Chapter 1

Introduction

1.1 INTRODUCTION

Weathering and erosion of rocks on continents are important processes in the geochemical cycles of elements. These processes regulate the composition of the atmosphere, the oceans and the sedimentary rocks. Rivers serve as the major pathways through which the continental rain and weathering products reach the oceans. The nature and extent of physical and chemical weathering, which together constitute continental denudation, are reflected in the sediment (suspended and bed) load and dissolved constituents of the rivers respectively. Chemical weathering of bedrocks depends on a number of variables, two of the important ones being lithology and availability of protons for chemical reactions. Protons are provided by carbonic acid, produced from solution of CO_2 and sulphuric acid, released from oxidative weathering of pyrites. This makes chemical weathering a major process in controlling the atmospheric CO_2 budget. Among the chemical weathering processes, silicate weathering is unique as it is responsible for CO_2 drawdown from the atmosphere and hence serves as a negative feedback in stabilizing the global temperature on a million-year time scale (Berner and Berner, 1997). Thus, geochemical and isotopic investigation of rivers provide valuable information on biogeochemical cycles, fluxes of elements and isotopes to the ocean, weathering and erosion rates of continents and contemporary CO_2 consumption via chemical weathering. Further, understanding the geochemistry of elements and isotopes, which serve as potential tracers to study various Earth System Processes at present and in the past, requires knowledge on their release via rock-water interaction in the natural aqueous environments and their behavior during transport in the rivers.

The origin and uplift of high mountains in a region, bring about climate change, influences the general hydrology and fluvial dynamics; and modifies the regional landscape (Ruddiman and Prell, 1997). One example of this is the Himalayan uplift and associated climate change. The Himalaya, 2400 km long and 250 to 300 km wide mountain barrier, rising to 500-8000 m above sea level, critically influences the atmospheric circulation of the Asian continent and exercises a dominant control on its climate. The mountain range is responsible for the unique monsoon climate that prevails in the subcontinent. There are about 1500 glaciers in the Himalaya, spreading over nearly 33,200 km^2 in the higher altitudes, which have an important role in the water budgets of the Himalayan rivers (Valdiya, 1998).

The rivers draining the Himalaya, a relatively young active mountain chain, contribute significantly to the global water and sediment discharge (Milliman and Meade, 1983; Berner and Berner, 1996) and influence the oceanic elemental and isotopic geochemistry. It is suggested that the uplift of the Himalaya and associated monsoonal rainfall, rapid physical erosion, all contribute to enhanced chemical weathering of silicates which in turn results in increased consumption of atmospheric CO_2. The drawdown of atmospheric CO_2 via silicate weathering in the Himalaya has been invoked as a driver of the Global Cenozoic cooling (Raymo and Ruddiman, 1992). This hypothesis is in line with the knowledge that chemical weathering of silicate minerals in the continents serves as the primary sink for atmospheric CO_2 on a multi-million year time scale. The enhanced chemical weathering in the Himalaya has also been thought to influence the major ion and various trace metal and isotopic budgets of the oceans. For instance, the steady rise in $^{87}Sr/^{86}Sr$ and $^{187}Os/^{186}Os$ of the seawater through late Cenozoic has been ascribed to weathering of silicates and organic rich sediments in the Himalaya (Raymo and Ruddiman, 1992; Richter et al., 1992; Pegram et al., 1992; Turekian and Pegram, 1997). Similarly, weathering in the Himalaya has also been proposed to be controlling the marine uranium budget (Sarin et al., 1990). Indeed, the Sr isotope evolution of the oceans through the Cenozoic has been used as supporting evidence in favour of enhanced silicate weathering in the Himalaya (Raymo and Ruddiman, 1992; Richter et al., 1992). This suggestion has become a controversy and the use of high radiogenic Sr isotopic composition in rivers as a proxy for silicate weathering has become a matter of debate. Such a controversy has sparked interests among a number of researchers to take up geochemical studies in the river basins of the Himalaya.

The results of Palmer and Edmond (1989) and Krishnaswami et al. (1992) showed that rivers draining the Himalaya, especially the head waters of the Ganga-Brahmaputra (G-B) system, have very high radiogenic Sr isotopic composition (high $^{87}Sr/^{86}Sr$) and high Sr abundance compared to other major rivers in the world. This lent support to the hypothesis of Raymo and Ruddiman (1992). Richter et al. (1992), based on the then available data on Sr fluxes from the Himalayan rivers, their $^{87}Sr/^{86}Sr$ and timing of the uplift of the Himalaya, concluded that chemical weathering associated with Himalayan Orogeny could have accounted for the observed increase in $^{87}Sr/^{86}Sr$ of the oceans during the Cenozoic.

Though there is a general consensus that rivers draining the Himalaya have contributed significantly to the Sr isotopic evolution of the oceans, the issues concerning the source(s) of high radiogenic Sr (^{87}Sr) in these rivers, its mass balance in them and the use of $^{87}Sr/^{86}Sr$ in the rivers as a proxy of silicate weathering have been a matter of intense debate and remain contentious. Krishnaswami et al. (1992) proposed that granites/gneisses in the Himalaya, with very high $^{87}Sr/^{86}Sr$ as possible source for high ^{87}Sr in the rivers of the Ganga-Brahmaputra (G-B) system. Harris (1995) suggested metasediments from the Higher Himalaya as candidates for the high $^{87}Sr/^{86}Sr$ in these river waters. Palmer and Edmond (1992), Quade et al. (1997), Blum et al. (1998) and English et al. (2000) proposed that the metamorphosed carbonates and calc-silicates in the Himalaya, which acquired high ^{87}Sr from the coexisting silicates during fluid exchange via widespread metamorphism, could be sources for high $^{87}Sr/^{86}Sr$ in the rivers draining the Himalaya. Galy et al. (1999) concluded that silicates in the Lesser Himalaya and in the Siwaliks are sources of the high $^{87}Sr/^{86}Sr$ in the Ganga-Brahmaputra rivers. Blum et al. (1998) and Jacobson and Blum (2000), based on studies of the Raikhot watershed in the Nanga Parbat region, proposed that disseminated calcite occurring in trace amounts in the silicate rocks is the predominant source of dissolved Ca and Sr to the streams draining the silicate bedrock. If carbonates or disseminated calcites truly control the Sr and its isotopic composition in rivers draining the Himalaya, the idea of using $^{87}Sr/^{86}Sr$ in the river waters as a proxy of silicate weathering in the Himalaya does not stand valid and needs to be re-evaluated.

Singh et al. (1998) carried out a detailed elemental and Sr isotopic study on the Precambrian carbonates, sampled extensively across the Lesser Himalaya and concluded that these carbonates can not account for the Sr load and its highly radiogenic isotopic composition of river waters in this region on a basin wide scale though they could be important for particular streams. Krishnaswami et al. (1999), in an attempt to characterize the sources of cations and Sr in the Ganga-Ghaghra-Indus (G-G-I) source waters, brought out the difficulty in making Sr mass balance in these rivers and underlined the importance of sources in addition to silicates and Precambrian carbonates in contributing to the Sr budget.

Estimation of contemporary weathering rate and CO_2 consumption via silicate weathering in the Himalaya requires understanding of proton sources that release solutes to rivers from rocks via chemical weathering. Considering that the lithological set up in the

Himalaya is diverse and complex, such exercises have proved to be difficult (Krishnaswami et al., 1999; Galy and France-Lanord, 1999). Further, the validity and accuracy of mass balance calculations in achieving these goals depend on the end member compositions used. One way of having better constraints on end member compositions is careful sampling of the streams draining predominantly single lithology. This is also not quite straightforward, as it is very difficult to find rivers draining monolithologic units. Inspite of this, estimates are available on the silicate weathering rates and associated CO_2 consumption for a few river basins in the Himalaya. These include the G-B system (McCauley and DePaolo, 1997; Galy et al., 1999), Ganga-Ghaghara-Indus system (Krishnaswami et al., 1999) and Chinese rivers (Gaillardet et al., 1999).

The river Yamuna, draining the western part of the Ganga catchment in the southern slopes of the Himalaya, is the largest tributary of the Ganga (Negi, 1991). The river, at its confluence at Allahabad, carries water one and half times that of the Ganga (Rao, 1975). In its course the Yamuna drains a variety of lithologies in the Lesser Himalaya giving ample opportunity to examine the influence of lithology on water chemistry. A part of this thesis is devoted to quantification of contributions of various sources to major cations in the Yamuna River System (YRS) in the Himalaya, estimation of weathering rate and CO_2 consumption flux via silicate weathering and mass balance of riverine Sr using data on chemistry and $^{87}Sr/^{86}Sr$ of water, bed load and various source rocks in the Yamuna basin and better constraints on the source composition. The contentious issues on source(s) of Sr in the rivers draining the Himalaya, as discussed earlier, would be addressed in some detail in this study. The importance of silicate weathering in the southern slopes of the Himalaya in consuming CO_2 from the atmosphere and in contributing to the ^{87}Sr budget of the rivers would also be discussed.

The origin and evolution of the Himalaya, as mentioned earlier, have influenced the onset of the Indian monsoon and affected the climate, vegetation (relative abundance of C4 and C3 grasses), erosion and weathering in the region (Cerling, 1997; Prell and Kutzbach, 1997). It is established that at present the Himalayan ranges control the monsoonal precipitation in the Indian subcontinent. The rivers in the Himalaya draw their water from the orographic precipitation as well as from melting of glaciers in the region. Understanding the influence of altitude, distance from the cloud source and hydrological processes operating in these catchments such as mixing, evaporation and evapotranspiration is important for the purpose of modeling water budget in the region. As a part of this thesis, stable isotopes (oxygen and hydrogen) have been measured in the waters of the YRS to characterize aources of river waters and processes controlling the stable isotopic composition of river waters in the region. Processes such as the "amount effect" and the "altitude effect" have been addressed in detail with the problems associated in deciphering them in a catchment, particularly in a Himalayan watershed, where the physiographic set up is diverse and complex. These data also provide inputs to the estimation of paleoaltitudes based on $\delta^{18}O$ in carbonates and for comparing the intensity of paleo-monsoon in the Himalaya with that of the present (Garzione et al. 2000a, b).

Analogous to Sr isotopes, marine records show that the Os isotopic composition ($^{187}Os/^{186}Os$ and $^{187}Os/^{188}Os$) of seawater has been steadily increasing through the Late Cenozoic (Pegram et al., 1992; Turekian and Pegram, 1997). The osmium isotopic composition in seawater is dictated by contributions from continental weathering (radiogenic component) and mantle material and cosmic dust (non-radiogenic component). The continental crust has an average $^{187}Os/^{186}Os$ of ~11 (Esser and Turekian, 1993) whereas the $^{187}Os/^{186}Os$ for the mantle material and cosmic dust is ~1 (Luck and Allegre, 1983; 1991). That of seawater value of 8.8 for $^{187}Os/^{186}Os$ (Levasseur et al., 1998) requires that continental weathering dominantly controls the seawater Os isotopic composition, consistent with the measured $^{187}Os/^{186}Os$ of river waters (Sharma et al., 1999; Levasseur et al., 1999). An increased flux of continental osmium or an increased supply of radiogenic osmium from continents can bring about an increase in the seawater $^{187}Os/^{186}Os$. The Cenozoic increase in $^{187}Os/^{186}Os$ has been ascribed to the uplift of the Himalaya and consequent enhanced chemical weathering, especially of the ancient organic rich sediments such as black shales in this region (Pegram et al., 1992; Turekian and Pegram, 1997). Since Re and Os have a tendency to get associated with organic matter, black shales and other organic rich sediments during their formation scavenge Re and Os from the aqueous environment (Ravizza and Turekian, 1989; Crusius et al., 1996; Morford and Emerson, 1999) with a preference for Re. Hence black shales, to start with, have elevated Re/Os compared to other rock types. The decay of ^{187}Re to ^{187}Os results in high $^{187}Os/^{186}Os$ in black shales. Hence rivers draining catchments containing black shales will have elevated $^{187}Os/^{186}Os$. Although the role of weathering of black shales in the Himalaya in influencing the $^{187}Os/^{186}Os$ of seawater has not been fully assessed, it has been found that rivers in the Himalaya have more radiogenic osmium isotopic composition compared to other major rivers in the world (Levasseur et al., 1999; Sharma et al., 1999). Black shale occurrences have been reported in the Himalaya, which are usually associated with pyrites. Pyrites, in oxic environment, undergo oxidation to produce sulphuric acid, a strong weathering agent. Considering that black shales are easily weatherable and during weathering they release a suite of cations along with Re and Os to the weathering solutions, rivers draining black shales in the Himalaya are expected to have elevated Re in their waters. Indeed, one sample from the Ganga measured and reported by Colodner et al. (1993b) does show Re concentrations of 8.2 pM compared to the global average value, 2.1 pM. There has been, however, no systematic attempt till date, to assess the impact of various lithologies including organic rich sediments in regulating the dissolved Re in river systems. Therefore, river waters of the YRS and various source rocks have been analyzed for Re to characterize its sources to these rivers. In addition to the source characterization, these data allow inferences on the comparative geochemistry of Re and Os during weathering and transport, as well as on the role of black shales in contributing to the riverine budget of various trace metals such as Re, Os and U. This study, for the first time, attempts to use dissolved Re in the waters as a proxy to study organic matter oxidation in the Himalaya and associated CO_2 flux to the atmosphere. Furthermore, the extent of mobility of Re and Os assessed in this study has implications to geochronometry of rocks/sediments using Re-Os systematics.

1.2 OBJECTIVES OF THE THESIS

This thesis focuses on chemical weathering in the Yamuna River Basin in the Himalaya and addresses to the following objectives based on a comprehensive study of major ion composition, $\delta^{18}O$, δD, Sr, Ba and Re abundances and $^{87}Sr/^{86}Sr$ in the Yamuna River and many of its tributaries in the Himalaya and in selected solid phases of their catchment.

1. To characterize nature and extent of chemical weathering in the Yamuna drainage basin.
2. To assess the relative contributions of various lithologies controlling the solute budgets in the YRS.

3. To constrain the role of silicate vs. carbonate weathering in controlling Sr, Ba abundances and $^{87}Sr/^{86}Sr$ in these rivers and the contemporary CO_2 consumption due to silicate weathering.
4. To evaluate the role of various hydrological and meteorological processes in the catchment in governing the stable isotopic composition of the rivers.
5. To determine the significance of black shale weathering in contributing dissolved Re to the Yamuna River System and its impact on the budgets of Os, U in rivers and CO_2 release to the atmosphere.
6. To assess the overall significance of rivers draining the southern slopes of the Himalaya (the Ganga, the Yamuna and the Indus) in influencing the global budgets of selected elements and isotopes and CO_2 consumption via silicate weathering through synthesis of the present results with those available in literature.

1.3 STRUCTURE OF THE THESIS

This thesis is divided into six chapters.

Chapter 1 introduces the thesis topic and the problems to be addressed in the present study. The chapter also gives a detailed background on the extent of studies carried out on this topic and the nature of controversies and debates existing on the issues discussed in this thesis.

Chapter 2 details the study catchment, sampling and analysis carried out for this study. Part I of this chapter focuses on general geology and climate of the catchment and describes some of the rivers sampled. Part II discusses sampling of river waters, sediments and source rocks, analytical methods employed to carry out various measurements as well as precision and accuracy of measurements.

Chapter 3 presents and discusses the stable isotope systematics in the YRS waters. In conjunction with available data on the local precipitation, influence of various processes such as evaporation, rainout from the clouds and local topography in regulating the isotopic composition of river waters is assessed. Further, this study has been integrated with available results on the Ganga and the Indus systems.

In ***Chapter 4***, abundances of major ions, Sr, Ba and $^{87}Sr/^{86}Sr$ in river waters, bed sediments and source rocks are presented. These data have been used to assess the nature and extent of contemporary chemical weathering in the catchment and to characterize sources of major ions, Sr and Ba in river waters. The role of various lithologies in contributing to the Sr isotopic budget of the YRS is also assessed. Finally, the present day weathering rates and CO_2 consumption fluxes via silicate weathering in the Yamuna basin in the Himalaya are estimated. The major ion data have also been used to derive "apparent activation energy" for overall silicate weathering in the Himalaya.

Chapter 5 presents Re abundances in the YRS streams/rivers, mine waters and various source rocks. Using these data, the contributions of Re to the YRS waters, from major and minor lithologies in the Yamuna basin in the Himalaya, has been estimated. Using dissolved Re in the YRS as a proxy, the role of weathering of organic rich sediments in contributing to various trace metals such as U and Os and CO_2 release to rivers/atmosphere via oxidation is assessed.

Synthesis of the results obtained in this study and broad conclusions drawn from them are presented in ***Chapter 6***. Future work that to address some of the issues that have borne out from this work are also outlined.