Chapter 1

Introduction

1.1 INTRODUCTION

The origin and evolution of the Himalaya and the impact of Himalayan Orogeny on long term global change and the chemical and isotopic evolution of the oceans has been a topic of considerable interest and debate among scientists in recent years (Ruddiman, 1997). The Himalaya and the Tibetan Plateau has had an unquestioned and significant effect on the atmospheric circulation patterns and hence global climate.

Uplift and climate change are linked together. Uplift can alter regional and global climate through a number of physical and chemical mechanisms that involve changes in the circulation of the Earth's atmosphere and chemical weathering patterns of the continents. Chemical weathering of silicate rocks on land is the primary long-term sink for atmospheric CO_2. Raymo *et al.* (1988) and Raymo and Ruddiman (1992) proposed that mountain building, especially that associated with the Himalayan Orogeny could increase the rate of removal of CO_2 from the atmosphere through enhanced silicate weathering resulting from the exposure of new rock surfaces, more mechanical weathering and more monsoonal rainfall. This hypothesis was based on the steady increase in oceanic $^{87}Sr/^{86}Sr$ ratio through the Cenozoic (Veizer, 1989; Richter *et al.*, 1992) which they attributed to increased contribution of radiogenic Sr from the chemical weathering of silicates from the Himalaya.

The observation (Palmer and Edmond, 1989; Krishnaswami *et al.*, 1992) that the rivers flowing through the Himalaya, particularly its headwaters are highly radiogenic in Sr isotopic composition with moderate Sr concentration lend support the above hypothesis. Richter *et al.* (1992) based on the available data on Sr fluxes from the Himalayan rivers, their $^{87}Sr/^{86}Sr$, their relation to erosion and the timing of increase in oceanic $^{87}Sr/^{86}Sr$ also concluded that Himalayan Orogeny and associated chemical weathering can account for the observed Sr isotope evolution of the oceans since the Cenozoic. The impact of chemical weathering on climate change through drawdown of atmospheric CO_2, can be better assessed if temporal variations in silicate weathering rates can be quantified.

Though it is recognised that weathering in the Himalaya could have contributed to the Sr isotope evolution of the ocean, there is considerable uncertainty regarding its sources to the G-B system, its isotopic mass balance and on the use of Sr isotopes as a proxy for silicate weathering (Palmer and Edmond, 1992; Derry and France-Lanord, 1997; Quade *et al.*, 1997; Harris *et al.*, 1998; Blum *et al.*, 1998). Krishnaswami *et al.* (1992) suggested that Precambrian granites/gneisses in the Himalaya would be supplying the radiogenic Sr to the headwaters of the G-B system. Harris (1995) proposed that weathering of metasediments from the Higher Himalaya are the source for the high $^{87}Sr/^{86}Sr$ of the Himalayan rivers. Contrary to this, Palmer and Edmond (1992), Quade *et al.* (1997) and Blum *et al.* (1998) have suggested that carbonates could be an important source of radiogenic Sr to the Himalayan rivers. If this hypothesis is valid, then the use of oceanic Sr record as a proxy of silicate weathering need to be re-evaluated. Palmer and Edmond (1992) hypothesised that the high radiogenic Sr in the G-B system is due to the weathering of metamorphosed carbonates which got enriched in ^{87}Sr derived from coexisting silicate rocks during the widescale regional metamorphism.

In order for silicates and /or carbonates to be a dominant source of Sr and high $^{87}Sr/^{86}Sr$ to the headwaters, it is necessary that they contain adequate Sr with quite radiogenic $^{87}Sr/^{86}Sr$ and that they are ubiquitous in the drainage basins. It is known that granites, gneisses and metasediments with high $^{87}Sr/^{86}Sr$ are widespread across the Himalaya all along the drainage basins of the headwaters of the Ganga, Ghaghara, Indus and the Brahmaputra. In this context, the Precambrian carbonates are quite abundant and widely dispersed in the drainage basins of many of the headwaters of the Ganga, Ghaghara and the Indus. These carbonates occur dominantly in the Lesser Himalaya, a region characterised by higher weathering rates, because of more rainfall, higher temperature and availability of more soil CO_2. A part of this thesis work addresses to the role of these carbonates in contributing to the Sr isotope mass balance in the headwaters, as evaluated through their chemical and isotopic analysis. Based on the available data on the chemical and isotopic composition of silicates of the Higher and Lesser Himalaya and the new measurements on Precambrian carbonates made in this study, efforts are made to quantify the sources of major ions and Sr isotopes to the headwaters of the Ganga-Ghaghara-Indus river systems and evaluate the rates of silicate and carbonate weathering and associated CO_2 consumption in their basins. While this work was in progress, Quade *et al.* (1997) reported $^{87}Sr/^{86}Sr$ in detrital carbonates from the basins of Nepal rivers to be in the range of 0.722 to 0.734. These results prompted them to suggest that these carbonates could be important in determining the $^{87}Sr/^{86}Sr$ of the Himalayan rivers and that the use of oceanic Sr record as proxies of silicate weathering needs to be reassessed. Harris *et al.* (1998) and Blum *et al.* (1998) based on the study of Bhote Kosi and Raikhot rivers concluded that carbonates, from bed loads and veins of silicates could be dominant source of radiogenic Sr to these rivers. These observations are also considered in the thesis while addressing to the Sr isotope mass balance in the Himalayan rivers.

Similar to $^{87}Sr/^{86}Sr$, the marine $^{187}Os/^{186}Os$ records also show a steady increase during the Cenozoic (Pegram *et al.*, 1992; Ravizza, 1993; Ehrenbrink *et al.*, 1995). The osmium isotopic composition of seawater is governed by the contribution of radiogenic Os via rivers from the weathering of continental crust and non-radiogenic Os from meteoritic and mantle derived materials. The $^{187}Os/^{186}Os$ of continental crust is in the range of 10 to 15 (Esser and Turekian, 1993) and that in meteoritic dust and recent basalts it is ~1 (Shirey and Walker, 1998). The $^{187}Os/^{186}Os$ of contemporary seawater is quite radiogenic, 8.6-8.8 (Ravizza and Turekian, 1992; Sharma *et al.*, 1997; Levasseur *et al.*, 1998) exhibiting the dominant influence of continental supply. Any enhancement in the relative contribution of Os from rivers would make the seawater Os isotopic composition more radiogenic whereas increased influx of mantle and meteoritic Os would drive the marine $^{187}Os/^{186}Os$ towards 1.

Studies of the past $^{187}Os/^{186}Os$ of sea water as recorded in the leachable fraction of pelagic clays (Pegram *et al.* 1992; Turekian and Pegram, 1997) and metalliferous sediments (Ravizza, 1993; Ehrenbrink *et al.*, 1995; Reusch *et al.*, 1998) all show steady increase in $^{187}Os/^{186}Os$ during the past ~50 Ma, the rate of increase being considerably more rapid during the recent ~16 Ma. This overall trend has been attributed to mountain building and associated chemical weathering, in particular to the weathering of continental materials and organic rich ancient sediments linked to the uplift of the Himalaya (Pegram *et al.*, 1992). The organic rich sediments scavenge both Re & Os during their formation with a preference for Re resulting in high Re/Os abundance ratio in them (Ravizza and Turekian, 1989; Ravizza, 1991). As these deposits age, their $^{187}Os/^{186}Os$ would be significantly higher than typical continental crust, making them a potential source of radiogenic Os to the oceans. Thus, changes in the $^{187}Os/^{186}Os$

composition of seawater are related to organic C cycle (Pegram *et al.*, 1992; Ravizza, 1993; Ravizza and Esser, 1993).

Pegram *et al.*, (1992); Ehrenbrink *et al.*, (1995) and Turekian and Pegram (1997) suggested that the weathering of black shales in the Himalaya could be the main source for the $^{187}Os/^{186}Os$ increase through the Cenozoic. Detailed comparison of Sr and Os isotope evolution in the oceans, however, show distinct differences in their covariation trend during different time segments, leading to the suggestion (Turekian and Pegram 1997; Reusch *et al.* 1998) that their temporal evolution is difficult to be explained in terms of their supply from the *same* source as was initially proposed (Pegram *et al.* 1992). Reusch *et al.*,(1998) have suggested that weathering of Australian Passive Margin-New Guinea Arc system can be important in influencing the Sr and Os marine record. The validity of these hypotheses can be tested only when data on Re-Os systematics and Os isotope composition of various crustal silicates and organic rich sediments exhumed during major tectonic events of the past ~50 Ma (uplift of the Himalaya, New Guinea-Australia collision) and in rivers draining them become available. Recently, Ravizza and Ehrenbrink (1998) have suggested that bulk of the increase in the marine $^{187}Os/^{186}Os$ during the past ~15 Ma can result from the aging of the sedimentary organic matter being weathered which causes steady increase in their $^{187}Os/^{186}Os$ from the decay of ^{187}Re in them. This hypothesis, if valid, would argue against the need to have significant enhancement in chemical weathering and associated supply of Os isotopes through time.

There are no reported measurements of Os concentration and its isotopic composition in Himalayan rivers. In the absence of river water data it is difficult to directly assess the role of the Himalayan black shales in contributing to the marine Os isotope record. The measurements of Re, Os concentrations and Os isotopic composition of black shales from the Himalaya, however, can help in assessing their potential to contribute to the marine $^{187}Os/^{186}Os$ evolution. The approach has been explored in this thesis.

Black shales are present in both the inner and outer sedimentary sequences of the Lesser Himalaya. Re-Os studies of these black shales can provide information on their chronology (Ravizza and Turekian, 1989) in addition to data to evaluate their potential in influencing the $^{187}Os/^{186}Os$ evolution of the oceans. The determination of chronology of these sequences is important in understanding their evolutionary history. The paucity of fossils records and problems associated with radiometric dating of sedimentary rocks have hampered the dating of these two sedimentary units and studies on their intercorrelation. Based on the lithological considerations Frank and Fuchs (1970) and Valdiya (1995) have suggested contemporaneous deposition of both inner and outer belt sequences, and therefore they are time equivalent. But according to Mehr (1977), Stocklin (1980), Shanker *et al.*, (1993) and Sharma (1998), outer belt sequence is much younger than the inner belt. This controversy can be settled if their "ages" can be determined. Another problem of relevance in the Lesser Himalaya is the precise age of the Krol-Tal boundary. Prior to the discovery of small shelly fauna and other microfossils, the entire Krol belt was believed to span the time period from Permian to Jurassic (Auden, 1937; Gansser, 1964). Recent discoveries of fossil records by many workers (Azmi, 1983, Bhatt and Mathur, 1990; Prasad *et al.*, 1990; Tewari and Azmi, 1992; Shanker *et al.*, 1993) have placed the whole sequence of Krol belt in Precambrian to Early Cambrian. Further, Ahron *et al.* (1987) and Banerjee *et al.* (1997) have characterised the Krol-Tal (Pc-C) boundary based on oxygen and carbon isotopes and trace element studies. These considerations has lead me to explore, as a part of this thesis, the possibility of dating these black shales from the various sedimentary formations of the Lesser Himalaya based on ^{187}Re-^{187}Os pair.

1.2 OBJECTIVES OF THIS THESIS

(i) to assess the role of Precambrian carbonates from the Lesser Himalaya in contributing to the present day major ion chemistry and Sr isotope composition of the headwaters of the Ganga-Ghaghara-Indus river systems through their detailed chemical and isotopic measurements.

(ii) evaluate Sr isotope mass balance in these rivers from data on the Precambrian carbonates (obtained in this study) and those reported for silicates from their drainage basins.

(iii) establish chemical extraction procedures and measurement techniques for the determination of subnanogram to nanogram levels of Re and Os concentrations and Os isotopic composition in the black shales based on available methods.

(iv) carry out Re-Os measurements on black shales from the Lesser Himalaya to evaluate their potential in contributing to the seawater Os isotope evolution.

(v) determine the chronology of black shales from the outer and inner belt sedimentary sequences of the Lesser Himalaya using ^{187}Re-^{187}Os pair to understand their interrelation.

1.3 OUTLINE OF THE THESIS

This thesis consists of five chapters. Chapter 1 contains the overall introduction to the thesis work, with a brief overview of current status in this field, the motivation behind the present work and its objectives. As the focus of this thesis work is on the weathering and chronology of the Lesser Himalayan sedimentaries, a brief summary of the available stratigraphy and general lithology of the Lesser Himalaya is given in Chapter 2. This chapter also contains the various experimental procedures adopted in this work. In this section, emphasis has been given on the extraction procedures and measurement techniques of Re and Os which has been established for the first time in our laboratory. The chemical and isotopic composition of the Precambrian carbonates and their role in contributing to the present day chemical and Sr isotope composition of the headwaters of the Ganga-Ghaghara-Indus river systems are discussed in Chapter 3. In addition, in this chapter attempts have been made to quantify the silicate and carbonate weathering contributions to major ions and Sr isotope composition of these rivers. Re-Os chronology of black shales from the inner and outer belts of the Lesser Himalaya forms the first part of Chapter 4, in the second part the potential of these black shales in determining the ^{187}Os/^{186}Os evolution of the oceans has been evaluated using a simple mass balance model. Finally in Chapter 5, the summary and conclusions of the present studies have been outlined with some suggestions for future work.