the ranges determined in the ores associated with magmatic hydrothermal deposits (Figs. 40a, b). It may, therefore, be stated that the nature of mineralisation of copper, lead and zinc was magmatic hydrothermal.
Various workers including Cannon et al. (1961), Rama Murthy and Patterson (1961), Kanasewich (1962), Moorbath (1962), Hayl et al. (1965), Brown (1962), Mitchell et al. (1971) have successfully utilized lead isotope data from the wall rocks of various ore deposits for genetic and geochronological purposes. The present author has made the first attempt to determine the isotopic composition of lead in galena from lead-zinc deposits and also in feldspars from the altered wall rocks of copper deposits and the younger granites (Table 26, Fig. 45) with a view to throw more light on the source of the mineralizing solutions.

Lead ratios in the feldspars belonging to the altered zones are found to be similar to those occurring in feldspars derived from the younger granites. These lead ratios in feldspars (Table 26) are strikingly similar to those found in the galena occurring in the lead-zinc deposits of Rishi area. Therefore, the isotopic similarity of lead in galena, feldspars in the wall-rocks as well as in the granitic rocks strongly suggests their common source. This view is further supported by a similar age of radiogenic lead in galena from lead-zinc deposit, in feldspars belonging to younger granites, and from the altered wall rocks of copper deposits. The age is found to be 20 ± 10 million years (with an average of 13 m.y.).

IV. Temperature of ore deposition

Some evidences are also available in support of the probable temperature of the ore fluids which has a direct bearing on the source of the deposits. Isotopic values of $^8_5\text{O}$ and assemblage of certain
Fig. 45

FIG. LEAD ISOTOPIC ANALYSIS OF GALEMA AND FELDSPATHS
FROM THE BASE METAL DEPOSITS
AROUND DHARIELING MINERALS
<table>
<thead>
<tr>
<th>No.</th>
<th>Nature of sample</th>
<th>Pb(^{206}/\text{Pb}^{204})</th>
<th>Pb(^{207}/\text{Pb}^{204})</th>
<th>Pb(^{208}/\text{Pb}^{204})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Galena : Rishi area</td>
<td>10.14</td>
<td>15.66</td>
<td>38.45</td>
</tr>
<tr>
<td>2</td>
<td>Galena : Rishi area</td>
<td>10.55</td>
<td>15.72</td>
<td>38.67</td>
</tr>
<tr>
<td>3</td>
<td>Galena : Rishi area</td>
<td>10.41</td>
<td>15.70</td>
<td>38.94</td>
</tr>
<tr>
<td>4</td>
<td>Galena : Rishi area</td>
<td>10.45</td>
<td>15.68</td>
<td>38.66</td>
</tr>
<tr>
<td>5</td>
<td>Galena : Rishi area</td>
<td>10.49</td>
<td>15.70</td>
<td>38.65</td>
</tr>
<tr>
<td>6</td>
<td>Galena : Rishi area</td>
<td>10.50</td>
<td>15.71</td>
<td>38.50</td>
</tr>
<tr>
<td>7</td>
<td>Galena : Rishi area</td>
<td>10.12</td>
<td>15.65</td>
<td>38.66</td>
</tr>
<tr>
<td>8</td>
<td>Galena : Rishi area</td>
<td>10.22</td>
<td>15.64</td>
<td>38.62</td>
</tr>
<tr>
<td>9</td>
<td>Galena : Rishi area</td>
<td>10.25</td>
<td>15.69</td>
<td>38.55</td>
</tr>
<tr>
<td>10</td>
<td>Galena : Rishi area</td>
<td>10.30</td>
<td>15.66</td>
<td>38.50</td>
</tr>
<tr>
<td>11</td>
<td>Galena : Rishi area</td>
<td>10.05</td>
<td>15.64</td>
<td>38.50</td>
</tr>
<tr>
<td>12</td>
<td>Galena : Rishi area</td>
<td>10.04</td>
<td>15.66</td>
<td>38.63</td>
</tr>
<tr>
<td>13</td>
<td>Galena : Rishi area</td>
<td>10.00</td>
<td>15.65</td>
<td>38.62</td>
</tr>
<tr>
<td>14</td>
<td>Potash-feldspar : from Wall-rocks, Peku copper deposits</td>
<td>10.67</td>
<td>15.70</td>
<td>38.95</td>
</tr>
<tr>
<td>15</td>
<td>Potash-feldspar : from Wall-rocks, Peku copper deposits</td>
<td>10.40</td>
<td>15.68</td>
<td>38.66</td>
</tr>
<tr>
<td>16</td>
<td>Potash-feldspar : from Wall-rocks, Peku copper deposits</td>
<td>10.12</td>
<td>15.65</td>
<td>38.65</td>
</tr>
<tr>
<td>17</td>
<td>Potash-feldspar : from Intrusive granites</td>
<td>10.75</td>
<td>15.71</td>
<td>39.01</td>
</tr>
<tr>
<td>18</td>
<td>Potash-feldspar : from Intrusive granites</td>
<td>10.85</td>
<td>15.72</td>
<td>39.16</td>
</tr>
<tr>
<td>19</td>
<td>Potash-feldspar : from Intrusive granites</td>
<td>10.20</td>
<td>15.64</td>
<td>38.55</td>
</tr>
</tbody>
</table>
minerals have mainly supplied such evidences.

A. Isotope ratios

Experiments on the use of oxygen isotopes as geothermometers have proved that oxygen isotope geothermometry is possible for the minerals like quartz, calcite, muscovite, alkali feldspars and water (Bigeleisen and Mayer, 1947; Urey, 1947; Silverman, 1951; Taylor and Epstein, 1962, 1963; O’Neill and Clayton, 1964; Taylor and Coleman, 1965; Clayton, O’Neill and Noyelles, 1966; O’Neill and Taylor, 1966; Taylor, 1967; Sheppard, Nielsen, and Taylor, 1971; Plackney and Eye, 1972). According to Taylor (1967), “Oxygen isotope geothermometers will have wide application in the field of hydrothermal mineral deposits because the isotopic fractionations are so much larger in the range of 100°–400°C than at higher temperature ranges, and it should be possible to obtain temperatures of formation of hydrothermal minerals within ±5°C if equilibrium is commonly established”. Hall and Friedman (1969) have suggested that patterns of δ 18O values in the altered rocks reflect the presence of a temperature gradient in the wall-rock during alteration.

An attempt is made here to correlate the results obtained from the study area, with the data from known assemblages to see where the δ 18O ratios of quartz and muscovite fall and thus to use the oxygen isotopes as geothermometers of the ore deposits. A comparison of the isotopic compositions of the quartz, calcite, and dolomite from the ore zone as well as the altered zone in lead-zinc deposits with the standard and known values indicates that the temperature of the ore fluids falls within a range of 150°C to 250°C ± 25°C. Similarly, the
$\delta^{18}O$ values obtained from the altered wall rocks and the ore zone in the copper deposits, and also the $\delta^{18}O$ variations in the quartz in the Pb-Zn deposits closely agree with the standard and known ranges and indicate that the temperature of ore fluids ranged from 185$^\circ$C to 350$^\circ$C.

B. Mineralogical assemblages

The mineralogic work done was not specially oriented towards the geothermometric investigations. Temperatures of ore deposition may also be determined by the study of mineral assemblages (Park Jr. and MacDiarmaid, 1964). Some of the evidences available are given below:

a) The total absence of such high temperature silicate minerals in the host rocks as wollastonite, tremolite, forsterite, periclase, etc. suggest that the upper limit of the temperature was not perhaps more than 400$^\circ$C or nearly so.

b) Since most of the copper ore deposits do not have associations of pyrrhotite or arsenopyrite, the temperature of the ore-bearing fluid was rather moderate.

The association of pyrite with marcasite in these deposits is also a significant feature. Recent experimental studies on pure Fe-S-O system in dry have shown that the formation of pyrite is possible with the upper stability limit at 743$^\circ$C, but marcasite was not formed. Kullerud (1960, 1961) prepared mixture of phases in Fe-S-O-H system, and maintained temperatures with a maximum of 432$^\circ$C $\pm$ 30$^\circ$C. Upto this temperature both pyrite and marcasite were formed but above this temperature only pyrite continued to form.