Abstract

Weathering of rocks is the fundamental geochemical process occurring on the surface of the earth and one of the principal mechanisms controlling the geochemical distribution of elements, which operates at the interface of atmosphere, hydrosphere, lithosphere and biosphere. This is also fundamental to major geomorphologic processes occurring on the surface of the earth. The weathering products in soluble ionic forms derived from an area determine the chemistry of the water bodies. Also the weathering products including the secondary minerals are eroded and transported as sediments to get deposited elsewhere and form most of the farmland areas. In this way all the geological components of the earth are directly or indirectly affected by the weathering of the rocks. Mobility of elements and their partitioning into various geochemical phases, as a result of weathering, play an important role not only in determining the chemistry but also decide the fertility of the farmland. The bioavailability of elements, especially nutrient elements, during the natural course of soil formation determines the fertility of farmland and hence the crop production. However, the mobility and bioavailability of elements in the environment are determined by the chemical form of an element which cannot be understood by the traditional study of bulk composition of rocks during weathering. The elements associated with sediments are also influenced by their specific chemical form(s) and transport dynamics. Study of partitioning of these elements amongst various geochemical phases helps to evaluate the process of their downstream transport, deposition and release under changing physical, chemical and biological conditions in terrestrial as well as aquatic environments. This distribution of elements amongst defined chemical species in a system is termed as speciation by the International Union for Pure and Applied Chemistry.

The study of speciation of elements during weathering will provide a better understanding of the geochemistry of soil, river and sea water and the elemental distribution therein. Most importantly, this also tells us about the factors responsible for the natural fertility of the soil, which is not yet understood clearly. Speciation studies have long been used to identify and quantify the heavy metals and toxic forms of elements present in various ecosystems, which pose threat to the health of living beings.
on transport mechanisms, mobilization and transformation of elements through various chemical forms under different environmental conditions e.g., acidic, alkaline, oxidizing or reducing. Realizing the importance of speciation of elements during weathering the present work has been undertaken to understand how various elements redistribute and attain different chemical forms during weathering of rocks, under different rainfall conditions in the Mysore plateau, southern India.

For the study of behavior of elements in a weathering system like the present work, the sequential extraction procedure helps to identify different phases formed in the soil as a result of weathering process. The presence of elements in specific fractions provides information about their probable chemical forms in the sample and helps to understand the pattern of their behavior during weathering. After extensive literature survey, the sequential extraction procedure developed by Leleyter and Probst (1998) was adopted for the present study which is a modification of established sequential extraction method used for sediments by Tessier et. al. (1979). It allows for differentiating and extracting seven distinct fractions and hence separating seven phases of soil in the present study which meets the requirements of study of weathering system the most. Since matrix effects are involved in heterogeneous processes of extraction and separation, there is no general agreement as to which chemicals should be used to extract elements from the various chemical phases. The aim of the study, type of samples and the elements of interest determine the choice of extractant for sequential extraction. However, repeatability of the extraction process supports its reliability and encourages the application of sequential extraction in varied fields.

The distribution of elements in seven different fractions is studied to understand their behavior and affinities for the different phases present in the soil during rock weathering. The rock chosen for the present study is amphibolites because of its high weatherability and widespread occurrence in southern India. Being basaltic in composition, this rock type is a major component of the earth's crust. Speciation of elements during the weathering of host gneisses is also studied under similar climatic conditions to compare the behavior of elements in two major rock types.

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. A very small quantity of Na, K and Mg are present in water soluble
forms during amphibolite's and gneisses weathering. Elements such as 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. Carbonate fraction represents the carbonate phases and 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. Mn-oxides are the reactive mineral phases formed in amorphous forms during
weathering of rocks. The fraction representing this phase hosts Mn, Co and Ba
specifically and in significant quantities for both types of rocks. A majority of transition
elements were found to get adsorbed on 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. As the weathering progresses the elements get enriched in this
fraction. 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 and mineral fractures as early as the
entry of water and alter the chemistry of the rocks promoting biological weathering. 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 amounts; however, the organic carbon content of
amphibolite weathered samples was found to be low. This fraction is also responsible for
mobilization of relatively less mobile elements like Fe and Al by the formation of soluble
organic compounds.

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.

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.

Presence of an element in soils does not ensure its availability to the plants, and 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. 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.

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. 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.

The major implication of the present study is in terms of realizing the importance of organic matter in the distribution of elements and determining the geochemistry of soil, sediments and water on the surface of the earth. The elements, especially nutrient
elements, are carried in the rivers in organic colloidal forms which are the major source of nutrient elements for the floodplain agricultural fields. Naturally occurring floods are essential to replenish the nutrients in soils/sediments, lost by harvesting in the farmland. However, constructions of dams on large scales is playing havoc on natural systems as these nutrient rich organic colloids present in the river water aggregate and settle at the bottom of reservoirs when the water is stagnant. Hence the use of stored water in dams is encouraging more complicated problems arising through excessive use of fertilizers and ultimately the productivity of the sea.