6.1 Behaviour of elements in different chemical species

The seven fractions separated to study the speciation of elements during weathering of amphibolites and gneisses, are defined operationally by using specific reagents to separate them. These fractions represent different phases formed during weathering and have their specific importance in terms of sequestering elements. In general it is found that distribution and behaviour of elements during weathering of rocks is related to their inherent chemical properties and the pressure, temperature and pE conditions of earth's surface (see GG425). However, being operationally defined procedures, sequential extractions inevitably give results that are dependent on the extraction parameters such as type, concentration, and pH of each reagent, sample weight to extractant volume ratios, extraction times and temperatures, methods of shaking and phase separation, etc (Shiowatana et al, 2001; Sahilquillo et al, 1999; Maiz et al, 1997). In the present study, the elements selected were observed to follow distinct pattern of their behaviour inspite of the differences in the lithology and the climate.

Alkali and alkaline earth elements, Ca, Mg, Na, K, Sr and Ba behaved in a similar manner and are found to be largely associated with water soluble, exchangeable and organic fractions. The ions like Na, Ca, Mg, K are easily mobilized in this form but their presence in the rock pores may facilitate rock weathering through precipitation and saturation (Puhringer, 1985). Although very little quantities of Na, K and Mg are present in water soluble forms during amphibolite and gneisses weathering, it provides important information about their mobility and bioavailability. These electropositive elements with constant valence states find appropriate binding sites at negatively charged surfaces of clay minerals such as montmorillonite and smectite formed during weathering (Grim, 1962). The elements Ca, Na, K are largely associated with exchangeable sites of the secondary clay minerals by electrostatic or Van-der-Walls forces. It is interesting to note that these elements are also the major nutrient elements for plants. Plants take up nutrient elements from soil through ion exchange process using H ions. It is observed that other alkaline earth elements Sr and Ba behave similar to Ca as per their association with the exchangeable fraction.
Carbonate fraction represents the carbonate phases formed due to precipitation of carbonates under specific conditions of pH and water availability. This is also a relatively temporary phase to hold elements absorbed by them which can be released under changed pH conditions of the environment (Yuan et al, 2004). Only a few elements such as Mg, Mn, Ba, Co and Ca in the fresh rock samples were found to get associated with this fraction. The importance of this fraction disappears as the weathering intensity increases. Again this fraction surprisingly plays some role in the gneissic rocks and not in amphibolites for reasons not readily understood; in general amphibolites have about 20% MgO and CaO, the carbonate forming oxides. Al, Fe, Cu, Ni and Zn are also present in carbonate fraction especially in the fresh rock samples of gneisses. Presence of Al in this fraction can be attributed to the use of highly acidic reagent (pH<5), acetic acid, for extraction of carbonate fraction. Low pH conditions might affect the dissolution of Al present in other phases or in some aluminosilicate minerals susceptible to be attacked by this reagent. It is not known if the differential behaviour of these elements in this particular fraction between mafic and felsic rocks is an artifact of experimental procedures followed here.

Mn-oxides are the reactive mineral phases in amorphous forms during weathering of rocks in soils and sediments. The fraction representing this phase hosted Mn, Co and Ba specifically and in significant quantities for both types of rocks. Mn oxides have high sorptive capacities and therefore adsorb a wide range of ions, controlling the distributions and bioavailability of many toxic and essential elements, especially in the aquatic ecosystem (Goldberg 1954).

A majority of transition elements were found to get adsorbed to iron oxide phases. This phase is separated into amorphous and crystalline fractions to differentiate the two forms of iron-oxide phases formed during weathering. Both amorphous and crystalline iron-oxide phases fractionated in the present study are secondary phases as it is not possible to break down primary iron oxide phases of the minerals by the present method of fractionation. The variable valences of the transition elements facilitate their adsorption on the iron oxide phases. Hence held in this phase the elements are not readily available for plant uptake or mobilization. As the weathering progresses the elements get enriched in this fraction. The present speciation study supports the low mobility of Al, Fe, V, Cr as observed in weathering studies (Middleberg, 1988) as they are held in iron oxide fractions.
The organic fraction emerged out to be the most significant fraction among the seven studied fractions. Invariably all the elements are found to be present in this fraction at some stage of weathering. This fraction represents the microbial population present in the weathering profiles which enter the rock crevices as early as the entry of water and alter the chemistry of the rocks exhibiting biological weathering. The microbes produce chemicals to disintegrate rocks and obtain energy through chemical reactions (Gorbushina, 2007). The metabolic products of the microbes as well as chemicals produced by them include a variety of ligands and chelating agents and bring about chemical weathering. Hence, this fraction provides binding agents to incorporate elements of different chemical properties as Al, Fe, alkali, alkaline earths and other transition elements (Allard, 2004; Neaman et al, 2005). The elements present in this fraction are either in the form of organometallic compounds, as ions bound to organic chelates or as dissolved organic complexes. During weathering of amphibolites under semi-arid conditions and of gneisses under all conditions, this fraction hosts elements in significant amount however the percent organic carbon content of amphibolite weathered samples was found to be low (Table 4.2). This fraction is also responsible for mobilization of relatively less mobile elements like Fe and Al by formation of soluble organic compounds (Tipping, 2002). Moreover, the transportation of organic colloids with water and as suspended load of rivers is highly relevant in relocation of elements into sediments and river water which can be further implied to the farmland geochemistry under the floodplain of the river.

6.2 Behaviour pattern with increasing weathering extent during progressive weathering

As weathering progresses in a weathering profile the elements attain different chemical forms and phases with the extent of weathering. The primary minerals break down, new minerals are formed and some ions are released. It is observed in the present study that elements either get enriched or depleted in the fractions hosting them, with the increasing weathering extent. As the weathering progresses Ca content of the rocks decreases significantly in the organic fraction except that Ca was lowest in this fraction in the freshest rock sample. Al and Fe increase with extent of weathering under high rainfall conditions but show a decrease in most weathered sample in all fractions. Trace elements such as V, Cr, Ba, Ni, Co, Cu and Zn tend to get enriched in Fe/Mn oxides as the weathering progresses in the profile. However, Mg, Sr, Na and K, present in exchangeable fraction, decrease with the increasing extent of weathering. Water soluble
and exchangeable fractions make the elements get carried away freely with flow of water as soon as they get mobilized in this fraction. This process of loss of elements is more pronounced under high rainfall conditions.

The observation shows that the elements bound with Fe/Mn oxides generally get enriched with the extent of weathering, that include Al, Fe, Mn and the trace elements. On the other hand alkali and alkaline earth elements such as Ca, Mg, Na and K, are highly mobile and are lost from the profile with the extent of weathering.

6.3 Speciation of elements during weathering in two rock types - amphibolites and gneisses

The speciation of elements during weathering of rocks of different lithology is observed to follow similar pattern. However, when observed closely, the differences lie in the quantitative distribution of elements among the defined fractions. Amphibolite weathering results in distinct distribution of elements in fractions such as alkali and alkaline earths in exchangeable and organic fractions and transition elements in Fe/Mn oxide fractions. While the weathering of gneisses do not show such distinction in the distribution of elements as some transition elements such as Cu, Ni and Zn are also found to be present in exchangeable fraction. The organic fraction formed during gneissic weathering concentrated more elements and in higher quantities than the amphibolites. As all the gneissic weathering profiles selected for the study are covered by soil on the top with vegetation cover, the organic fraction here seem to play even more important role in distribution of the elements. The organic acids produced at the top of the profile, due to litter decomposition and activities of variety of soil microbes, is likely to leach through the weathering profile and reach the bedrock. In this way probably additional organic matter is available for biological weathering of the gneisses which affects the association of more and more elements with organic fraction (Huang et al, 2002). The amorphous iron oxide fraction also hosted V, Al, Ni and Fe in higher quantities during weathering of gneisses which was lower in amphibolites. Carbonate fraction was observed to hold Fe, Cu, Ni and Zn in gneisses, particularly in the fresh rock samples. However, for amphibolites, only Mg, Mn, Ba, Co and Ca are present in carbonate fraction.

In conclusion there is no fundamental difference in the distribution of elements during weathering of the two rock types, amphibolites and gneisses, implying that the behaviour of elements is primarily decided by the chemical properties of the elements and
their affinities for the different phases under physical and chemical conditions of the environment.

6.4 Speciation of elements under different rainfall conditions

The weathering profiles developed under contrasting rainfall conditions for both amphibolite and gneissic rocks were selected to study the effect of rainfall on the distribution of elements. The weathering of amphibolites is observed to be affected by the amount of rainfall received by the area. Under high rainfall conditions (> 400 cm/year) the mobile elements such as Ca, K and Na are lost from the system; the loss of Na was higher than that of K as the smaller size of Na help it to escape all the structural hindrances present in the soil while K gets associated within the interlayer positions in the clay minerals. Under high rainfall conditions Al and Fe get enriched in crystalline Fe-oxide fraction whereas organic fraction is the main host for these two elements under low rainfall conditions. Ca, Mg and Cr are not affected much by the amount of rainfall except that in low rainfall conditions Ca was lost from organic fraction significantly. Under high rainfall conditions Sr is concentrated in exchangeable fraction but in low rainfall it is spread in more fractions. Ba and V have decreased in low rainfall conditions but distributed significantly in carbonate fraction along with other fractions which is not visualized under high rainfall conditions. Mn, Co, Cu and Ni are low in semi-arid conditions.

The amphibolite weathering profiles developed under semi-arid regions are observed to have higher concentration of Ca and K in exchangeable fraction and Mg in carbonate and organic fractions. This implies that rate of loss of elements under low rainfall conditions are minimum. The weathering of gneisses under different rainfall conditions does not show major differences in the distribution of elements. However, some elements are quantitatively less in their respective fractions under low rainfall conditions such as concentration of Mg in carbonate fraction, Fe and V in crystalline Fe-oxide, Mn and Co in Mn-oxide and Ni in organic fraction. Na is enriched in exchangeable fraction in semi-arid conditions but is lost from the profile under high rainfall. Differences are also evident in the clay mineralogy and degree of weathering experienced by the rocks under different rainfall conditions. Under high rainfall conditions, gibbsite and goethite are formed while the weathering was restricted to smectite under semi-arid conditions.
6.5 Distribution of nutrient elements in soil, sediment and water

The speciation of elements during weathering of rocks is studied here to understand the distribution and bioavailability of elements required by the plants for their growth and metabolic activities. It is known that plants obtain all major and trace nutrients except C, H and O from the soil; hence they are called mineral nutrients (Hopkins, 1999). We understand that the elemental composition of the soil, and the soil itself, is derived from rocks through the process of weathering. Breaking down of rocks through physical, chemical and biological forces is also accompanied with many physical changes in the system as new phases and minerals appear in the weathering profile. The elements released from the rocks in the process of weathering acquire various chemical forms and get distributed in different geological components. Presence of an element in soils does not ensure its availability to the plants, bioavailability is a complex function of many factors including total concentration and speciation of elements, mineralogy, pH, redox potential, temperature, total organic content (both particulate and dissolved fractions), and suspended particulate content, as well as volume of water, water velocity, and duration of water availability, particularly in arid and semi-arid environments (John and Leventhal, 1995). Nutrient elements studied in the present work, such as Ca, K, Mg and Fe, Sr, Mn, Ba, Co, Cu and Zn are also distributed among different phases according to their chemical properties, local physical conditions as well as the structural chemistry of the phases. It has been observed that Ca, K and probably Mg are mainly associated with exchangeable fraction, and hence readily available to the plants through the natural process. The presence of Mg in carbonate fraction makes it available when pH of the system changes. Plants take up nutrients in the form of soluble ions from the soil solution through passive absorption (Hopkins, 1999). This process occurs through osmosis when the concentration of nutrients is higher in the soil. However, the abundance of all the nutrient elements in the soil is not possible under natural conditions. Hence major proportion of nutrient uptake by plants occurs through active absorption which happens through exchange of nutrients present at the exchangeable sites in the soil with H ions. This makes the exchangeable fraction the most suitable fraction to hold the elements required by the plants hence restricting them from getting washed away in soluble forms.

Another important aspect is the presence of elements required by the plants in organic fraction. All the nutrients present in exchangeable fraction are also present in organic fraction. Moreover, trace nutrients required by plants in fewer quantities also
occur in organic fraction (Stordal, 1996). This is of special significance because organic fraction acts as reservoir for these elements and releases them time to time with changes in pH and Eh conditions of the environment (Viets, 1962). In many instances trace elements move through biological membranes in the form of complexes of chelates with organic ligands (Stewart, 1963; Jones, 1998). The microbial activities and the presence of organic compounds make the elements bioavailable and increase their mobility. Trace elements such as Cr, Sr are required by plants but become toxic when present in large quantity. Thus aggregation of these elements with organic matter and their controlled release is a part of biological management to maintain favourable conditions in the soil for the growth of plants.

Organic fraction not only provides nutrients to the plants but also act as important structural and active component of the weathered material which pave the way for formation of soil at a faster rate (Rogers and Bennett, 2004). This fraction along with exchangeable fraction constitutes the colloidal suspended load of rivers and help in the long distance transport of the nutrient elements. The dissolved components of river water contributed by the water soluble fraction of weathering products, and along with the nutrient rich suspended load, contribute to the fertility of floodplains and deltas of rivers. Natural irrigation of agricultural fields with river water provides the necessary plant nutrients in various forms. Hence periodic and seasonal flooding is necessary for the productivity of a farmland as river flooding results in the deposition of its suspended load.

The weathering products are carried away from the source of their generation through various geological agents and form sediments elsewhere. The nutrient rich weathering products as sediments, obtained from low rainfall region, are expected to contribute more to the fertility of the farmlands of which they are part as they are observed to retain nutrient elements in high quantities. The nutrient elements in ionic forms dissolved in the river water, the suspended load of the rivers comprising clay and organic colloidal organic matter also determine the fertility of farmland, especially in the areas irrigated with river water.

6.6 Major implications of the study

The role of organic matter in the distribution of elements during weathering of amphibolites and gneisses is the most important finding of the present study. As
weathering progresses and soil is formed, the organic fraction plays more important role of not only reservoir of nutrients of soil but also the structural component of the soil. The higher the organic matter content of the soil, the better is its quality for the growth of the plants.

The present study shows that all the nutrient elements are present in at least some quantities in the organic fraction. This fraction acts as a store house for major as well as trace nutrients and release them in bioavailable forms (Viets, 1962). A variety of elements get associated with this fraction, which also included heavy metals such as Cr, Sr, Ni, Cu that are harmful for living beings if present in available forms in the environment. The binding of these metals with the organic matter through various ligands can make them available in the soluble forms and help in their free mobility to other geological components such as sediments, surface water and ground water (Williams, 1967).

Very small organic particles are carried away in water bodies as colloidal particles (0.2-0.4 microns). The elements in exchangeable and organic fractions, which are mostly nutrient elements, constitute the major portion of suspended load of the rivers (Pacini and Gachter, 1999). These organic compounds carried by the rivers as suspended load are the best medium for translocation of elements in places farther and wider from their sources of origin thus allowing their distribution in different geological environments, from mountains to plains for example. Through periodic floods the nutrient load of the rivers is deposited on the floodplains and help in the replenishment of the fertility of the farmland. Floods cause hydraulic disturbance that determines the composition of biotic communities within the channel, the riparian zone and the floodplain (Junk et al., 1989; Webb et al., 1999). As observed by Dupre and coworkers (1999), the lighter suspended particles are carried by the rivers throughout its course only to deposit them at the delta when coagulation and segregation of organic matter occurs. The spatio-temporal heterogeneity and chemistry of river systems is responsible for a diverse array of dynamic aquatic habitats and hence ecological diversity, all of which is maintained by the natural flow regime. It is flooding and the consequent transfer of material that makes rivers and floodplains among the most fertile, productive and diverse ecosystems in the world. The delta region is therefore rich in nutrients and is highly productive. The old practice of using unbounded river water for irrigation is natural method to provide nutrients to the farmland.
Construction of dams on the rivers to hold the water for long periods affects the natural process of replenishment of farmlands. Dams alter the natural distribution and timing of stream flows in order to meet human needs. As such, they also alter essential processes for natural ecosystems; constitute obstacles for longitudinal exchanges along rivers by altering the pattern of downstream flow (i.e. intensity, timing and frequency), change sediment and nutrient regimes and alter water temperature and chemistry. When the flow of water is held for a long period of time, the suspended load which comprises of ions, clay particles and organic compounds tend to flocculate and settle at the bottom of the reservoir. The water discharged from reservoirs can be of a different composition to that flowing into the reservoir as water storage in reservoirs induces physical, chemical and biological changes and it is devoid of its large proportion of the suspended load which is actually responsible for the fertility of soil. This poses serious environmental problems as availability of water do not match with the nutrient requirement of farmland and more and more artificial fertilizers are required to obtain the same crop yield. Heavy use of fertilizers is also a threat to soil and aquatic ecosystems and thus the cyclic process of environmental degradation starts. Under natural conditions sediment feeds floodplains, creates dynamic successions, and maintains ecosystem variability and instability (Petts, 1996). Changes in sediment transport have been identified as one of the most important environmental impacts of dams. The reduction in sediment transport in rivers downstream of dams not only has impacts on channel, floodplain and coastal delta morphology (Acreman et al, 2000), but also alters habitat for fish and other groups of plants and animals through changes in river water turbidity.

Reduction in stream flow of rivers can also have considerable impacts on vegetation in downstream delta and coastal areas. For example, dam construction and operation in the Indus basin has reduced flow by more than 80% (McCully 1996). The Tabela Case Study (2000) of World Commission on Dams reports that with the increased abstraction of water upstream in the Indus basin, the quantity of silt reaching the delta has been reduced. The greatest impact is on estuarine mangroves that once covered over 1 million ha. The sediment brought down to the delta is now estimated at about 60 Mt per year, about one fifth of original quantities (Warsi, 1991; Kijine et al., 1992; Ahmad, 1993a; Mohtadullah, 1997). Only 10% of original delta is left as active delta and the reduction in the sediment discharge has changed the balance between erosion due to high energy waves and sediment deposition, towards erosion. Mangrove forest needs sediment
as part of its habitat renewal mechanism. The reduced freshwater and sediment flow plus human encroachment contributes to further mangrove degradation. These changes have even affected the total site biodiversity as mangrove species in the delta have decreased from the eight recorded species to a virtually mono-specific mangrove stand.

Freshwater flows support marine fish production due to abundance of nutrients in the dissolved and suspended load of the rivers, which makes the estuarine area highly productive. Hence the reduction in freshwater flow affects fish population, greatest in the first year of the life of fish population. As fish abundance is normally determined during the egg and larval stages (Drinkwater and Frank 1994), a decrease in freshwater flow and nutrients with the river discharge may affect the nursery areas by reducing the available food supply. Other problems associated with low and untimely discharge of river waters will be increased salinity and invasion by predatory marine fishes. These impacts are well illustrated by the effect of the Aswan High Dam on the coastal waters of the Mediterranean (Aleem 1972; Drinkwater and Frank 1994) where reduction in nutrients transported to the sea has reduced production at all trophic levels, resulting in a decline in catches of sardines and other fish (Chen, 2002). In the Zambezi delta the impact of modified seasonal flows on shrimp fisheries has been estimated at 10 million dollars per year (Gammelsrod, 1992).

The most important implication of the present study is that we have understood that nature has its ways to decide the chemistry of soil, river water as well as sediments in favour of mankind unless disturbed by anthropogenic activities. The processes occurring at the basic level in nature, which includes weathering, precipitation, natural course of river and periodic flooding are responsible to build fertile farmlands and sustain farming for at least several millennia.