Chapter-IV

GEOCHEMISTRY
4. GEOCHEMISTRY

4.1 SAMPLING AND ANALYTICAL TECHNIQUES

Fresh samples (measuring about 6”x 4”) of the pelites, shales, sandstones and quartzites were collected from the outcrops. Locations of the samples are shown in Fig. 6. The rock samples have been collected from the Paleoproterozoic Sakoli and Sausar basins and the Neoproterozoic Chhattisgarh and Indravati basins of the Bastar craton with a view to observe spatial as well as stratigraphic variations. Extensive care has been taken to collect only the fresh samples from the outcrops. Prior to geochemical analysis, the rocks were studied under the microscope. Effects of alterations were observed in thin sections, and the samples which show least alteration effects, were opted for geochemical studies. After careful petrographic studies from the point of view of secondary alterations, and also for representation of maximum possible spatial and temporal variations of the clastic rocks, altogether twenty three samples were selected for geochemical analysis. Out of the twenty three samples, four pelite and three quartzite samples belong to the Bhiwapur Formation and the Pawni Formation of the Sakoli basin, and the Junewani Formation of the Sausar basin. Seven shale and five sandstone samples belong to the Gunderdehi Formation, the Tarenga Formation, the Lohardih Formation, the Chopardih Formation and the Kansapathar Formation of the Chhattisgarh basin, and two sandstone and two shale samples belong to the Tiratgarh Formation and the Jagdalpur Formation of the Indravati basin (Appendix II).

Rock samples were reduced to smaller size (~3cm) to observe any alteration. The chips were further crushed to yet smaller sizes (~2mm) then washed with distilled water and sun dried. These were then pulverized to ~200 mesh in agate mortar. Major elements
were analyzed on WD-XRF (Siemens SRS 3000) at Wadia Institute of Himalayan Geology (WIHG), Dehradun. The accuracy (% RSD) for major oxide is less than 5 % and the precision is better than 1.5 % (Saini et al., 1998). Details of the analytic techniques, precision and accuracy of the machine are described by Saini et al. (1998). Trace elements including rare earth elements (REE) were analyzed on ICP-MS (Perkin Elmer Sciex ELAN DRC II) at National Geophysical Research Institute (NGRI), Hyderabad. The precision of ICP-MS trace and rare earth element (REE) data is < 5 % RSD for all the trace and rare earth elements. Details of the analytical techniques, accuracy and precision of the instrument are described by Balram et al. (1996). International standards like GSR-4 (sandstone), GSR-5 (shale), ASK-2 (schist), and JG-2 (quartzite) were used for calibration and testing of accuracy. Whole rock major and trace element data of the pelites, shales, sandstones and quartzites are presented in Appendix II.

4.2. GEOCHEMICAL CHARACTERISTICS

4.2.1. NEOPROTEROZOIC SHALES AND PALEOPROTEROZOIC PELITES

4.2.1.1 MAJOR ELEMENTS

The major element analysis of the Neoproterozoic shales of the Chhattisgarh and Indravati basins, and the Paleoproterozoic pelites of the Sakoli and Sausar basins of the Bastar craton are given in Appendix II. Under microscope, the Neoproterozoic shales of the Bastar craton display compositional variation from typical shale to calcite rich shale. This is best depicted by the abundance of CaO in these shales. Therefore, this allows separation of our shale samples into the calcareous shales (the Gunderdehi Formation of the Chhattisgarh basin) at >6 % CaO and the non-calcareous shales (the t'arenge
Formation of the Chhattisgarh basin and the Jagdalpur Formation of the Indravati basin at < 0.3 % CaO. The calcareous shales have lower SiO₂ (43 %), Al₂O₃ (10 %) and Fe₂O₃ (3.3 %) content and higher CaO content (21 %), whereas the non-calcareous shales have higher SiO₂ (64 %), Al₂O₃ (17 %) and Fe₂O₃ (7.39 %) content and lower CaO content (0.1 %). The calcareous shales show large variations in Al₂O₃ content (7 % - 14.23 %) and in CaO content (6.84 % - 35 %). In these shales Al₂O₃ and K₂O content increases with the increase in SiO₂ content and decreases with the increase in CaO content, indicating clay minerals dominantly controlling Al₂O₃, K₂O and SiO₂ contents and calcite controlling the CaO content. The inverse linear trend of CaO against SiO₂ in the calcareous shales may indicate carbonate in these shales to be primary rather than secondary, because the influence of secondary carbonate should result in scatter on CaO – SiO₂ plot (Fig. 13) (Feng and Kerrich, 1990; Gu, 1994).

In comparison to NASC (North American Shale Composite; representative of continentally derived sediments) (Gromet et al., 1984), the non-calcareous shales show enrichment in Fe₂O₃ and K₂O and depletion in Na₂O and CaO. The non-calcareous shales also show concentrations of SiO₂, Al₂O₃, TiO₂, MnO and P₂O₅ similar to NASC. The calcareous shales show depletion in all major elements except for CaO and MnO relative to NASC and the depletion is most in SiO₂, Al₂O₃ and Na₂O (Appendix II).

In contrast, the Paleoproterozoic pelites are characterized by lower SiO₂ (59 %) and higher Fe₂O₃ + MgO (10.41 %) compared to the non-calcareous shales (8.6 %) and NASC. Immobile constituents like TiO₂ (0.75 %), Al₂O₃ (22.02 %) and Fe₂O₃ (8.62 %) are enriched in the pelites compared to the non-calcareous shales, calcareous shales and NASC. Mobile constituents like Na₂O (0.5 % for the pelites and 0.2 % for the non-
calcareous shales) and CaO (0.25 % for the pelites and 0.1 % for the non-calcareous shales) are strongly depleted in the pelites and the non-calcareous shales compared to NASC, whereas the calcareous shales with reference to NASC are depleted only in Na₂O and not in CaO. K₂O is enriched in both the non-calcareous shales (5.5 %) and the pelites (4.8 %) than NASC. However, in the calcareous shales K₂O is lower (2.6 %) compared to the non-calcareous shales, pelites and NASC (Appendix II). The non-calcareous shales and pelites contain very low CaO concentration (<0.3 %), which can be expected to be present in feldspar minerals. Petrographic observation of thin sections also confirms the absence of carbonates and presence of minor amount of plagioclase minerals in these non-calcareous shales and pelites. The calcareous shales and the non-calcareous shales show lower TiO₂ values than do the pelites. The Jagdalpur shales have higher TiO₂ content among the non-calcareous shales and the calcareous shales.

Before we begin to understand how and when major and trace element monitor composition in detrital sedimentary rocks, we need to know which minerals control the element distribution and how the proportions of these minerals vary with lithological composition. One good approach to this problem is to look at a possible correlation between specific elements that monitor the relative abundances of specific minerals.

In the calcareous shales most of the major oxides (except CaO) show positive correlation with SiO₂, Al₂O₃ and K₂O indicating these elements are controlled by clay minerals (Figs. 13, 14 and 15). The plots of Fe₂O₃, K₂O and TiO₂ vs. Al₂O₃ and K₂O yield linear plots for the calcareous shales indicating all these elemental oxides are
Fig. 13. Major oxides (wt. %) vs. SiO₂(wt. %) for the non-calcareous shales and the calcareous shales of the Neoproterozoic Chhattisgarh and Indravati basins and the pelites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
Fig. 14. Major oxides (wt. %) Vs. $\text{Al}_2\text{O}_3$ (wt. %) for the non-calcareous and calcareous shales of the Neoproterozoic Chhattisgarh and Indravati basins and the pelites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
Fig. 15. Major oxides (wt. %) vs. K₂O (wt. %) for the non-calcareous shales and calcareous shales of the Neoproterozoic Chhatisgarh and Indravati basins and the pelites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
incorporated into the clay minerals (Figs. 14 and 15). For the calcareous shales, CaO content decreases with the increase in Al₂O₃ content indicating CaO in the calcareous shales is controlled by calcite (Fig. 14) (Parekh et al., 1977; Cullers, 2002). In the non-calcareous shales and pelites Fe₂O₃, K₂O and TiO₂ also show linear trend against Al₂O₃, indicating all these elemental oxides are incorporated into the clay and mica minerals (Fig. 14).

The positive correlation of Fe₂O₃, MgO and TiO₂ with Al₂O₃ and K₂O in the calcareous shales, non-calcareous shales and pelites indicate clay-mica minerals (phyllosilicates) control on these elements (Figs. 14 and 15). This is suggested by linear trend between Al₂O₃ and K₂O (Fig. 14). All the non-calcareous shales, calcareous shales and pelites have low P₂O₅ and MnO contents. However, the calcareous shales have higher P₂O₅ and MnO content than the non-calcareous shales and pelites (Appendix II). The MnO and P₂O₅ do not show good positive correlation with either Al₂O₃ or K₂O (Fig. 14 and 15). This may suggest that mica and clay (phyllosilicates) fraction are not the only phases controlling these elements in the calcareous shales, non-calcareous shales and pelites. It is possible that minor accessory minerals like Fe-Ti oxides, sphene, apatite, epidote and monazite contain at least some of the Fe, Mg, Ti, Mn and P.

In the non-calcareous shales and pelites. SiO₂ shows negative correlation with Al₂O₃ (Fig. 13), indicating dilution of Al₂O₃ with increase in quartz content. The K₂O/Al₂O₃ ratio of sediments can be used as an indicator of original composition of ancient sediments. The K₂O/Al₂O₃ ratios for clay minerals and feldspars are different (0-0.3, 0.3-0.9 respectively. (Cox et al., 1995). The average K₂O/Al₂O₃ ratio for the calcareous shales varies from 0.19 to 0.27 and for the non-calcareous shales, it varies
from 0.22 to 0.37. In most of the samples, the $K_2O/Al_2O_3$ ratios are close to the upper limit of the clay mineral range, which suggests illite to be dominant clay mineral in these shales.

### 4.2.1.2. TRACE ELEMENTS

Large ion lithophile elements such as Rb, Sr, Ba and Cs behave similarly to related major elements during weathering processes. Like $K_2O$, Rb and Cs will be incorporated into clays during chemical weathering. In contrast, CaO, Sr and Na$_2$O tend to be leached (Nesbitt et al., 1980). Ca, Na along with Rb and Cs are mainly controlled by feldspar, so depletion of Ca, Na, Rb and Cs in the samples may suggest depletion of feldspar in studied samples. The absence of feldspar can be explained either by (i) removal of feldspar by post-depositional dissolution or through weathering in the source area or (ii) by their depletion in the source rocks. Considering the higher concentrations of Rb and Cs in shales and pelites compared to CaO and Na$_2$O, the former seems more probable.

Most of the trace elements have higher concentration in the non-calcareous shales compared to the calcareous shales except for Sr and Ba (Appendix II). Plots of transition elements like Sc, V, Ni, Cr vs. Al$_2$O$_3$ and K$_2$O yield linear plots for both the calcareous and the non-calcareous shales (Fig. 16). This may suggest that these elements in the calcareous and the non-calcareous shales are housed in the clay minerals (Parekh et al., 1977, Cullers, 2002). When Rb and Sr are plotted against Al$_2$O$_3$ and K$_2$O in the calcareous shales, Rb shows a positive linear trend against Al$_2$O$_3$ and K$_2$O, whereas Sr shows a negative linear trend with Al$_2$O$_3$ and K$_2$O (Fig. 17). However, Sr in the
calcareous shales shows a positive correlation with CaO ($r = 0.82$). This indicates Sr is housed in calcite and Rb is housed in clay minerals in the calcareous shales.

The other trace elements (LILEs and HFSEs) like Cs, Nb, U and Zr also show linear trend against $\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}$ (Figs. 17 and 18). However, elements like Ba, Y and Ta do not show linear trend against $\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}$ (Figs. 17 and 18) indicating some accessory minerals other than clay minerals (e.g. allanite for Y and barite for Ba) controlling their abundance.

Overall, the average concentrations of most of the trace elements are quite different in the calcareous shales compared to the non-calcareous shales. Those trace elements that are concentrated in clay minerals are higher in the non-calcareous shales compared to the calcareous shales. In contrast, those major and trace elements that are concentrated in calcite (CaO, Sr) are higher in the calcareous shales when compared with the non-calcareous shales. Most elemental concentrations decrease from non-calcareous shales to calcareous ones. This variation is presumably due to the fact that most elements are concentrated in clay minerals compared to calcite. When compared with NASC, both the calcareous and non-calcareous shales are depleted in transition elements like V, Ni, Cr and Co. However, the non-calcareous shales are enriched in other trace elements (large ion lithophile elements and high field strength elements) like Rb, Cs, Th, Ta and Nb, and show similar concentrations of Sc and Hf relative to NASC. On the other hand the calcareous shales are enriched in trace elements like Sr, Cs, Ba and Th, and show similar concentration of Sc and Th relative to NASC (Appendix II).

Relative to the Neoproterozoic calcareous and non-calcareous shales, Paleoproterozoic pelites are highly enriched in all transition elements especially in Cr
Fig. 16. Plot of transition elements vs. $\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}$ for the non-calcareous shales and calcareous shales of the Neoproterozoic Chhattisgarh and Indravati basins and pelites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
Fig. 17. Plot of large ion lithophile elements (LILE) vs. Al₂O₃ and K₂O for the non-calcareous shales and calcareous shales of the Neoproterozoic Chhattisgarh and Indravati basins and pelites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
Fig. 18. Plot of high field strength elements (HFSE) vs. Al₂O₃ and K₂O for the non-calcareous shales and calcareous shales of the Neoproterozoic Chhattisgarh and Indravati basins and pelites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
In pelites transition elements like Ni and Co show good positive correlation with Al₂O₃ or K₂O while Cr and Sc do not correlate with Al₂O₃ and K₂O (Fig. 16). Average contents of LILE (except Sr and U) like Rb, Cs and Th of pelites are lower than those of the calcareous and the non-calcareous shales. The calcareous and the non-calcareous shales are enriched in LILE especially in Th compared to pelites, while pelites are enriched in HFSE like Zr, Hf, Nb compared to the calcareous and the non-calcareous shales. In comparison to NASC, pelites are enriched in transition elements like Sc, V, Ni and Cr. The pelites are also enriched in other trace elements like Rb, Nb, Cs, Ta, Th, U and depleted in Sr, Y, Zr, Hf relative to NASC (Appendix II). Most of the LILE and HFSE (e.g. Th, U, Rb, Sr) in pelites show good positive correlation against Al₂O₃ and K₂O indicating mica (phyllosilicate) control on their contents (Fig. 17 and 18).

4.2.1.3. RARE EARTH ELEMENTS (REE)

The sedimentary rocks preserve a record of the provenance and the processes of weathering (McLennan, 1989). Rare earth elements (REE) have very similar geochemical properties and are not easily fractionated during sedimentary processes and will not be affected to any great extent during a silicification episode (McLennan, 1989). The REEs are considered to be essentially uniform in abundances in fine grained clastic sedimentary rocks and are not significantly affected by weathering, diagenesis and most forms of metamorphism (Haskin et al., 1966; Nance and Taylor, 1977; Chaudhri and Cullers, 1979). The REEs are therefore very important in understanding crustal evolution. Total REE concentration (ΣREE) in the calcareous and the non-calcareous shales is variable.
with the highest mean value in the non-calcareous shales to be 263 ppm and the lowest
mean value in the calcareous shales being 122 ppm. The $\sum$REE concentrations of the
non-calcareous shales are higher than those of the NASC (183 ppm). The total REE
concentration of the calcareous shales is very much lower than that of the NASC
(Appendix II). The large differences in REE content between the calcareous and the non-
calcareous shales may be due to the reason that REE normally reside in fine fraction (silt
or clay) and it has also been inferred that the trivalent REE are readily accommodated in
most clay-mica minerals (phyllosilicates) enriched with alumina and ferric iron (Cullers
et al., 1987, Cullers, 1988). Therefore, the calcareous shales contains the lowest REE
content due to its higher calcite content, while the non-calcareous shales contain the
higher REE concentrations due to absence of calcite (Haskin et al., 1966). The moderate
positive correlation between REEs and Al$_2$O$_3$, K$_2$O in the calcareous and non-calcareous
shales (Fig. 19) suggests that clay and micas are important in hosting the REEs (Condie.
1991). Aluminum is the main constituent of the clay and mica minerals. It is now
considered that the REE generally reside in minerals like zircon, monazite, allanite and
apatite etc. (McLennan, 1989). The lack of good correlation between LREE and HREE
with Zr in the non-calcareous shales (Fig. 16) suggests zircon does not control the REE
abundances in the non-calcareous shales. However, in the calcareous shales Zr correlates
positively with LREE and HREE indicating zircon control on REE in the calcareous
shales (Fig. 19). In the calcareous and the non-calcareous shales LREE show linear trend
with Th (Fig. 19), while HREE show linear trend with Y (Fig. 19), indicating monazite
control for the LREE abundances and allanite control for the HREE. A negative or
insignificant correlation is observed between P$_2$O$_5$ vs. LREE ($r = 0.27$ for the calcareous
shales).
Fig. 19. Plot of REE vs. Al₂O₃ and K₂O and REE vs. Y, Th and Zr for the non-calcareous and calcareous shales of the Neoproterozoic Chhattisgarh and Indravati basins of the Bastar craton.
shales and \( r = 0.56 \) for non-calcareous shales) and HREE (\( r = 0.44 \) for the calcareous shales and \( r = -0.96 \) for the non-calcareous shales). This suggests that apatite is not controlling either LREE or HREE in the calcareous and the non-calcareous shales (Fig. 19).

In chondrite normalized REE plot (Sun and McDonough, 1989) (Fig. 20), both the calcareous and the non-calcareous shales show highly LREE enriched and flat HREE patterns with negative Eu anomaly. The non-calcareous shales have higher \((La/Yb)_{n}\) ratio (18) compared to the calcareous shales (7), while the \((Gd/Yb)_{n}\) ratio in both the non-calcareous and the calcareous shales do not show much variation (1.9 and 1.4, respectively). The calcareous and the non-calcareous shales also exhibit significant negative Eu anomaly (\(Eu/Eu^{*} = 0.65\) for the non-calcareous shales and 0.8 for the calcareous shales).

The chondrite normalized LREE pattern of the pelite sample no. DS-524 are also fractionated but less than that of the non-calcareous and calcareous shales (Fig. 20) with LREE enrichment \((La/Yb)_{n} = 8.86\) and flat HREE \((Gd/Yb)_{n} = 1.83\) and small negative Eu anomaly \((Eu/Eu^{*} = 0.80)\).

In Figure 20, the REE patterns of the calcareous shales shows strong negative Ce anomaly (especially for the sample no. RD-512) compared to the non-calcareous shales. Ce may oxidize in sea water from the \(3^{+}\) to the more insoluble \(4^{+}\) oxidation state, but the other REEs are not oxidized. The Ce\(^{4+}\) in well oxygenated sea water may then be incorporated into marine sediment thus enriching the sediment in Ce relative to the other REE (Bellanca et al., 1997; German and Elderfield, 1990, Cullers, 2002). This process depletes seawater in Ce relative to the other REEs (Bellanca et al., 1997; German and
Fig. 20. Chondrite-normaized REE patterns for the non-calcareous and calcareous shales of the Neoproterozoic Chhattisgarh and Indravati basins, and a pelite sample of the Paleoproterozoic Sakoli basin of the Bastar craton.
Elderfield, 1990; Cullers, 2002). The Ce/Ce* has been used in sedimentary rocks to interpret the redox conditions in sea water at the time when the REE were incorporated into the marine sediment (German and Elderfield, 1990). The calcareous shales analyzed in this study contain lower average Ce/Ce* (0.86) than the non-calcareous shales (0.93). Present sea water is characterized by Ce/Ce* values of 0.4-0.7 (Elderfield and Greaves, 1982), whereas the average shales typically yield Ce/Ce* values of about 1.0 (Cox et al., 1995; Cullers and Berendsen, 1998). Therefore, the calcareous shales with the average Ce/Ce* value slightly lower than the non-calcareous shales and slightly higher than the present ocean water indicates suboxic conditions for the calcareous shales compared to the non-calcareous shales.

4.2.2. NEOPROTEROZOIC SANDSTONES AND PALEOPROTEROZOIC QUARTZITES

4.2.2.1. MAJOR ELEMENTS

The major element analysis of the Neoproterozoic sandstones of the Chhattisgarh and Indravati basins, and the Paleoproterozoic quartzites of the Sakoli and Sausar basins of the Bastar craton are given in Appendix II. The major element composition of sandstones of all the three formations of the Chandarpur Group does not show much variation. In general the SiO₂ concentration is high (avg. 92.96 wt. %) in all the sandstones of the Chandarpur Group and the Tiratgarh Formation. Pettijohn et al. (1972) employed a diagram to classify terrigenous sands on the basis of log (Na₂O/K₂O) vs. log (SiO₂/Al₂O₃) (Fig. 21). According to this classification scheme, the sandstones are mostly sublitharenite, subarkose and arenite. On the log (SiO₂/Al₂O₃) vs. log (Fe₂O₃/K₂O) diagram (Heron, 1988) (Fig. 22), the sandstones plot in the sublitharenite, subarkose and
arenite fields, similar to Figure 21. The sandstones do not show much variation in concentration of major elements, but oxides like SiO₂, Al₂O₃ and K₂O show little variation in their concentration. The Lohardih Formation has slightly higher abundance of Al₂O₃ and K₂O and lower abundance of SiO₂ compared to the Kansapathar Formation. This is corroborated by the observed decrease in unstable components (like K-feldspar and rock fragments) and an increase in mineralogical maturity from the Lohardih Formation to the Kansapathar Formation stratigraphically. When the major element composition of the Tiratgarh Formation of the Indravati Group is compared with all the three formations of the Chandarpur Group, it shows very much similarity with the Lohardih Formation and the Chopardi Formation of the Chandarpur Group in terms of abundance of all the major elements. This is consistent with petrological observations.

The Paleoproterozoic quartzites show large variation in SiO₂ (75.94 - 95.89 %), Al₂O₃ (1.15 - 10.98 %), Fe₂O₃⁴ (0.09 - 2.22 %), Na₂O (0.05 - 4.79 %) and K₂O (0.25 - 5.09 %). The variation in these major oxides is due to variation in the amount of mica, opaques and quartz as revealed from petrographic studies (Appendix I).

In general, major element abundances of the sandstones and quartzites do not show much difference, except for SiO₂, Al₂O₃, K₂O and Na₂O. Relative to the sandstones, quartzites have higher concentration of Al₂O₃ (6.19 % for the quartzites, 2.5 % for the sandstones), Na₂O (0.07 % for the sandstones, 1.65 % for the quartzites) and K₂O (0.89 % for the sandstones, 2.93 % for the quartzites). The other major elements like Fe₂O₃⁴, P₂O₅, CaO, MgO, MnO are almost similar, while SiO₂ and TiO₂ show very little difference between the sandstones and quartzites. The higher concentration of Al₂O₃.
Fig. 21. Geochemical classification of sandstones of the Chandarpur Group and the Tiratgarh Formation using Log (SiO$_2$/Al$_2$O$_3$) vs. Log (Na$_2$O/K$_2$O) (Pettijohn et al., 1972).
Fig. 22. Geochemical classification of sandstones of the Chandarpur Group and the Tiratgarh Formation using Log(SiO$_2$/Al$_2$O$_3$) vs. Log(Fe$_2$O$_3$/K$_2$O) (Heron, 1988).
K₂O and Na₂O in the quartzites compared to the sandstones is due to the presence of higher amount of mica in the quartzites than in the sandstones (Appendix II).

Relative to the shales, pelites and NASC, sandstones and quartzites are enriched in SiO₂ and depleted in all other major elements. This is due to higher quartz content and lower abundance of feldspar, mica, rock fragments and absence of clay minerals in the sandstones and quartzites. The major oxides like Al₂O₃, K₂O, TiO₂ and MgO show a negative trend against SiO₂ (Fig. 23). On the other hand Na₂O, CaO, P₂O₅ and MnO do not show any linear trend against SiO₂, Al₂O₃ and K₂O (Figs. 23, 24 and 25). In Figure 24 a linear trend of TiO₂, MgO and K₂O can be observed against Al₂O₃. However, TiO₂ and MgO show a linear trend against K₂O (Fig. 25). The little variation of CaO and Na₂O compared to K₂O against SiO₂ and Al₂O₃, and the strong depletion of CaO and Na₂O indicate absence of plagioclase, which is consistent with petrographic observation of dominance of K-feldspar over plagioclase (palgioclase/K-feldspar ratio <1). The oxides like MnO and P₂O₅ have low concentrations and do not show good positive correlation with Al₂O₃ and K₂O (Figs. 24 and 25). This may suggest that minor accessory minerals like apatite, epidote, sphene contain at least some of the Mn and P.

4.2.2.2. TRACE ELEMENTS

Trace elements like large ion lithophile elements (LILE) and high field strength elements (HFSE) are incompatible elements and are thus preferentially partitioned into melts during crystallization and as a result these elements are enriched in felsic rather than mafic rocks. Transition elements like Sc, Cr and Ni are compatible elements and therefore get enriched in mafic rocks (Feng and Kerrich, 1990). In Chandarpur Group.
Fig. 23. Major oxides (wt. %) vs. SiO₂ (wt. %) plots for the sandstones of the Neoproterozoic Chhattisgarh and Indravati basins and quartzites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
Fig. 24. Major oxides (wt. %) vs. Al$_2$O$_3$ (wt. %) plots for sandstones of the Neoproterozoic Chhattisgarh and Indravati basins and quartzites of Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
Fig. 25. Major oxides (wt. %) vs. K₂O (wt. %) plots for sandstones of the Neoproterozoic Chhattisgarh and Indravati basins and quartzites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
abundance of most of the trace elements (e.g. transition elements, LILE and HFSE) decrease from the Lohardih Formation to the Kansapathar Formation stratigraphically, presumably due to decrease in feldspar and rock fragments. In sandstones of the Chandarpur Group and the Tiratgarh Formation, the average contents of transition elements like Ni, Cr, V and Sc, LILEs like Rb (25 ppm), Cs (1 ppm), Sr (16 ppm) and HFSEs like U (0.70 ppm), Th (3.19 ppm), Nb (2.2 ppm), and Y (4.9 ppm) are strongly depleted relative to NASC while trace elements like Co, Zr, Hf and Ta are enriched compared to NASC (Appendix II).

The lower abundances of most of the trace elements in the sandstones may be due to high quartz concentration and low abundances of feldspar, rock fragments and heavy minerals which are consistent with the petrography (Appendix I). Statistically, the Chandarpur Group and the Tiratgarh Formation are indistinguishable in abundance of transition elements, LILE and HFSE except for the higher Ba, Rb, Y, Zr, Th and U contents in the latter (Appendix II).

Relative to the quartzites, the sandstones are slightly depleted in transition elements like Cr, Co and slightly enriched in V and Ni. However, they show similar values for Sc. The LILE and HFSE like Rb, Cs, Sr, Th, U, Nb, Y and Zr are enriched in the quartzites compared to the sandstones. Relative to NASC, the quartzites are depleted in most of the trace elements, while the trace elements like Co, Zr, Hf, Ta, Th and U are enriched in the quartzites relative to NASC. When the average concentration of transition elements, LILE and HFSE of the sandstones and the quartzites are compared with the shales and the pelites, it is observed that the sandstones and the quartzites are strongly depleted in trace elements (except for Co and Zr) (Appendix II). The higher values of
trace elements like Co, Zr, Hf, Ta, Th and U in the sandstones and the quartzites relative to the NASC may be due to sedimentary sorting of certain accessory minerals like zircon (for Zr and Hf) and monazite (for Th). The higher value of Zr in sandstones is consistent with petrography which reveals zircon grains in sandstones. Most of the trace elements show good positive correlation between Al₂O₃ and K₂O indicating K-feldspar or mica control on their abundances (Figs. 26, 27 and 28). Plots of transition elements like Sc, Cr, Ni against Al₂O₃ and K₂O yield linear plots for both the sandstones and the quartzites (Fig. 26). The LILE and HFSE like U, Cs, Th, Rb, Ba and Ta show linear trend against Al₂O₃ and K₂O (Figs. 27 and 28). However elements like Zr, Y, Nb do not show linear trend against Al₂O₃ and K₂O (Figs. 27 and 28) indicating some accessory minerals (e.g. allanite for Y, zircon for Zr) other than feldspar and mica to be controlling their abundance in the sandstones and the quartzites.

Overall, the average concentrations of most of the major and trace elements are quite similar in the sandstones and the quartzites. The minor differences in composition are due to the higher concentration of mica and opaque minerals in the quartzites compared to the sandstones.

4.2.2.3. RARE EARTH ELEMENTS (REE)

Total REE concentration in the sandstones of the Chandarpur Group is variable with the highest value in the Chopardih Formation (39 ppm) and the lowest value in the Kansapathar Formation (13 ppm). However, the ΣREE concentration of the Tiratgarh Formation of the Indravati Group is higher than all the three formations of the Chandarpur Group (76 ppm). The REE patterns of all the three
Fig. 26. Plots of transition elements vs. Al$_2$O$_3$ and K$_2$O for the sandstones of the Neoproterozoic Chhattisgarh and Indravati basins and quartzites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
Sandstones • Quartzites

![Graphs showing plots of large ion lithophile elements (LILE) vs. Al₂O₃ and K₂O for sandstones of the Neoproterozoic Chhattisgarh and Indravati basins and quartzites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.]

Fig. 27. Plots of large ion lithophile elements (LILE) vs. Al₂O₃ and K₂O for sandstones of the Neoproterozoic Chhattisgarh and Indravati basins and quartzites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
Fig. 28. Plots of high field strength elements (HFSE) vs. Al₂O₃ and K₂O for sandstones of the Neoproterozoic Chhattisgarh and Indravati basins and the quartzites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
formations of the Chandarpur Group of the Chhattisgarh basin and the Tiratgarh Formation of the Indravati basin are uniform and there are no systematic differences in REE patterns among different formations of the Chandarpur Group and the Tiratgarh Formation (Fig. 29).

When the mean REE concentration of the Paleoproterozoic quartzites are compared with the Neoproterozoic sandstones, it is observed that the quartzites have higher REE mean value (145 ppm) than the sandstones (34 ppm). However, on an average, the sandstones and the quartzites have REE abundances lower than that of the shales and NASC. The REE contents show large variations between the quartzites and the sandstones. It may be due to the reason that REEs are normally reside in fine fraction and it has been inferred that trivalent REEs are readily accommodated in most of the clay-mica minerals (phyllosilicates) enriched with alumina and ferric iron (Cullers et al., 1987: Cullers, 1988). This is also corroborated by the observed positive correlation of REE with Al₂O₃ and K₂O (Fig. 30). Thus, the sandstones with lower mica content have lower REE content, while the quartzites with higher percentage of mica content have higher content of REE than the sandstones (Haskin et al., 1966). Good positive correlation of LREE and HREE with Zr, Th and Y of the sandstones indicate allanite, monazite and zircon control on REE (Fig. 30). In contrast, LREE and HREE in the quartzites do not show good correlation with Zr, Th and Y indicating little or no control of allanite, monazite and zircon on REE in the quartzites (Fig. 30).

In chondrite normalized plot (Sun and McDonough, 1989) both the sandstones and the quartzites show LREE enriched and flat HREE patterns with negative Eu anomalies (Fig. 29). Although there are variations in absolute concentration of REE
Fig. 29. Chondrite-normalized REE patterns for sandstones of the Neoproterozoic Chattisgarh and Indravati basins and quartzites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
Fig. 30. Plots of REE vs. Al₂O₃ and K₂O and REE vs. Y, Th and Zr for the sandstones of Neoproterozoic Chhattisgarh and Indravati basins and the quartzites of the Paleoproterozoic Sakoli and Sausar basins of the Bastar craton.
between the sandstones and the quartzites, they have almost similar ratios of LREE/HREE (10.50 for the sandstones and 11 for the quartzites). The REE patterns of the sandstones and the quartzites are highly fractionated and uniform with LREE enrichment \((\text{La/Yb})_n = 12.5\) for the sandstones and 12 for the quartzites, flat HREE \((\text{Gd/Yb})_n = 1.56\) for the sandstones and 1.42 for the quartzites, and significant Eu anomaly \((0.67\) for the sandstones and 0.47 for the quartzites). There are no systematic variations in REE patterns between the sandstones and the quartzites (Fig. 29).