SECTION C
MAJOR AND TRACE ELEMENT GEOCHEMISTRY
Chapter C -I

MAJOR ELEMENT GEOCHEMISTRY

General Statement

The present chapter deals with geochemistry of major elements and various geochemical factors that control the formation of bauxites. The major elements which have been analysed are Si, Al, Fe$^{2+}$, Fe$^{3+}$, Ti, P, Na, K, Ca, Mg and Mn. In addition to these, loss on ignition ( L.O.I. ) has been determined which includes moisture and other volatile matters such as CO$\text{2}$, SO$\text{2}$, etc. The elements mentioned above have been determined in the form of their oxides. These oxides have been converted to their elements and vice versa wherever necessary with the help of conversion factors (Table XVIII ). Among these Si, Al and Fe are more important in interpreting the genesis of bauxite. As a general rule, bauxite deposits are formed by gradual removal of silica, enriching thereby in Al and Fe. The bauxites are characterized by Al/Fe ratios which depend upon the source rocks. Bauxites rich in iron i.e., ferralites, generally form on igneous rocks and are also associated with most of the Karst deposits. Bauxites rich in silica i.e., siliclite develop if iron is removed faster than silica. These form as saprolite zone on igneous rocks and develop from highly aluminium clays and transitional stages to flint clay on sediments. Aluminous bauxite i.e., allite is formed under the conditions of removal of silica and iron.
### Table-XVIII: Conversion factors for elements and their oxides.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Found</th>
<th>Sought</th>
<th>Factor</th>
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<tbody>
<tr>
<td>Aluminium</td>
<td>Al</td>
<td>Al₂O₃</td>
<td>1.8898</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>Al</td>
<td>0.5291</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>CaO</td>
<td>1.3992</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>Ca</td>
<td>0.7146</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>Cr₂O₃</td>
<td>1.4614</td>
</tr>
<tr>
<td></td>
<td>Cr₂O₃</td>
<td>Cr</td>
<td>0.6942</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>CoO</td>
<td>1.2714</td>
</tr>
<tr>
<td></td>
<td>CoO</td>
<td>Co</td>
<td>0.7865</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>CuO</td>
<td>1.2510</td>
</tr>
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<td></td>
<td>CuO</td>
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<tr>
<td>Gallium</td>
<td>Ga</td>
<td>Ga₂O₃</td>
<td>1.3442</td>
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<tr>
<td></td>
<td>Ga₂O₃</td>
<td>Ga</td>
<td>0.7438</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>FeO</td>
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<td></td>
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<td>Fe₂O₃</td>
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<td>Fe</td>
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<td>Lead</td>
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<td></td>
<td>PbO</td>
<td>Pb</td>
<td>0.9283</td>
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<td>Magnesium</td>
<td>Mg</td>
<td>MgO</td>
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<td></td>
<td>MgO</td>
<td>Mg</td>
<td>0.6031</td>
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<td>Manganese</td>
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<td>MnO</td>
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<td></td>
<td>MnO</td>
<td>Mn</td>
<td>1.2255</td>
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<td>Molybdenum</td>
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<td>MoO₃</td>
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<td>MoO₃</td>
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<td>0.6665</td>
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<tr>
<td>Nickel</td>
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<td>NiO</td>
<td>1.2726</td>
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<td></td>
<td>NiO</td>
<td>Ni</td>
<td>0.7957</td>
</tr>
<tr>
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<td>---------</td>
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<tr>
<td>Phosphorus</td>
<td>P</td>
<td>P₂O₅</td>
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<td>0.6301</td>
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<td>Silicon</td>
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<td>0.4672</td>
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<tr>
<td>Sodium</td>
<td>Na</td>
<td>Na₂O</td>
<td>1.3478</td>
</tr>
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<td></td>
<td>Na</td>
<td>Na</td>
<td>0.7419</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr</td>
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</tr>
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<td></td>
<td>Sr</td>
<td>Sr</td>
<td>0.8456</td>
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<td>Titanium</td>
<td>Ti</td>
<td>TiO₂</td>
<td>1.6660</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>Ti</td>
<td>0.5995</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
<td>V₂O₅</td>
<td>1.7050</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>V</td>
<td>0.5602</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>ZnO</td>
<td>1.2447</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>Zn</td>
<td>0.8033</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Zr</td>
<td>ZrO₂</td>
<td>1.3508</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>Zr</td>
<td>0.7403</td>
</tr>
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</table>
Chemical composition of bauxite deposits is controlled by many factors.

(a) Elemental composition of the source rock.
(b) Affinity of specific elements in forming minerals during weathering.
(c) The drainage conditions during weathering which governs relative enrichment i.e. precipitation in situ and absolute enrichment i.e. vertical or horizontal ground water transport of elements.
(d) Polygenetic alterations i.e. late diageneric and epigenetic.

A comparison of various elements in bauxites has been made with the elements of earth's crust (Table-XIX).

Table - XIX: The relative enrichment of elements in bauxites with respect to earth's crust (after Benesalevsky, 1963).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Bauxites</th>
<th>Earth's crust</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>30.16</td>
<td>7.45</td>
<td>4.05</td>
</tr>
<tr>
<td>Fe</td>
<td>9.99</td>
<td>4.20</td>
<td>2.38</td>
</tr>
<tr>
<td>Si</td>
<td>3.90</td>
<td>26.00</td>
<td>0.15</td>
</tr>
<tr>
<td>Ti</td>
<td>1.64</td>
<td>0.64</td>
<td>2.56</td>
</tr>
<tr>
<td>Ca</td>
<td>0.81</td>
<td>3.25</td>
<td>0.25</td>
</tr>
<tr>
<td>K</td>
<td>0.36</td>
<td>2.35</td>
<td>0.15</td>
</tr>
<tr>
<td>P</td>
<td>0.13</td>
<td>0.12</td>
<td>1.08</td>
</tr>
<tr>
<td>Mg</td>
<td>0.09</td>
<td>2.35</td>
<td>0.038</td>
</tr>
</tbody>
</table>
The chemical analyses of about ninety samples from the granite and granitic rocks at the base to the laterite at the top was made in order to understand the geochemical behaviour of the major constituents. The data in their oxide form are given in Table −XX. These data have been recalculated to their elemental form and are presented in Table−XXI. Histograms of these data have also been prepared to see the variation of elements at a glance (Fig. 7−14).

The most important elements are iron, aluminium and silica which are also present in the country rocks i.e. granites and granitic rocks. Silica is obviously make up the bulk in the country rock, the alumina is considerably present but the iron is missing or in very minute amount.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Bauxites</th>
<th>Earth's crust</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.08</td>
<td>2.40</td>
<td>0.03</td>
</tr>
<tr>
<td>Mn</td>
<td>0.076</td>
<td>0.10</td>
<td>0.76</td>
</tr>
<tr>
<td>V</td>
<td>0.062</td>
<td>0.02</td>
<td>2.10</td>
</tr>
<tr>
<td>Cr</td>
<td>0.055</td>
<td>0.03</td>
<td>1.03</td>
</tr>
<tr>
<td>Cu</td>
<td>0.023</td>
<td>0.01</td>
<td>2.30</td>
</tr>
<tr>
<td>Zn</td>
<td>0.021</td>
<td>0.02</td>
<td>1.05</td>
</tr>
<tr>
<td>Ga</td>
<td>0.0035</td>
<td>−</td>
<td>−</td>
</tr>
</tbody>
</table>

Geochemical variation
Sufficiently high iron in lateritic bauxites and laterites pose a problem about the substrate rock which gave rise to residual bauxite deposits. Chemically the soft matrix on lithification remains steady in MgO, CaO, CO₂ and SiO₂ while Al₂O₃ and TiO₂ increase proportionately.

A positive relation exists between nature of substrate rock and their residual products in their chemical constituents as is evidenced by Table XXII.

Table XXII: Chemical analyses of residual bauxites derived from various rock types in Malaya (P.L.C. Grubb, 1963).

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.55</td>
<td>1.9</td>
<td>6.85</td>
<td>44.47</td>
<td>8.65</td>
<td>17.79</td>
<td>16.16</td>
<td>14.92</td>
<td>16.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>11.40</td>
<td>8.0</td>
<td>50.35</td>
<td>3.39</td>
<td>6.70</td>
<td>4.84</td>
<td>44.70</td>
<td>22.34</td>
<td>15.26</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>57.70</td>
<td>59.1022.35</td>
<td>34.34</td>
<td>55.00</td>
<td>50.15</td>
<td>25.22</td>
<td>52.98</td>
<td>40.72</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.95</td>
<td>0.55</td>
<td>1.35</td>
<td>0.24</td>
<td>0.70</td>
<td>0.10</td>
<td>0.96</td>
<td>1.25</td>
<td>3.32</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>29.40</td>
<td>30.45</td>
<td>19.60</td>
<td>17.50</td>
<td>28.95</td>
<td>27.72</td>
<td>12.96</td>
<td>9.51</td>
<td>24.70</td>
</tr>
</tbody>
</table>

100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00

1. Bauxite on andesite - rhyolite
2. " " rhyolite
3. " " rhyolite tuff
4. " " granite
5. " " micropegmatite
6. " " diaspore pyrophyllite hornfels
7. " " graphitic muscovite-quartz schist
8. " " leucite tephrite
9. " " nepheline basalt
The samples were analysed for their aluminium, silicon, iron, titanium, phosphorus, manganese, calcium, magnesium, sodium, potassium and loss on ignition content which includes moisture content as well as volatiles like CO₂, SO₂ etc. These were calculated in the form of their oxides. The conversion of oxides to their elements was made with the help of Table-XVIII wherever needed.

Petrochemistry of granites and granitic rocks

The petrochemistry of the country rock has been studied to know the nature of the rock (Fig. 15).

Granitic rock samples were taken from different outcrops which include graphic granite, porphyritic granite and granite gneiss. Along with bauxites and laterites, these were also analysed for the major elements. The analytical data were recalculated as percentage by Osmann (Johannsen, 1962) where

\[
\begin{align*}
S &= \text{SiO}_2 + \text{TiO}_2 \\
\text{Al} &= \text{Al}_2\text{O}_3 \\
F &= (\text{CaO} + \text{FeO} + \text{MgO}) - C \\
C &= (\text{Al}_2\text{O}_3 - \lambda) \\
\text{The total of } S + \text{Al} + F &= 100
\end{align*}
\]

In the diagram out of eight plottings seven fall in the igneous field and only one reading falls outside igneous field. This belongs to the granitic gneiss in the
FIG. 15 AI SF DIAGRAM FOR GRANITE & GRANITIC ROCKS.
north of Salmatia pat. This means that besides igneous granitic rocks, there exists probably the granitic rocks of nonmagmatic origin as well.

Further an attempt has been made to define a common chemical trend for the parent rock i.e. granites and granitic rocks and their weathering products such as bauxites, laterites and lithosargic clays. Chemical differentiation effected in sedimentary and weathering processes is remarkably efficient. Main stages in the differentiation are the formation of resistates, hydrolysates, oxidates, carbonates, evaporates and redusates. Many writers have emphasized the greater range in content of various major elements in sediments as compared to igneous rocks. This applies especially to Si (as oxide), Al and Fe (as hydrated oxides) and Ca and Mg (as carbonates).

There are various factors which play a greater role in the weathering processes, leaching and deposition of sediments than in the case of igneous rocks. Some of the important factors are climatic conditions, salinity, redox potential, H⁺ ion concentration, topography and source rock composition. Chemical adjustments in rock weathering tend to produce new mineral phases in equilibrium with surface temperatures and pressures and in accord with the chemical composition of the system.

Fig. 16 shows residual averages plotted according to a system suggested by Mason (1966). It is to be noted
that $\text{Al}+\text{Fe}$ in most of the bauxites and laterites is more than 90% and in the lithomargic clays it ranges between 65 and 75 percent. Silica on the other hand diminishes to nil as compared to parent rock which has high silica, 65 to 75% and $\text{Al}+\text{Fe}$ only around 30%, Ca+Mg being low in both the cases (Table-XXIII).

The Ca-Na-K diagram (Fig. 16) shows a strong scatter of points widening towards the Na-K side and median intersecting approximately at Na-K ratio 17:3 as compared to granites and granitic rocks which has Na-K ratio as 5:15 (Table XXIV). The reversal of Na-K ratio and good enrichment in the bauxites and laterites may be due to the formation of illite mineral which consumes Na. The presence of illite mineral has also been detected by XRD analysis (Chapter-B-III).

Fig. 17 and 18 show the series of 11 triangular diagrams. Recalculated values have been shown in Tables XXV-XXXV. The Si-Al-Mg diagram shows few interesting features. In granitic rocks most points lie near Si corner, whereas in bauxites and laterites near Al corner. The lithomargic clays come in between them serving as the intermediate stage during bauxitization. Almost all the lithological units show similar behaviour with respect to Mg which is low in content not exceeding 18%. It indicates that bauxitization did not have much effect on Mg content and it remains in the clay lattices during weathering.
whereas silica is depleted.

The next ten diagrams show the variation of Al, total iron, Mg, Ca and (Na+K) in various combinations. The three groups could be distinguished on the bases of these diagrams.

Group 1. Three diagrams with corner Ca, Fe or Mg and with a side Al—(Na+K), in which granitic rocks fall in a zone extending towards a point midway along the Al—(Na+K) side. Whereas in bauxites and laterites it is observed that in Ca-Al—(Na+K) diagram the points spread from Al corner towards Ca—(Na+K) side. In Fe-Al—(Na+K) diagram the (Na+K) content does not increase more than 5% and the spreading of the data is almost linear along the Al-Fe line. The Mg-Al—(Na+K) diagram represents the concentration of points on alumina corner with slight spreading towards Mg corner.

Group 2. Three diagrams with corner Al, Ca or (Na+K) and with a side Fe-Mg show interesting features. In the Mg-Ca-Fe diagram (Fig. 17) the granitic rocks fall almost in the centre of the diagram, whereas their daughter rocks, bauxites and laterites fall on Fe corner and show a spread towards Mg-Ca line within the Ca:Mg ratios 17:13 to 6:14. In Mg-Fe-Al diagram (Fig. 17) the ionous trend varies from Mg-Fe side to Al corner whereas bauxites and granites lie along the Fe-Al line in which Mg does not increase beyond 5% which indicates that bauxites and laterites are
the weathering products of granites. In Fe-Mg-(Na+K) diagram (Fig. 19) the granitic zone curves towards the (Na+K) corner which ends at a point along the Fe-(Na+K) side, approximately at (Na+K) : Fe= 18:2 in both the Fe-Mg-Al and Fe-Mg-(Na+K) diagrams there is a group of points with low proportion of Mg and high sodic content which favour strongly a sodic granite provenance.

It is observed in Fe-Mg-(Na+K) diagram (Fig. 19) that the bauxites and laterites fall on Fe corner with spreading towards Mg-(Na+K) line in which Mg/(Na+K) does not increase 12:9. Hence it is inferred that (Na+K) content of the granites has been depleted during weathering.

Group-3. Four diagrams with Ca in one corner and without either of the pairs Al-(Na+K) or Fe-Mg fall in this group. Here the granitic rocks fall in a zone which is convex towards the Ca corner and curves between the other two corners whereas the bauxites and laterites show spreading of the points from Al corner towards Ca-Fe or Ca-Mg side with slight variation in Ca-Fe-Al and Mg-Ca-Al diagrams. (Fig. 19) which indicates that due to bauxitization the Ca content was depleted whereas Fe or Mg content increased.

In the last two diagrams with Ca-Fe-(Na+K) and Mg-Ca-(Na+K) the laterites spread towards Fe and Ca corner whereas bauxites spread towards Ca and Mg corner.
Inter element relationships

\( \text{SiO}_2 \) vs \( \text{Al}_2\text{O}_3 \): The geochemistry of silicon is more important as it is the main electronegative constituent which is gradually removed in solution. There is a direct relationship between silica removal and the intensity of the drainage i.e., with the increase in drainage, there is a depletion in silica. This is one of the main reasons that is why we find great variation in \( \text{SiO}_2 \) content vertically as well as horizontally in the bauxite profile. Generally we find more of silica in the upper and lower part of the profile. This may be because silica freed from different horizons settles at the bottom and the \( \text{SiO}_2 \) in uppermost zone may be due to the plant vegetation which may be responsible for the fixation of the silica.

Aluminium is the chief constituent of bauxites in the form of alumina (\( \text{Al}_2\text{O}_3 \)) and it is most abundant metal in igneous rocks. Al in the upper lithosphere is pronouncedly oxophile element. It is always found with oxygen in the form of oxides and hydroxides.

Silica in the present bauxites is as low as zero and as high as 19.61% with an average of only 1.44%. In laterites variation in minimum and maximum is similar but the average falls higher which is 4.04%. In lateritic clay, silica is appreciably high, varying between 24.7 and
27.3% (average 25.06%). In the parent rock i.e. granites and granitic rocks silica is very high ranging between 52.40 and 70.08% (average 64.61%).

Alumina also shows great variation in various lithological units. In bauxites the variation is maximum and 63.4% ranging between 45.60% (average 39.29%). In lithocargos and granitic rocks, the variation is in narrow range between 27.45 - 31.50% and 15.69 - 18.97% with an average of 30.01 and 17.51% respectively. (Table 46).

$SiO_2$ and $Al_2O_3$ have been plotted for the bauxites and laterites in the Fig. 19 and the slope of the graph is on the negative side. This means that with the increase of $Al_2O_3$, there is a decrease in $SiO_2$ content. This is the most obvious relationship because in beaunitisation there is a gradual removal of silica and enrichment of alumina.

It is known that silica and alumina solutions of a concentration of approximately 0.1% quickly precipitate each other. During weathering of micas, disintegration is often incomplete and mainly alkali metals are extracted. The $Si-O$ framework is largely unattacked and may be converted by reactions with weathering solutions to clay minerals. The clay minerals are hydrous aluminium silicates. Some $Al$ may be replaced by $Fe^{3+}$ and $Mg^{2+}$. 
FIG. 19 RELATIONSHIP OF SiO₂ WITH TiO₂ AND Al₂O₃ IN BAUXITES/LATERITES.
The clay minerals present are illite, montmorillonite and kaolinite.

An interesting feature of these bauxite deposits is that its silica modulus does not depend on the alumina content but is controlled by the silica content (Fig. 20). Thus in rocks with a similar alumina content, the silica modulus varies 10 fold, whereas in those with a specific silica content its variation is small. This suggests that main factor controlling the bauxitization was the leaching of silica, which is the fundamental process of bauxite weathering, whereas a slight effect of alumina reflects the general inertness of alumina during lateritization.

From the XRD analyses (Chapter D-III) it is known that kaolin is present in significant amount as clay mineral in most of the bauxites. This indicate that leaching of SiO₂ was relatively slower.

The graphs constructed on the basis of the data obtained show the dependence of density on amount of alumina (Fig. 21) for the rocks containing free alumina (bauxites and laterites) have shown the presence of an association between these parameters. In the first case, a statistical correlation close to linear, has been identified, and in the second there is a hyperbolic curve. In the parent igneous rock i.e. granite and granitic rocks,
FIG. 20 SILICA MODULUS VERSUS SILICA CONTENTS OF BAXIIYIC ROCKS.
FIG. 21  GRAPHS SHOWING DEPENDENCE OF DENSITY OF BAUXITE ROCK DEPOSITS ON THE AMOUNT OF $\text{Al}_2\text{O}_3$ (a) AND THE SILICA MODULE ($\text{Al}_2\text{O}_3/\text{SiO}_2$) (b).
such an association is absent.

\[ \text{Fe}_2\text{O}_3 \text{ vs } \text{Al}_2\text{O}_3 - \]

Iron is one of the chief constituent which is removed in the formation of bauxites. Iron is generally present in two states, divalent ferrous and trivalent ferric state. However, almost all of the iron is in ferric state and ferrous iron if present is less than one percent.

The content of ferric iron (\( \text{Fe}_2\text{O}_3 \)) in bauxites varies widely 0.01 to 27.47% (average 7.76%) and in laterites 9.70 - 39.25% (average 26.71%). In lithosaurus and granites it is 13.67 - 19.60 % (average 16.69%) and 0.0-0.31% (average 0.16%) respectively.

Ferrous iron (FeO) is very low in both laterites and bauxites ranging upto 0.28% (average 0.57%). In bauxites and laterites \( \text{Fe}_2\text{O}_3 /\text{FeO} \) ratio is much higher than parent igneous rocks. This is so because oxidation of ferrous minerals in igneous rock takes place by atmospheric oxygen during weathering.

In the early stages of bauxitization, increasing degree of drainage with increasing speed of \( \text{SiO}_2 \) removal, leads to relative enrichment of aluminium. Commonly there is intergrowth of Al & Fe minerals in gibbsite and boehmite bauxite and generally have similar Al/Fe
tatio and their separation improves with the increased drainage, diagenesis and epigenesis.

TiO₂ vs Al₂O₃

According to Migdisow (1910) titanium enrichment is highest in bauxites during weathering. Titanium in the source rock is generally present in silicates which are unstable to weathering and is converted to minerals like anatase and incorporated into iron minerals. Ilmenite and rutile in the primary rocks on the other hand remain mostly stable and appear as relic minerals. Titanium is the most abundant of all the trace elements. Since its percentage is high enough in the bauxites, it has been dealt here in the major element geochemistry.

Concentration of titanium in the bauxites is quite rich varying between 4.28 and 13.14% (average 7.69%). In laterites it is somewhat lower as it ranges between 2.17 and 10.43% (average 5.46%). In lithomarge it is relatively poor and varies in between 3.80 and 4.60% (average 4.20%). In granites and granitic rocks, its concentration being very low reaching maximum at 0.51 (average 0.24%).

TiO₂ and Al₂O₃ values have been plotted to study the relationship between the two if any (Fig. 22).

The correlation is strongly sympathetic in both bauxites
CORRELATION DIAGRAM OF
(a) Al₂O₃ V/S Fe₂O₃
(b) TiO₂ V/S Fe₂O₃ AND
(c) TiO₂ V/S Al₂O₃ IN THE
BAUXITES (*) AND LATERITES (○).

FIG. 22
and laterites with a difference that slope line of the correlation is steeper in bauxites than in the laterites. This gives an indication that titanium is partitioned preferentially in Al₂O₃ i.e. more in bauxites than in the laterites.

It is noticed that in many of the bauxites, titanium is concentrated to the same degree as aluminium but the geochemical coherence is not strong. The rather high Al₂O₃/TiO₂ ratio of the bauxites suggests that in the laterite, detrital Ti minerals play a more prominent part.

TiO₂ vs Fe₂O₃

The values of TiO₂ and Fe₂O₃ have been plotted in the Fig. 22 to study their relationship. This also reflects a changed behaviour in bauxites and laterites. The correlation is strongly positive in the case of bauxites whereas in laterite also it is positive but to a lesser degree. This could mean that partitioning of titanium is more in Fe₂O₃ in bauxites than in laterites. It reveals that in bauxite laterite profile the enrichment of titanium is more in bauxite zone than in the lateritic zone. Chemical analyses of bauxites from many localities bear frequent sympathetic relationship with titania and iron oxide, but exceptions are not hard to find.
Plot of TiO₂ and SiO₂ also exhibit a negative correlation (Fig. 19 A). This relationship stands equal for both, bauxites and laterites. This is because during weathering and residual concentration silicon is being replaced by titanium (Kunitz, 1936). The replacement is limited however owing to the difference in the radii of Si⁴⁺ and Ti⁴⁺.

Titanium does not form simple silicates. Thermochemical studies of TiO₂ - SiO₂ system reveals that there is no binary compound known in the system. Titanium silicates are complex silicates containing some other cations with a co-ordination number differing from Ti⁴⁺ such as Ca²⁺, Na⁺, K⁺ etc. Among these cations, heat of formation of Ca is highest, hence it combines with Ca to form apatite. Titanium is also incorporated in the structures of most felsic rock forming minerals e.g. titanaugite and wodanite (Lebedev and Lebedev, 1934).

During weathering titanium remains largely as resistates, because the titanium forming minerals like ilmenite and rutile being fairly stable against weathering, could remain more or less unaltered in the resistate sediments. Titanium contained in the structures of felsic minerals is brought into solution during weathering.
but it is readily hydrolysed and carried into hydrolysates.
It is present in the form of sphene, ilmenite, brookite
and anatase.

\[ TiO_2 \rightarrow Al_2O_3 \rightarrow Fe_2O_3 \]

The average compositions of various lithological
units in terms of \( TiO_2 \rightarrow Al_2O_3 \rightarrow Fe_2O_3 \) have been plotted
on a triangular co-ordinated graph paper (Fig. 23) in
order to decipher the chemical changes in the three
component system of \( TiO_2 \), \( Al_2O_3 \) & \( Fe_2O_3 \) during weathering
of granites and granitic rocks which resulted in the
formation of laterites, bauxites and lithosargic clays.
Weathering profiles appear to be enriched in titanium with
respect to parent rock. More lithosargic clay appears
to be the intermediate product and the two trends are
distinctly noticed. The one is the lateritic trend where
\( Fe_2O_3 \) increases with a decrease in the \( TiO_2 \) content and
the other bauxitic where \( Al_2O_3 \) increases with an increase
in the \( TiO_2 \) content. From the lithosargic clay, the
degree of \( Fe_2O_3 \) enrichment in the lateritic trend is much
less than that of \( Al_2O_3 \) enrichment in the bauxitic trend.
The ternary diagram (Fig. 18) further indicate that
partitioning of titanium is more in the bauxitic trend
than that in the lateritic trend.
FIG. 23 PLOTTING OF AVERAGE COMPOSITIONS OF VARIOUS ROCK UNITS OF BAUXITE PROFILE IN TERNARY DIAGRAM OF TiO$_2$, Fe$_2$O$_3$ & Al$_2$O$_3$. 
Alkalies vs \( \text{Al}_2\text{O}_3 \)

In the bauxites and laterites \( \text{K}_2\text{O} \) varies between 0.00% and 0.50% (average 0.05%), while in lithomargic clay it varies between 0.22% and 0.40% (average 0.32%) and in granites between 5.30% and 10.00% (average 7.32%). Na\(_2\text{O}\) content in bauxites ranges between 0.1-3.0% (average 0.39%) and in laterites 0.05 - 0.85% (average 0.34%) in lithomarge between 0.23 to 0.37% (average 0.31%) and in granites 1.40 to 3.17% (average 2.17%).

Potassium is lowest in the bauxites and highest in granites and granitic rocks, the distribution of K in granites is no doubt related to their felspar content. The K content of the lithomargic clay is higher than that of bauxites.

Bauxites and laterites contain more of Na than K, averaging about 0.22% but the parent rock i.e. granites and granitic rocks possess higher K than Na. Compared with country rocks, the bauxites show lesser depletion of Na than K. This is because illite which is dominant mineral in clay fraction of bauxites has low K and high Na is added during weathering by the removal of K through the agencies of leaching and cropping by plants. Most of sodium in the bauxites is contained in the illite.
Which is one of the dominant clay mineral in the bauxite profile of the area of study.

$K_2O$ and $Na_2O$ values have been plotted against their alumina content in order to understand the correlation between them if any (Fig. 24, 25). In the plotting of $K_2O$ vs $Al_2O_3$, a negative correlation is observed. It reveals that increase of alumina brought a decrease in the $K_2O$ content in all the three types of residual i.e. bauxite, laterite and lithomarge. However in granites no definite correlation is noticeable. Similar plots were made for $Na_2O$ also. The plots with sodium reveals no definite trend. In granites and other granitic rocks and lithomarge, the trend is slightly negative. This is so because solubility of sodium is very high and it is more mobile during weathering than $K$ (Anderson & Hawkes, 1958, Short, 1961).

$Mn/Al$ vs $Na$

Geochemically manganese is a lithophile metal but in the upper lithosphere it is rather exophile. During weathering processes, manganese is dissolved mainly as carbonate and a small quantity of manganese come in the sulphate form. Mn in comparison to iron gets dissolved faster in the carbonate bearing solution. Carbonate decomposition leads to the formation of Mn compounds.
FIG. 24 RELATIONSHIP OF $K_2O$ AND $Al_2O_3$ IN DIFFERENT ROCK TYPES.
FIG. 25 RELATIONSHIP OF $\text{Na}_2\text{O}$ & $\text{Al}_2\text{O}_3$ IN DIFFERENT ROCK TYPES.
In weathering zone carbonate is directly converted into manganic oxides and hydroxides. In the lowest stage of oxidation or redox potential, manganese compounds give most mobile ions, whereas higher stages of oxidations are connected with immobilization or fixation of manganese. Having large ionic radius of divalent Mn which means low ionic potential of trivalent and quadrivalent manganese, leads to precipitation e.g. MnO₂ even from acid aqueous solution. The oxidation potential prevalent generally in weathering processes are too low to form permanganate ions.

Balance of the two processes i.e. leaching and precipitation will decide about the fate of manganese compounds in the weathering of rock forming minerals. Under oxygen deficiency conditions manganese will be liable to scoulution and leaching, whereas under available oxygen conditions, manganese is liable to be precipitated. Besides access of oxygen, pH plays an important role in the geochemistry of manganese, a low pH favours the solution and leaching of manganese.

In the bauxites of present study region MnO content is quite low with maximum reaching to 1.97% with an average of 0.36 percent. In the laterites also the
concentration of manganese is low, lower than the
bauxites with a maximum 0.62% (average 0.35%). In
lithomarge and granites, manganese is absent, however
slight presence is evidenced in some samples of the later.

The plotting of Mn/Al vs Mn (Fig. 26) indicate
that with the increase in Mn/Al ratio Mn increases which
means that Mn is not associated with Al but it is leached
out during weathering. This element has been depleted
to a greater extent indicating reducing environmental
conditions, because Mn readily dissolves in a reducing
environment.

\[ \text{Mn/Fe vs Mn} \]

Similar plots were made for Mn/Fe vs Mn (Fig. 26)
Two different trends appear for bauxites and laterites.
In both the cases the slope is positive. In bauxites the
slope is inclined towards Mn side whereas in laterites
it is inclined towards Fe.

Some separation of Mn and Fe is evident as the
Mn/Fe ratio is higher in the lithomarge and bauxites than
the parent rock. Mn is dissolved at low Eh and pH
and much of the variation in Mn/Fe ratio (Table-XXXVII)
is attributed to their separation at or near the site of
weathering (Vogt, 1906, Hanson, 1932, Ljunggren, 1953).
At the site of weathering, Mn, like Fe enters in the
lattices of developing minerals such as montmorillonite,
FIG. 26 PLOTTING OF Mn/Al \times 10^2 V/S Mn(\%) AND Mn/Fe \times 10^2 V/S Mn(\%) IN LATERITE & BAUXITE.
illite etc., or it may be co-precipitated with Fe. The lower Mn/Fe ratio of lithomarge suggests a preferential retention of Fe with relative concentration of Mn.

Mg/Al

Magnesium is generally poor in the weathering products of kaolitization. In the bauxites of the present area of investigation, however, Mg content is varying between 0.28% and 5.51% (average 1.15%). In laterites its concentration is lower, between 0.07% and 1.32% (average 0.66%). In granites, however, Mg content is higher and the values range between 0.42 and 10.81% (average 2.8%).

Mg values have been plotted against Al and some interesting relationships have been noticed. The bauxites have a sympathetic relationship with respect to Mg and Al whereas in laterites and lithomorphic clays it has an antipathetic relationship (Fig. 27).

Mg/Al ratio in most of the bauxites is more or less constant with only a minor variation (Table-XXXVII). It suggests that Mg lies chiefly in the clay fractions. Mg is probably included into the structure of montmorillonite at the site of weathering. With the changes in the physico-chemical conditions, Fe replaces Al structurally in illite and montmorillonite.
FIG. 27 PLOTTING OF Mg V/S AI AND Mg V/S Fe
DIFFERENT LITHOLOGICAL UNITS.
**Mg vs Fe**

The plotting of Mg versus Fe (Fig. 27) indicate a sympathetic relationship in the bauxites whereas in laterites it is antipathetic.

The laterites, which possess more of iron has inverse relationship because of the fact that there is similarity between Mg$^{2+}$ and Fe$^{2+}$ ion that caused mutual substitution of one offer another under similar physico-chemical conditions resulted in enrichment of one at the expense of other, depending upon Eh – pH of the medium.

**Loss on ignition (L.O.I.)**

Water content of bauxites and laterites is determined as loss on ignition which includes some volatiles also. The volatile contents of major bauxite minerals are H$_2$O, CO$_2$, and SO$_2$.

L.O.I. content of bauxites varies from 15.69% to 29.53% (average 25.52%) and in the laterites 11.85 to 26.39% (average 21.03%). Lithomargic clays also have high L.O.I. content ranging between 19.85 and 22.18% (average 20.07%). On the other hand, granites and granitic rocks have very low content with as low as 0.38% and as high as 6.42 (average 2.24%).
Most of the water of bauxites is contained in the aluminium minerals. Aluminium content or the quality of bauxites may be inferred from ignition loss under certain conditions particularly when clay mineral is very low and hematite, gibbsite are the only iron and aluminium minerals respectively.

Role of ionic potentials and bondings.

The problem of migration and fixation of various major as well as trace elements has been well understood by Goldschmidt (1937), who divided the various elements into three main categories on the basis of their ionic potentials (Fig 28). Category-I, have the lowest potentials, representing simple ionic compounds and are readily soluble under subaerial conditions. Category-II, elements are typically insoluble being easily hydrolysed and precipitated in the form of hydroxides, Category-III elements though possess highest ionic potentials and forming complex anions with oxygen are in contrast, comparatively soluble.

Wickman (1944) who supported the Bernal and Megaw (1935) for the interpretation of hydrogen and hydroxyl bondings, proposed that this grouping could alternatively be ascribed to the effect of cation size.
FIG. 28 RELATION OF IONIC POTENTIAL AND HYDROXIDE FORMATION (AFTER GOLDSCMIDT, 1927)
on the polarization power in hydroxyl groups. Thus the soluble cations of Category-I having electrostatic valencies towards the hydroxyl groups of less than 1/2, have simple ionic bonds in their hydroxides, whereas those in Category-II with valencies of 1/2 to 1 have hydroxyl bonds. In Category-III, on the other hand, the complex ions have hydrogen bonds due to the cation valencies being greater than 1.

A notable practical limitation in both of these hypotheses is their apparent overlooking the effects of physical or chemisorption, which particularly in the presence of organic matter, have a significant role. Thus assuming existence of higher Eh and pH conditions in the upper lateritic horizons of jungle covered hills, the writer considers that solubility of hematite, limonite and quartz would have been exceeded resulting in their precipitation. The feasibility of such behaviour seems to be further substantiated by the fact that the ionic potentials of Fe^{2+}, Mn^{2+} and Si^{4+} all lie close to the insoluble hydrolysates of Category-II, whereas evidences of these processes may be seen in the characteristically coarse hard iron rich lateritic crusts to bauxite horizons in the Lohardaga deposit.
The distribution of minor elements (Table XXVII) is also chemically significant and not apparently due to the presence of detrital heavy mineral constituents. TiO$_2$ and to a lesser extent MnO and P$_2$O$_5$ all vary sympathetically with the Fe$_2$O$_3$ content, indicating more concentration in extremely coarse iron rich laterites. Further more, with the exception of TiO$_2$ and to a lesser extent MnO, these elements also possess ionic potentials bordering on the very limits of Goldschmidt's precipitated Category IX of hydrolysates. It seems likely, therefore, that they too may have been concentrated by the combined effects of absorption followed by increased Eh conditions as it is generally present near the surface of most weathering profiles.

Geochemical significance of kaolinitic clays

Kaolinitic clays have been observed at many places beneath the bauxite horizon and the bed rocks. (Chapter B-III). Several thoughts are prevalent for the genesis of these clays. One idea is that given by Harrison (1911) who studied under microscope the direct alteration of feldspar into gibbsite and its subsequent silicification to kaolinite in the weathering crust of dolerite in humid tropical climate, on the other hand, Goldich (1940) considered that bauxite is a primary weathering product of bed rock, but with a change
in weathering conditions e.g. establishment of permanent water table, kaolinitic clays begin to form directly from the bed rock beneath the bauxite.

In zone-1 which has dominantly kaolinitic clays, alkalies and alkaline earths have been removed. There is not much change in Al₂O₃ and Fe₂O₃ contents, silica has increased a little in respect to fresh bed rock (Table-XX).

The intermediate zone-2 shows a pronounced decline in silica content with an increase in Al₂O₃ and Fe₂O₃ relative to zone-1. At top of this zone there is a pronounced enrichment in Al₂O₃ and lowering in Fe₂O₃ content than the remaining part of this zone (Table-XX).

The top zone which constitutes the bauxite horizons in characterized by a very high Al₂O₃ and low SiO₂ and Fe₂O₃ content. TiO₂ is strongly enriched in this zone, at some localities reached up to 17% (sample No.7, 10, 34, 49, 65).

Extent of accumulation or removal of three major components of the weathered profile has been illustrated in Fig. 29. The marked increase of iron in zone-2 is due to the presence of considerable amount of ferruginous nodules up to a size of 2 cm. As there is only small depletion of SiO₂ and no depletion of Al₂O₃
FIG. 29 COMPARISON OF MAJOR CONSTITUENTS OF BAUXITIZED MATERIAL WITH BED ROCK
in this zone, the pronounced enrichment of iron does not merely reflect a residual accumulation. There is not any marked depletion of iron beneath this zone but the bauxites are clearly leached of iron in comparison with lower part of the profile. This seems most likely that iron was gradually leached out of the bauxites and then redeposited at a lower level in the profile. Since ferric iron is practically immobile under normal ground water conditions, it might be that mobilization of iron was brought about by reducing or complexing action of organic material. Harden and Bateson (1963) have reported the presence of organic carbon up to the extent of 1.3% in some clay bands in the bauxite body.

With the foregoing discussions, the author has come to the conclusion that bauxites were formed by leaching of upper portion of kaolinitic clays which are supposed to be the weathering product of aluminous bed rocks. The iron which was removed in the process was redeposited near the water table to give horizons containing ferruginous nodules. Removed $SiO_2$ appears to have remained in solution and left the system entirely. Some silica was however redeposited at lower levels below the water table.
The kaolinitic clays were formed under poor drainage conditions so that more soluble components of the bed rock, i.e., sodium, potassium, calcium, and magnesium were removed. This could be under swampy conditions which would provide humic material needed to mobilize the iron out of the kaolinitic clays.

Iron rich zone under the bauxites may not always be present because conditions may not favour iron precipitation at any particular level below the bauxites. However, presence of iron rich zone is considered to support the Harder's view (1949) that the boharanga bauxites have been formed by the desilicification of material originally similar to the underlying kaolinitic clays.

Role of titanium in the genesis of bauxite

In the bauxitization and lateritization, various physico-chemical factors got involved. Titanium plays a significant role with the aid of others in the development of bauxite profile.

Most of the silicate minerals are hydrolysed in the weathering environment where surface and ground water are freely available. The released ions, particularly of low ionic potentials are adsorbed by clays. Ilmenite and rutile, the two titanium bearing minerals are
resistant against weathering, thus remain in the resistates. Titanium of the mafic minerals to some extent must have been dissolved which later on reprecipitated in the other polymorphs of Ti e.g. anatase. This phenomenon is a reconstruction phenomenon (Frederickson, 1948) which requires an aqueous medium. The atoms involved in the process must be hydrated at one stage and then dehydrated and recrystallised into one of the polymorphs of the TiO₂.

\[
\text{TIO} (\text{OH})_2 \rightarrow \text{TIO}^{4+} + 2 \text{OH} \rightarrow \text{TiO}_2 + \text{H}_2\text{O}.
\]

As a result of hydrolysis, dispersion colloidal system is generated in the weathering zone. This system is dominated by soils of negatively charged SiO₂, positively charged Al (OH)₃, and negatively charged Fe (OH)₃ (Rankama and Sahama, 1949). Al (OH)₃ might be negatively charged in an alkaline medium. Marshall (1964) stated that if there is concentration of ions having valency higher than 2, Al (OH)₃ would show reversal of sign. It seems therefore more likely that Ti⁴⁺ ions are important in reversing its charge.

Bauxitization and laterization mainly involves removal of SiO₂, flocculation and precipitation of main soils namely Fe (OH)₃ and Al (OH)₃. This is
controlled by fluctuating conditions of Eh-pH and the presence of Ti$^{4+}$ ions.

The other important factor which controls the flocculation in the system is the cota potential (Chasteen, 1962). The cota potential must be lowered in order to cause flocculation. Ti$^{4+}$ may bring down the cota potential of Fe (OH)$_3$ sol and cause its flocculation (Sinha Ray, 1973). As a result Ti will be adsorbed. Similarly Al may be adsorbed by Fe (OH)$_3$ because of similar ionic potentials of Al$^{3+}$ (5.26) and Ti$^{4+}$ (6.25). It could thus be inferred that titanium is present either in the gibbsite structure as replacement of Al or as adsorbed layer on gibbsite. The preferential partitioning of titanium in the bauxite trend is the result of titanium protecting the Al in the sol state, and of replacement and adsorption relationship in the crystalline state of Al sesquioxide.
Chapter C-XX

TRACE ELEMENT GEOCHEMISTRY

Knowledge of trace elements and its significance have been known since the beginning of 20th century. Washington (1913) probably was the first to study the distribution of trace elements in different rock types. He pointed out that trace elements did not relate only to rock types but also to major elements present in the rock. Vog (1919) and Huddington (1933) stated some complications in the distribution of the trace elements.

In the last few decades, knowledge of geochemistry of trace elements has developed fast. A good work is being done on the distribution of trace elements in igneous rocks and their geochemical behaviour during the fractional crystallization of magmas. Goldschmidt (1937) a pioneer worker in the field of geochemistry, observed some facts regarding element distribution in rocks and minerals and proposed a classification based on chemical affinity. He classified all the elements into five groups namely siderophile, chalcophile, lithophile, atmophile and biophile based on the preference of the elements to go with iron, sulphides, silicates, atmospheres and organisms respectively. He also found that chemical
properties of elements are related with electronic configuration. Further he assumed that mutual replacement of ions in magmatic rocks was purely ionic. He explained certain geochemical relationships on the basis of ionic radii and charge. Ionic radius which is very often used in the geochemical phenomenon has been defined by Bragg (1937) that ions come closer and closer to some distance, then repulsive forces act, this minimum distance which is characteristic for a certain ion is ionic radius.

Modern researches in geochemistry revealed that Goldschmidt's rules need to be modified. More emphasis has been given to chemical bonding. According to Fyfe (1951) partial covalent bond in certain compounds show certain deviations from the phenomenon of isomorphism. Ramsey (1925), Shaw (1953) and Ahrons (1953) were of the view that chemical bondings could explain most of the geochemical behaviour during crystallization.

Hingwood (1955) used electronegativity as criteria for bond type in minerals and rocks. However the credit of applying electronegativity originally goes to a chemist, Pauling (1935). He defined it as "The power of an atom in a molecule to attract an electron unto itself". Pauling (1946) was of the view 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 electronegativity 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 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". This rule satisfactorily applies to such cases in which the difference in the electronegativity is more than 0.1.

Ringood's (1955) modifications to Goldschmidt's rules was criticized 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. Rockolds (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
(Krauskopf, 1967).

**Distribution of Trace elements**

Distribution of 12 trace elements namely Cu, Ni, Co, Ga, Cr, Sr, Sn and V in the country rock i.e., granites and granitic rocks and bauxite-laterite profile has been studied in this chapter. Pb and Sn were determined only in case of granites and granitic rocks because these were insignificantly present in the bauxites and laterites. The samples were analysed on atomic absorption spectrophotometer for determining quantitatively the trace elements which may have some significance in the present investigation. Other elements sought but below detection level were Mo, Sn, Bi, Sn, Be, Sn, Be, Sc, B, Pb, Li and Y.

Although the chemical nature of the precursor of the bauxites and laterites is not known in detail because nowhere, within the area of investigation, there is a contact of bauxite bed with parent rock. The subjacent rock which is granite and other granitic rocks is quite fresh. However relative enrichment or depletion has been worked out by assuming the basement rock as to have the original composition.

As revealed by chemical analysis of fragment portions, the partition of various elements between the whole rock, -12, and -200 portions of a sample over the entire profile
brings out certain affinities as shown by Fig. 30. Enrichment in the whole rock which includes gibbsite and iron oxide nodules and fragments, suggests that Fe, V, P, Ga and Cr are fixed in concretionary amorphous materials while Sr, Ca appears to be preferentially absorbed on clay sized material.

The relative geochemical response of various elements to conditions of extreme leaching and selective precipitation was examined by making inter element comparisons of successive samples in each horizon of the entire section. The chemical variance within the bauxite laterite profile may be due to primary effects in which an element or a compound containing it, has undergone absolute movement and secondary effects wherein the element is positionally fixed but shows relative concentration change due to changes in the other elements in the sample. The primary effects are believed to be the result of downward transport in solution or suspension. Mobility is thus a function of solubility, sorptive phenomenon, and possibly translocation. The addition of cyclic salts from the atmosphere may also play a role in the observed distribution of the elements.

The trace element abundances in the bauxite laterite profile as well as in the country rock i.e. granites and
FIG. 30 PARTITION OF ELEMENTS BETWEEN SIZE FRACTIONS.
granitic rocks have been presented in the Table-XXXVIII. These data have also been represented by histograms for a view at a glance (Fig. 31-34).

The following arbitrary scale has been used for the purpose of comparing relative abundances of trace element concentrations.

<table>
<thead>
<tr>
<th>ppm values</th>
<th>Scale symbol</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000</td>
<td>EH</td>
<td>Exceptionally high</td>
</tr>
<tr>
<td>1000 - 5000</td>
<td>VH</td>
<td>Very high</td>
</tr>
<tr>
<td>500 - 1000</td>
<td>H</td>
<td>High</td>
</tr>
<tr>
<td>100 - 500</td>
<td>M</td>
<td>Moderate</td>
</tr>
<tr>
<td>50 - 100</td>
<td>L</td>
<td>Low</td>
</tr>
<tr>
<td>10 - 50</td>
<td>Vl</td>
<td>Very low</td>
</tr>
<tr>
<td>10</td>
<td>N</td>
<td>Exceptionally low</td>
</tr>
</tbody>
</table>

Geochemical dispersion of trace elements

Variation diagrams (Fig. 35, 36, 37) were used to represent graphically the geochemical dispersion of Cu, Pb, Zn, Cr, Co, Ni, Ga, Zr, and V in the different rock types of Lohardaga deposit. These diagrams illustrate
the dispersion pattern of these trace elements and their relative abundance in a particular set of rock. An attempt has been made to use them to present the analytical data of geochemical dispersion both for ore rock as well as country rock. All the rocks were divided into three groups namely granite and granitic rocks, bauxites and laterites. The range of variation is not very wide, the lower limit is as low as 2 ppm and the higher limit is 600 ppm. The minimum, maximum and average compositions of trace elements in various lithological units have been represented in Table-XCXIX.

Concentration circles were drawn in ppc range on logarithmic scale for the values of 1,000 ppc, 500 ppc, 100 ppc, 50 ppc, 20 ppc, 10 ppc, and 5 ppc to suit the range of variation of these data. Circular graph was divided into many segments to fit every element in each rock to be presented. Each segment was further divided into present frequency having sectors of 25 percent, 50 percent, 75 percent and 100 percent.

Trace element concentration values have been grouped with an interval of 10 ppm for values up to 100 ppm, and an interval of 50 ppm for more than 100 ppm. (Table XXX, XXXI and XXXII).

Circular diagrams for the graphical representation
FIG. 35  GEOCHEMICAL VARIATION DIAGRAM OF Cu, Pb, Zn IN DIFFERENT ROCK TYPES.
FIG 36 GEOCHEMICAL VARIATION DIAGRAM OF Cr, Co, Rh, IN DIFFERENT ROCK TYPES.
FIG. 37. GEOCHEMICAL RATION DIAGRAM OF Zr, Z, Y
IN DIFFERENT ROCK TYPES
of geochemical data have been used as proposed by Baisalibelli (1964, Fig-35, 36, 37). The diagrams represent all the parameters clearly with the scope to accommodate any other relevant record. The dispersion patterns were later discussed with a view to study the geochemical behaviour of trace elements in a particular set of rocks and their variation trends.

Table-XXXIII: Explanation of geochemical diagram for granites and granitic rocks.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of the element</th>
<th>Average Concentration</th>
<th>Range of values</th>
<th>Max. frequency group/group and % frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu</td>
<td>16.5 ppm</td>
<td>3-22 ppm</td>
<td>10-20 ppm (50%)</td>
</tr>
<tr>
<td>2</td>
<td>Pb</td>
<td>20.1 ppm</td>
<td>11-29 ppm</td>
<td>10-20 ppm (62.5%)</td>
</tr>
<tr>
<td>3</td>
<td>Zn</td>
<td>42.1 ppm</td>
<td>32-54 ppm</td>
<td>30-40 ppm (50%) &amp; 40-50 ppm (50%)</td>
</tr>
<tr>
<td>4</td>
<td>Ni</td>
<td>7 ppm</td>
<td>3-11 ppm</td>
<td>5-10 ppm (62.5%)</td>
</tr>
<tr>
<td>5</td>
<td>Co</td>
<td>3 ppm</td>
<td>1-6 ppm</td>
<td>0-5 ppm (57.5%)</td>
</tr>
<tr>
<td>6</td>
<td>Cr</td>
<td>19 ppm</td>
<td>12-24 ppm</td>
<td>10-20 ppm (75%)</td>
</tr>
<tr>
<td>7</td>
<td>Ga</td>
<td>17.5 ppm</td>
<td>12-24 ppm</td>
<td>15-20 ppm (50%)</td>
</tr>
<tr>
<td>8</td>
<td>Zr</td>
<td>174.4 ppm</td>
<td>120-220 ppm</td>
<td>100-150 ppm (37.5%) &amp; 200-250 ppm (37.5%)</td>
</tr>
</tbody>
</table>
Table 4: Distribution of chemical elements in rocks. (ppm = parts per million)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Element</th>
<th>Average Concentration</th>
<th>Range of Values</th>
<th>Max. Frequency Group/ Values</th>
<th>% Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Sr</td>
<td>303.12 ppm</td>
<td>250-350 ppm</td>
<td>250-300 ppm (50%)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>V</td>
<td>31.62 ppm</td>
<td>24-60 ppm</td>
<td>20-30 ppm (50%)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5: Explanations of geological diagram for bauxites.

1. Cu: 
   - 33 ppm
   - 12 ppm to 20 ppm to 30 ppm (34.69%)

2. Pb: 
   - HOT
   - Determined

3. Sn: 
   - HOT
   - Determined

4. Ni: 
   - 37 ppm
   - 12 ppm to 40 ppm to 50 ppm
   - 50 ppm (42.35%)

5. Co: 
   - 27 ppm
   - 7 ppm to 40 ppm
   - 40 ppm (40.81%)

6. Cr: 
   - 275 ppm
   - 190 ppm to 300 ppm
   - 300 ppm (34.69%)

7. Ga: 
   - 32.4 ppm
   - 21 ppm to 20 ppm to 26 ppm
   - 30 ppm (44.9%)

8. Sr: 
   - 440.6 ppm
   - 350-330 ppm
   - 350-400 ppm (32.6%)

9. Zr: 
   - 139.6 ppm
   - 40-230 ppm
   - 100-150 ppm (36.7%)

10. V: 
    - 224.0 ppm
    - 170-230 ppm
    - 200-250 ppm (55.1%)
Table XXXIII—Explanation of geochemical diagram for latorites.

<table>
<thead>
<tr>
<th>S.NO.</th>
<th>Name of the element</th>
<th>Average concentration</th>
<th>Range of values</th>
<th>Max. frequency group/group &amp; % frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu</td>
<td>36 pppm</td>
<td>12-90 pppm</td>
<td>30-40 pppm (26.66%)</td>
</tr>
<tr>
<td>2</td>
<td>Fe</td>
<td>DETERMINED</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Si</td>
<td>DETERMINED</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Hf</td>
<td>36 pppm</td>
<td>17-40 pppm</td>
<td>40-50 pppm (42.95%)</td>
</tr>
<tr>
<td>5</td>
<td>Ce</td>
<td>DETERMINED</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Sr</td>
<td>235 pppm</td>
<td>190-370 pppm</td>
<td>200-300 pppm (43.10%)</td>
</tr>
<tr>
<td>7</td>
<td>Ga</td>
<td>31.6 pppm</td>
<td>20-47 ppm</td>
<td>230-250 pppm (43.10%)</td>
</tr>
<tr>
<td>8</td>
<td>Sr</td>
<td>440.3 pppm</td>
<td>280-540 pppm</td>
<td>400-500 pppm (30.00%)</td>
</tr>
<tr>
<td>9</td>
<td>Sr</td>
<td>159.7 pppm</td>
<td>170-280 pppm</td>
<td>200-250 pppm (43.2%)</td>
</tr>
</tbody>
</table>

Relative mobility of trace elements

The rock samples clearly show low dispersion of Cu while the residual products derived apparently from granites and granitic rocks show enrichment in Cu contents. It appears that during chemical weathering of the rock and sorting out of various elements, Cu resisted considerably and as a result of which there is concentration of copper.
in the residual soil.

The rock samples distinctly show higher dispersion of Pb & Sn as compared to the residual soil samples. The effect of chemical weathering on Pb & Sn to be unlike that of Cu. It indicates that in general Pb & Sn was leached out considerably during the chemical weathering leaving the residual deposit depleted in its Pb & Sn content.

Similarly, the relative degree of enrichment or depletion for all trace elements is worked out as follows (Table-SOCXIII).

Table-SOCXIII—Scheme of relative mobility of trace elements.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Enriched on average</th>
<th>Elements</th>
<th>Deplated on average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>15.27 times</td>
<td>Sn</td>
<td>∞ times</td>
</tr>
<tr>
<td>Co</td>
<td>9.00 times</td>
<td>Pb</td>
<td>∞ times</td>
</tr>
<tr>
<td>Y</td>
<td>7.03 times</td>
<td>Sr</td>
<td>0.45 times</td>
</tr>
<tr>
<td>Ni</td>
<td>5.23 times</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>2.52 times</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>2.00 times</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>1.35 times</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The observations and the general quantitative assessment made in the above table led the author to suggest the following scheme of relative mobilities of trace elements during the process of chemical weathering in the present area of study. Maximum resistant being Cr and least resistant being Sn.

\[ \text{Cr} > \text{Co} > \text{V} > \text{Ni} > \text{Sr} > \text{Cu} > \text{Ga} > \text{Sr} > \text{Ph} > \text{Sn} \]

This occurrence does not conform in detail to anticipated changes under lateritisation in accordance with the ionic potential of these elements. Fixation of some elements such as the theoretically soluble V and Cr by selective absorption on developing iron oxide concentrations, precipitation of P as an insoluble iron phosphate or changes in pH as a function of soil, atmosphere and depth may all play a part in this divergence of observation from traditional ionic potential theory.

Copper

Copper is cosmically abundant in comparison with other heavy metals. Average content of Cu in the upper lithosphere has been estimated about 100 ppm. Chemical analyses have shown that very little copper is present
in the silicates. More of copper occurs in the metal phase and it is still higher in the sulphide phase. Copper thus geochemically has a chalcopyrite with some siderophile tendency.

Copper in silicates form in less commonly found, mainly chrysocolla CuSiO₄. H₂O and diaspore Cu₃(Si₃O₉) 3H₂O are the most important species, mainly restricted to hydrothermal veins. Small amounts of Cu may replace ferrous iron in mineral structures in the absence of appropriate supply of sulphur. The reason for such substitution is the similarity of the radii of Cu²⁺ (~0.83 Å) and Fe²⁺ (~0.84 Å).

The following table gives the data for various copper radii ions, according to L. Pauling and H. Huggins (1934).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺</td>
<td>0.33</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>0.95</td>
</tr>
<tr>
<td>Cu metal</td>
<td>1.23</td>
</tr>
<tr>
<td>Cu 'tetrahedral'</td>
<td>1.35</td>
</tr>
</tbody>
</table>

During weathering superficial parts of copper ore bodies are oxidized. The copper iron sulphide
(chalcopyrite) are broken up and taken to solution as cupric sulphate. The copper sulphate solution migrates downward below the zone of oxidation but above the water table. They react with undecomposed sulphide minerals, and native Cu and copper rich sulphide are thereby formed. Other copper minerals like cuprite, tenorite, asurite and celadonite may also be deposited. The copper bearing solution may migrate to surrounding rocks through cracks and fractures. Some part of copper is trapped in hydroxylate sediments by absorption.

The best condition for oxidation and leaching which involves large amounts of rock-water-given-by-air contact, atmospheric or dissolved in circulating waters which in turn depends upon the porosity and permeability. Greatest oxidation is expected in the areas where water table is far below the ground as in desertic conditions, some other factors like topography and hydrologic conditions which control surface drainage and ground water circulation are also effective in the oxidation. In a humid climate, the metal ions e.g. cupric ions in this case will be carried away in solution to the sea. On the other hand if rainfall is scarce and ground water tends to stagnate, large amounts of soluble metal ions can be accumulated by precipitation, either at ground water level or where reducing conditions are
The copper content in residual clays, bauxites and soils is generally less than that of parent rock, because copper in the course of weathering has been removed in solution. Copper amount in soils of humid condition is averaged at 10 ppm and rarely exceeding 20 ppm, but some arid region soils have been reported to contain up to 50 ppm.

In spite of high solubility of copper, there is fairly good enrichment of it in the bauxitic profile. Copper is high particularly in the upper profile, might be due to its association with organic material. Copper which is generally related with Mn does not develop any relationship in these bauxites.

The concentration of Cu in the granites and granitic rocks is moderately low, 8 ppm to 22 ppm, with an average of 16 ppm. There is a considerable enrichment of Cu in the bauxites and laterites which varies 12 ppm to 70 ppm and 12 ppm to 90 ppm respectively. On an average, bauxite is found to contain 33 ppm and laterite 36 ppm of Cu. Cu is however depleted completely in lithomargic clay. Krauskopf (1956) has shown that Cu is effectively absorbed by Fe(OH)$_3$, Mn (OH)$_4$, and clay minerals. Cu/Al ratio in the bauxites and laterites is remarkably constant.
with only minor variations (Table -XXXIV). Cu/Al ratio has been plotted against Al content and the graph shows their constancy which gives the idea that Cu is mainly associated with clay minerals (Fig. 38). During weathering, copper like Ga, Cr and V remained structurally combined in the lattices of clay minerals.

Table-XXXIV and the graph in the Fig. 38 shows the Cu/Mg ratio which reveals an inverse relationship suggesting thereby that Cu is not related to Mg. Mg is generally found to be associated with montmorillonite.

Zirconium

Zirconium chemically resembles very closely with Hafnium, though their atomic numbers are very much different ( Zr 40 and Hf 72 ). The most characteristic valency of zirconium is 4. Its ionic radius is 0.87 Å which indicates that zirconium should have a coordination of 6 relative to oxygen. However the most abundant Zr mineral is zircon ( Zr SiO₄ ) possess a 8 fold coordination structure. This coordination number is too high for the dimension of Zr⁴⁺ ion. Some external forces e.g. radioactive radiation are believed to have broken the zircon, is however, a stable orthosilicate found in rocks.
FIG. 38 PLOT OF Cu/Al x 10^4 V/S Al AND Cu V/S Mg IN DIFFERENT LITHOLOGICAL UNITS.
This mineral carries bulk of zirconium about 67% of $ZrO_2$ in igneous rocks.

Geochemically zirconium is lithophile occurring in silicate form. Zirconium in sedimentary rocks are derived from igneous rocks. The distribution and behaviour of zirconium in sandstones is because of high weathering resistance of zircon, the principal zirconium carrier. The exceptionally high zirconium content in kaolins, halloysites, and other clay minerals is attributed to their formation during weathering of zirconium rich nepheline syenites.

During weathering zirconium in the form of zircon remains largely in the residuum, which contains more of zirconium than hydrolyzates. Some zirconium also goes into solution and it is removed from solution by hydrolysis and does not form secondary minerals.

Zirconium concentration is high in all the weathered products i.e., bauxite, laterite and lithomorphic clay. The range is in between 250 ppm and 550 ppm (average 440 ppm). In granites and granitic rocks it is however low, varying between 120 ppm and 220 ppm (average 174.4 ppm).

Zirconium has been plotted against Ti and Al (Fig. 39). In both the cases a general trend appears to be sympathetic. This is so because $Zr$ is mostly incorporated
FIG. 39 RELATIONSHIP BETWEEN Zr V/S Al AND Ti IN BAUXITIC ROCKS.
into titanium minerals e.g. anatase during neomineralization. Sr is accommodated with aluminium hydroxide as well. Evidence for substitution of Al by Sr in kaolinite was presented by Degenhardt (1957) who also suggested that any Sr ions in solution would enter the lattice of developing montmorillonite.

**Nickel**

Nickel belongs to the iron family (Goldschmidt, 1929) or the ferrides (Landergräns, 1943). It is very close to iron in the periodic system also. The average content of Ni in igneous rocks as given by clark and Washington (1924) is 0.20 percent. Vogt (1931) thought this value to be very high and he gave an 0.01% Ni. Geochemically nickel follows magnesium as their ionic radii are similar (Mg 0.79 Å, Ni 0.78 Å).

nickel together with cobalt are strongly concentrated in the metal phase of the meteorites. Geochemically Ni and Co are strongly siderophile, though Co is less siderophile than Ni. In the upper lithosphere Ni and Co are found to be chalcophile as it occurs in sulphide form in many minerals. Along with siderophile with a chalcophile tendency, this element possesses lithophile tendency as well. Geochemically Ni resembles very much with Co but in case
of weathering they differ from each other considerably.

During weathering Ni largely remains in solid products of disintegration and is deposited in hydrolyzate sediments. In the process of weathering nickel is locally concentrated relative to its content in the original silicate rock. The concentrated Ni may be partly derived from nickel magnesium silicates and partly from sulphides and arsenides of nickel which are found associated with magmatic magnesium silicate rocks.

Nickel bearing silicate minerals on weathering may accumulate to form veins of pure nickel silicates. During lateritic weathering of serpentine, nickel becomes enriched in the insoluble residue. Serpentine first gets converted to magnesite by \( \text{CO}_2 \) bearing weathering solution then magnesite goes into solution as magnesium bicarbonate and only silica, hydrosilicates of \( \text{Ni} \) and \( \text{Mg} \) and iron oxide remain as residue. The bulk of nickel is retained in the solid products of weathering and only a very little amount is transported to the sea.

The concentration of Ni in the weathering environment can be controlled by two major processes, firstly attacked by percolating ground water of serpentine minerals which results in the release of \( \text{Ni}^{2+} \) ions by precipitation &
incorporation of Ni into lattices of newly formed minerals. Ni$^{2+}$ ions are soluble in solution upto pH range of 6-6.7 and higher pH will result in precipitation of Ni. It is apparently stable in the upper ferruginous horizons where acid conditions prevailed. There are other factors besides these for the control of distribution of Ni. It is suggested that Ni if incorporated into the aluminous goethite lattice, downward movement of this element could be severely restricted.

Ni with Zn are carried in goethite, a hydroxide of iron. Ni & Co due to similar ionic radii behave similarly. These elements are concentrated when SiO$_2$ and HgO are leached out.

Nickel concentration in the bauxites and laterites vary from 12 ppm to 50 ppm, the average being 37 ppm. Nickel is high in lithomargic clays varying between 63 and 90 (average 80). However in the granites and granitic rocks it is very low, 3-11 ppm with an average of 7 ppm.

The Ni/Ni ratio is fairly constant in almost all types of lithological units. This constancy suggests that Ni contents are related to montmorillonite clay
content. To study Ni/Al ratio in more detail, it has been plotted against % Al (Fig. 40) a tendency towards an inverse relationship is exposed. It might indicate that there is mutual ionic substitution in clay mineral lattice at or near the site of weathering.

Ni/Mg ratio decreases in the bauxites and their plot indicate a negative correlation (Fig. 41). Mg is generally lost relative to Ni during weathering thus it seems reasonable to say that under the conditions required for the formation of montmorillonite, where Mg is retained (Hirst, 1962) both Ni and Co are also retained. Thus the absolute enrichment of Co and Ni contents will be higher in bauxites containing montmorillonite than in those containing illite alone, their ratios to Mg should be lower.

**Cobalt**

This element also is an important member of G Goldschmidt's iron family. The average content of Co as given by clarks and Washington (1924) is 0.001%. This was however revised by many authors. In 1933 Goldschmidt working with White and Humann gave the average content of Co as 0.004%. Because of similarity in ionic radius, cobalt is geochemically closer to divalent iron.

\[
\text{Co} \ 0.82 \text{Å}, \ \text{Fe}^{2+} \ 0.83 \text{Å}
\]
FIG. 40 PLOT OF Ni/Al x 10^4 V/S Al AND Ni V/S Co IN LITHOLOGICAL UNITS.
FIG 41 Ni PLOTTED AGAINST Fe AND Mg IN DIFFERENT LITHOLOGICAL UNITS.
Cobalt like nickel is strongly siderophile though less than the nickel. In the upper lithosphere it possesses chalcophile tendency as well. It combines readily with sulphur. The lithophile tendency is also not ruled out as it is a frequent constituent of silicate rocks. In acid igneous rocks cobalt has been found to be more than the nickel.

Unlike nickel, cobalt passes easily into trivalent cobalt which has 6 coordination number, whereas coordination number of divalent cobalt is 6 or 4.

In the weathering process, cobalt does not form hydroxysilicates. It remains in weathering solutions as bicarbonate or colloidal hydroxide. In lateritic weathering Co as well as Ni gets enriched. Its content in sea water is very low.

Cobalt content in the basaits and laterites in the present area of investigation varies from 7 ppm to 40 ppm (average 27 ppm). In lithomarge it is somewhat higher, 57 ppm to 79 ppm (average 66 ppm). In granites and granitic rock its content is exceptionally low, ranging between 2 ppm and 6 ppm (average 3 ppm).

The Co/Al ratio is fairly constant (table XXXXV) in almost all types of lithological units. This constancy
suggests that Co contents are related to montmorillonite clay content. To study Co - Al relationship in more detail, it has been plotted against % Al (Fig. 42) a tendency towards an inverse relationship is exposed. It might be due to mutual ionic substitution in clay mineral lattice at or near the site of weathering.

Cobalt is found to vary linearly with MgO and the ratio of Co/MgO is approximately 0.00006. Sendell and Goldich (1943) also reported similar trend in a number of granite samples. This value thus may be used to determine the Co content in common igneous rocks if MgO value is known.

There is a good relationship between Co and total Fe₂O₃, reflecting the similar behaviour of the two elements. No direct relationship exists between the amount of Mn and Co, but it is generally accepted that Co is associated with the manganese minerals. However Co together with Ni are more depleted than Mn. Co & Ni are particularly strongly complexed by organic ligands and Co CO₃ is very insoluble and thus may be important in the formation of laterites.

So far as its concentration in bauxites is concerned, Gordon & Murata (1953) found average Co concentration in Arkansas bauxites to be 0.00014% or 1.4 ppm, with a
FIG. 42. PLOT OF $\text{V}_0/\text{Al} \times 10^4$ VS. $\text{V}_0$ VS. $\text{Al}$ VS. $\text{Al}$ VS. $\text{Al}$ DIFFERENT LITHOLOGICAL GROUPS.

BAUXITES
LATERITES
CLAYS
GRANITE
maximum of 20 ppm, Cobalt concentrations in the bauxites and laterites are quite high. It has been as low as 12 ppm in both bauxites and laterites but the maximum value is 70 ppm in bauxites & 90 ppm in laterites. The average values being 33 ppm in case of bauxites and 36 ppm in the laterites. Most of it is associated with the manganese oxide and hydroxides. There exists a positive linear relationship between cobalt and magnesium & cobalt and total iron. This relationship is more pronounced in case of iron.

If, however, sum of magnesium & iron is plotted against the cobalt concentration, a slope of 45° is obtained which indicates a proportionality between the variables (Fig. 43). This means that there is a better coherence between Co and either Fe or Mg. It seems quite reasonable to imply that the cobalt concentration of bauxites and laterites are dependant on the number of sites available for cobalt to occupy. Cobalt values are higher, upto 40 ppm in clayey bauxites, e.g. bauxites of Haidarpur and Garhpat, strengthens the above observations.

Strontium

This is the most abundant trace element of upper lithosphere. Its content as given by Clarke and Washington and Vinogradov is 0.34%. It occurs dispersed in the native state as well as with minerals. Its atomic number is 38 and atomic radius 1.27 Å. The bulk of
FIG. 4.3 Co plotted against Fe and Mg in different rock types.
strontium is concealed in the rock forming minerals of igneous rocks. Due to close ionic radius strontium accompanies Ca constantly in igneous and sedimentary rocks. It replaces K in many minerals. The ionic radii of closer elements are given as

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>1.06</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>1.27</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.33</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Both Sr and Ba may substitute K because ionic radius of K is intermediate between the other two elements. The feldspar structure is most suitable for the strontium and barium to fit in. Strontium is present in plagioclases and potash feldspars.

Sr do not replace the rare earths because the substitution for a tripositive ion by a bipoistive ion is unfavourable to the stability of the structure with regards to energy relationship. Sr may accompany the rare earth metals in many minerals but it replaces K$^+$ & Ca$^{2+}$.

During weathering most of the strontium dissolves as bicarbonate. Chlorides and sulphates are also formed. Strontium may be precipitated as carbonate through loss of CO$_2$ from carbonate bearing weathering solutions and
as sulphate if acted upon by sulphuric acid. The bulk portion of strontium however migrates to the sea. In hydrolyzate sediments and in the clay minerals of soils, Sr may be fixed on a very moderate scale by base exchange.

The concentration of strontium in bauxites and laterites of the area under study varies from 40 - 230 ppm and 50 - 230 ppm respectively. Their average concentrations are 130 ppm and 150 ppm respectively. In lithophylite it is slightly higher ranging between 70 - 110 ppm (average 94 ppm) and in the granites it is further high & varies between 255 - 350 ppm (average 303 ppm).

This element is characteristically depleted in the weathering processes. Strontium is preferentially absorbed on clay sized material. Kaolin rich bauxites, therefore, are found to have relatively higher concentration.

According to Goldschmidt's (1954) famous concept that there is a tendency for certain trace element to follow major element that are similar to them in radius and bond type. Following this, strontium may be found in Ca rich minerals. This relationship is however reversed in basaltic rocks.

There is a good linear relationship of Ca & Sr. It is evident from the Fig. 44 that there is a positive slope which means that there is an increase in Sr content with
the increase of Ca content. This relationship is not simple linear relationship but log of their concentrations shows a better trend. This relationship is true for granitic rocks only and does not apply to basaltic rocks where this relationship reveres to negative slope (Turekian, et al. 1956). The concentration of strontium will depend upon total amount of Ca bearing minerals. Feldspar group of minerals particularly plagioclase are thus the carriers of Sr. This is the reason why we find more Sr in the clayey bauxite.

**Gallium**

The geochemistry of gallium is very closely related to aluminium. The atomic radius of trivalent gallium is 0.62 Å, and aluminium 0.57 Å, they are quite similar and therefore most of the gallium in the lithosphere is hidden in aluminium minerals. The distribution of gallium among various aluminium minerals of magmatic rocks follows the rule that the isomorphous substitution tends to concentrate the more strongly bonded components in the earliest and more weakly bonded components in the latest crystallizes of some minerals.

Geochemically gallium is a siderophile as well as lithophile. The valency of Ga is variable 1⁺, 2⁺ and 3⁺. Ga³⁺ compounds are most stable. An important factor in the
geochemical behaviour of gallium is its ability to form complex ions with oxygen and fluorine in the similar way as aluminium and iron.

During weathering, gallium follows aluminium closely and is deposited from the resulting solution into the hydroxylates. Bauxites are especially rich in Ga. The larger part of the gallium from the decomposition of primary aluminosilicates is collected with aluminium in clay minerals or in bauxites when aluminium hydroxides are the product of weathering.

Ga is more abundant trace element more than Pb, U, Sn, Mo or As. It may be seen from the Table XXXVIII the Ga content of bauxites varies from 21 ppm to 46 ppm. The general average content of Ga is 32 ppm. Fig. 37 shows variation of Ga content in the bauxitic profile of the area under study. The moderately high content of Ga in these bauxites indicate possible basaltic source rock. Behaviour of Ga in laterites is similar to bauxites. Ga in the granites and granitic rocks is moderately low. It varies from 12 ppm to 20 ppm, the average being 17.5 ppm. In lithomarge the variation is in between 16 and 21 ppm, (Average 18 ppm).

The constancy of Ga/Al ratio (generally varying between $0.67 \times 10^{-4}$ and $2.00 \times 10^{-4}$) (Table XXXV)
between bauxites and laterites suggests that Ga enters the basin structurally combined with in the lattices of the degraded clay minerals. The average Ga/Al ratio for parent igneous rock is closely similar to the ratio in bauxites and laterites suggests that there is a little separation of Ga and Al during weathering processes. Absorption of Ga with the clays would be favoured by very small grain size of the clays. ( Kirsch, 1963 ).

The Ga/(Na + K) ratio is by no means as constant as the Ga/Al ratio. The ratio is as low as \(0.12 \times 10^{-13}\) and as high as \(99.00 \times 10^{-3}\). Assuming the bulk of Na plus K to be sited in illite and montmorillonite suggests that the coherence of Ga is better with total clay content than with illite plus montmorillonite. It is presumed that a considerable proportion of the Ga might have replaced Al in kaolinite. This is contrary to the view, expressed by N. Laughlin (1959), that the amount of Ga proxying for Al in the kaolinite structure is small. The Ga/Al ratios and Ga contents of the iron rich fractions are low and are in fair agreement with Goldschmidt and Peters (1931) who report a maximum of 3.7 ppm Ga in oxidate Fe ores.

To understand the variation of Al, Ti and Ga,
(Ga \times 10^4)/Al has been plotted against the ratio Ti/Al (Fig. 45). The median line in the figure is only tentative and has been drawn to show the trend. It may be noted that (Ga \times 10^4)/Al tend to increase in Ti/Al. This indicates a close relationship of Al or Ti with respect to Ga.

In the product of bauxitisation, Fe and Al contents may vary within extreme limits among different layers. With such a large variation in concentration over the total thickness of weathered products, it will be difficult to correlate the distribution of Ga with either Al or Fe. Whereas Ti contents in the different zones of bauxite-laterite profile vary within a narrow range, there is a close relationship of Ga and Ti.

Vanadium.

It is one of the most abundant trace element of the upper lithosphere. It is a member of iron family (Goldschmidt, 1929) or the ferrides (Landorgren, 1943). In the upper lithosphere, it is occurring in oxygen compounds of trivalent vanadium. The vanadium is associated with trivalent iron. Vanadium is oxidised to the quinquevalent state in the course of weathering cycle and sedimentation. Vanadium in its quinquevalent
FIG. 45 RELATIONSHIP BETWEEN GALLIUM AND TITANIUM.
state closely resembles with phosphorus.

For divalent vanadium compounds, VO and VS can be mentioned. VS and VO have a close similarity with FeS and FeO. It is clear that V\(^{3+}\) is more closely related to ferric iron and trivalent chromium than to aluminium.

During weathering some of the vanadium is incorporated in the clay minerals formed. The most important phenomenon during weathering of vanadium compounds is the oxidation of V to vanadate ion (\(\text{VO}_4\))\(^{3-}\). \(\text{V}_2\text{O}_5\) readily combines with water to form vanadic acid, which in presence of suitable cations give rise to vanadates. The trivalent vanadium ion is relatively immobile because of precipitation as it is sparingly soluble even at low pH. Quinquivalent vanadium is easily mobilised, and if heavy metals are present in weathering solution, base metal vanadates may be formed. It is likely that quinquivalent vanadium will concentrate in ferruginous horizons in soils and concretions of limonite, while trivalent vanadium will concentrate in the clay fraction.

There is fairly good enrichment of V in bauxites and laterites. It ranges from 170 ppm to 230 ppm. The average value is about 224 ppm. V in the lithomarge is
somewhat higher. Its values ranges between 275 ppm and 338 ppm (average 300 ppm).

There is constancy of V/Al and V/Fo ratios with minor variations (Table-XXXVI). This is probably indicative of close association with the clays. During weathering considerable V may be incorporated into the developing clay minerals possibly due to low solubility and hence relative immobility of V (Cr)₃. Variation in V/Hg ratio could be explained in the same way as variation in the Cr/Hg ratio although the relatively higher Cr/V ratios of bauxites may indicate a concentration of V relative to Cr in montmorillonite.

The higher V/Al ratio and lower Cr/V ratios of the laterites relative to bauxites may be attributed to the adsorption of V onto Fe₂O₃ and Fe (OH)₃.

Chromium.

The geochemistry of chromium may be said to be characterized by the strongly chalcophile character in sulphide-metal system of iron meteorites, a somewhat more strongly lithophile character in oxidized silicate meteorites and by a very strongly lithophile character in the lithosphere of the earth.

Chromium occurs in many valency states. Divalent Cr is found in sulphide compounds of meteoric irons, but
Trivalent Cr is the most important valency state in the geochemistry of the element. The chronic ion radius is very similar to aluminium and ferric iron, so that we have isomorphous substitution in aluminous and ferric minerals. The hydrated trivalent ions are also closely similar. Their ionic radii are Al$^{3+}$ 0.57, Cr$^{3+}$ 0.64, Fe$^{3+}$ 0.67 Å. Under intense oxidation, trivalent Cr is oxidised to equivalent state forming chromate ion ($\text{CrO}_4^{2-}$). This results in mobilisation of the rather immobile chronic ion by transformation into an easily soluble anion. Only little Cr remains in solutions formed during weathering. As a result the precipitates, oxides and evaporates are nearly devoid of Cr, which become enriched in resistates and particularly in the hydrolysates.

The concentration of Cr in the bauxites and laterites is 190 ppm, averaging at 230 ppm. In lithomorphic clay, the variation of Cr is from 150 to 193 ppm (average 163 ppm). The concentration of Cr in the granites and granitic rocks is 12-24 ppm with an average of 18 ppm.

On the basis of Cr/Mg ratio (Fig. 46). It appears that the bauxites have been originated from basaltic rocks (Schroll et al. 1961). This is the most suitable ratio for geochemical characterization of bauxite provenances.
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*Binary correlation diagram of log C of Cu in different rocks.*
There is strong enrichment of chromium in the bauxite/
laterite profile. It seems that chromium is associated with
manganese and iron hydroxides.

The Cr/Al and Cr/Fe ratios (1.5 and 2.0) are moderately
constant suggesting some degree of association of Cr with the
clay fraction (Table-XII). Chromium thus probably enters
in lattice positions within the degraded clays. The Cr/Mg
ratio is higher (15) in the bauxites where less montmorillonite
is present relative to illite. Cr is probably associated
with both illite and montmorillonites reflecting some preference
to the former in accordance with the expected conditions of
formation of the respective clay minerals during weathering.
Illite is formed under rather acid and reducing conditions
which probably allow retention of Cr (as Cr\(^{3+}\)) and its inclusion
in the lattice. On the other hand montmorillonite is formed
under oxidizing and alkaline conditions where Cr may be
converted to the anionic complex Cr\(_2\)\(^{2-}\) and removed in solution.

Frohlick (1960) postulates that bulk of Cr present in bauxites
is associated with clays, particularly illite.

The ferruginous bauxites and the laterites have lower
Cr/Fe ratio than bauxites due to the presence of limonitic
concretions which contain little or no Cr above that included
in the contaminant clay minerals. The conditions under which
Fe\(_2\)O\(_3\) or Fe\((OH)\(_3\)\) are precipitated are such that Cr would
probably be mobilised as Cr\(_2\)\(^{2-}\). Apparently co-precipitation of
Cr \((OH)\(_3\) with iron as the hydroxide has played no significant
part, nor has there been any tendency to form ferric
chromates.