# Isotopic and Geochemical Studies of the Lesser Himalayan Sedimentaries

by

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#### **Certificate**

I hereby declare that the work presented in this thesis is original and has not formed the basis for the award of any degree or diploma by any university or institution.

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Dedicated To Maa & Babujee

#### ABSTRACT

The role of silicate and carbonate weathering in contributing to the major cations and Sr isotope geochemistry of the headwaters of the Ganga-Ghaghara-Indus system is evaluated by making *new* chemical and isotopic measurements of Precambrian carbonates from the Lesser Himalaya and from the available data on silicates. Samples of Precambrian carbonate outcrops collected across the Lesser Himalaya have been analysed for their mineralogy, chemical composition and isotope ratios of Sr, O and C. Their Sr concentrations range from 20 to 363 ppm with <sup>87</sup>Sr<sup>/86</sup>Sr 0.7064 to 0.8935,  $\delta^{18}O_{PDB}$  -1.4 to -12.8 ‰ and Mn 11 to 2036 ppm. The petrography of the samples, their low Sr concentrations and wide range of  $\delta^{18}O$  values are all suggestive of their postdepositional alteration.

Comparison of the <sup>87</sup>Sr/<sup>86</sup>Sr and Sr/Ca ratios among the carbonates and silicates from the Lesser Himalaya and the source waters of the Ganga, Ghaghara and the Indus shows that the values for the source waters overlap with those of the silicates but are much higher than those in carbonates. An upper limit of carbonate Sr in the various source waters is calculated to be between 6%-44% (mean 18%), assuming that *all* the Ca in the rivers is of carbonate origin. The results show that on the average, weathering of the Precambrian carbonates is unlikely to be a major contributor to the highly radiogenic Sr isotope composition of these source waters; however, they can be a dominant supplier of radiogenic Sr to some rivers on a regional scale.

The silicate Sr component in these headwaters range from 2% to 100% with a mean of 40%. The calculation shows that only in few of the headwaters Sr balance would be achieved based on a two component, silicates and Precambrian carbonates, mixing. This indicates the need of a third end member. Tibetan/Tethyan carbonates, evaporites, phophorites are the possible end member.

The second part of the thesis deals with the study of Re-Os isotope systematics in black shales from the Himalaya for determining the chronology and evaluating their potential to contribute to the steady increase in <sup>187</sup>Os/<sup>186</sup>Os of the oceans since past ~25 Ma. Towards this, chemical procedures and Negative Thermal Ion Mass Spectrometry techniques have been established for the precise measurements of Re-Os concentrations in environmental samples and the Os isotope composition in them for the first time in our laboratory. The precision of <sup>187</sup>Os/<sup>186</sup>Os ratios and Os concentration determination are better than 1% ( $\pm 2\sigma_{\mu}$ ) and 2-3% ( $\pm 2\sigma$ ) respectively in a few tens to few hundreds of picograms of Os.

Re and Os abundances and Os isotope composition have been measured in a number of black shales sampled from outcrops and two underground phosphorite mines, Maldeota and Durmala, in the Lesser Himalaya. The black shales from the Maldeota and Durmala mines, collected ~15 m above the Krol-Tal (Pc-C) boundary, yield <sup>187</sup>Re-<sup>187</sup>Os isochron ages of  $535 \pm 11$  Ma consistent with stratigraphy and those assigned for the Pc-C boundary at various other locations. The age of these samples from the outer belt seems to be a few hundred millions of years younger than the <sup>187</sup>Re-<sup>187</sup>Os age of  $839 \pm 138$  Ma for black shales from the inner belt.

The role of weathering of these black shales in contributing to the Os isotope evolution of seawater over the past ~25 Ma was assessed using a simple budget model. If the <sup>187</sup>Os/<sup>186</sup>Os of global rivers (including those draining the Himalaya) is kept constant at today's value of 11.0 (based on available data for rivers) then the Os flux required from HTP rivers to reproduce the oceanic <sup>187</sup>Os/<sup>186</sup>Os would have to increase from 0.51 moles y<sup>-1</sup> at 16 Ma ago to 830 moles y<sup>-1</sup> at present. The present day flux would correspond to Os concentration of ~40 pg  $\lambda^{-1}$  in HTP rivers. This concentration is sustainable by weathering of black shales from the region, though it is about a factor of ~2 more than the highest Os concentration reported in rivers.

Similar calculations, assuming global <sup>186</sup>Os flux to be constant over the past 16 Ma at 15.8 moles y<sup>-1</sup> (calculated from available data for rivers), show that <sup>187</sup>Os/<sup>186</sup>Os in HTP rivers have to increase from 7.7 at 16 Ma ago to 40.5 at present to reconstruct the observed seawater <sup>187</sup>Os/<sup>186</sup>Os variations. The present day ratio of 40.5 is within the range measured in black shales from the Himalaya, but it is higher than the mean of ~23 in the Maldeota and Durmala black shales and the reported value of ~16.2 in the leachable fraction of the Ganga river sediments in the plains. The measured Os concentrations and <sup>187</sup>Os/<sup>186</sup>Os in black shales from the Lesser Himalaya though can meet the model requirements, the demands on them can be more easily accommodated if the <sup>187</sup>Os/<sup>186</sup>Os of HTP rivers is taken as 16.2 and that in all the other rivers as 11.0.

This study has brought the need (i) to look for other possible source(s) to balance the Sr budget in the head waters and (ii) more detailed study of black shales from the inner and outer belts to determine their chronology and inter-relation.

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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<sub>2</sub>. 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<sub>2</sub> 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 <sup>87</sup>Sr/<sup>86</sup>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<sub>2</sub>, 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 <sup>87</sup>Sr/<sup>86</sup>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 <sup>87</sup>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 <sup>87</sup>Sr/<sup>86</sup>Sr to the headwaters, it is necessary that they contain adequate Sr with quite radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr and that they are ubiquitous in the drainage basins. It is known that granites, gneisses and metasediments with high <sup>87</sup>Sr/<sup>86</sup>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<sub>2</sub>. 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<sub>2</sub> consumption in their basins. While this work was in progress, Quade et al. (1997) reported <sup>87</sup>Sr/<sup>86</sup>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 <sup>87</sup>Sr/<sup>86</sup>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 <sup>187</sup>Os/<sup>186</sup>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 <sup>187</sup>Os/<sup>186</sup>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 <sup>187</sup>Os/<sup>186</sup>Os would be significantly higher than typical continental crust, making them a potential source of radiogenic Os to the oceans. Thus, changes in the <sup>187</sup>Os/<sup>186</sup>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 <sup>187</sup>Os/<sup>186</sup>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 <sup>187</sup>Os/<sup>186</sup>Os during the past ~15 Ma can result from the aging of the sedimentary organic matter being weathered which causes steady increase in their <sup>187</sup>Os/<sup>186</sup>Os from the decay of <sup>187</sup>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 <sup>187</sup>Os/<sup>186</sup>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 <sup>187</sup>Os/<sup>186</sup>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

#### **1.2 OBJECTIVES OF THIS THESIS**

the Lesser Himalaya based on <sup>187</sup>Re-<sup>187</sup>Os pair.

- (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 <sup>187</sup>Re-<sup>187</sup>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 <sup>187</sup>Os/<sup>186</sup>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.

Chapter 2

Materials and Methods

#### **A. MATERIALS**

#### 2.1 STRATIGRAPHY AND LITHOLOGY OF THE AREA

This section provides the lithological and stratigraphical framework for the study area. This thesis work is predominantly in the Lesser Himalaya and as mentioned earlier, focuses on (i) the determination of chronology of the sedimentary sequences of this region, (ii) evaluate the role of carbonates and silicates of the region in regulating the chemical and Sr isotopic compositions of rivers draining through them and (iii) assessing the importance of weathering of black shale deposits from this area in controlling the seawater  $^{187}$ Os/ $^{186}$ Os evolution during the past ~25 Ma. Knowledge of the stratigraphy of the area and available data on their ages provide the base line information for chronological studies carried out in this work. For evaluating the role of these sedimentaries and silicates in determining the chemical and isotopic fluxes, emphasis will be on the lithology. Keeping these in view, efforts have been made in this chapter to summarise from the available information the origin, lithology, stratigraphy and suggested intercorrelation of the different geological units. In the north, the Lesser Himalaya is separated from the Higher Himalaya by the Main Central Thrust (MCT) while the Main Boundary Thrust (MBT) defines its southern boundary (Gansser, 1964). The Lesser Himalaya represents a relatively matured topography made of Middle Proterozoic to Early Cambrian sedimentary strata with small amount of displaced crystallines (Valdiya, 1995). The crystalline klippe divides the Lesser Himalayan sedimentaries into two NW-SE elongated sequences. The northern sedimentary sequence is known as the *inner belt* while the southern part, as the *outer belt* (Valdiya, 1980; Fig. 2.1).

#### (i) Outer belt sedimentary sequence

The outer belt consists of several exposed but detached synclines between Solan in Himachal Pradesh to Nainital in Uttar Pradesh. These synclines are made of thick pile of unmetamorphosed sedimentary rock sequences, which have been studied by various workers (Medlicott, 1864; Auden, 1934; Rao, 1968; Bhargava, 1972 and Shanker *et al.*, 1993) who have recognised various groups and formations in these synclines. The sedimentary successions composed of the Blaini, Infra-Krol, Krol and the Tal Fig. 2.1

formations together are called as *Krol belt* (Fig. 2.2). There are lot of controversies about their origin. Rao (1968) considered the Krol-Belt as autocthonous while Auden (1934, 1937) regarded it as an allochthon, which have been transported from the inner sedimentary belt. According to Valdiya (1995) these sedimentary sequences are para-auctothonous and they have advanced 4-21 km southward over the Siwalik zone.

The Krol belt sediments are exposed along the drainage basins of the tributaries of the Ganga, Ghaghara and the Indus rivers and their weathering may have significant influence the chemistry and isotopic composition of these rivers. In the following paragraphs brief description of the various units of the Krol belt is presented.

#### (a) Blaini formation

The Blaini formation, named after the river Baliana, northwest of Solan in Himachal Pradesh (Fig. 2.1), is a conglomerate with siltstones, grey, olive-green and black coloured shales and pink colour limestone. It is comprised of diamictite interbeded with quartz arenite, shale/slate and limestone. The type section is in Baliana River and the proposed reference section is on the right bank of Mussorie Syncline (Shanker *et al.,* 1993). It is represented by four horizons of diamictite. The Blaini boulder beds are composed of unsorted clast of various rock types in a structureless matrix of variable composition. Near Maldeota, clasts and matrices are dominantly dolomitic in composition and are probably derived from the underlying Shali and Deoban formations while in the Simla the Jaunsar Groups are the source of argillaceous and arenaceous clasts. This formation is inferred to have been formed in glacio-marine environment (Shanker *et al.,* 1993).

#### (b) Infra-Krol Formation

Infra-Krol formation overlies the Blaini formation (Fig. 2.2) and is composed of grayish black and bleached shale/slate interbedded with thin silty layers. The contact between the Infra-Krol and the Blaini formations is gradational and often difficult to demarcate. The type section for Infra Krol formation is Krol Hill, Krol Syncline near solan (Fig. 2.1). It is represented by black and bleached ash gray shale/slate. The presence of various types of bedding have led to the suggestion that these were deposited in a low energy tidal flat and lagoonal environment (Bhargava and Singh, 1980).

Fig. 2.2

#### (c) Krol Formation

Krol formation is a thick succession of carbonate rocks with shales and sandstones. It conformably overlies the Infra-Krol formation. Valdiya (1975) and Kumar (1984) classified it into three members-Lower, Middle and Upper. The proposed type area for the Krol group is Krol Hill in Solan, H.P. and Kauriyala village in Tehri Garhwal district, Uttar Pradesh (Fig. 2.1; Shanker *et al.*, 1993). Lower Krol consists of argillaceous limestone interbedded with greenish gray calcareous shale with fine-grained calcites, some sericite and clay minerals. Middle Krol consists of purplish and greenish shale with thin lenticular limestone with or without gypsum. This member is wide spread throughout the Krol basin. The Upper Krol is represented by blue crystalline limestone and dark gray thickly bedded massive dolomitic limestone.

The Krol formation generally represents deposits of a shallow tidal sea where sediments of mostly intertidal to superatidal zone dominate (Singh *et al.*, 1978; Shanker *et. al.*, 1993). Ripple marks and other flow structures on the quartz arenite and calcareous bands of upper part of the Middle Krol member have been interpreted to represent the restoration of connection with the open sea (Shanker *et. al.*, 1993).

#### (d) Tal formation

This formation is composed of chert-phosphorite, areno-argillaceous and arenaceous calcareous rocks (Shanker *et al.*, 1993). It conformably overlies the Krol formation (Fig. 2.2). Mussoorie area (Mussoorie Syncline), Dehradun is proposed as reference area for the Tal formation where all its litho-units are well exposed. In this area, it is well exposed in the **Maldeota** and **Duramala** phosphorite mine sections from where black shale samples were collected for this study. It is divided into two members, the Lower and the Upper Tal.

The Lower Tal formation consists of black chert interbedded with shale and rock phosphate, *black shale*, calcareous siltstone and siliceous limestone. The lower Tal is divided into four units, the chert-phosphorite, argillaceous, arenaceous and the calcareous units (Fig. 2.2). The chert-phosphorite unit consists of black chert interbedded with black shale and rock phosphate with occasional limestone bands. Above the chert-phosphorite band, the argillaceous layer composed of *black shales* (often pyritic and micaceous in nature) occur. Black shales of this layer are fine grained, consisting of muscovite,

sericite, clay minerals and fine silica. The arenaceous and the calcareous units lie above the argillaceous units. The Upper Tal formation is made of quartz arenite, shale, siltstone and limestone. It conformably overlies the calcareous member of the Lower Tal formation.

The presence of chert unit has led to the suggestion of a facies change from carbonate tidal flat deposition to protected tidal flat deposition and that of rock phosphate to restricted circulation, relatively shallower water depth (Shanker, 1971). The presence of pyritiferous black shales in argillaceous member suggests euxinic environment and deoxygenated conditions (Shanker *et al.*, 1993).

#### (ii) Palaeontological records and ages of the various formations

Many workers have studied the fossils records of the Blaini-Infra Krol-Krol-Tal sequence. Prior to the discovery of small shelly fauna, trilobites and small brachiopods in the Lower Tal formation, this entire sequence was believed to span the time period from Permian to Jurassic (Auden, 1937). Recent discoveries of fossils (Azmi, 1983) has placed the Tal formation in the Early Cambrian (Table 2.1). Consequently, the sequences underlying the Tal group of sediments assume Neoproterozoic status. The identification of stromatolitic beds, acritarchs and filamentous-coccoidal microfossils in the Krol formation further supports this idea (Bhatt and Mathur 1990; Prasad *et al.*, 1990; Shanker *et al.*, 1993; Tewari and Azmi, 1992).

The chert-phosphorite layer of the lower Tal has been correlated with Meishucunian I of South Chinese section based on the presence of small shelly fossils and with the Tomotian Stage of Russia based on family of calcareous algae and stromatolites (Shanker *et al.*, 1993). The micro and trace fossils of the arenaceous unit of the Lower Tal formation is correlatable to Meishucunian Zone III of South China. The calcareous unit of the Lower Tal formation contains brachiopods and microgastropods, which are known from Qiongzhusian Stage of South China or the Atdabanian Stage of Siberian section.

Many workers have attempted to precisely date the sedimentary rocks from the close vicinity of Pc-C boundary of known stratotype sections, with a view to assign "age" for the Pc-C boundary. The Rb-Sr ages of black shales collected just above the boundary from the South Chinese section range from 569 to 602 Ma (Xue, 1984; Zhang *et al.*,

Formation	Fossils/Stromatolites	Assigned	Ref.
		ages/period	
Tal	conodonts and other small	Early	Azami et al., 1981; Azmi
	shelly fossils, trace fossils,	Cambriam	1983; Singh & Rai 1983;
	small brachipods, gastropods		Bhatt et al., 1985; Brasier
			& Singh, 1987
Krol	Several forms of stromatolites,	Late	Singh & Rai, 1977;
	Ediacaran fossils	Proterozoic	Shanker et al., 1993;
		to Vendian	Shanker & Mathur, 1992,
Blaini/Infra	Acritarchs, cyanobacterial	Late	Prasad et al., 1990; Tewari
-Krol	filaments, coccoids	Proterozoic	& Azmi, 1992
Mandhali	Stromatolites e.g. Jurusania,	Upper	Valdiya, 1980
	Collenia parva	Riphean	
Deoban	Stromatolites e.g. Baicalica	Middle	Valdiya, 1980
	baicalia, Masloviella	Riphean	
	Columnaris		

Table 2.1: Various stromatolites/fossils findings and probable ages of various formations

1984). Similarly, Sharma *et al.*, (1992) have dated black shales from the chertphosphorite unit of the Lower Tal by Rb-Sr and obtained an age of  $626\pm13$  Ma. These Rb-Sr ages are a few million years older compared to U-Pb ages, 520-545 Ma, obtained on the zircon separates from the volcanic ash interlayered between sedimentary rocks near the Pc-C boundary of Canada, Morocco, China, Siberia and South Australia (Bowring *et al.*, 1993; Brasier *et al.*, 1994). Based on these U-Pb ages, the Pc-C boundary has been assigned an age of ~545 Ma (Brasier *et al.*, 1994). The only radiometric age available for the Krol belt section from the Lesser Himalaya, as mentioned earlier, is that based on Rb-Sr for the black shales of chert-phosphorite unit of the Lower Tal formation (Sharma *et al.*, 1992). Ahron *et al.* (1987) and Banerjee *et al.*(1997) have characterised the Krol-Tal boundary (Pc-C boundary) in this section based on carbon and oxygen isotopes and trace element studies of Krol carbonates and Tal phosphorites. One of the goals of this study is to explore the possibility of dating the black shales from the Lower Tal section using the Re-Os chronometer and thereby provide an "age" for the Pc-C boundary. With this view, as well be discussed later, black shales samples from these sections have been collected and analysed for Re, Os isotopes systematics and their composition.

Another objective of this thesis is to assess the role of weathering of carbonates and silicates in regulating the chemical and Sr isotope compositions of the rivers flowing through the southern slops of the Himalaya. In this context, the lithologies of the different formations are important which were briefly described earlier. Many of these formations are exposed in the drainage basins of the Tons, the Yamuna, the Ganga and the Kali rivers (Fig. 2.1). The extensive carbonate outcrops of the Krol formation is of particular interest as it has been shown that major ion chemistry of the rivers is dominated by the weathering of carbonates. In this study the contribution of the Lesser Himalayan carbonates to the Sr abundance and <sup>87</sup>Sr/<sup>86</sup>Sr of the rivers will be evaluated. The presence of evaporites along with the carbonates are reported in the Krol formation (Shanker *et al.*, 1993). They may also be important in contributing to the Sr isotope systematic of the Ganga headwaters. In view of this, several carbonate samples have been collected from the Krol formation exposed in Solan (H.P.) to Nainital (U.P.) in the outer belt; for their chemical and isotope composition, these are discussed in the later sections.

The presence of black shales in the Tal, Blaini-InfraKrol and Krol formations has been discussed earlier and form important exposures of black shales in the Lesser Himalaya. Many of these have been sampled during this study (see section 2.1) to determine their chronology (and hence that of Pc-C boundary) and to assess their potential in contributing to the Os isotope evolution of the oceans. It is suggested (Pegram *et al.*, 1992, Ehrenbrink *et al.*, 1995; Turekian and Pegram, 1997) that weathering of black shales from the Himalaya may have caused the steady increase in the Os isotopic composition of the oceans through the past few tens of Ma. As these black shales are quite old, the Os isotopic ratios in them could be very high, weathering of which can supply highly radiogenic Os to the rivers and finally to the oceans.

#### (ii) Inner belt sedimentary sequence

The inner belt sedimentary sequence of the Lesser Himalaya lies to the north of the outer belt towards MCT. It is a tightly folded repeatedly faulted auctothonous sedimentary pile (Valdiya, 1995). The autocthonous unit of the inner belt is divided into two groups, *Damtha and Tejam* (Fig. 2.3). The Damtha is conformably succeeded by the *Tejam group*, comprising of Deoban (≈Shali) and Mandhali (Sor) formations (Fig. 2.3). The Deoban is made predominantly of dolomites and contain in them branching stromatolites (Valdiya, 1980). This formation grades upwards into the pyritous-carbonaceous slates, marls and interbeded calcitic marbles of the Mandhali formation. As the Deoban (≈Shali) and Mandhali are made of huge carbonate deposites, they are of interest to this work in assessing the role of carbonates in contributing chemical constituents and Sr to the rivers flowing through them. Many of the rivers such as the Beas, Sutlej, Alaknanda, Pindar, Ramganga, Sarju and the Kali all flow through the Deoban (≈Shali) and Mandhali carbonate deposits. Carbonates from these areas have undergone low degree of metamorphism.

Occurrences of black shales have been reported in the Deban and Mandhali formations (Rupke, 1974; Valdiya, 1980). These black shales also have been sampled in this study (see section 2.1) for determining their chronology and use the data for stratigraphic inter-correlation with outer belt black shale deposits.

In veiw of the above, these two formations have been discussed in some detail below.

#### (a) Deoban formation

The Deoban formation consists of stromatolite bearing, cherty dolomite and dolomitic limestone with bands and intercalations of blue limestone and grey slate (Valdiya, 1980). There are two facies of the Deoban lithology, one is developed in southeast of the Alaknanda river in the Gangolihat area of Pithoragarh district and other that is recognizable in the Deoban mountain in the Chakrata area (Fig. 2.1). The first one falls in the drainage area of the Alaknanda, Pindar (headwaters of Ganga) and Sarju, Ramganga, Kali (headwaters of Ghaghara) rivers while the later one forms a part of the drainage basins of the Yamuna and the Tons rivers. Shali formation in the Himachal Pradesh is equivalent to the Deoban formation (Valdiya, 1995) and it forms a part of the

Fig. 2.3

drainage basin of the Sutlej river. In the Thal-Tejam-Girgaon area these limestones are metamorphosed and the degree of metamorphism increases towards the MCT (Bhattacharya, 1982). In the Baram area these are in contact with Toli gneisses. Based on the sedimentary structures and associated stromatolites Kumar and Tewari (1978) suggested an inter-tidal to a carbonate tidal flat deposition for these carbonates. The occurrence of oolites in these deposits has led to the suggestion of a shallow, warm and agitating marine environment for their deposition.

#### (b) Mandhali formation

Mandhali succeeds the Deoban discordantly in the Chakrata area, but with break or unconformity elsewhere. It consists of greyish green and black carbonaceous pyritc phyllites or slates interbedded with blue limestones and a vareity of conglomerate made of clasts. In the Gori (tributary of Kali) valley it contains pyritous slates massive dolomite limestone with chert laminae. In this area limestones are intruded by dolerite which have given rise to marble in contact zones. In the Thal-Tejam area (Ramganga valley) it is represented by pyritous carbonaceous phyllites interbebed with limestone. According to Valdiya (1980), the presence of carbonaceous substances in them denotes poorly ventilated euxinic environment for their deposition. The conglomeratic horizons within the succession indicate intervals of disquiet and interrupted sedimentation in an unstable shelf-environment.

#### **2.1** (iii) Intercorrelation between Inner and outer belt sedimentaries

Intercorrelation between the inner and outer sedimentary sequences is a difficult task due to the lack of sufficient fossil records and radiometric ages. Many workers have tried to correlate these two sequence based on lithology and more recently based on the available few fossil records.

West (1939) has correlated the Deoban (=Shali) formation of the inner belt with the Krol of the outer belt and Rautgara (inner) with Blaini (outer) based on lithology (Fig. 2.4). Frank and Fuchs (1970) and Valdiya (1995) have followed the same convention.

But other workers (Mehr, 1977; Stocklin, 1980; Shanker *et al.*, 1993) suggest that the Krol belt of the outer belt is much younger than the Tejam group of rocks (Fig. 2.5)



Fig. 2.4:The inter-correlation between inner and outer sedimentary sequences as suggested by West (1939) and Valdiya (1995)





and that the Mandhali formation is the base of the Jaunsar group (Chandpur and Nagthat formation) on which the Krol belt is overlying.

Recently, Sharma (1998) proposed that the inner and outer belt sediments deposited in the same basin and due to tectonic activity sometime in Precambrian, sea regressed southward in the Lesser Himalaya resulting in the cessation of sedimentation in the inner belt and continued in the outer belt. As a result, there is no sedimentary rocks present above the Mandhali formation in the inner belt. He supports the model in which Mandhali is considered as the base of Chandpur (Fig. 2.5).

It should be possible to check on the stratigraphic correlation between the inner and outer belt sediments and thereby check the validity of the above models, if their chronology can be ascertained. The attempt in this thesis to date black shales from the inner and outer belt is a step in this direction.

As discussed earlier a part of the work in this thesis deals with the weathering of the different lithologies and their contribution to the chemical and isotopic composition of the headwaters of the Ganga, Ghaghara and Indus. In the following (Table 2.2) the broad lithology of the drainage basins of different river system has been summarised.

# Table 2.2: Lithology of drainage basins of major rivers of the G-G-I source waters

Ganga System	
Bhagirathi	Originates in the Higher Himalaya and flows through the Crystallines before
	entering the Lesser Himalaya, where it drains metasediments (quartzites and
	dolomitic limestones) and metabasics.
Bhilangna	It flows mostly through the Higher and Lesser Himalayan Crystallines. Near its
	confluence with the Bhagirathi it drains Nagthat quartzites, phyllites, greywackes
	and limestones.
Alaknanda	In the Higher Himalaya, it originates and drains the Higher Himalayan
	Crystallines. In the Lesser Himalaya it flows through carbonates of Deoban and
	Mandhali, massive quartzites and slates, phyllites and greywackes of Nagthat
	formation.
Ganga Ganga takes its name at Devprayag after the confluence of the Bhagirathi and the Alaknanda. Downstream of Devprayag it passes through Nagthat quartzites, Krol limestones, phyllites of InfraKrol, the Siwaliks and alluvium in the plains.

# Ghaghara

- Sarju At its origin, Sarju passes through the Higher Himalayan Crystallines. It flows towards south west, predominantly through famous Calc Zone of Tejam carbonates, slates and quartzites of Rautgara before joining Ramganga.
- Ramganga Ramganga drains relatively larger stretch of Higher Himalayan Crystallines in its upper reaches. Downstream, it flows through lithologies similar to those described for the Sarju and in addition through a band of Lesser Himalayan Crystallines (Askot Klippe).
  - Kali The river Kali drains a number of lithologies. In its upper reaches it flows through the Higher Himalayan Crystallines, and downstream it drains carbonates and slates of Deoban and Mandhali formation, quartzites and phyllites of Rautgara formation, the Lesser Himalayan Crystallines (Almora Nappe), and the Siwaliks.

## **Indus System**

- Sutlej Originates near Mansarovar Lake and flows through the crystallines, gneisses, granites, phyllites, schists, carbonates and quartzites. Further downstream, it drains the carbonates of Shali Fomation.
- Beas It originates near Rohtang Pass (Higher Himalaya), flows through the crystallines, carbonates and Tethys sediments

# **B. METHODS**

The objectives of this thesis, as mentioned in the earlier chapter, are to (i) determine the chronology of black shales from the Lesser Himalaya, (ii) assess the role of weathering of these black shales in controlling the <sup>187</sup>Os/<sup>186</sup>Os of seawater and (iii) evaluate the impact of weathering of carbonates and silicates in governing the chemical and Sr isotopic composition of the Himalayan rivers.

To achieve these goals, it is necessary to collect suitable samples and analyse them for their mineralogy, petrology (microscopic studies), chemical and isotopic composition. Sample characterisation has been done based on the microscopic studies of their thin sections and using x-ray diffraction. Chemical analyses of the samples have been carried out using a variety of analytical techniques such as Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Atomic Absorption Spectrometry, UV-Visible spectrophotometry, Ion chromatography, CN analyser and coulometer. For isotopic analysis Negative Thermal Ionisation Mass Spectrometry (N-TIMS), Thermal Ionisation Mass Spectrometry (TIMS) and Stable Mass Spectrometry techniques were used. These are discussed in some detail below.

# **2.2 FIELD SAMPLING**

Sampling is a critical component of this work and considerable efforts were put in for their collection. The samples analysed in this study were collected in five field campaigns conducted during 1992, 1994, 1995, 1996 and the last in 1998. I had participated in the campaigns of 1994, 1996 and 1998, the samples from the other campaigns were made available to me for this work.

#### (i) Black shales

Black shale samples were collected from the various geological formations and locations in the Lesser Himalaya. For chronological work, black shale samples were collected from the two underground phosphorite mines, Maldeota and Durmala near Mussoorie These sites were chosen, as sufficient lithological and stratigraphical information were available from these areas (see section 2.1). In addition, the Rb-Sr age for the Lower Tal formation provided an idea of the chronology of these formations. Also sampling from underground mines is likely to minimise weathering and mobilisation effects. These samples were collected from the argillaceous unit of the Lower Tal formation (Fig. 2.2) in both the mines which is ~10 m above the Krol-Tal (Pc-C ) boundary.

The samples UK98-1 to UK98-11 were collected from the Maldeota phosphorite mine at three altitudes in strike direction of the bed, from a stretch of ~1 km. Two more samples KU92-56 and 58 are also from the same mine but were picked from the pile of

black shales kept outside the mine during phosphorite mining. They also belong to the same argillaceous unit of the Lower Tal (Fig. 2.2).

The UK98-17 to 31 were sampled from the Durmala mine. These samples were collected from the two limbs of the anticlinal bed of argillaceous unit separated by  $\sim$ 3 km. UK98-17, 18 and 19 were from one end whereas UK98-28 and 31 from others.

All these black shale samples, in hand specimen, were black, hard and compact with presence of thin laminations. Fresh shining pyrites were present in almost all of them. In some samples pyrites were distributed through out the matrix whereas some of them contained larger size (few millimeter to centimeter) pyrite concretions. It can be inferred from the presence of these shining pyrites that effects of weathering in these samples is unlikely to be significant.

For the chronology of the inner belt sediments of the Lesser Himalaya, samples were collected from the Shali formation in Theog. These samples are from road cut exposures and were collected a few centimeters below their exposed surfaces. HP94-22 to 26 were sampled from this region.

To evaluate the impact of weathering of black shales from the Lesser Himalaya on the seawater Os isotopic composition, a reconnaissance study of the Os isotopic composition has been done in which samples from several drainage basins of the major headwaters of Ganga-Ghaghara-Indus river system were analysed. The samples for this purpose come mainly from surface exposures of four localities, Nainital, Almora, Mussoorie and Simla (Fig. 2.1). The Nainital samples (KU92-49 to 51) belong to the Upper Krol formation, the Almora samples (KU92-2 and 6) are from Almora crystallines and are basically black graphite schist. These exposures form a part of the drainage basins of the headwaters of the Ganga and Ghaghara systems. KU92-53, 57, UK94-51 to 66 were sampled from the road cut exposures of different localities of the Mussoorie hills. They are from Upper Krol and the Lower Tal formations. This area falls in the drainage basin of the Ganga River system.

As discussed above inner belt samples were collected from the Shali formation at Theog near Simla (Fig. 2.1).

# (ii) Carbonates

To determine the influence of the Lesser Himalayan carbonates on the chemical and Sr isotopic composition of the headwaters of G-G-I, a detailed sampling of these carbonates have been done covering a wide geographical area from Bilaspur in Himachal Pradesh to Pithoragarh (near Nepal border) in Uttar Pradesh,. Samples collected for this study are from almost all the carbonate bearing formations of the inner and outer Lesser Himalaya, discussed in section 2.1. The samples from the inner belt are from Deoban and Mandhali formations of the Tejam group and Shali formation (equivalent of Deoban in Himachal Pradesh) whereas the outer belt samples primarily belong to the different units of the Krol formation and one from Blaini formation. These formations are sampled from the road cuts or the natural exposures.

The samples KU92-9, 13, 22, 26, 36, 43, 46 and UK95-12, 19 were collected from the Deoban and Mandhali formations in the Gangolihat- Pithoragarh and Thal-Tejam-Pipalkoti area of the inner Lesser Himalaya. The sample KU92-26 is from the northern Tejam region, where these units have gone through a low degree of metamorphism due to the proximity of Main Central Thrust (Bhattacharya, 1982). The samples KU92-13, 43 and UK95-19 are from regions near Gangolihat where evidence of carbonate diagenetic processes of dolomitization and silicification have been reported (Kumar and Tewari, 1978). The sample KU92-22 is from the southern part, and KU92-36 and UK95-12 are from northern part of the Thal-Tejam exposure. The sample KU92-36 was in contact with augen gneisses. UK95-12 is from Pipalkoti, where massive deposits of rhythmites are exposed. The sample KU92-46 is collected at the contact of carbonate and slate. All the above samples are part of the drainage basins of Ghaghara system except UK95-12, which is a part of the Alaknanda basin (Ganga system) (Fig. 2.1).

The samples HP94-41, 42 and 43 are from the Shali formation a part of the drainage basin of Sutlej. These samples are generally intercalated with slates.

The samples UK94-76, 77, 78 and 97 are from the Deoban formation exposed in Chakrata-Deoban-Tiuni area. These are a part of the drainage basins of the Tons and Yamuna rivers (Fig. 2.1).

The sample VBL-1 is from the Blaini formation. Other samples are all from Krol formation collected from the Mussoorie hills except HP94-13 which comes from the Krol formation of Solan (HP) area (Fig. 2.1).

### (iii) Water samples

Water samples were collected from the Ganga, Alaknanda, Pindar, Sarju, Ramganga and the Kali rivers during the field campaign of 1996 for major ion chemistry. The samples were collected in pre-cleaned plastic bottles as far away as possible from the river bank. After collection, one aliquot of the water (~250 ml) was filtered at site through 0.45  $\mu$ m nucleopore filter contained in an acrylic set-up (Sarin *et al.*, 1992). Two other aliquots one ~500 ml and the other ~1000 ml were also collected and brought to laboratory as such for analysis.

# **2.3 POWDERING**

In the laboratory, the carbonate and black shale samples were powdered from the field samples. Towards this, the field samples were broken to chips of mm to sub mm size using agate mortar and pestle. From these chips about 250 grams of samples were finely powdered using agate Tema mill and stored in cleaned plastic containers. In last phase of the work, the final powdering was done with SPEX mill using an acrylic container and methylcrylate balls. These powdered to ensure that the entire sample is brought to <100  $\mu$ m. Care was taken to avoid any contact with metals and metal surfaces during this entire operation. Typically an amount of about 40-60 grams of samples were powdered using the SPEX mill. These powders were used for various chemical, isotopic and XRD analyses.

# **2.4 ANALYTICAL TECHNIQUES**

The analytical techniques were employed depending on the type of the samples and the information sought from them. Of all the analytical techniques employed in this study, considerable efforts and time was spent in establishing the chemical procedures for the extraction and purification of Re and Os from black shales and their isotopic analysis by negative thermal ionisation mass spectrometry (Trivedi *et al.*, 1999). These procedures, established for the first time in our laboratory (and in India) are based on

# **ANALYTICAL SCHEMES FOR THE SAMPLES CARBONATES** Sample Composition Isotopic Charaterisation Composition $\begin{array}{c} \text{Stable isotope MS} \\ \delta^{18}\text{O}, \, \delta^{13}\text{C} \end{array}$ Microscopy AAS X-ray diff. TIMS (<sup>87</sup>Sr/<sup>86</sup>Sr) **ICP-AES BLACK SHALES** Composition TC, TN CaCO<sub>3</sub> **Re-Os** isotopes AAS CN Coulometer NTIMS **ICP-AES** Analyser Spectrophotometer **RIVER WATER** Major Ion Chemistry Ion Chromatography **ICP-AES** Spectrophotometer AAS SO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> (Na, K, Ca, Mg) $(SiO_2)$ (Ca, Mg)

those available in literature. The chemical procedure and measurement technique have been described in detail in this section, whereas other analytical methods are briefly presented as they are routinely used in our laboratory.

#### (i) **Re-Os isotope measurement techniques**

Os and Re abundances in geological and environmental samples are quite low, typically of the order of a few tens of picograms to nanograms per gram (Table 2.3; Esser and Turekian, 1993; Ravizza and Turekian, 1991; Shirey and Walker, 1998).

Samples	$\operatorname{Re}\left(\operatorname{ng}\operatorname{g}^{-1}\right)$	Os (ng $g^{-1}$ )	<sup>187</sup> Os/ <sup>186</sup> Os
Meteorites			
Chondrite	42 - 97	417 - 1050	~1
Iron	0.78 - 4820	8.8 - 65,740	~1
<u>Mantle</u>			
MORB	0.5 -2	0.001 - 0.05	~1
OIB	0.1 - 1	0.01 - 0.5	~1
Average continental crust	<1	< 0.05	10 - 15
Granitoids	0.076 - 0.125	0.004 - 0.007	13 - 31
Mn Nodules		0.25 - 2.39	5.13 - 10.96
Black sea sediments	21 - 184	0.23 - 0.69	5.71 - 7.44
Pelagic sediments	0.076 - 1.49	0.135	6.0 - 6.7
Black Shales	30 - 1000	0.36 - 7.4	24.3 - 70.3

Table 2.3: Re, Os abundances and <sup>187</sup>Os/<sup>186</sup>Os in some geological and environmental samples

The precise determination of Os and Re concentrations in these samples and their Os isotopic composition, therefore, requires the extraction and purification of subnanogram to nanogram quantities of these metals from several grams of samples. Low concentrations of Re and Os in the materials analysed in this study also requires the chemical and procedural blanks to be as low as possible. In this work these have been achieved using high purity chemicals.

# (a) Re, Os standards, Spikes and Reagents

The Re and Os standards and spike solutions, used for the calibration and standardisation of mass spectrometric procedures and the determination of Re and Os concentrations were obtained from G. Ravizza (WHOI) and W. Pegram (Yale University). The Os standard solution is a spec pure solution of  $(NH_4)_2OsCl_6$  in 6N HCl and had a concentration of 411 µg Os g<sup>-1</sup> solution (Esser, 1991). The Os spike solution is enriched in <sup>190</sup>Os with an isotopic composition of 96.6% <sup>190</sup>Os, 1.9% <sup>192</sup>Os, 1.0% <sup>189</sup>Os, 0.5% <sup>188</sup>Os and < 0.1% <sup>187</sup>Os, and a concentration of 13.720±0.129 µg g<sup>-1</sup> solution (Esser, 1991). The Re standard is a nitric acid solution of 99.999% potassium perrhenate. The Re spike is an acid solution of enriched Re metal (94.5% <sup>185</sup>Re (Ravizza, 1991). These standards and spikes were suitably diluted for our use using appropriate high purity acids and were recalibrated to ascertain their strengths. The recalibration results are as follows:

## Os Standard and Spike

The Os standard of 411  $\mu$ g g<sup>-1</sup> was diluted with high purity 6N HCl to yield a strength of 7.802 ng g<sup>-1</sup>. The spike was diluted to yield two working solutions with the concentrations of 19.23 ng g<sup>-1</sup> (OS2) and 0.74 ng g<sup>-1</sup> (OS3). All the diluted standards and spikes were kept in pre-cleaned fluon bottles fitted with Teflon dropper. The diluted standard was calibrated with OS2 thrice. The repeats are

(i)	7.89 ng $g^{-1}$	(10.12.1997)
(ii)	8.04 ng g <sup>-1</sup>	(12.12.1997)
(iii)	$7.92 \text{ ng g}^{-1}$	(20.01.1998)

Mean  $7.95 \pm 0.08 \text{ ng g}^{-1}$ 

This is consistent with the expected value of  $7.80 \text{ ng g}^{-1}$  from the dilution.

# **Re Standards and Spikes**

Similar to Os standard and spike, Re standard and spike solutions were also acquired from Yale University. The Re standard has a strength of 118.3  $\mu$ g g<sup>-1</sup>. This was diluted in high purity 1N HNO<sub>3</sub> to yield strength of 37.6 ng g<sup>-1</sup>. This standard was calibrated using a spike obtained from Dr. G. Ravizza, WHOI with a strength of 1.568 ng g<sup>-1</sup>. Repeat measurements yield for the concentration in standard solution values of

 $37.48 \pm 0.02 \text{ ng g}^{-1}$  $36.60 \pm 0.09 \text{ ng g}^{-1}$  $37.15 \pm 0.08 \text{ ng g}^{-1}$  $37.50 \pm 0.07 \text{ ng g}^{-1}$ 

Mean  $37.22 \pm 0.03 \text{ ng g}^{-1}$ 

This is consistent with the expected value of 37.6 ng g<sup>-1</sup> based on dilution. Using this standard, another Re spike (from Yale) was calibrated. The strength of the spike is 65.88  $\pm$  0.07 ng g<sup>-1</sup>. This was labelled as SPIKE 1C and used for our work.

The need to extract and purify subnanogram to nanogram quantities of Os and Re from various samples places stringent requirements on the purity of reagents and cleanliness of glass and Teflon wares used for the analysis as the procedural blank levels have to be extremely low, less than a few picograms. The acids,  $H_2SO_4$ ,  $HNO_3$  and HBr were procured from SeaStar Chemicals Inc., Canada; HCl was purified in the laboratory by distilling analytical grade acid at sub-boiling temperatures first using a quartz still and then redistilled with a Teflon distillation set-up (Mattinson, 1969). Ni powder was obtained from Aldrich Inc. (99.999% purity; mesh size 100). The reagents for fusion,  $Na_2CO_3$ ,  $Na_2B_4O_7$  10H<sub>2</sub>O; and S were all of analytical grade quality.  $H_2O_2$  is analytical grade from Qualigens, Bombay. Commercially available distilled water was first purified using Milli-Q system and redistilled twice at sub boiling temperatures in quartz (QD  $H_2O$ ) for wet chemistry.

All glasswares used were first cleaned in Milli-Q water, then boiled in hot conc. HNO<sub>3</sub>, rinsed profusely in Milli-Q water and finally with QD H<sub>2</sub>O. The Teflon wares used were procured mainly from Savillex Corporation, USA. They were first cleaned in milli-Q water, then in hot conc. HNO<sub>3</sub> for 3-4 days. They were then filled with a cleaning solution containing HNO<sub>3</sub>, HF and H<sub>2</sub>O in 2:2:1 ratio, sealed, wrapped in transparent cling films and kept under infra red lamp for several hours to days. The acid is emptied, rinsed several times with Milli-Q water and then with QD H<sub>2</sub>O prior to use.

# (b) Os Chemistry

#### Sample Decomposition Technique

The Os from various geological samples (black shales, igneous rocks, river and sea sediments) was extracted by NiS fusion and purified by distillation and ion exchange methods (Fig. 2.6; Luck and Allegre, 1983; Esser, 1991; Pegram et al., 1992). Typically, 0.5 - 2.0 gm of samples were used for the analysis. The samples were first mixed with the fusion flux ( $Na_2B_4O_7$  10H<sub>2</sub>O,  $Na_2CO_3$ ) in the ratio 1:2 and the Borax to sodium carbonate ratio is 2:1, and then with Ni (~250 mg) and S (~175mg) using a small agate mortar and pestle. After homogenising the sample and fusion mixture about half of it is placed in a "Coors" porcelain crucible (acquired from Thomas Scientific, USA) and made a crater at its centre. To this, a known weight of Os spike solution was added, and covered with the rest of the sample mixture. The small crucible containing the sample fusion flux mixture was kept in a bigger crucible, covered with lid and placed in a muffle furnace at 800°C. The temperature was raised to  $\sim 1080^{\circ}$ C and kept at this temperature for 2 - 3 hrs. The furnace was switched off, the melt allowed to cool in the furnace and crucible was broken to remove the NiS bead. Usually one large NiS bead was recovered, sometimes one large and many smaller beads were also found. The beads were usually smooth with metallic lustre and free from any adhering glass. The NiS bead was weighed to determine yield, which generally was in the range of 70%-90%. The bead was dissolved by refluxing it for several hours with distilled 6N HCl in a conical flask covered with a Teflon lid at subboiling temperature. The NiS bead generally dissolved in about 6-8 hours. The solution was cooled to room temperature, filtered through 25 mm dia 0.45 µm Millipore filter set up to separate the insoluble sulfides which are known to retain Os quantitatively. The filter paper was carefully removed, folded and placed in a precleaned 250 ml distillation flask.

#### Distillation

This step is necessary to separate Os from less volatile (Re) and non volatile elements whose molecular and atomic species interfere during Os mass spectrometry, e.g.  $^{187}$ Re with  $^{187}$ Os. This process takes the advantage of high volatility of Os as OsO<sub>4</sub> at 104°C. About 10 ml conc. H<sub>2</sub>SO<sub>4</sub> was added to dissolve the filter paper and then ~80 ml QD H<sub>2</sub>O to make the acid strength ~4N (water was added slowly to minimise heating) so



Fig. 2.6: Flow diagram for Os chemistry

that boiling point of the solution will be ~ $105^{\circ}$ C. To this ~3 ml of 4N H<sub>2</sub>SO<sub>4</sub> containing ~ $300 \text{ mg CrO}_3$  was added as oxidant. The 250 ml round bottom flask containing the solution was connected to a condenser system. The outlet tube of the condenser was dipped into a test tube containing 8 ml H<sub>2</sub>O<sub>2</sub>. The H<sub>2</sub>O<sub>2</sub> trap was kept cool with ice. All the joints were sealed with Teflon tape. Both condensers were cooled with running tap water. The mixture was distilled using purified air as carrier gas following the procedure outlined by Luck (1982) and modified at Yale (Martin, 1990). The solution was brought slowly to boiling. When the solution started boiling the water in the reflux condenser was turned off and the Os distillate was collected in the ice cooled H<sub>2</sub>O<sub>2</sub>.

The Os distillate in  $H_2O_2$  was further purified by distilling it into ~8ml HBr by second distillation. For this, the  $H_2O_2$  distillate was transferred to a 125 ml round bottom flask and Os was distilled into 8 ml HBr (Esser, 1991).

#### Conversion to Osmium hexa bromide and grain chemistry

The HBr containing the Os was transferred to 15 ml Savillex digestion well, sealed and kept at  $80^{\circ}$ - $100^{\circ}$ C overnight in an oven. The solution was then slowly evaporated to 0.5 ml on a hot plate, transferred to the cap of the digestion vessel and taken to near dryness (~1µl). This was diluted to 10 µl with QD H<sub>2</sub>O to make the acid strength 1N. One grain of precleaned Chelex-20 (20-50 mesh) ion exchange resin is picked and placed in a 5 ml Savillex vial. It is cleaned with conc. HBr and conditioned with 1 N HBr by ultrasonicating. To this, the 10 µl sample solution was loaded, ultrasonicated for 45 minutes and the solution was pipetted off using a microsyringe. The resin bead was washed with 10 µl of 1N HBr, ultrasonicated for three minutes and the solution was repeated thrice. The Os from bead was eluted with Conc. HBr. Towards this, 10 µl of conc. HBr was put on the bead and ultrasonicated for 45 minutes. This HBr fraction was carefully collected as it contains Os. This step was repeated to ensure quantitative retrieval of Os.

#### Loading and Metal conversion

The purified Os was slowly evaporated to  $<1\mu$ l and carefully loaded onto Os-Re free, Pt filament (H. Cross Company, USA) using a Teflon capillary coupled to a microsyringe. Prior to loading, the Pt filament was spot welded on the posts of filament holder and degassed under vacuum (10<sup>-7</sup> torr) at ~900°C (orange red colour) for 3-4 hours. The Os

fraction after loading on the degassed Pt filament was dried at ~0.5 amp. current. It was then heated to dull red heat (~ $600^{\circ}$ C) under vacuum (< $10^{-7}$  torr) for 8-10 hours to reduce it to Os. Now this is ready for isotope measurements using NTIMS.

# (c) Re Chemistry

For the determination of Re concentration, in the earlier phase of measurements, samples were brought into solution by acid digestion and Re purified by ion exchange procedure (Ravizza, 1991; Shen *et al.*, 1996), later the procedure was modified slightly and samples were ashed at 450°C prior to acid dissolution (Fig. 2.7).

#### Acid dissolution

About 0.25 g of powdered samples were taken in 15/30 ml Savillex digestion vessels, wetted with QD H<sub>2</sub>O and a few drops of conc. HNO<sub>3</sub>. To this, Re spike was added followed by ~10 ml conc. HNO<sub>3</sub>. The vessel was sealed and kept at 80°-100°C on a hot plate for ~24 hours after which it was opened and placed on a hot plate to evaporate the HNO<sub>3</sub>. The residue was digested twice, each time with ~ 5 ml HF, taken to dryness first with HNO<sub>3</sub> and then with aqua-regia to bring it to solution. In some samples, particularly in black shales from the Himalaya, there was often a small amount of dark residue; even after repeated HNO<sub>3</sub> and aqua-regia treatments which interfered with the Re chemistry and mass spectrometry. Therefore, the samples were ashed to oxidise the organic carbon before dissolution.

#### Ashing and Acid Dissolution

To avoid interference of organic matter with the Re chemistry the black shale samples were first ashed at  $450^{\circ}$ C for ~12 hrs. (Colodner *et al.*, 1993). The ashed samples were later brought to solution by acid digestion. The sample solution is brought to dryness and taken in about 7 ml 0.8N HNO<sub>3</sub>. Re was separated from this solution using an anion exchange resin (1ml Dowex 1X8, 100-200 mesh size, pre cleaned with 6N HCl and 8N HNO<sub>3</sub>) conditioned in 0.8 N HNO<sub>3</sub> medium. After loading the sample, the resin is washed four times, each with 3 ml 0.8 N HNO<sub>3</sub>. The Re from the column was eluted with 12 ml 8N HNO<sub>3</sub>. The eluate is evaporated to near dryness and taken in 1 ml of 0.8 N HNO<sub>3</sub> and the Re repurified by passing through 100 µl anion exchange resin. The column is washed thrice, each time with 0.5 ml 0.4N HNO<sub>3</sub>. The Re from the column is eluted with 3 ml 8N HNO<sub>3</sub>. The solution containing Re is evaporated to dryness, digested with a





drop of conc.  $HNO_3$ , dried and taken in 0.2 N  $HNO_3$  (~0.5 µl). A part of this solution is loaded on the filament for mass spectrometric measurements. In a few black shale samples Re concentration was measured by wet oxidation and after ashing. The results (Table 2.4) are consistent within errors, suggesting that there is no measurable loss of Re during the ashing processes.

Further, a few control experiments were done to determine the optimum temperature for ashing. Towards this, a few black shale samples were ashed at three different temperatures. The results (Table 2.5) show that samples ashed between 450- $600^{\circ}$ C all yielded Re concentrations which are within errors. Based on these results we maintained an ashing temperature of 450°C for ~12 hrs, as it was the minimum.

Sample	R		
-	(a)	(b)	
KU92-56(1) KU92-56(2)	$255 \pm 18$ $264 \pm 4$	266 ± 6	
KU92-58(1) KU92-58(2)	$18.8 \pm 0.12$ $18.4 \pm 0.30$	$18.1\pm0.08$	

**Table 2.4: Inter-comparison of Re measurements** 

a: acid digestion, b: ashing followed by acid digestion

Table 2 5.	. D			- 4 J:CC 4	• • • • • • • • • • • • • • •
1 able 2.5	: Re concentr	ation in sail	ipies asneu a	at unterent	temperatures

Sample #	600°C	<u>Re (ng g<sup>-1</sup>)</u> 550°C	450°C
KU92- 49	-	$5.25\pm0.06$	$5.18 \pm 0.2$
UK94-55	$0.39\pm0.05$	$0.34\pm0.02$	$0.36 \pm 0.01,  0.35 \pm 0.01$
UK98-1	$8.81\pm0.12$	-	$8.64 \pm 0.13$
UK98-2	69.7 ± 0.28	-	68.6 ± 1.6
UK98-3	145 ± 1.2	-	153 ± 2.5
UK98-4	$3.25\pm0.08$	-	3.16 ± 0.10

# (d) Os and Re mass spectrometry

The isotopic analysis of some of the Pt group elements by NTIMS was pioneered by Heumann (1988) which was later extended to Re, Os and Ir (Creaser *et al.*, 1991; Volkening *et al.*, 1991; Hauri and Hart, 1993). The NTIMS technique have been established at PRL for the measurement of Re and Os isotope composition following the available procedures. The mass spectrometer used in these studies is an indigenously built, 23 cm radius,  $60^{\circ}$  sector magnetic field, single focusing instrument equipped with faraday cup collector (Trivedi, 1990). This machine was used earlier for Rb-Sr isotope measurements (Trivedi, 1990; Trivedi *et al.*, 1995). The polarities of the magnet and ion acceleration high voltages were reversed to suit the NTIMS operation. Following is the mass spectrometric parameters used for Re and Os measurements (Table 2.6):

Element	Accelerating Potential	Magnetic Field	Filament current
	(KV)	Gauss	(A)
Re	4.66	5700-5725	2.2-2.4
Os	4.87	5670-5730	2.1-2.3

 Table 2.6: Mass spectrometric settings for Re & Os measurements

The Os metal fraction on the Pt filament was removed from the degassing chamber. About 20 µg of spec. pure Ba(NO<sub>3</sub>)<sub>2</sub> (from Spex Industries Inc., USA) as a solution was loaded on the top of the Os metal and dried at 0.5 amp to enhance the production of negative thermal ions of OsO<sub>3</sub> (Creaser *et al.*, 1991). This was loaded in the mass spectrometer and kept overnight to pump down to the required vacuum. The mass spectrometric measurements of Os were carried out by bleeding oxygen into the mass spectrometer at a pressure of  $\sim 2 \times 10^{-6}$  torr (Hauri and Hart, 1993) which is known to promote ionisation efficiency of  $OsO_3^-$  and  $ReO_4^-$ . Typical ion currents were about  $10^{-13}$ A at mass 240 per 100 pg Os load. Os isotopic ratios were measured at masses  $240(^{192}\text{Os}^{16}\text{Os}^{-1}), 238(^{190}\text{Os}^{16}\text{Os}^{-1}), 237(^{189}\text{Os}^{16}\text{Os}^{-1}), 236(^{188}\text{Os}^{16}\text{Os}^{-1}), 235(^{187}\text{Os}^{16}\text{Os}^{-1})$  and  $234(^{186}Os^{16}O_3)$ . Backgrounds were measured at masses 233.5 and 240.5. The oxide ratios were corrected for interferences from  $(Os^{16}O_2^{17}O^{-})$  and  $(Os^{16}O_2^{18}O^{-})$  and mass dependent isotope fractionation using <sup>188</sup>Os/<sup>192</sup>Os abundance ratio of 0.32439 (Nier, 1937) to obtain elemental isotope ratios. In addition, corrections for Os isotope contributions from the spike were also made. A typical spectrum of Os standard and Os extracted from one of the black shales is shown in Fig. 2.8.

For Re also, ~ 10  $\mu$ g of Ba(NO<sub>3</sub>)<sub>2</sub> solution was loaded on the top of it on the Pt filament and placed in the mass spectrometer for analysis. Typical ion current for a 100 pg load Re standard was about  $5 \times 10^{-13}$  A at mass 251. In sample loads the currents were

Fig.2.8

lower probably because of interference from organic matter and/or other ions such as chromate (Shen *et al.*, 1996). Similar to Os data reduction, corrections for oxide interference ( ${}^{185}\text{Re} \, {}^{16}\text{O}_{3}{}^{18}\text{O}^{-}$  on  ${}^{187}\text{Re}^{16}\text{O}_{4}^{-}$ ) were made for calculating Re concentration. The Os and Re data reduction procedures followed those being used at Yale and WHOI (Williams and Ravizza pers. comm.).

Date	Standard (pg)	<sup>187</sup> Os/ <sup>186</sup> Os	<sup>190</sup> Os/ <sup>192</sup> Os
05.12.1997	1025	$0.8751 \pm 0.0062$	$0.6424 \pm 0.0024$
06.12.1997	470	$0.8973 \pm 0.0080$	$0.6451 \pm 0.0012$
13.12.1997	100	$0.9075 \pm 0.0234$	$0.6455 \pm 0.0115$
22.12.1997	300	$0.8766 \pm 0.0125$	$0.6422 \pm 0.0019$
17.01.1998	250	$0.8872 \pm 0.0096$	$0.6446 \pm 0.0007$
19.01.1998	200	$0.8926 \pm 0.0099$	$0.6469 \pm 0.0010$
09.02.1998	250	$0.8915 \pm 0.0064$	$0.6462 \pm 0.0025$
01.04.1998	400	$0.8790 \pm 0.0068$	$0.6430 \pm 0.0011$
04.06.1998	60	$0.8912 \pm 0.0087$	$0.6431 \pm 0.0013$
10.11.1998	2000	$0.8860 \pm 0.0009$	$0.6439 \pm 0.0002$
Mean		$0.8884 \pm 0.0198$	$0.6441 \pm 0.0033$
Martin (1990	)	$0.897 \pm 0.016$	$0.6417 \pm 0.0075$
Allegre(1983	)		0.64382

Table 2.7: Os isotopic composition of standard with time

Table 2.7 lists the isotopic composition of Os measured over several months in standard loads. The standard loaded are within  $\pm 10\%$  of the values given. The <sup>187</sup>Os/<sup>186</sup>Os is calculated from the measured <sup>187</sup>Os/<sup>192</sup>Os and using a value of 0.03907 for <sup>186</sup>Os/<sup>192</sup>Os (Luck and Allegre, 1983). The results show that the <sup>187</sup>Os/<sup>186</sup>Os and <sup>190</sup>Os/<sup>192</sup>Os in the standard runs are 0.8884  $\pm$  0.0198 and 0.6441  $\pm$  0.0033 respectively in agreement within errors with those reported (Table 2.7). Individual errors (within run) are  $\pm 2\sigma$  uncertainty on the mean whereas the error given for the mean is twice of standard deviation calculated from the ten numbers listed in the table for both <sup>187</sup>Os/<sup>186</sup>Os and <sup>190</sup>Os/<sup>192</sup>Os.

The <sup>185</sup>Re/<sup>187</sup>Re ratio measured in the standard is 0.594  $\pm$  0.003, consistent with reported values within errors and are reproducible within  $\pm$ 0.5%. The precision of Re concentration measurements ( $\pm$ 2 s.d. within runs) is typically ~2-3% and the reproducibility, based on replicate analysis of six pairs of samples, show excellent agreement within experimental uncertainties.

# (e) Procedural blanks

Four procedural blanks for Os were run for the NiS fusion and wet chemistry using 250-500 mg Ni. It includes all steps starting from fusion, dissolution of bead, filtration, distillation, grain chemistry and loading. The sample-powdering step is not included in the blank run, but this unlikely to contribute to blank as utmost care was taken to avoid any metal contact with the samples during this process. The Os blank for the entire procedure (Table 2.8) ranged between 0.7 to 4.2 pg with an average  $1.8 \pm 1.6$  pg. Os isotopic measurements could not be made on these blanks, as the Os load on the filament were quite low ( $\leq 1$  pg). Re blank comes mainly from the Pt filament (Hauri and Hart, 1993). We ran four procedural blanks for Re; it ranged from 1.7 pg to 4.5 pg, with a mean of  $3.5\pm1.2$  pg (Table 2.8). Re and Os blanks were run four times during the study, they are listed in Table 2.8.

Element	Date	Blank (pg)	Element	Date	Blank (pg)
Os	06.11.1997	4.2	Re	14.10.1997	1.7
	01.01.1998	0.7		15.03.1998	3.8
	21.01.1998	0.8		16.03.1998	4.5
	12.06.1998	1.6		26.08.1998	3.9
Mean		$1.8\pm1.6$	Mean		$3.5 \pm 1.2$

 Table 2.8: Procedural blanks of Re and Os

# (f) Precision and accuracy of Re and Os measurements

## Inter laboratory comparison

To check the accuracy and precision of the entire procedure, NiS fusion and wet chemistry, we analysed two samples of black shales of known Os and Re concentrations and isotope composition. These samples were obtained from Dr. G. Ravizza and their Os and Re analysis were made earlier by the SIMS technique (Ravizza, 1991 and pers. comm.). Table 2.9 lists the inter-comparison between the two sets of measurements which shows reasonable agreement.

Sample	[Re] ng g <sup>-1</sup>	[Os] pg g <sup>-1</sup>	<sup>187</sup> Os/ <sup>186</sup> Os
NA10			
Present study	119.9	904	$67.00 \pm 0.51$
Ravizza (1991)	119.7	943	$70.26\pm0.74$
NA11			
Present study		7390	$69.19 \pm 0.54$
Ravizza (1991)		7374	$67.98 \pm 1.02$

# Table 2.9: Os & Re concentrations and <sup>187</sup>Os/<sup>186</sup>Os ratio in black shales : Inter laboratory comparison

# Table 2.10: Results of Re, Os and <sup>187</sup>Os/<sup>186</sup>Os repeat measurements

Sample	Re	Os	<sup>187</sup> Os/ <sup>186</sup> Os
1	$(ng g^{-1})$	$(ng g^{-1})$	
UK98-1(i)	$8.81 \pm 0.24$	$0.60 \pm 0.01$	15.373 ± 0.093
(ii)	$8.64\pm0.26$	$0.60\pm0.04$	$15.439\pm0.108$
UK98-2(i)	$69.7\pm0.57$	$1.57\pm0.04$	$30.490 \pm 0.164$
(ii)	$68.6 \pm 3.13$	$1.45\pm0.05$	$30.464 \pm 0.154$
UK98-17(i)	-	$2.84\pm0.08$	$31.853 \pm 0.179$
(ii)	-	$2.95\pm0.06$	$31.494 \pm 0.072$
KU92-56(i)	$255 \pm 18$	$13.2 \pm 0.40$	$18.098 \pm 0.218$
(ii)	$264 \pm 4$	$13.5\pm0.35$	$18.002 \pm 0.134$
(A)	$266 \pm 6$	-	-
KU92-58(i)	$18.8\pm0.12$	$0.79\pm0.002$	19.864 ± 0.139
(ii)	$18.4\pm0.30$	$0.80\pm0.004$	$19.869 \pm 0.070$
(A)	$18.1\pm0.08$	-	-

All Re measurements by ashing followed by acid digestion, except in KU92-56 and KU92-58, where measurements were made by both the procedures; (i) and (ii) refer to wet oxidation and (A) ashing followed by acid digestion.

#### *Reproducibility*

In addition, we also analysed a few samples of black shales from the Lesser Himalaya in duplicate to assess the reproducibility of the measurements. The results (Table 2.10) show good agreement between the replicates.

#### (ii) **Rb & Sr Measurements**

Measurements of Rb and Sr abundances and Sr isotopic composition in carbonate samples from the Lesser Himalaya were made using Thermal Ionisation Mass Spectrometer (TIMS). Sr isotopes were measured both in the whole rock and their mild acid leachates (Singh et al., 1998). For the whole rock analysis, about 100 mg of powdered samples were brought to solution by digesting them in HF-HNO<sub>3</sub>. The solution were spiked with <sup>87</sup>Rb, <sup>84</sup>Sr tracers, and the tracers were equilibrated with sample by heating them in closed containers and dried. The dried residue was taken in 2.5 N HCl and Sr and Rb were separated and purified by cation-exchange (Dowex 50X8, 200-400 mesh) following the procedures used in our laboratory (Trivedi, 1990). The separated Rb and Sr fractions were dried, taken in a drop of orthophosphoric acid and evaporated directly onto an outgassed tantalum filament of the ion source (Trivedi 1990). To determine the isotope ratios of the carbonate fraction, the whole rock samples were leached using either dilute acetic acid or hydrochloric acid (Singh et al., 1998). For the acetic acid leach, about 100 mg of powdered samples were treated with 20 ml of 5% acid at 60°C for 1 h. The slurry was cooled, let stand for 2-3 h and centrifuged. For hydrochloric acid leach ~ 100 mg of the powdered samples (or in some cases ~ 1 gm of a few mm size chips) were treated with ~20 ml of 0.1 N HCl at room temperature for 1-2 h and centrifuged. The leachates were dried, taken in 2.5 N HCl and Rb, Sr are separated and further purified by ion exchange procedure. The purified Rb and Sr were run for their isotopic composition using 9" radius single focussing mass spectrometer fitted with faraday cup collector and the ion current was recorded digitally.

The Sr isotopic ratios were normalized to  ${}^{86}\text{Sr}/{}^{87}\text{Sr} = 0.1194$ . The long-term stability of the mass spectrometer was checked by measuring the ratio  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  of NBS-987 standard periodically. The mean  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  value of the standard, over the past few years being 0.71025 ± 0.00007. The overall precision in the determination of  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  is

 $\pm$  0.0005 (two standard error on the mean based on ~50 measurements). These error are quite small compared to the scale of Sr isotope variation in carbonates analysed (Trivedi *et al.*, 1995; Singh *et al.*, 1998). In addition, to check on the accuracy of <sup>87</sup>Sr/<sup>86</sup>Sr measurements sample of seawater from the Arabian Sea and CaCO<sub>3</sub> from a living coral from the Lakshadweep were analysed (Trivedi *et al.*, 1995). These analyses yielded <sup>87</sup>Sr/<sup>86</sup>Sr of 0.7097  $\pm$  0.0006 and 0.7092  $\pm$  0.0002, respectively, in good agreement with contemporary seawater values. The total Rb and Sr procedural blanks were ~0.5 ng and ~4 ng respectively (Trivedi *et al.*, 1995).

# (iii) O & C isotopes measurements

The oxygen and carbon isotope measurements were made in the stable isotope mass spectrometry group. The oxygen and carbon isotopes were measured in the CO<sub>2</sub> liberated from ~5 mg of samples by treating them with 100% phosphoric acid for ~72 h. The measurements were made using a VG 903 mass spectrometer with respect to a laboratory standard calibrated against V-PDB. The precision for  $\delta^{18}$ O and  $\delta^{13}$ C measurements are ±0.2‰ (Sarkar *et al.*, 1990). The  $\delta^{18}$ O and  $\delta^{13}$ C data are expressed with respect to V-PDB, without any additional fractionation correction for  $\delta^{18}$ O in dolomite.

# (iv) Determination Elemental Abundances

#### (a) Sample preparation for elemental analysis

The chemical composition of carbonates and black shales were measured using either AAS or ICP-AES techniques. A common sample preparation procedure was followed for these measurements. For the whole rock analysis of black shales, 0.5 to 1 g of samples were dissolved using HF, HClO<sub>4</sub>, HNO<sub>3</sub> and HCl. The samples were brought in to solution using 1N HNO<sub>3</sub>. For the carbonate whole rock measurements, samples were first treated with dilute HCl to dissolve the carbonate and after the reaction was over, the slurry was centrifuged. The solution was carefully decanted into a beaker. The residue was transferred to Teflon beaker quantitatively and brought into solution after treatment with HF, HNO<sub>3</sub>, HCl. This solution was mixed with the superanate collected earlier, dried and taken in 1N HNO<sub>3</sub> for elemental measurements. For the carbonate leach measurement ~ 1g of the sample powder was treated with ~200 ml of 0.1 N HCl for 1-2 h

at room temperature with occasional stirring, The slurry was centrifuged, the superanate was made to known volume and analysed to yield elemental composition of the carbonate phase. In a few samples the residue of the 0.1N HCl leach were treated with HF, HNO<sub>3</sub>, HCl and brought to solution. These solutions were also analysed separately. The elemental composition was measured either by AAS or ICP-AES. Few of the elements were measured by both the techniques. In the following section, measurement details using the AAS and ICP-AES are discussed.

### (b) Atomic Absorption Spectrophotometry

The elemental analyses of carbonates, black shales and river water samples were done using atomic absorption spectrophotometer, Perkin Elmer models 305 and 4000, following our laboratory procedures (Sarin *et al.*, 1979; Sarin *et al.*, 1992). The instruments were calibrated using either single or multi-element laboratory standards. Wherever required the sample solutions were suitably diluted to bring the concentration to the linear portion of the absorption curve. To check the accuracy, USGS standard, W-1, was run along with the samples for several elements and the results are given in Table 2.11

Element	Measured	Recommended*
Fe (%)	8.0	7.79
Mg (%)	3.81	3.99
Ca (%)	7.6	7.82
Na (%)	2.17	1.57
Al (%)	7.63	7.86
Cu (ppm)	124	121
Mn (ppm)	1346	1364

 Table 2.11: Results of USGS standard, W-1

\* From Potts et al. (1992)

Few samples are run in duplicate to assess the reproducibility, these results are given in Table 2.12. Based on these duplicate analyses the coefficient of variation for the AAS measurements were calculated using the formula,

$$CV(\%) = \left(\frac{1}{2n}\sum_{i}\left(\frac{d_{i}}{x_{i}}\right)^{2}\right)^{\frac{1}{2}} \times 100$$

where  $d_i$  is difference between the duplicates with mean  $x_i$  and n is the total sets of duplicates. The results are given in Table 2.13.

Sample	Fe(%)	Mg(%)	Ca(%)	Na(%)	K(%)	Al(%)	Mn(ppm)	Cu(ppm)
KU92-10(1)	8.02	1.28	0.37	0.37	7.02	10.61	37	2
(2)	7.52	1.36	0.23	0.28	6.36	9.83	35	2
KU92-17(1)	2.29	1.53	0.28	0.81	3.54	9.51	57	15
(2)	2.26	1.50	0.25	0.61	3.30	9.38	59	12
KU91-39(1)	4.61	2.80	0.13	0.49	3.99	10.34	269	10
(2)	4.56	2.80	0.13	0.55	4.14	10.45	264	12
KU92-41(1)	3.64	1.75	0.15	1.21	2.81	9.62	258	13
(2)	3.93	1.80	0.16	1.46	3.04	9.78	262	15
					- · ·		-	-
KU92-53(1)	0.30	0.45	0.92	0.15	0.30	0.47	100	23
(2)	0.26	0.46	0.97	0.12	0.30	0.51	104	23

Table 2.12: Replicate measurements of different elements in blackshales using AAS

Table	2.13:	Coefficients	of	variation	for	different	elements	for	AAS
8									
measu	remen	nts							

Element	Coeff. Var.(%)		
Fe	5.5		
Mg	2.3		
Ca	15.4		
Na	15.9		
Κ	4		
Al	3		
Mn	2.5		
Cu	10		
	1		

#### (c) Inductively Coupled Plasma- Atomic Emission Spectrophotometry

Elemental composition in some of the carbonate samples were measured using a Jobin Yvon ICP-AES (model 38S;) in sequential mode. The instrument was calibrated using either commercially available or laboratory made multi-element standards. Several USGS standards were analysed to check the accuracy of the measurements. The results





Fig. 2.9: Comparison of measurement made with ICP-AES with reported values for different USGS standards. Reported concentration are from Potts *et al.* (1992)

are given in Fig. 2.9. The concentrations measured in the USGS standards are in good agreement with those reported (Potts *et al.*, 1992). During the course of this work a few of the black shale samples were analysed for their elemental concentrations both by ICP-AES and by AAS. The comparison of results shows (Fig. 2.10) that the concentrations of various elements obtained by both the techniques are in excellent agreement.

In carbonates, Sr concentration were measured by isotope dilution mass spectrometry. In a few samples, it was also measured using ICP-AES. The comparison of



Fig. 2.10: Comparison of concentration of various elements in black shales measured by ICP-AES and AAS.

TIMS and ICP-AES data is shown, Fig. 2.11. The two techniques show good agreement particularly in lower concentration range, though the ICP-AES values are generally lower by ~10%.

## (d) UV-Visible Spectrophotometry

Phosphorus in the black shales and dissolved silica in the river water samples were measured using a Beckman UV-visible spectrophotometer, model 26. Dissolved silica was measured using the molybdenum blue method (Strickland and Parsons, 1968). Phosphorus measurements in the black shale were done by dissolving ~0.5 g samples using HF, HClO<sub>4</sub>, HNO<sub>3</sub>, HCl acids. An aliquot of the solution was used for P determination using molybdenum blue method (Strickland and Parsons, 1968). The concentration-absorption curve was established with known phosphorus standards. USGS standard W-1 was run with the samples. The P measured in W-1 was 619 ppm, this compares well with the recommended value of 611 ppm (Potts *et al.*, 1992). Few black shale samples were run in duplicate. They are given in Table 2.14.



Fig. 2.11: Sr in carbonates, measured by isotope dilution mass spectrometry and by ICP-AES

Table	2.14:	Replicate	analyses	of	phosphorus	in	black	shales	using
spectr	ophoto	ometer							

P (ppm)
957
1039
738
695
365
370
460
464
493
521

Based on the above replicate results, the coefficient of variation of P measurements is calculated to be 3.7%.

Dissolved silica in river waters was measured directly from filtered water samples. Typically 5 ml samples were used for each measurements. In addition, silica concentration in a few water samples was measured by both spectrophotometry and ICP-AES. The results are given in Table 2.15:

Sample #	SiO <sub>2</sub> Concer	<u>itration</u>	
-	(a)	(b)	
RW96-1	$111 \pm 0.7$	$110 \pm 0.8$	
RW96-7	$56 \pm 0.3$	$56 \pm 0.7$	
RW96-10	$265 \pm 1.5$	$277 \pm 7$	
24/89	$118\pm0.7$	$120 \pm 1.5$	

Table 2.15: Silica concentration in river waters ( $\mu M \lambda^{-1}$ ) by spectrophotometer and ICP-AES

(a): by Spectrophotometry and (b): by ICP-AES

The errors in spectrophotometry measurements are  $\pm 1$  sigma uncertainties in the calibration. Therefore it represents the minimum error. Errors given on ICP-AES measurements are standard deviations based on three measurements of the same aliquot.

# (e) Inorganic, Organic carbon and Nitrogen analysis

Total carbon and nitrogen contents in the samples were measured using a CN analyser (FISONS model NA1500; Sarin *et al.*, 1997) while the inorganic carbon (CaCO<sub>3</sub>) using a coulometer. For CN analysis ~20 mg of samples were packed in tin cups and combusted in the furnace of CN analyser in presence of chromium trioxide and silver cobaltous cobaltic oxide catalysts. The evolved  $CO_2$  was purified from the combustion products on chromatography column and measured by thermal conductivity detector. The measured  $CO_2$  provides measure of total carbon (organic + inorganic) in the sample. The analyser was calibrated using Deer-River black shale standard and checked for its accuracy using shales of known carbon concentration. In addition, to check the precision of the measurements several black shale samples were run in duplicate for total carbon and CaCO<sub>3</sub> by coulometer (Table 2.16).

Sample	Total C (%)	Inorganic Carbon(%)
KU92-8(1)	3.47	
(2)	3.45	
KU92-17(1)	0.71	
(2)	0.68	
KU92-51(1)	1.57	
(2)	1.61	
KU92-56(1)		1.01
(2)		0.99
UK94-55(1)	1.63	
(2)	1.60	
HP96-26(1)	0.67	
(2)	0.65	
UK98-2(1)	5.57	
(2)	5.82	
UK98-9(1)		1.27
(2)		1.29
UK98-20(1)	6.89	5.08
(2)	6.80	5.08

 Table 2.16: Replicate measurements of total carbon and inorganic

 carbon in black shales

To measure the inorganic carbon ~ 50 mg of black shale samples were treated with 30% phosphoric acid in a test tube and the liberated  $CO_2$  was measured by coulometer. The duplicate analyses of the samples are given in Table 2.16.

The coefficient of variation for total carbon measurements is  $\sim 2\%$  and that for inorganic carbon measurements is 1% calculated based on the replicate measurements (Table 2.16). From these measurements, the abundance of organic carbon in the sample was calculated as:

$$C_{org} = C_T - C_I$$

where  $C_T$  is the total carbon and  $C_I$  is the inorganic (CaCO<sub>3</sub>) carbon.

## (f) Anion measurements by ion chromatography

The anions Cl, SO<sub>4</sub>, NO<sub>3</sub> and F in river water samples were measured using ion chromatograph, (Dionex model # Series 2000*i*-SP). For analyses, Dionex Ion-Pac AS4A separator column coupled with AG4A guard column were used. Samples were injected in the column where the anions were separated based on their retention time and then they were selectively eluted and their conductance were measured to determine their concentrations. The system was calibrated using multi-anion working standards. The overall precision of measurements is ~5% (Sarin *et al.*, 1992).

# (g) Mineralogical Studies

Carbonate samples were analysed for their mineralogy using Philips X-ray diffractometer and thin section microscopy. For X-ray analysis, sample powders were mounted on Al holder and scanned between  $20^{\circ}-60^{\circ}$  using copper K $\alpha_1$  radiation as X-ray source. Along with samples standards of dolomite (Thornwood, New York), calcite, limestone braccia (Boulder County) and quartz (Park County, Colorado) acquired from Ward's Natural Science Establishment, Inc., Rochester, N.Y. and a coral sample from Gulf of Kutch were also run. Various minerals present in the samples were identified based on the peaks.

Thin section studies of carbonate samples were done to study their petrography, effects of alteration (cements, veins) and presence of opaque minerals. Few of the thin sections were made at Indian Institute of Technology, Kharagpur (courtesy Prof. Amitabh Chakraborty) and others were made at Geological Survey of India, Gandhinagar. The microscopic studies of these thin sections were done using NICON UFX - 11A microscope at the Department of Geology, University of Delhi, Delhi under supervision of Prof. S.K. Tandon.

Chapter 3

Silicate & Carbonate Weathering in the Himalaya: Impact on major ion chemistry and <sup>87</sup>Sr/<sup>86</sup>Sr of the Ganga Headwaters

The impact of silicate and carbonate weathering in regulating the major ion composition and <sup>87</sup>Sr/<sup>86</sup>Sr of the headwaters of the Ganga-Ghaghara-Indus is discussed in this chapter. This has been achieved by (i) making new measurements on the chemical composition and <sup>87</sup>Sr/<sup>86</sup>Sr of the extensive Precambrian carbonate deposits from the Lesser Himalaya and in a few headwaters of the Ganga-Ghaghara-Alaknanda system (Singh *et al.*, 1998) and (ii) analysing available data on the chemical and Sr isotope composition of these rivers (Sarin *et al.*, 1989; Krishnaswami *et al.*, 1992; Sarin *et al.*, 1992; Pande *et al.*, 1994 and Trivedi *et al.*, 1995) and granite/gneisses/metasediments from the Lesser and Higher Himalaya (Kashyap 1972; Misra *et al.*, 1973; LeFort, 1975; Rao, 1983; Bhattacharya *et al.*, 1984; Rawat 1984; Nautiyal and Rawat, 1990; Choudhury *et al.*, 1991; Gupta *et al.*, 1994; Kaur and Chamyal, 1996)

It is well established that the <sup>87</sup>Sr/<sup>86</sup>Sr of the oceans has been steadily increasing through the Cenozoic (Veizer, 1989; Richter et al., 1992). The sources contributing to this increase has been a topic of considerable interest and debate. It has been attributed to recent mountain building activities, e.g. the Himalaya, and associated enhanced chemical weathering of silicates (Raymo and Rudimann, 1992). This will have effect on global climate change as enhanced silicate weathering would cause drawdown of CO<sub>2</sub> from the atmosphere contributing to cooling. Subsequently, Palmer and Edmond (1992) suggested that the high <sup>87</sup>Sr/<sup>86</sup>Sr in the Himalayan rivers is due to the weathering of metamorphosed carbonates which have acquired high <sup>87</sup>Sr/<sup>86</sup>Sr from the mobilisation of radiogenic Sr from silicates during metamorphism. This inference was based on the observation that the major ion chemistry of the Ganga is dominated by carbonate weathering and the mixing line between <sup>87</sup>Sr/<sup>86</sup>Sr and (1/Sr) of the river waters predicted a value of 0.7209 for the high Sr endmenber generally taken to be carbonates. If carbonates are indeed the source for the high  ${}^{87}$ Sr/ ${}^{86}$ Sr in the headwaters, then under steady state it would not affect CO<sub>2</sub> balance of the atmosphere. Thus it is important to understand the source(s) of the high <sup>87</sup>Sr/<sup>86</sup>Sr in these rivers, which will provide better insight into the coupling between tectonics, chemical weathering and global change. In this context, a major emphasis of this thesis has been to assess the role of silicate and carbonate weathering in contributing to the major ion chemistry and Sr isotope composition of rivers draining the southern slopes of the Higher and Lesser Himalaya. Data on the chemical and isotopic

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composition of granite/gneissess of the region are available in literature, whereas there is almost no data on carbonates. Therefore, a detailed investigation of the large carbonate outcrops of the Lesser Himalaya through which the headwaters of the major rivers flow was undertaken.

The Precambrian carbonate deposits, occurring in abundance all across the Lesser Himalaya, in the drainage basins of the several of the headwaters of Ganga-Ghaghara-Indus, were collected from different locations (Fig. 3.1) and were analysed for their mineralogy, chemical composition and Sr, C, O isotopes to study their importance in contributing to the present day chemistry and Sr isotope composition of the Himalayan rivers. In addition, the studies of the composition of ancient sedimentary carbonates provide a means to constrain the chemical and isotopic evolution of the seawater through time. The measured isotopic and chemical composition of ancient carbonates is a result of their original composition (i.e., at the time of their deposition) and postdepositional overprinting on their original signatures. Veizer (1983), Hall and Veizer (1996) have used covariation trends in the elemental and stable isotope systematics to identify and to select "least altered" carbonates for paleoceanographic research. Some of these approaches have been followed to obtain *qualitative* information on the alteration effects in the samples analysed. Main goal of this study, however, is to assess the importance of these carbonate deposits in contributing to major ions and Sr isotopes to the river waters which currently flow through them.

# **3.1. MINERALOGY, CHEMICAL AND ISOTOPIC COMPOSITION OF THE PRECAMBRIAN CARBONATES**

#### (i) Mineralogy and Chemical Composition

Thin section microscopy and XRD studies helped in the identification of various minerals present in the Precambrian carbonates analysed in this study. Chemical composition measurements also provided an idea of their mineralogical composition of the carbonates. The mineralogical and chemical composition of the samples analysed are given in Table 3.1. Microscopic studies reveal that most of the samples are micrites, some are made of spars and microspars. Polycrystalline rhombs of calcite are scattered within the micrite/micro-sparite groundmass. The grain margins are often blurred due to

Fig.3.1
recrystallisation. The micrite ground mass are often cut with veins filled with secondary calcite or quartz (Fig. 3.2). Secondary silica growth and opaque hexagonal grain are also seen in some of the samples (Fig. 3.3). In many samples, pore spaces or veins are filled with cements whereas in some of them original carbonate fragments are distributed in cements deposited later. In some of the samples, particularly those collected close to the MCT, effects of metamorphism is seen from the presence of schistosity (Fig. 3.4). During mountain building process, near the MCT, due to high temperature and pressure part of the carbonates could have been converted to marble. The thin section studies, thus show evidence for alteration of these carbonates.

X-Ray diffraction studies show pronounced peaks of dolomite and calcite in most of the samples (Fig. 3.5) whereas in a few of them quartz peaks are also present. Microscopic and XRD studies and chemical composition measurements all suggest that many of these carbonates are predominantly made of dolomite, the few exceptions being the limestones from Shali-Bilaspur in the inner belt and Dehradun-Mussoorie in the outer belt (Table 3.1).

The average **bulk** chemical composition of dolomites and limestones from the inner and outer belts are given in Table 3.1 and their average in Table 3.3. Most of the samples contain abundant Mg, consistent with that expected based on X-ray diffraction studies. Among the samples analysed only five of them had Mg  $\leq \sim 1\%$  (UK95-19, HP94-41, HP94-42, UK94-76, UK94-44 and UK94-45) others had Mg 3.3-12.8% (Table 3.1) with Mg/Ca (molar) 0.008 to 1.25. The Al content of carbonate rocks were generally low, except in three samples from the inner belt where it was in excess of 1% (KU92-43, KU92-46 and UK94-78). The high Al content in the inner belt samples is due to their association with shale/slate (rhythmites). Often they are intercalated with layers of varying thickness of shales or slates. The low Al, particularly in the outer belt samples, suggests that these carbonate rocks are generally pure with very low aluminosilicate contamination. The concentration of Rb showed considerable variation, 0.05-165 ppm, the highest concentration was in sample KU92-46 which also had the highest Al (Table 3.1). Statistical analysis of Rb and Al data show a strong positive correlation between them (correlation coefficient 0.94) indicating a common source for both, aluminosilicates. A covariance plot of Mn with Al doesn't show any discernible trend

Fig.3.2

Fig.3.3 Fig.3.4 Fig.3.5

which indicates that Mn has been added to the carbonates during their alterations. Broadly, among the dolomites, the samples from the inner belt have higher Al, Rb and <sup>87</sup>Sr/<sup>86</sup>Sr (Table 3.3). The high Al in the inner belt samples is consistent with field observations that many of them occur as intercalations of carbonates and shales/slates with significant spatial variability in their relative thicknesses.

The chemistry of the bulk samples (Table 3.1) and their mild acid leaches (0.1N HCl or 5% Acetic acid) show that most (>90%) of the Ca, Mg, Sr and Mn are leachable



Fig. 3.6: Histogram of leachable fractions of Ca, Mn, Sr and Al in mild acid. Figures show that most of the Ca, Sr and Mn is leachable and hence are associated with the carbonate phase. Leachable Al shows considerable range, probably due to its association with more resistant alumino-silicates

from the bulk rock suggesting that these elements reside almost entirely in the carbonate phase (Fig. 3.6). In contrast, the fraction of leachable Al shows a wide scatter (3% to 64%), averaging ~30%. Among the elements in the carbonate fraction, the abundances of

Sr and Mn are determined by the extent of alteration of the samples (Veizer 1983, Hall and Veizer 1996). During alteration, the carbonate matrix loses Sr and gains Mn and their



Fig. 3.7: Scatter diagram of Sr/Cs vs Mn in the carbonates analysed. The abundances in the bulk samples are plotted as most of the Sr and Mn are associated with carbonate phase. The overall negative trend is indicative of gain of Mn and loss of Sr suggestive of alteration of the samples.

covariation trend provides a measure of the preservation of their original signatures. The mean concentration of Sr in the dolomites and the limestones from the inner belt are 48 and 148 ppm respectively, in the outer belt samples these are about a factor of two higher (Table 3.3). In general, the concentration of Sr in the carbonates from the Lesser Himalaya are significantly lower than those in recent marine carbonates but are similar to those of Precambrian carbonates (Mirota and Veizer, 1994).

Figure 3.7 is a scatter diagram of (Sr/Ca) vs Mn in the samples analysed, the bulk composition has been plotted as most of the Sr and Mn are contained in the carbonate phase. The data in Fig. 3.7 show an overall negative trend. A possible cause for the

scatter in Fig. 3.7 may be the extent and nature of their alteration and the properties of the endmembers involved. Further in Fig. 3.7 the data of all the samples analysed have been pooled which include limestone and dolomites that are derived from different carbonate formations, Krol, Deoban, Mandhali and Shali which were deposited at different time periods.

### (ii) Oxygen and Carbon isotopes

The mean  $\delta^{18}O_{(PDB)}$  and  $\delta^{13}C_{(PDB)}$  data for the dolomites and limestones from the inner and outer belts overlap with each other, with mean values of ~ -9‰ and ~1‰ respectively (Table 3.3). The  $\delta^{18}O$  data show a wide range, -1.4 ‰ to - 12.8 ‰ (Table 3.2) similar to those reported for the Krol carbonates (Bhattacharya *et al.*, 1996 ; Sarkar *et al.*, 1996; Kumar, 1998) and for the Precambrian carbonates from other geographical regions (Veizer and Hoefs, 1976; Hall and Veizer, 1996). The  $\delta^{13}C$  values, in comparison show a narrow range, -1‰ to +3.3‰ (Table 3.2), as the carbon isotope pool is dominated by the carbonates. It is known (Mirota and Veizer, 1994) that oxygen isotopes shift towards lighter  $\delta^{18}O$  values during dolomitization. Development of fractures and



Fig. 3.8: Covariation plot of  $\delta^{13}$ C vs Sr. The overall positive trend observed may result from alteration of the carbonates by fresh water causing depletion in  $\delta^{13}$ C and removal of Sr.

microfractures due to compaction and/or tectonic activity can provide passage for fluids and pore space that can be filled with cements. Cementation associated with influx of extraneous water commonly leads to alteration of isotopic composition. In fact in many of the samples thin section studies show evidence for cementation. Fig. 3.8 is a plot of  $\delta^{13}$ C –vs- Sr, which shows an overall positive trend. The factor(s) contributing to the trend is unclear, a possible explanation could be the alteration of carbonates by fresh water (containing biogenic CO<sub>2</sub>) causing depletion in  $\delta^{13}$ C and removal of Sr. The quantitative significance of this hypothesis, however, needs to be assessed. Analysis of  $\delta^{18}$ O –vs- Mn and  $\delta^{18}$ O –vs- Sr data in the carbonates from the Lesser Himalaya, however, did not show any significant covariation.

The present studies based on thin sections microscopy,  $\delta^{13}$ C,  $\delta^{18}$ O, Mn, Sr and  $^{87}$ Sr/ $^{86}$ Sr on the Precambrian carbonates from the Lesser Himalaya all seem to suggest that many of these carbonates have been altered. Attempts were **not** made to study the extent of alteration in greater detail, as it is **not** directly relevant to the main goal of this study, which is to evaluate the role of weathering of these carbonates in contributing to the **present day** major ion and Sr isotope budget of the rivers draining through them. Such a study only requires the knowledge of the chemical and isotopic composition of the carbonates being **currently** weathered and not the details of how their composition has evolved.

### (iii) Sr isotope systematics

The Sr isotopic composition of the bulk carbonate rocks and their mild acid leaches show considerable variation, from 0.7064 to 0.8935 (Table 3.2). Most of the samples, however, have <sup>87</sup>Sr/<sup>86</sup>Sr in the range of 0.7064 - 0.7300, with two samples from the Gangolihat - Pithoragarh region having extremely high values, 0.8535 and 0.8935 respectively (Table 3.2). The <sup>87</sup>Sr/<sup>86</sup>Sr of the leaches are similar to those of the bulk samples (Table 3.2) consistent with that expected as most of the Sr in the bulk rock is leachable (Fig. 3.6). While this work was in progress, Sarkar *et al.* (1996) reported <sup>87</sup>Sr/<sup>86</sup>Sr in the carbonate fraction of a few samples from Krol-Tal formations, their <sup>87</sup>Sr/<sup>86</sup>Sr in carbonates from the Lesser Himalaya are sparse; Galy (1999) reports value of 0.7395-0.8572 with low Sr and Quade *et al.* (1997) values of ~0.73 for detrital carbonates from Nepal rivers. Among

the samples analysed, those from the inner belt have higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios. The samples having the most radiogenic ratios are KU92-43 and 46 (Table 3.2) also have high Al content (Table 3.1). Both these samples are rythmites made of layers of carbonates and silicates. The Sr isotope ratio of the carbonate fraction of these samples also are highly radiogenic with values in excess of 0.85 (Table 3.2). Two other bulk samples which have <sup>87</sup>Sr/<sup>86</sup>Sr in excess of 0.73 are KU92-26 and 36 (Table 3.2). KU92-26 is from the northern Thal-Tejam region an area which is reported to be affected by enhanced metamorphism (Bhattacharya, 1982) and KU92-36 was collected at the contact with gneiss. The Sr isotope composition of mild acid leaches of these samples are also quite radiogenic, attesting to the influence of alteration processes in the redistribution of Sr isotope systematics of many carbonates. These results lead us to infer that the Sr isotope systematics of many carbonates from this region have been modified by postdepositional addition of radiogenic Sr.

The chronology of the carbonates analysed in this study is not well established. However, based on stromatolites Valdiya (1980) has inferred that the Deoban, Mandhali, Shali were deposited during Middle Riphean to Vendian and the Krol during Late Precambrian. The <sup>87</sup>Sr/<sup>86</sup>Sr during this period was 0.705-0.707 (Veizer, 1989). The <sup>87</sup>Sr/<sup>86</sup>Sr of the carbonate fraction of many samples analysed in this study are significantly higher than that of seawater of that time, 0.705-0.707 (Veizer, 1989) suggesting postdepositional addition of radiogenic Sr to the carbonates. Widespread metamorphism and magmatism in the Himalaya involving large-scale fluid transport could have caused loss of Sr from the carbonate and redistribution of Sr isotopes between coexisting silicates and carbonates resulting in the formation of carbonates with low Sr content and high <sup>87</sup>Sr/<sup>86</sup>Sr. Sr isotope composition can also be modified near the carbonate-silicate boundary by diffusive processes. During metamorphism fluids containing Sr can diffuse into the carbonates and silicates and modify their isotopic signatures (Bickle *et al.*, 1995; Gazis *et al.*, 1998).

Code		Sr ppm	Whole Rock <sup>87</sup> Sr/ <sup>86</sup> Sr	Leach <sup>87</sup> Sr/ <sup>86</sup> Sr	δ <sup>13</sup> C(PDB)* (‰)	δ <sup>18</sup> O(PDB)* (‰)
INNER	BELT					
Gangolik	hat - Pithoragarh					
KU92-9		41	0.7102	_	-0.5	-11.5
KU92-13	3	66	0.7064	_	0.4	-9.1
UK95-19	)	114	0.7067	-	-0.6	-9.0
UK95-19	$\partial(\mathbf{R})$		0.7068			
KU92-43	3	84	0.8786	0.8935	0.6	-12.5
KU92-46	5	48	0.8901	0.8535	-0.3	-9.1
Thal -Te	jam - Pipalkoti					
KU92-22		30	0.7147	-	-0.1	-10.2
KU92-26	5	22	0.7323	0.7314	-0.7	-6.4
KU92-36	5	68	0.7314	0.7173	-0.7	-10.9
UK95-12	2	24	0.7286	0.7246	1.0	-9.0
Shali - B	ilaspur					
HP94-41	-	104	0.7219	0.7219	-0.8	-9.7
HP94-42		124	0.7171	0.7159	-1.0	-11.2
HP94-42	(R)	-	-	0.7158		
HP94-43		20	0.7144	0.7138	-0.5	-6.5
Chakrata	ı - Deoban - Tiuni					
UK94-76	õ	325		0.7087		
UK94-77	7	33		0.7162		
UK94-78	3	363		0.7102		
UK94-97	7	52		0.7081		
OUTER	BELT					
Dehradu	n-Mussoorie					
UK94-44	ŀ	282	0.7093	0.7089	1.0	-12.8
UK94-45	5	305	0.7124	0.7097	2.7	-9.2
UK94-50	)	173	0.7098	0.7095	1.9	-12.5
UK95-3		147	0.7102	-	1.2	-11.8
KU92-55		141	0.7142	-	0.1	-8.7
UK94-67	7	52	-	0.7147	0.7	-9.8
UK95-6		33	0.7093	-	2.8	-3.9
UK95-7		240	0.7096	-	1.8	-1.4
VKC-11		62	0.7128	-		
VBL-1		53	0.7139	-		
Nainital	<b>、</b>	~ ~	0 =1 11	0 =1 10		
KU92-48	3	95	0.7141	0.7148	3.3	-3.6
UK95-22	2	52	0.7088	-	2.0	-9.7
UK95-23	5	67	0.7108	-	0.4	-10.3
UK95-24	ŀ	44	0.7107	-	0.5	-12.1
Solan				0.7100	1 7	7 (
HP94-13		-	-	0./109	1./	-/.6
SPITI V		1029	0.7092			
5P1-5(G	ypsum)	1028	0.7082	-		

Table 3.2 : Sr,O & C isotopic data on carbonate rocks from the Lesser Himalaya

( R ) - repeat measurement \* no fractionation correction was made for dolomites

Inner Belt				Outer Belt				All samples		
	Dolomi	te	Limeste	one*	Dolomi	te	Limesto	one*		
Element	mean <sup>+</sup>	log1σ	mean <sup>+</sup>	log1σ	mean <sup>+</sup>	log1 <del>o</del>	mean <sup>+</sup>	log1σ	mean	σ
Ca (%)	18.0	0.15	34.0	0.05	23.8	0.08	38.0	0.03	24.3	7.7
Mg (%)	9.6	0.13	0.42	0.38	9.6	0.20	0.50	0.43	8.3	4.7
Al (%)	0.32	0.94	0.21	0.46	0.06	0.67	0.02	0.49	0.43	0.95
Sr (ppm)	48	0.34	148	0.23	83	0.28	293	0.02	109	98
Mn (ppm)	219	0.52	172	0.34	349	0.59	14	0.13	501	635
Rb (ppm)	12	0.69	6	0.51	0.89	0.78	0.05	-	15	34
Isotopes	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ
$\delta^{13}$ C (‰)	-0.1	0.6	-0.8	0.2	1.5	1.0	1.9	1.2	0.7	1.2
$\delta^{18}$ O (‰)	-9.5	2.1	-10.0	1.1	-8.3	3.8	-11.0	2.6	-9.1	2.9
<sup>87</sup> Sr/ <sup>86</sup> Sr	0.745	0.066	0.714	0.007	0.712	0.002	0.711	0.002	0.725	0.043

### Table 3.3 : Mean composition of carbonate rocks from the Lesser Himalaya

+ geometric mean, all other arithmatic mean, data from Tables 3.1 and 3.2

\* Carbonates having  $\leq$  ~1% Mg is considered as limestones. Samples UK95-19, HP94-41 & 42 and UK94-76 of the inner belt, UK94-44 & 45 of the outer belt fall in this category.

## Table 3.4: Range in Sr abundance and <sup>87</sup>Sr/<sup>86</sup>Sr in carbonates from the Lesser Himalaya

Sample/location	Sr (ppm)	<sup>87</sup> Sr/ <sup>86</sup> Sr	Ref.
Lesser Himalaya Pc. Carbonates	20-363	0.7064-0.8901	This work <sup>+</sup>
Detrital Carbonates Nepal, Siwalik	NA	0.722 - 0.734	Quade et al., 1997
Lesser Himalaya	28-55	0.7395-0.8572	Galy, 1999
Krol Belt	252-588	0.70976-0.72918	Sarkar <i>et al.</i> , 1996

+ : Whole rock data (Table 3.2) NA: Not Available

## (iv) Impact of carbonate weathering on <sup>87</sup>Sr/<sup>86</sup>Sr of the Ganga-Ghaghara-Indus Headwaters

One of the unique characteristics of the G-G-I source waters is their high <sup>87</sup>Sr/<sup>86</sup>Sr and Sr concentration (Palmer and Edmond, 1989; Edmond, 1992; Krishnaswami et al., 1992;Palmer and Edmond, 1992; Pande et al., 1994; Trivedi et al., 1995). The source(s) for the high <sup>87</sup>Sr/<sup>86</sup>Sr is still debated and includes weathering of granites/gneisses (Krishnaswami et al., 1992; Edmond, 1992), metasediments (Harris, 1995) and metamorphosed carbonates (Palmer and Edmond, 1992). Quade et al. (1997) based on <sup>87</sup>Sr/<sup>86</sup>Sr studies of soil carbonates from the Siwaliks and detrital carbonates from the rivers of Nepal have suggested that carbonates are important and perhaps dominant source for the high  ${}^{87}$ Sr/ ${}^{86}$ Sr in the rivers of the Himalava. Harris *et al.* (1998) and Blum et al. (1998) based on the analysis of Bhote Kosi and Raikhot rivers, two minor tributaries of the Ganga and Indus respectively, for their major ion chemistry and Sr isotopes also have highlighted the importance of carbonate weathering in contributing to the Sr flux and high <sup>87</sup>Sr/<sup>86</sup>Sr of the Himalayan rivers. The suggestion of Palmer and Edmond (1992) stems from the observation that the major ion chemistry of G-B rivers is dominated by carbonate weathering and that the covariation trend between <sup>87</sup>Sr/<sup>86</sup>Sr and (1/Sr) predicts a value of 0.7209 for the high Sr end member, generally taken to be carbonates. Interestingly the mean  ${}^{87}$ Sr/ ${}^{86}$ Sr of the bulk carbonates analysed in this study, 0.725 (Table 3.3) is very similar to that estimated by Palmer and Edmond (1992). Our results on carbonates show that their  ${}^{87}$ Sr/ ${}^{86}$ Sr are generally <0.72, though a few samples have values as high as ~0.85 (Table 3.2; Fig. 3.9). The river water <sup>87</sup>Sr/<sup>86</sup>Sr are always in excess of 0.72 (Krishnaswami et al., 1992, Pande et al., 1994, Trivedi et al., 1995; Fig. 3.9). Therefore, if carbonates have to be an important source for the high  ${}^{87}$ Sr/ ${}^{86}$ Sr of the headwaters, then carbonates with adequate Sr and high <sup>87</sup>Sr/<sup>86</sup>Sr (comparable to those in headwaters) have to be exposed over wide areas of the Himalaya. Both these conditions are not met by the Precambrian carbonate outcrops of the Lesser Himalaya, the largest carbonate exposure in the drainage basins of many of these headwaters. These carbonates have low Sr and <sup>87</sup>Sr/<sup>86</sup>Sr generally <0.720. These observations lead to the conclusion that the weathering of these Precambrian carbonates cannot be a major source for the high radiogenic Sr to these rivers on a basinwide scale, though they can be important for some tributaries which flow through carbonates with extraordinarily radiogenic Sr isotope composition. A more detailed discussion on the source(s) of radiogenic Sr to the headwaters is presented in the next section.



Fig.3.9: Histograms showing the comparison <sup>87</sup>Sr/<sup>86</sup>Sr and Sr/Ca in the G-G-I source waters and Precambrian carbonates. Both <sup>87</sup>Sr/<sup>86</sup>Sr and Sr/Ca in the headwaters are much higher than those of the Precambrian carbonates.

### (v) Sr contribution from Precambrian carbonates to the headwaters

An upper limit on the carbonate Sr to the headwaters can be derived by assuming that (i) *all* Ca in the rivers is of carbonate origin and (ii) the Sr/Ca ratio in the carbonates is  $0.20\pm0.15$  (nM/µM), the mean value measured in the Precambrian carbonate outcrop (this study; Table 3.3; Fig. 3.9) and (iii) Ca and Sr in these carbonates are getting weathered congruently. The results (Fig. 3.10) show that the carbonate Sr can account for 6 to 44% (mean 18%) of measured riverine Sr. The limit would increase to 11 to 77%, (mean 31%) if the Sr/Ca ratio in the carbonates is taken as 0.35; one sigma over the mean

value. Considering that Ca can also be supplied to these rivers from the weathering of silicates, evaporites, and phosphates the Precambrian carbonate component of Sr in the Himalayan rivers is likely to be lower than that estimated above. These estimates indicate



Fig. 3.10: Carbonate Sr component in the G-G-I source waters. The values are *upper limits* and are calculated by assuming that *all* the Ca in the headwaters is of carbonate origin and Sr/Ca in carbonates as 0.2 nM/ $\mu$ M, their mean abundance ratio in Precambrian carbonate outcrops (top) and 0.35 nM/ $\mu$ M, 1 $\sigma$  over the mean abundance ratio in carbonates (bottom).

that bulk of the Sr in most of these rivers has to originate from sources other than Precambrian carbonates of the Lesser Himalaya such as weathering of silicates, evaporites, and phosphates and other carbonates.

The role of carbonates in contributing to the high strontium isotope composition of the source waters is governed by their  ${}^{87}$ Sr/ ${}^{86}$ Sr and their supply of Sr to the rivers. Thus, rivers draining carbonates with  ${}^{87}$ Sr/ ${}^{86}$ Sr of ~0.85, such as those from Gangolihat-

Pithoragarh would have  ${}^{87}$ Sr/ ${}^{86}$ Sr in excess of 0.74, even if the fraction of carbonate Sr in them is only ~18%, the balance Sr being supplied from silicates with  ${}^{87}$ Sr/ ${}^{86}$ Sr of 0.720.

Sarkar et al. (1996) and Quade et al. (1997) have recently proposed that carbonates are important and perhaps dominant source of high <sup>87</sup>Sr/<sup>86</sup>Sr in the rivers of the Himalaya. Sarkar et al. (1996) arrived at this conclusion based on the analysis of Krol - Tal carbonates from the Garhwal (Kumaun) Himalaya whereas the suggestion of Quade et al. (1997) relies on the <sup>87</sup>Sr/<sup>86</sup>Sr measurements of soil carbonates from the Siwalik and detrital carbonates from the rivers of Nepal. The Sr isotope data measured by these two groups and in the present study in the various carbonates overlap with each other and show that many of these are quite radiogenic in composition (Table 3.4). This by itself, however, does not make the carbonates to be a dominant source of the high <sup>87</sup>Sr/<sup>86</sup>Sr in rivers, as it would also depend on their contribution to the Sr budget of the rivers. Out of eight samples analysed by Sarkar et al., (1996) five have <sup>87</sup>Sr/<sup>86</sup>Sr between 0.720 to 0.729 and the average of all the samples is 0.719 which is slightly higher than the vaverage value of 0.711 obtained in this work for the Krol belt (outer belt) samples (Table 3.3). The Sr concentration measured by acid leaching of the samples are 252 to 588 ppm (Sarkar et al., 1996); their Sr/Ca however is not available as Ca data is not reported. The samples analysed by Sarkar et al. (1996) are from the same formation (Krol-Tal) in which measurements have been made in this study. If the mean Sr/Ca ratio of the Krol belt samples analysed in this study ( $0.21\pm0.14$  nM/ $\mu$ M) is typical of Krol-Tal carbonates from all locations, then they are unlikely to be a major source of Sr to the rivers as their Sr/Ca is significantly lower than in rivers. It is seen from above, that data on both Sr isotopic ratio and Sr/Ca in carbonates are needed to make proper assessment of their role in contributing Sr isotope budget of the rivers. The estimate based on Sr/Ca ratios of Precambrian carbonates measured in this study suggest that on the average they account for only one fifth of the Sr in the source waters. Based on above calculations it can be inferred that the Precambrian carbonates are unlikely to be a major source of high <sup>87</sup>Sr/<sup>86</sup>Sr to the rivers on a basinwide scale, however, they could be significant for particular streams.

Harris *et al.*, (1998), based on the study of cations and Sr abundances and <sup>87</sup>Sr/<sup>86</sup>Sr in dissolved phase, bed load bulk samples and their leachates of the Bhote Kosi

river, a minor tributary of Ganga, in the Nepal Himalaya concluded that Sr isotope compositions of the headwaters is determined by a small contribution ( $\sim 10\%$ ) from highly radiogenic silicates and ~90% from carbonates which can have  ${}^{87}$ Sr/ ${}^{86}$ Sr upto ~0.8. This inference relies on the Sr isotopic composition determined in leachates of bed loads and an assumed value of  $10^{-3}$  for the molar ratio of Sr/(Ca+Mg) in the carbonates. The leachates have values of <sup>87</sup>Sr/<sup>86</sup>Sr in range of 0.712 to 0.792, with a mean of ~0.720, typical of those observed from carbonates analysed in this study. The Sr/(Ca+Mg) of  $10^{-3}$ is much higher than those measured for Precambrian carbonates in this work and suggest the need to have measurements of Sr/(Ca+Mg) in the carbonates drained by the Bhote Kosi. In another study, Blum et al. (1998) suggested that vein carbonates present in granite/gneisses of the Higher Himalayan Crystalline Series are contributing to about three fourth of the Sr budget of the Raikhot river in the Higher Himalayan watershed. Based on a Ca/Sr vs <sup>87</sup>Sr/<sup>86</sup>Sr plot, they infer that the vein calcites to have Ca/Sr molar ratio 5000 and <sup>87</sup>Sr/<sup>86</sup>Sr ~0.82. High <sup>87</sup>Sr/<sup>86</sup>Sr of the vein calcite is due the migration of radiogenic Sr to the calcite from the silicates during metamorphism. This is an interesting suggestion and its importance in contributing to the Sr isotope budget of the headwaters can be better assessed if more data on the abundance of vein calcites, their Ca/Sr ratios and  ${}^{87}$ Sr/ ${}^{86}$ Sr become available.

In the following, attempts are made to make elemental and Sr isotope budget for the G-G-I headwaters based on contributions from various sources. Towards this, it is necessary to chemically and isotopically characterise the various endmembers and quantify their contribution to the major ions and Sr isotope composition of the source waters of the Ganga-Ghaghara-Indus. These are discussed below.

# **3.2.** SILICATE AND CARBONATE WEATHERING IN THE GANGA-GHAGHARA-INDUS BASIN: CONTRIBUTION TO THE CHEMICAL AND Sr ISOTOPE BUDGETS OF RIVERS.

### (i) Major ion chemistry of the G-G-I source waters

Considerable amount of data on the major ion chemistry of the headwaters of the G-G-I system draining the southern slopes of the Himalaya are available (Sarin *et al.*, 1992; Pande *et al.*, 1994; Trivedi *et al.*, 1995; this study). These results have been

summarised in this section and are used to derive information on the role of silicate and carbonate weathering in the drainage basins. The major rivers of the source waters of the Ganga (Bhagirathi, Bhilangna, Alaknanda, Pindar), the Ghaghara (Sarju, Ramganga, Kali) and the Indus (Beas) all originate in the Higher Himalaya, however, a large fraction of their drainage basins and those of their tributaries lie in the Lesser Himalaya (Fig. 3.1). Sutlej, another major tributary of the Indus has its origin in the Tibetan Plateau and flows through Laddakh and Zanskar before it crosses the Higher Himalaya.

Data on the major ion composition of the source waters of the Ganga, Ghaghara and the Indus and their Sr isotope composition (Table 3.5) are compiled from the earlier publications (Sarin *et al.*, 1989; Krishnaswami *et al.*, 1992; Sarin *et al.*, 1992; Pande *et al.*, 1994; Trivedi *et al.*, 1995). In addition, new measurements on a few samples of the Alaknanda, Pindar, Sarju and Kali are included (RW series, Table 3.5), these samples were collected as a part of this work during Sept 1996, towards the end of the monsoon season.

The chemical composition of rivers at any given site is governed by contributions from the following:

- (i) supply of solutes from upstream of the site,
- (ii) weathering of local bed rocks and detritus transported to the site from upstream and
- (iii) contributions from various tributaries.

Thus, the major ion composition of the Bhagirathi at Devprayag (Fig.3.1), for example, will depend on the input of solutes by weathering all through its drainage basin, from its source in the Gangotri glacier in the Higher Himalaya to Devprayag in the Lesser Himalaya and the supply from its tributaries. Analogous to Bhagirathi, the water chemistry of many major rivers of the Ganga-Ghaghara source waters (e.g. Bhilangna, Alaknanda, Pindar, Kali, Sarju, and Ramganga) would be determined by the bed rock lithologies of both the Higher and Lesser Himalaya as they flow through both these terrains. The chemical weathering rates in the Lesser Himalaya, however, is expected to be higher than those in the Higher Himalaya because of higher temperature, rainfall and the availability of more soil  $CO_2$  for weathering. The material being weathered may involve bed rocks and soils from the Lesser Himalaya and detritus transported from the

Himalayan Crystallines. It is established that significant part of sediments depositing in the Bay of Bengal Fan is transported from the Higher Himalaya (France-Lanord *et al.*, 1993).

Source					~		~	87~ 86~	
Code	River	Date	Na	Κ	Ca	Mg	Sr	°'Sr/°°Sr	
Ganga									
13	Bhagirathi <sup>+</sup>	April, 89	141	64	291	103	331	0.7667	
16	Bhagirathi	April, 89	131	47	392	170	694	0.7482	
10	Bhagirathi	April, 89	145	48	367	139	524	0.7614	
11	Bhagirathi	April, 89	193	51	348	144	503	0.7604	
8	Bhagirathi	April, 89	150	52	373	134	502	0.7561	
4	Bhagirathi	April, 89	163	53	396	149	560	0.7570	
5	Bhagirathi	April, 89	154	51	377	136	420	0.7583	
23	Bhagirathi	April, 89	154	51	385	134	529	0.7589	
RW-3	Bhagirathi	Sept, 96	65	35	249	89			
14	Kedarganga <sup>-</sup>	April, 89	98	83	373	93	262	0.7420	
15	Son gad	April, 89	55	56	367	52	315	0.7300	
17	Helgu gad	April, 89	51	29	135	31	168	0.7659	
9	Pilang gad	April, 89	68	34	179	52	181	0.7902	
12	Asiganga	April, 89	42	51	229	60	184	0.7624	
7	Nagun gad	April, 89	249	29	555	190	1390	0.7574	
6	Seansu gad	April, 89	294	28	394	139	1000	0.7572	
19	Bhilangna	April, 89	89	46	288	54	224	0.7554	
22	Bhilangna	April, 89	107	49	298	67	246	0.7600	
3	Bhilangna	April, 89	115	44	310	93	265	0.7656	
20	Jola gad	April, 89	184	31	160	82	273	0.7986	
21	Nailchami gad	April, 89	132	61	388	187	431	0.7482	
18	Balganga	April, 89	119	36	310	108	367	0.7714	
28	Alaknanda <sup>+</sup>	Oct, 90	44	19	175	23	141	0.7569	
29	Alaknanda	Oct, 90	70	40	422	185	650	0.7350	
24	Alaknanda	April, 89	107	51	429	175	644	0.7385	
RW-4	Alaknanda	Sept, 96	47	36	438	135			
RW-5	Alaknanda	Sept, 96	44	35	420	165			
RW-6	Alaknanda	Sept, 96	51	46	564	232			
RW-7	Alaknanda <sup>+</sup>	Sept. 96	44	18	187	27			
RW-8	Pindar	Sept. 96	46	37	472	202			
2	Ganga	April. 89	143	51	496	242	676	0.7425	
RW-1	Ganga	Sept. 96	65	43	355	122		_	
RW-2	Ganga	Sept. 96	61	37	316	103			
1	Song	April. 89	283	28	842	432	1310	0.7315	
Ghagh		<u>r</u> i, 0)	_00	_0	÷.=		1010	0	
ara									
R-1	Sariu	Sept. 92	77	33	577		263	0.7585	
R-6	Sariu	Sept. 92	71	34	551		311	0.7514	
	~~~	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	, <b>1</b>		001		~ 1 1		

Table 3.5: Major ion and Sr concentrations and <sup>87</sup>Sr/<sup>86</sup>Sr in G-G-I source waters.

<b>R-7</b>	Sarju	Sept, 92	75	33	551		286	0.7553
RW-9	Sarju	Sept, 96	66	31	645	521		
R-2	Ramganga	Sept, 92	126	30	379		296	0.7757
RW-10	Ramganga	Sept, 96	133	29	338	201		
R-3	Ghat gad	Sept, 92	92	34	609		316	0.7508
R-4	Kali	Sept, 92	65	39	551		1320	0.7276
RW-11	Kali	Sept, 96	53	34	585	367		
R-5	Gori	Sept, 92	78	41	456		768	0.7490
R-8	Panar	Sept, 92	325	52	545		1245	0.7408
R-9	Suyal	Sept, 92	190	39	211		413	0.7351
Indus								
IND-1	Sutlej	Aug, 91	84	82	622	193	1962	0.7166
IND-2	Beas <sup>+</sup>	Aug, 91	48	25	148	39	169	0.7448
IND-20	Beas <sup>+</sup>	Aug, 91	22	14	61	18	105	0.7225
IND-3	$Chandra^+$	Aug, 91	24	21	353	76	1118	0.7239
IND-4	$Bhaga^+$	Aug, 91	28	19	332	114	718	0.7342
IND-5	Darcha <sup>+</sup>	Aug, 91	24	20	189	54	255	0.7595

<sup>+</sup> samples collected from the Higher Himalaya, all the others from the Lesser Himalaya. RW-series samples collected in 1996 during this study; R-series Ghaghara source waters [Trivedi *et al.,* 1995]; IND from Pande *et al.,* 1994; others from Krishnaswami *et al.,* 1992; Sarin *et al.,* 1992. The major ion concentrations in μM, and Sr in nM.

Rivers receive major cations and anions from different sources such as atmospheric deposition, weathering of silicates, carbonates and evaporites (Table 3.6). The contribution of these sources to the major ion budget can be assessed if the chemical and isotopic properties of these endmembers are known. These are generally constrained from available data on the bedrocks, soil profiles and stream sediments. Mass balance calculations provide a means to evaluate the contribution from various sources to the river water chemistry.

The mass balance equations for the major cations in rivers are:

$$Na_r = Na_a + Na_e + Na_s \tag{1}$$

 $\mathbf{K}_{\mathrm{r}} = \mathbf{K}_{\mathrm{a}} + \mathbf{K}_{\mathrm{s}} \tag{2}$ 

$$Ca_r = Ca_a + Ca_e + Ca_s + Ca_c \tag{3}$$

 $Mg_r = Mg_a + Mg_s + Mg_c \tag{4}$ 

$$Sr_r = Sr_e + Sr_s + Sr_c \tag{5}$$

where the subscripts r, a, e, s and c refer to river, atmospheric, evaporite, silicate and carbonate. The concentrations of major ions in rivers are generally expressed in  $\mu$ M and that of Sr in nM.

Element	Major Sources
Na	Atmospheric deposition, solution of evaporites, saline and/or alkaline
	encrustations, silicate (plagioclase) weathering.
Κ	Atmospheric deposition, silicate (K-feldspar, biotite) weathering.
Mg	Silicate (olivine, pyroxenes) and carbonate (dolomite) weathering.
Ca	Silicate (plagioclase) and carbonate (limestone, dolomite) weathering,
	solution of gypsum/phosphorites.
Sr	Same as Ca.

Table 3.6: Primary sources of major elements and Sr to river waters.

Atmospheric deposition can be an important source of several major ions to rivers. Major ions in the atmosphere are derived from marine, terrestrial and anthropogenic sources. The contribution of atmospheric deposition to the major ion budget of rivers would depend on factors such as vegetation cover, industrial activities in the drainage basins and proximity to the seacoast. Atmospheric deposition fluxes to rivers can be determined through the chemical composition of precipitation (rain and snow) in that region. The chemistry of snow and ice from the Chota Shigri Glacier (Higher Himalaya) and rain water from the foot-hills of Kumaun Himalaya show that atmospheric deposition on an average could account for ~15% of Na and K in the Bhagirathi, Alaknanda and their tributaries (Sarin *et al.*, 1992). For the other major ions, Ca, Mg and SO<sub>4</sub>, the atmospheric component is much lower,  $\leq 5\%$ , and hence are neglected in the balance calculations. The Na concentrations in the snow and rain water samples approximately equal that of chloride and hence chloride can serve as the index to determine the Na contribution via atmospheric deposition.

Weathering of evaporites from the drainage basin can be of significance to the mass balance of Na and Ca. As halite is very soluble, its presence in the drainage basins provides an easily weatherable source of Na and Cl to the rivers. The halite component of Na in rivers equals the abundance of chloride. Other sources for Na and K to rivers can

be dissolution of salt encrustations, borax and from alkaline and saline soils. These sources can be important for specific streams (e.g. Yamuna in plains; Indus tributaries flowing through salt encrustations, borax etc.) but are not of significance for rivers discussed in the study.

The silicate component of sodium and potassium in rivers, Na<sub>s</sub> and K<sub>s</sub>, can be calculated based on the above discussions as:

$$Na_s = Na_r - Cl_r \tag{6}$$

$$K_s = 0.85 K_r$$
 (7)

where  $Cl_r$  is the measured chloride concentration ( $\mu M$ ) in the rivers The Na<sub>s</sub> contribution to the Na abundance in the various rivers is calculated as

$$f \operatorname{Na}_{\mathrm{s}} = \left[\frac{\left(\operatorname{Na}_{\mathrm{r}} - \operatorname{Cl}_{\mathrm{r}}\right)}{\left(\operatorname{Na}_{\mathrm{r}}\right)}\right] \times 100$$
(8)

$$f(\mathrm{Na}_{\mathrm{s}}+\mathrm{K}_{\mathrm{s}}) = \left[\frac{(\mathrm{Na}_{\mathrm{r}}-\mathrm{Cl}_{\mathrm{r}})+0.85\mathrm{K}_{\mathrm{r}}}{(\mathrm{Na}_{\mathrm{r}}+\mathrm{K}_{\mathrm{r}})}\right] \times 100$$
(9)

The silicate Na component, Na<sub>s</sub>, ranges between 27% to 94% of total Na (Fig. 3.11). These calculations show that on an average ~77% of Na and K (range 53 to 90%) in these waters is of silicate origin (Fig. 3.11). The Na<sub>s</sub> and K<sub>s</sub> together account for 6%-36% (molar fraction) of the total cations and represent the *minimum* contribution of cations to these rivers via silicate weathering. This is a minimum, as silicate weathering would also supply Ca and Mg to the rivers.

The calculation of silicate component of Ca and Mg in rivers is a more difficult exercise as they can be supplied to rivers from several sources and requires some simplifying assumptions to assess the various contributions. In the following, three different approaches are described to determine the silicate Ca or Mg in the rivers. All these methods rely on the estimation of Ca or Mg to Na ratio released to solution from silicates during their weathering. Based on this ratio and the Na<sub>s</sub> concentration in rivers estimated earlier, Ca<sub>s</sub> is calculated as:

$$Ca_{s} = \left(\frac{Ca}{Na}\right)_{sol} Na_{s}$$
(10)

where  $\left(\frac{Ca}{Na}\right)_{sol}$  is the (Ca/Na) ratio (molar) released to rivers during silicate weathering.

The first approach is to assume that weathering is congruent i.e., during weathering Ca (or Mg) and Na are released to the rivers in the same proportion as their abundances in silicates. The Ca/Na abundance ratios in the granites and gneisses of the



Fig. 3.11: The contribution of Na and Na+K to the G-G-I source waters via silicate weathering. On an average, in the headwaters silicate weathering contributes accounts for ~72% Na and ~77% of (Na+K).

Higher and Lesser Himalaya and in metasediments of the Lesser Himalaya are given in Table 3.7 and their frequency distribution is shown in the Fig. 3.12. The data for the Higher Himalaya are mainly from the Gangotri and the Badrinath regions, the drainage basins of the Bhagirathi, Ramganga, Alaknanda in their upper reaches. The Lesser Himalaya data are mainly from the Kumaun-Garhwal which constitute a major fraction of the drainage basins of the Ganga- Ghaghara source waters. The Ca/Na ratios ( $\mu$ mole/ $\mu$ mole) in the HH and LH samples exhibit a very wide range, spanning nearly three orders of magnitude (Table 3.7, Fig. 3.12). The mean Ca/Na in these fall in the

	Granites/Gneisses						Ν	Metasediments		
	HH			LH			LH			
	Range	Mean	n	Range	Mean	n	Range	Mean	n	
Ca/Na	0.04-1.33	0.27±0.27	58	0.03-7.74	0.68±1.14	78	0.003-2.33	0.39±0.39	77	
	0.10-1.33	0.32±0.29	45	0.11-1.33	0.46±0.28	61	0.10-1.44	0.44±0.31	61	
Mg/Na	0.004-10.5	$0.40 \pm 1.40$	56	0.01-20.0	1.51±2.96	78	0.07-8.15	0.77±1.28	77	
	0.04-1.31	0.31±0.28	37	0.11-2.02	0.65±0.45	57	0.12-1.64	0.52±0.32	71	
K/Na	0.37-9.02	1.25±1.28	58	0.37-184	6.29±21.3	78	0.13-14.7	2.40±2.36	77	
	0.37-3.39	$1.06 \pm 0.62$	56	0.37-2.95	1.23±0.60	63	0.47-3.99	1.89±1.05	60	
Sr/Na	0.17-33.8	1.75±4.44	56	0.08-36.55	2.77±6.69	51				
	0.36-3.0	1.22±0.65	<b>48</b>	0.35-3.0	1.68±0.72	39				

### Table 3.7: Elemental abundance ratios in the HH and LH granites/gneisses and metasediments\*

All ratios in units of µmole/µmole except Sr/Na which is in nmole/µmole. For all ratios two numbers are given. The numbers in bold are the range and the mean obtained by discarding extreme values in the distributions. n: number of samples.

\* Sources of data: HH granites/gneisses - [LeFort, 1975; Rao, 1983; Choudhary *et al.*, 1991; Kaur and Chamyal, 1996]; LH granites/gneisses - [Bhattacharya *et al.*, 1984; Rao, 1984; Nautiyal and Rawat, 1990; Gupta *et al.*, 1994;]; LH metasediments - [Kashyap, 1972; Mishra *et al.*, 1973; Rawat, 1984].

range of 0.3 - 0.7 (Table 3.7) with large uncertainties. To obtain a more representative value for the mean Ca/Na with less uncertainties, the Ca/Na data were reanalysed by discarding the extreme values on either end of their distribution (Table 3.7). The recalculated mean Ca/Na and associated errors are given in Table 3.7 which shows that



Fig. 3.12: Frequency distribution of Ca/Na and Mg/Na abundances(μmole/μmole) in granites and gneisses of the Higher (HH) and Lesser Himalaya(LH). Data from Le Fort, 1975; Rao, 1983; Bhattacharya *et al.*, 1984; Nautiyal and Rawat, 1990; Choudhury *et al.*, 1991; Gupta *et al.*, 1994; Kaur and Chamyal, 1996.

the mean values in all three groups of samples are nearly the same and centre around a value of  $0.45\pm0.3$ . The weathering of these silicates, as assumed earlier, would release Na and Ca to rivers in the mole ratio 1:0.45.

Another approach to determine the ratio of  $(Ca/Na)_{sol}$  is from the measured Ca/Na ratios of streams flowing predominantly through silicate lithology. The Jola gad stream, a tributary of the Bhilangna (Fig. 3.1) meets this requirement. Of all the rivers and streams for which data are available (Table 3.5) Jola gad has the highest <sup>87</sup>Sr/<sup>86</sup>Sr, lowest Ca/Na and SO<sub>4</sub>/HCO<sub>3</sub> (signifying minimum contribution of Ca from carbonates and sulphates). The Ca/Na<sub>s</sub> in this sample is 1.15. This value could also be an upper limit of input of (Ca/Na) from silicates as even minor amount of carbonates present in the terrain would add to the Ca in river as they weather far more easily than the silicates.

The third method to estimate the (Ca/Na)<sub>sol</sub> is from the chemical composition of soil profiles and their parent rocks. Gardner and Walsh (1996) have reported the chemical composition of three soil profiles formed from metamorphic rocks in the Lesser Himalaya. Their results, summarized in Table 3.8, show that Na, Ca and Sr in the soil profiles are significantly less than those in the parent rock, K and Mg in the rocks and soils are quite similar and that Al in the soils is higher than that in the parent rock. These results would indicate that Na, Ca and Sr are mobilised from rocks and soils far more efficiently than Mg and K. The increase in Al (and that of K and Mg in the GW profile) reflects the mass loss during weathering and the resistant nature of Al. From these data, the ratio of various elements to sodium released to rivers during weathering of bed rocks is calculated as:

$$\frac{\left[\left(\frac{\mathbf{X}_{i}}{\mathbf{Al}}\right)_{ro} - \left(\frac{\mathbf{X}_{i}}{\mathbf{Al}}\right)_{so}\right]}{\left[\left(\frac{\mathbf{Na}}{\mathbf{Al}}\right)_{ro} - \left(\frac{\mathbf{Na}}{\mathbf{Al}}\right)_{so}\right]}$$
(11)

where  $X_i$  represents the elements Ca, Mg and Sr and the subscripts *ro*, *so* refer to bed rock and soil profile (Table 3.8). The calculations are normalised to Al as it is resistant to weathering and corrects for mass loss. The average value calculated for Ca/Na solution ratio based on the three soil profiles is 0.47 (range 0.37 to 0.52) nearly identical to the mean Ca/Na ratio in the source rocks suggesting that Ca and Na are released to solution by and large in the same proportion as their abundances in the source rocks. The soil profile data provides the element to Na ratio supplied to rivers over the time of soil formation. The three methods employed to determine the (Ca/Na)<sub>sol</sub> yield values which

<b>Element/Ratio</b>	<b>Bed rock</b> <sup>+</sup>	Soil Profile <sup>++</sup>				
		BW1	BW2	GW		
Al	2807	3356	3184	3352		
Na	644	31	43	135		
Κ	649	622	578	760		
Ca	342	19	33	151		
Mg	470	425	479	527		
Sr	2040	496	699	1114		
Na/Al	0.24	0.01	0.01	0.04		
Ca/Al	0.12	0.01	0.01	0.05		
Mg/Al	0.17	0.13	0.15	0.16		
K/Al	0.23	0.19	0.18	0.23		
Sr/Al	0.75	0.15	0.22	0.33		

Table 3.8: Elemental concentrations and ratios in bed rocks and soil profiles\*

<sup>+</sup> Average of five samples.

<sup>++</sup> BW1 average of 11 samples upto a depth of 3m; BW2 11 samples, depth 5m; GW 11 samples, depth 5m.

are within a factor of ~2 of each other, 0.45-1.15. A value of  $0.7\pm0.3$  for  $(Ca/Na)_{sol}$  has been used to estimate the Ca contribution to the rivers by silicate weathering. This ratio coupled with Na<sub>s</sub> estimated show that silicate Ca in the G-G-I source waters vary widely, 2%-61% of the total Ca in rivers (Fig. 3.13) but on an average accounts for only ~16%. Thus, on an average bulk of the Ca in these waters has to be from sources other than silicates, such as weathering of carbonates and evaporites.

The major sources of Mg to the river waters are weathering of carbonates and silicates. The primary silicate minerals which supply Mg to river water are biotite, chlorite and amphiboles. The silicate Mg in rivers can be estimated following the approaches outlined for Ca. The Mg/Na abundance ratio (Table 3.7) in the three groups of silicate lithologies are indistinguishable from each other within errors, though the value for the HH granites/gneisses appear lower. The Mg/Na ratio in these silicates centre around a value of  $0.5\pm0.3$ . This compares with the ratio of ~0.6 for the Mg/Na<sub>s</sub> in the Jola



Fig. 3.13: Silicate Ca and Ca+Mg in the headwaters of G-G-I source waters. On an average ~ 16% of Ca and ~17% of (Ca+Mg) in these source waters are of silicate origin.

gad water, which as mentioned earlier, flow predominantly through silicate terrains. The above Mg/Na ratios are much higher than the  $(Mg/Na)_{sol}$  derived from the soil profile data (Table 3.8). The Mg/Al in the bed rock and soil profiles are quite similar indicating that loss of Mg during weathering is small and that Mg and Na are not weathered congruently from silicates. The  $(Mg/Na)_{sol}$  calculated from data in Table 3.8 range between 0.05-0.17 for the three soil profiles. Based on above three estimates a value of  $0.3\pm0.2$  for  $(Mg/Na)_{sol}$  is adopted for calculating the silicate Mg component of the G-G-I source waters. The silicate Mg ranges between 2% to 52% of the total Mg with an average of 21%. Analogous to Ca, bulk of Mg in these waters is also derived from sources other than silicates, such as carbonates.

The (Ca+Mg)/Na ratio released to the source waters of the G-G-I from silicates of the Higher and Lesser Himalaya is  $1.0\pm0.35$  based on the (Ca/Na)<sub>sol</sub> ( $0.7\pm0.3$ ) and (Mg/Na)<sub>sol</sub> ( $0.3\pm0.2$ ) estimated earlier. This value is used for deriving the silicate contributions of Ca and Mg in rivers draining both the Higher and Lesser Himalaya. With the available data, it is difficult to estimate (Ca+Mg)/Na solution ratios separately for the Higher and Lesser Himalaya; though it is recognized that they may differ because of differences in the composition of bed rocks and intensity of weathering. The (Ca+Mg) derived from silicates vary between 2%-57% of their abundance with an average of 17%

(Fig. 3.13). This, as mentioned earlier, requires that on an average these rivers acquire bulk of their (Ca+Mg) from sources other than silicates, such as carbonates and evaporites. The (Ca+Mg)/Na ratio estimated in this study is similar to that reported (Harris *et al.*, 1998) for the Bhote Kosi river,  $0.81\pm0.2$ .

### (ii) Silicate weathering: Contribution of cations to headwaters

The silicate weathering contribution of cations ( $\Sigma$ Cat)<sub>s</sub> is calculated as:

$$(\Sigma \operatorname{Cat})_{s}(\mu M/\mu M) = \left[\frac{\Sigma(X_{i})_{s}}{(\Sigma \operatorname{Cations})_{r}}\right] \times 100 = \left[\frac{(\operatorname{Na}_{r} - \operatorname{Cl}_{r}) \times 2 + 0.85 \mathrm{K}_{r}}{(\operatorname{Na}_{r} + \mathrm{K}_{r} + \mathrm{Mg}_{r} + \mathrm{Ca}_{r})}\right] \times 100$$

The  $(\Sigma Cat)_s$  to the G-G-I source waters range between 8% to 67% (Table 3.9, Fig. 3.14) and suggest that on an average about 30% of the cations in these source waters is of silicate origin. This is nearly identical to the ( $\Sigma$ Cat)<sub>s</sub> in the Ganga waters (30%) at the foot-hills of the Himalaya, sampled at Rishikesh (Fig. 3.1) which integrates the contributions from all its source waters weathering the Higher and Lesser Himalaya. It is also interesting to note that the average silicate component calculated in this study is consistent with the estimates made by Sarin et al. (1992). A lower limit for the silicate contribution to these waters, as mentioned earlier, is 6%-36% (average 18%) by assuming that only Na and K are released to rivers during the weathering of silicates. The main ambiguity in the  $(\Sigma Cat)_s$  estimate is that associated with the values of  $[(Ca+Mg)/Na]_{sol}$ . Propagation of an  $+1\sigma$  uncertainty on this value (i.e. [(Ca+Mg)/Na]<sub>sol</sub> =1.35) would increase the average ( $\Sigma$ Cat)<sub>s</sub> to 35%, whereas using a value of 0.65 for [(Ca+Mg)/Na]<sub>sol</sub> (i.e. -1 $\sigma$  uncertainty) decreases the average ( $\Sigma Cat$ )<sub>s</sub> to 26%. Further, though ( $\Sigma Cat$ )<sub>s</sub> has been calculated for all the rivers and streams (Tables 3.5 and 3.9), it should be more reliable for the larger rivers which integrate contributions from tributaries draining through different bed rock lithologies.

The  $(\Sigma Cat)_s$  in the Bhagirathi along its course centres around 40% for samples collected during the same period, except at Gangotri near its source in the Higher Himalaya where it is marginally higher, ~52% (Table 3.9). The Bhilangna waters derive about 40% of their cations from silicate weathering. The  $(\Sigma Cat)_s$  in the Alaknanda sampled at Badrinath in the Higher Himalaya is ~36% which, as in the Bhagirathi,

Code	River	$(\Sigma Cations)_r$	$f(Na_s+K_s)^+$	$f(Ca+Mg)_{s}^{+}$	$(\Sigma Cat)_s$	
Ganga		(µ111)			(1)	(2)
Gungu					(1)	(2)
13	Bhagirathi	599	89	33	31	52
16	Bhagirathi	740	82	19	20	34
10	Bhagirathi	699	82	23	23	40
11	Bhagirathi	736	74	28	24	43
8	Bhagirathi	709	78	23	22	38
4	Bhagirathi	761	76	22	22	38
5	Bhagirathi	718	78	23	22	39
23	Bhagirathi	724	77	22	22	38
RW-3	Bhagirathi	438	69	12	16	25
14	Kedarganga	647	90	20	25	39
15	Son gad	530	85	11	19	27
17	Helgu gad	246	83	25	27	44
9	Pilang gad	333	84	25	26	43
12	Asiganga	382	82	11	20	29
7	Nagun gad	1023	88	29	24	45
6	Seansu gad	855	82	45	31	59
19	Bhilangna	477	85	22	24	40
22	Bhilangna	521	84	24	25	42
3	Bhilangna	562	83	23	23	40
20	Jola gad	457	77	57	36	67
21	Nailchami gad	768	66	13	17	27
18	Balganga	573	79	22	21	38
28	Alaknanda	261	88	20	21	36
29	Alaknanda	717	83	9	13	21
24	Alaknanda	762	82	14	17	28
RW-4	Alaknanda	656	57	3	7	10
RW-5	Alaknanda	664	53	2	6	8
RW-6	Alaknanda	893	79	5	9	13
RW-7	Alaknanda	276	81	16	18	31
RW-8	Pindar	757	74	5	8	12
2	Ganga	932	82	16	17	30
<b>RW-1</b>	Ganga	585	73	9	13	21
RW-2	Ganga	517	78	11	15	24
1	Song	1585	87	19	17	33
Ghaghara						
RW-9	Sarju	1263	72	4	6	9
RW-10	Ramganga	701	77	19	18	32
RW-11	Kali	1039	83	5	7	11
Indus						
IND-1	Sutlej	981	78	7	13	19

 Table 3.9: Silicate weathering contribution of cations to G-G-I source waters.

IND-2	Beas	260	55	10	16	23
IND-20	Beas	115	55	10	17	24
IND-3	Chandra	474	64	3	6	8
IND-4	Bhaga	493	71	4	7	10
IND-5	Darcha	287	77	7	12	18

 $(\Sigma \text{Cations})_r = (\text{Na}_r + \text{K}_r + \text{Mg}_r + \text{Ca}_r); f \text{ and } \Sigma \text{ are molar fractions.}$ 

$${}^{*}f(\operatorname{Na}_{s}+\operatorname{K}_{s}) = \left[\frac{\left(\operatorname{Na}_{r}-\operatorname{Cl}_{r}\right)+0.85\operatorname{K}_{r}}{\left(\operatorname{Na}_{r}+\operatorname{K}_{r}\right)}\right] \times 100; \ f(\operatorname{Ca}_{s}+\operatorname{Mg}_{s}) = \left[\frac{\operatorname{Na}_{r}-\operatorname{Cl}_{r}}{\operatorname{Ca}_{r}+\operatorname{Mg}_{r}}\right] \times 100$$

$$(\Sigma\operatorname{Cat})_{s}{}^{*}(1) = \left[\frac{\operatorname{Na}_{s}+\operatorname{K}_{s}}{\left(\Sigma\operatorname{Cations}\right)_{r}}\right] \times 100; \ (\Sigma\operatorname{Cat})_{s}(2) = \left[\frac{\left(\operatorname{Na}_{r}-\operatorname{Cl}_{r}\right) \times 2+0.85\operatorname{K}_{r}}{\left(\Sigma\operatorname{Cations}\right)_{r}}\right] \times 100$$

\* minimum silicate contribution assuming only Na and K are released during silicate weathering (i.e. no contribution of Ca and Mg from silicates).

decreases as it traverses through the Lesser Himalaya where it encounters more carbonates in the drainage basin. In general, the ( $\Sigma$ Cat)<sub>s</sub> in the Alaknanda is less than that in the Bhagirathi and the Bhilangna, consistent with the lithology of its drainage basin which has more carbonates than those in the Bhagirathi and in the Bhilangna basins. The ( $\Sigma$ Cat)<sub>s</sub> in the Alaknanda show considerable variation, 8% to 36%, the lower values associated with samples collected during the monsoon (September). The silicate cations in the Pindar, a major tributary of the Alaknanda is ~12% (Table 3.9) quite similar to the value for the Alaknanda collected from nearby location during the same season. Among the source waters of the Ghaghara, the Kali and the Sarju have ~10% of their cations from silicates whereas in the Ramganga the ( $\Sigma$ Cat)<sub>s</sub> is ~32% (Table 3.9). The Indus source waters have ( $\Sigma$ Cat)<sub>s</sub> 8%-24%, the Chandra sample collected after passing through outcrops of Paleozoic carbonates in the Spiti valley (Kanwar and Ahluwalia, 1979) has the lowest ( $\Sigma$ Cat)<sub>s</sub> of all the rivers analysed in this study. These results show that there is an overall consistency between the ( $\Sigma$ Cat)<sub>s</sub> in the rivers and their lithology of the drainage basins.

The  $(\Sigma Cat)_s$  in the Bhagirathi, Alaknanda and the Ganga, seems to show seasonal variations (Table 3.10) with lower values in samples collected during the monsoon (September). This observation, if confirmed through more measurements, would suggest

that during stages of high water discharge silicate weathering is relatively less intense probably because of the dominance of physical erosion which may aid in preferentially dissolving the easily weatherable carbonates relative to the more resistant silicates.



Fig. 3.14:  $(\Sigma Cat)_s$  in the headwaters of G-G-I system. The three histograms correspond to estimates based on three values for  $(Ca_s+Mg_s)/Na_s$ , 0.65, 1 and 1.35. The values 0.65 and 1.35 are  $\pm 1\sigma$  uncertainty in the estimates of  $(Ca_s+Mg_s)/Na_s$ . On an average,  $(\Sigma Cat)_s$  accounts for ~30% of the total cations in the source waters (middle figure). The arrows represent the mean of the distribution.

River (Location)	Sampling date	% ( $\Sigma Cat$ ) <sub>s</sub>	Ref.
Bhagirathi (Devprayag)	March, 82	36	Sarin <i>et al.</i> , 1989
	Nov, 83	37	Sarin <i>et al.</i> , 1989
	April, 89	38	Sarin <i>et al.</i> , 1992
	Sept, 96	25	this study
Alaknanda (Bhagwan) <sup>+</sup>	Nov, 83	27	Sarin <i>et al.</i> , 1989
	April, 89	28	Sarin <i>et al.</i> , 1992
Alaknanda (Devprayag) <sup>+</sup>	Sept, 96	10	this study
Ganga (Rishikesh)	March, 82	29	Sarin <i>et al.</i> , 1989
	Sept, 82	17	Sarin et al., 1989
	Nov, 83	28	Sarin et al., 1989
	April, 89	30	Sarin <i>et al.</i> , 1992
	Sept, 96	21	this study

Table 3.10: Seasonal variation in  $(\Sigma Cat)_s$  in the Ganga source waters

<sup>+</sup> Devprayag is about ~10 km downstream of Bhagwan.

In the preceding paragraphs the  $(\Sigma Cat)_s$  in the source waters of G-G-I have been constrained using better controls on the (Ca/Na) and (Mg/Na) ratios released to the rivers during silicate weathering. These results suggest that on an average about a third of the cations in these rivers is of silicate origin and bring to focus the significance of silicate weathering in these basins in contributing to the cation budget of these rivers. The ( $\Sigma Cat$ )<sub>s</sub> values obtained depend critically on the values of (Ca/Na)<sub>sol</sub> and (Mg/Na)<sub>sol</sub>. As mentioned earlier, a single value is used for these ratios for all the source waters draining through both the Higher and Lesser Himalaya. Such an assumption, though may be an oversimplification, it places useful constraints on the cation contributions via silicate weathering to these source waters. Further, the uncertainty of ±35% in the [(Ca+Mg)/Na]<sub>sol</sub> is likely to account for the variations in the Ca and Mg inputs from the different lithologies.

### (iii) Carbonate (Ca+Mg) in the headwaters

Carbonates occur widespread in the Lesser Himalaya and is a dominant lithology in the drainage basins of the several headwaters of the G-G-I system. These carbonates are predominantly dolomites and can contribute both Ca and Mg to the rivers which flow Fig. 3.15: Frequency distribution of molar fraction of evaporite Ca in the source waters. These calculations assume that all the SO<sub>4</sub> in the water is from the dissolution of evaporites and hence are upper limits.

through them. The carbonate component of Ca to the rivers is difficult to estimate as both carbonates and evaporites (in addition to silicates discussed above) can contribute to its mass balance in rivers, whereas for Mg, carbonates are the only other source. Many of the G-G-I source waters have high SO<sub>4</sub> concentration, 18 to 460  $\mu$ M (Sarin *et al.*, 1992), and account for 1% to 67% (molar fraction) of the anion budget of these rivers. The SO<sub>4</sub> in these waters can originate from (i) dissolution of evaporites, in this case equimolar concentration of Ca and SO<sub>4</sub> would be released to the waters, (ii) oxidation of sulphide minerals in the basin and (iii) from sulphurous springs. The observation (Sarin *et al.*, 1992) that in two samples, Bhagirathi and Kedarganga, collected at Gangotri after they flow through the Higher Himalaya, SO<sub>4</sub> concentration exceeds Ca (SO<sub>4</sub>/Ca = 1.2 - 1.3  $\mu$ M / $\mu$ M), suggests that a significant component of SO<sub>4</sub> in these waters has to be from oxidation of sulphide minerals and/or from sulphurous springs. Data on the abundance and distribution of evaporites and sulphide minerals in the drainage basin are sparse, however, presence of pyrites and other sulphide minerals disseminated in shales,

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quartzites and other sedimentary rocks of the basins (Tewari and Gaur, 1977) and deposits of gypsum in dolomites of Krol formation have been reported (Valdiya, 1980). An *upper limit* on the evaporite component of Ca in river can be derived by assuming that all the  $SO_4$  in the water is from its dissolution. This upper limit is presented in Fig. 3.15, which shows that in the Bhagirathi, Bhilangna, Alaknanda and a few source waters of the Indus, and the Ghaghara, the gypsum Ca is quite high, averaging about  $\sim 34\%$  (molar fraction), comparable to or even more than the carbonate component of  $Ca [Ca_c = Ca_r - Ca_r]$  $(Ca_s + Ca_e)$ ;  $Ca_e = SO_4$ ]. This is unlikely considering that gypsum/anhydrite is expected to be less abundant relative to carbonates in the drainage basins of the rivers, though their occurrence has been reported (Valdiya, 1980) from several locations of the Lesser Himalaya. The observation that waters with high SO<sub>4</sub> (>100  $\mu$ M) generally have low Cl, with SO₄/Cl 3.5 to 77, and low to moderate TDS (≤100 mg/l) are other indications that evaporites may not be an important source of SO<sub>4</sub> to these waters. Thus, Ca<sub>e</sub> in these waters is very likely to be lower than that calculated assuming it to be equivalent to SO<sub>4</sub>. This inference, if valid, would suggest that significant fraction of  $SO_4$  in these rivers is from the oxidation of pyrites. Here again, to account for the measured concentration of  $SO_4$  in the waters, the pyrite abundance has to be adequate in the drainage basins. Pyrite disseminated in the shales of the Lesser Himalaya from several locations though are reported, more data on its abundances along the drainage basins are needed to better assess their role in contributing to the  $SO_4$  in these waters. Thus, with the available data it is not possible to calculate separately the input of SO<sub>4</sub> to the rivers via dissolution of evaporites and oxidation of pyrites. Studies on sulphur isotopes in the dissolved sulphate of these rivers may help resolve this issue.

In the present study, therefore only an *upper limit* on the carbonate Ca could be estimated assuming that the rivers receive Ca only two sources, silicates and carbonates (i.e. there is no contribution of Ca to the rivers via dissolution of evaporites). The calculated carbonate Ca ranges between 39% to 98% of Ca<sub>r</sub>. In rivers where SO<sub>4</sub> concentrations are relatively low compared to Ca, the upper limit on Ca<sub>c</sub> estimated above would be close to the true carbonate component of Ca in them. The (Ca+Mg)<sub>c</sub> in the source waters (upper limit) range between 71 to 1123  $\mu$ M. This accounts for 43% to 98% (molar fraction) (Ca+Mg) in the rivers.

### (iv) Sr and <sup>87</sup>Sr/<sup>86</sup>Sr of the Ganga, Ghaghara and the Indus source waters

In this section, the impact of silicate and carbonate weathering on the Sr budget of the G-G-I river system is assessed. The silicate and carbonate Sr have been calculated based on the approach followed for major ions. Endmember values are assigned based on the three approaches, i.e. their values in granite/gneisses of the Higher and Lesser Himalaya, water composition flowing through mainly silicate lithology and from the soil and its parent rock chemistry. It must be mentioned here that in section 3.1 (iii), it was concluded based on Sr/Ca and <sup>87</sup>Sr/<sup>86</sup>Sr in Precambrian carbonate outcrops that these carbonates are unlikely to be a dominant source for the high radiogenic Sr isotope composition of the G-G-I headwaters.

Figure 3.16 is a comparison of the frequency distribution of <sup>87</sup>Sr/<sup>86</sup>Sr in the source waters of the Bhagirathi, Alaknanda, Ghaghara and the Indus and those in the carbonates and whole rock granites/gneisses from the Lesser and Higher Himalaya. Sr isotopic data of whole rocks from the Lesser and Higher Himalaya have been used for comparison, as a large fraction of the drainage basins of the Bhagirathi, Alaknanda, Ghaghara and Sutlej is in these regions. France-Lanord et al. (1993) concluded that the primary source of the sediments to the Bay of Bengal are the higher Himalayan Crystallines (or its close analogue with only minor contributions from the Lesser Himalaya) based on studies of clay mineralogy, Sr, Nd and oxygen isotope systematics in them. More recently, Derry and France-Lanord (1996), while attesting to the earlier conclusions of France-Lanord et al. (1993) regarding the provenance of detritus in the Bay of Bengal sediments, alluded to the possibility of a relative increase in the contribution of the Lesser Himalaya materials to the Bay of Bengal sediments during the Pliocene. Many of the G-G-I source waters have significant fraction of the drainage in the Lesser Himalaya. Chemical weathering is likely to more pronounced in the Lesser Himalaya where the general temperature is higher than the Higher Himalaya the difference in temperature could result in increase in dissolution rate (Lasaga et al., 1994). Soil formation in the Lesser Himalaya (Gardner and Walsh, 1996) and availability of more biogenic  $CO_2$  could also enhance the chemical weathering in this part of the Himalaya compared to the Higher Himalaya. It is therefore possible that sites of maximum mechanical erosion and maximum chemical weathering are decoupled, with Lesser Himalaya contributing more to the dissolved load than the



Fig. 3.16: Comparison of <sup>87</sup>Sr/<sup>86</sup>Sr and Sr/Ca in G-G-I source waters, silicates (granite/gneisses) and Precambrian carbonate outcrops of the Lesser Himalaya. The data show that bulk of the carbonates have <sup>87</sup>Sr/<sup>86</sup>Sr and Sr/Ca much less than those measured in the headwaters whereas those in silicates bracket the source water values. Granites/gneisses having <sup>87</sup>Sr/<sup>86</sup>Sr >1.0 though reported, are excluded from the histogram.

Higher Himalaya. The observation, however, that the Bhagirathi (at Gangotri) and Alaknanda (at Badrinath) have high <sup>87</sup>Sr/<sup>86</sup>Sr with moderately high Sr concentration before they enter the Lesser Himalayan basin (Krishnaswami *et al.* 1992) points to the important influence the rocks in the Higher Himalaya also have in regulating the Sr isotope composition of these rivers. Currently, however, the relative contributions from the drainage basins of the Higher and Lesser Himalaya to the Sr flux and isotopic
composition of these rivers are uncertain as data on their water flux along the flow path is unavailable.

The Sr isotope composition of the source waters overlaps with those of the granites/gneisses, but are significantly higher than that in most of the carbonates. A similar pattern is also seen in the comparison of the Sr/Ca ratios (Fig. 3.16), the source waters have a mean Sr/Ca ratio ( $1.41\pm0.69$ ) nmol/µmol that is much higher than that of the carbonates ( $0.20\pm0.15$ ) nmol/µmol.

In order to better constrain the sources of Sr to these rivers similar approach has been followed as for major ions to characterise the silicate end member values. The Sr/Na ratios (mole) in the HH and LH granites and gneisses show considerable range, over two orders of magnitude (Table 3.7). The mean Sr/Na, after discarding the extreme values on either end of its distribution are  $1.22\pm0.65$  and  $1.68\pm0.72$  respectively for the HH and LH samples (Table 3.7) and overlap with each other within errors. The Sr/Na in the Jola gad waters is 1.96 (Singh et al., 1998). The (Sr/Na) solution ratio based on the results from three soil profiles (Gardner and Walsh, 1996) is in the range of 2.5-2.9. The difference between the three values may be due to the incongruent weathering of the Sr and Na or regional differences in Sr/Na in source rocks. Following the same assumptions used for the major ions, the ratio of (Sr/Na) released to rivers from weathering of silicates can be in the range of 1.2-2.9. For estimating the silicate Sr in the rivers we have adopted a value of 2.0±0.8 This is 25% lower than that used by Singh *et al.* (1998), but falls within  $\pm 1\sigma$ uncertainty. The Sr<sub>s</sub> in the source waters range between 2% to  $\sim 100\%$  of Sr<sub>r</sub> with a mean of ~40% (Table 3.11). In the Bhagirathi (Devprayag), Bhilangna (Tehri), Alaknanda (Bhagwan) and the Ganga (at Rishikesh) the Sr<sub>s</sub> constitutes  $43\pm17\%$ ,  $71\pm28\%$ ,  $27\pm11\%$ and  $34\pm14\%$  of Sr<sub>r</sub> respectively. Among the Ganga source waters, Bhilangna has bulk of its Sr from silicates ( $\sim$ 70%), whereas in the Bhagirathi silicate Sr accounts for about half of its Sr budget. In the Alaknanda, the silicate Sr decreases from ~55% in the samples collected at Badrinath, to ~27% at Devprayag, following the trend in  $(\Sigma Cat)_s$ . The Sr<sub>s</sub> contribution to the Sr budget in the Sutlej, Beas, Chandra and Bhaga; the source waters of the Indus are small,  $\leq 20\%$  (Table 3.11), consistent with the estimates for ( $\Sigma Cat$ )<sub>s</sub> in these waters.

The significance of silicate weathering in determining the <sup>87</sup>Sr/<sup>86</sup>Sr of the G-G-I source waters can be gauged from the trend in Fig. 3.17 which shows a strong positive correlation of <sup>87</sup>Sr/<sup>86</sup>Sr with ( $\Sigma$ Cat)<sub>s</sub> (r = 0.75). It is borne out from this trend that silicate weathering is primarily responsible for the high <sup>87</sup>Sr/<sup>86</sup>Sr in the source waters (a plot of <sup>87</sup>Sr/<sup>86</sup>Sr vs. Sr<sub>s</sub> also shows similar trend). It is noteworthy that the end member values of <sup>87</sup>Sr/<sup>86</sup>Sr for ( $\Sigma$ Cat)<sub>s</sub> = 0 and ( $\Sigma$ Cat)<sub>s</sub> = 100% derived from Fig. 3.17 are 0.715 and 0.82 respectively, close to the mean ratios in the Precambrian carbonates and granites/gneisses in the Lesser Himalaya (Krishnaswami and Singh, 1998).

Importance of carbonates in regulating the Sr budget of the rivers can be evaluated by estimating the carbonate Sr in them. The primary sources of Sr to rivers are silicates, carbonates and evaporites. As discussed earlier, it is not possible to estimate the evaporite contribution to major ions (and Sr) from the available data. Carbonate Sr can be calculated based on the carbonate Ca component of rivers which equals the difference between the measured Ca in them and their calculated silicate Ca. The Sr input to these rivers from carbonates is calculated as:

$$Sr_{c}(nM) = (Ca_{r} - Ca_{s}) \times \left(\frac{Sr}{Ca}\right)_{c}$$
$$= [Ca_{r} - (0.7 \pm 0.3)Na_{s}] \times \left(\frac{Sr}{Ca}\right)_{c}$$
(12)

 $(Sr/Ca)_c$  is taken to be the abundance ratio in Precambrian carbonate outcrops,  $(0.2\pm0.15)$  nmole/µmole. It is assumed in this calculation that Ca<sub>r</sub> in rivers is derived from two components, Ca<sub>s</sub> and Ca<sub>c</sub>. The results of these calculations yield value of 5% to 42% (mean 15%) for the carbonate Sr contribution. The contribution of silicate and carbonate Sr in the source waters are compared in Fig. 3.18. The data inspite of substantial uncertainty, show that in most of the source waters the silicate Sr component exceeds that of the carbonate Sr, exceptions being some of the tributaries of the Ghaghara and the Indus, where Sr<sub>s</sub>  $\approx$  Sr<sub>c</sub> (Krishnaswami and Singh, 1998). Thus the extensive outcrops of the Precambrian carbonate deposits of the Lesser Himalaya, as inferred earlier (section 3.1 (iii)) in general is not a major source for both Sr and <sup>87</sup>Sr/<sup>86</sup>Sr of the G-G-I source waters.



Fig. 3.17: Variation of measured <sup>87</sup>Sr/<sup>86</sup>Sr in G-G-I source waters with their calculated ( $\Sigma$ Cat)<sub>s</sub> [Table 3.9 (2)]. There is an overall positive correlation between the two (r = 0.75) suggesting that silicate weathering is an important source for the highly radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr of the rivers (Krishnaswami and Singh, 1998). The horizontal bars represent the range in ( $\Sigma$ Cat)<sub>s</sub> calculated by considering ±1 $\sigma$  uncertainty.

It is seen from the data in Table 3.11 that for many rivers the  $(Sr_s+Sr_c)$  do not add upto 100%, though in some of them Sr balance can be achieved within uncertainties.

The fraction of riverine Sr that is supplied from the weathering of silicates and Precambrian carbonates is presented in Fig. 3.19 which show that only in a few of the source waters the Sr budget can be balanced if input is solely from these sources. It is possible to balance the Sr budget in a few more rivers in which the sum of silicate and carbonate Sr contribution exceed 70% by considering  $1\sigma$  uncertainties associated with the estimates (Fig. 3.19). It is seen from this exercise that in a number of source waters, particularly Kali, Gori (Ghaghara system), Sutlej, Beas, Chandra, Bhaga and Dharcha (Indus system) it is difficult to account for their measured Sr if the two end members

chosen (silicates and Precambrian carbonates) are their only sources and if the approaches used for estimating their contributions are valid (Krishnaswmi and Singh, 1998 and Krishnaswami *et al.*, 1998). These results seem to suggest that in addition to silicates and the Precambrian carbonates, some of the rivers may be receiving Sr supply from sources such as evaporites, phosphates and carbonates (other than the Precambrian outcrops) and the assumption of a two component system for Ca and Sr may not be valid.



Fig. 3.18: Scatter plot of Sr<sub>s</sub> vs Sr<sub>c</sub>. The silicate Sr exceed the carbonate Sr in a majority of the headwaters. The data for the Ganga, Ghaghara and the Indus headwaters are shown by by separate symbols. In the Kali, Gori (Ghaghara system) Sutlej, Beas, Chandra, Bhaga, Dharcha (Indus system) Sr<sub>s</sub>≈Sr<sub>c</sub>.

This, as discussed below, is also evident from the Sr isotope data. In Fig. 3.20 <sup>87</sup>Sr/<sup>86</sup>Sr of the G-G-I source waters is plotted as a function of their measured Ca/Sr ratios (Krishnaswmi and Singh, 1998 and Krishnaswami *et al.*, 1998). Also presented in the Fig. 3.20 are the Sr isotope and Ca/Sr values for silicate (granites and gneisses from HH and LH) and Precambrian carbonate end members. The silicate endmember has Ca/Sr

centring around 0.25 ( $\mu$ M/nM) with <sup>87</sup>Sr/<sup>86</sup>Sr close to 0.80 based on data for about 50 granites/gneisses each from the LH and the HH. The river water data do not fall on the mixing line between the silicate and Pc-Carbonate end members (Fig. 3.20), but seem to be contained in a triangle bound by silicate, carbonate and an additional end member. The <sup>87</sup>Sr/<sup>86</sup>Sr and Ca/Sr of the additional end member as seen from Fig. 3.20 is ~0.715 and ~0.2 ( $\mu$ mole/nmole) respectively. The low <sup>87</sup>Sr/<sup>86</sup>Sr and Ca/Sr (i.e.high Sr) end member

Table 3.11: Silicate and carbonate weathering contribution of Sr toG-G-I source waters

River	Sr <sub>r</sub> *	f Sr <sub>s</sub>	f Sr <sub>c</sub>	$f(\mathrm{Sr_s}+\mathrm{Sr_c})$
	(µM)			
Bhagirathi	331	77	12	90
Bhagirathi	694	31	9	40
Bhagirathi	524	45	11	56
Bhagirathi	503	54	10	64
Bhagirathi	502	45	12	57
Bhagirathi	560	43	11	54
Bhagirathi	420	56	14	70
Bhagirathi	529	44	12	55
Kedarganga	262	70	24	94
Son gad	315	30	21	51
Helgu gad	168	50	13	63
Pilang gad	181	63	15	78
Asiganga	184	36	22	58
Nagun gad	1390	32	6	38
Seansu gad	1000	48	5	52
Bhilangna	224	68	21	89
Bhilangna	246	72	19	92
Bhilangna	265	71	18	89
Jola gad	273	102	5	106
Nailchami gad	431	35	16	51
Balganga	367	50	13	64
Alaknanda	141	55	21	76
Alaknanda	650	18	12	29
Alaknanda	644	27	12	38
Ganga	676	34	12	47
Song	1310	38	10	48
Sarju	263	34	42	75
Ramganga	296	64	21	85
Ghat gad	316	44	36	79
Kali	1320	7	8	15
Gori	768	17	11	27
Sarju	311	30	33	64

Sarju	286	34	36	70
Panar	1245	45	6	50
Suyal	413	63	6	68
Sutlej	1962	6	6	12
Beas	169	23	16	38
Chandra	1118	2	6	8
Bhaga	718	5	9	14
Dharcha	255	13	14	27
Beas	105	15	11	26

\* Krishnaswami *et al.* (1992); Pande *et al.* (1994) and Trivedi *et al.* (1995)  $f \operatorname{Sr}_{s} = (\operatorname{Sr}_{s}/\operatorname{Sr}_{r}) \times 100$  $f \operatorname{Sr}_{c} = (\operatorname{Sr}_{c}/\operatorname{Sr}_{r}) \times 100$  $f (\operatorname{Sr}_{s}+\operatorname{Sr}_{c}) = [(\operatorname{Sr}_{s}+\operatorname{Sr}_{c})/\operatorname{Sr}_{r}] \times 100$ 

is commonly taken to be carbonates. The results of this study (Fig. 3.20) suggest that the extensive outcrops of Precambrian carbonates of the Lesser Himalaya because of their relatively lower Sr abundance (i.e. high Ca/Sr) is not this additional end member. Possible candidates for this endmember are Tethyan/Tibetan carbonates (present in the drainage basins of some of the Ghaghara and Indus source waters) and/or evaporites rich in Sr (gypsum, celestite). Harris et al. (1998) reported a range of values for <sup>87</sup>Sr/<sup>86</sup>Sr in Tibetan carbonates based on measurements of acid leaches of bedload samples of the Bote Kosi river in the Tibetan Sedimentary Series. The studies of Galy (1999), indeed, show that the Tibetan carbonates have Sr concentrations ranging from 252 to 1600 ppm with <sup>87</sup>Sr/<sup>86</sup>Sr varying from 0.7079-0.715 which can satisfy the values required for the third endmember. Very recently, Blum et al. (1998) based on the chemical and Sr isotope study of Raikhot watershed from the Higher Himalayan Crystallines have suggested that weathering of vein calcites contributes to their high <sup>87</sup>Sr/<sup>86</sup>Sr. The Raikhot waters have Ca/Sr (1.4-3.6  $\mu$ M/nM) slightly higher than that in the Ganga headwaters (0.32-2.2  $\mu$ M/nM). Further, the drainage basin of the Raikhot river is only in the Higher Himalaya, whereas the G-G-I headwaters discussed in this study flow through both the Higher and Lesser Himalaya with large fraction of their drainage in the Lesser Himalaya. Blum et al. (1998) also conducted leaching experiments on gneisses and granites and bed load samples and came to the conclusion that these samples have a highly radiogenic leachable Sr component, which they attributed to vein calcites. Based on the <sup>87</sup>Sr/<sup>86</sup>Sr and Ca/Sr of the Raikhot river waters the authors (Blum et al., 1998) suggested that vein calcites with  ${}^{87}$ Sr/ ${}^{86}$ Sr (~0.8) and Ca/Sr ~5 would be an endmember to explain the Raikhot river data. The vein calcite is a high  ${}^{87}$ Sr/ ${}^{86}$ Sr, low Sr endmember (Ca/Sr ~5 µmol/nmol), properties which are quite opposite to that required for the endmember in Fig. 3.20, low  ${}^{87}$ Sr/ ${}^{86}$ Sr and high Sr (i.e. low Ca/Sr). These results suggest the need to get more data on the distribution and Sr isotope systematics of the vein calcites directly and



Fig. 3.19: The sum of silicate and carbonate Sr contribution to the Sr budget of the G-G-I source waters. The data show that only in very few of the headwaters, thr Sr budget can be balanced based on the approaches discussed in the text. Samples with  $(Sr_s+Sr_c)$  contribution >70% can be made to balance the budget by considering 1 $\sigma$  uncertainty.

also look for differences if any in the Sr isotope contribution from various sources to the rivers of the Higher and the Lesser Himalaya.

The inferences about the need for a third source based on Fig. 3.20 rests on the assumption that the silicate and carbonate end members have unique  ${}^{87}$ Sr/ ${}^{86}$ Sr and Ca/Sr

values. If this assumption is not valid, for example, if the silicates can have  ${}^{87}$ Sr/ ${}^{86}$ Sr ranging between 0.75-0.80 with Ca/Sr 0.2-2.0, the observed trend (Fig. 3.20) can result from mixing of these silicates with an end member having  ${}^{87}$ Sr/ ${}^{86}$ Sr of ~0.715 with Ca/Sr ~0.2. This suggestion, as in the previous case, also requires an end member with low  ${}^{87}$ Sr/ ${}^{86}$ Sr and low Ca/Sr. An alternative hypothesis is to suggest that the Sr isotope



Fig. 3.20: Plot of reported <sup>87</sup>Sr/<sup>86</sup>Sr vs Ca/Sr in the G-G-I headwaters. The endmember values for silicates (Sil), Precambrian Carbonates (Pc. Carb.) and vein calcites (Blum *et al.*, 1998) are also given. The river water data do not plot on the mixing line of silicate and Precambrian carbonates, but fall in the field of a triangle defined by silicate, Precambrian carbonate and an additional third endmember. Possible candidates for this endmember are Tethyan/Tibetan carbonates and/or Sr rich evaporite phases.

composition of the headwaters result from mixing of silicates (Ca/Sr = 0.25,  ${}^{87}$ Sr/ ${}^{86}$ Sr=0.80±0.02), vein calcites (Ca/Sr=5,  ${}^{87}$ Sr/ ${}^{86}$ Sr=0.80) and a third endmember (Ca/Sr  $\cong$  0.2,  ${}^{87}$ Sr/ ${}^{86}$ Sr  $\cong$  0.715). Both the above suggestions discount the significance of contribution of Ca and Sr to rivers from the weathering of Precambrian carbonates of the Lesser Himalaya, which is unlikely to be realistic for the G-G-I source waters which have

a significant fraction of their drainage through Precambrian carbonates. Further, the available data show that silicates from the LH and HH rarely have Ca/Sr > 0.8 ( $\mu$ mole/nmole; Fig 3.16).

It is borne out from the above discussions and material balance calculations that silicate weathering contributes more to the present day Sr budget of many of the G-G-I source waters than weathering of Precambrian carbonate outcrops and that it plays an important role in determining their <sup>87</sup>Sr/<sup>86</sup>Sr. The variations in the Sr concentration and <sup>87</sup>Sr/<sup>86</sup>Sr of these source waters seem to be dictated by three end members, silicate (Ca/Sr = 0.25, <sup>87</sup>Sr/<sup>86</sup>Sr= $0.80\pm0.02$ ), Precambrian carbonates (Ca/Sr = 5, <sup>87</sup>Sr/<sup>86</sup>Sr =  $0.715\pm0.01$ ) and a third component (Ca/Sr  $\approx 0.2$ , <sup>87</sup>Sr/<sup>86</sup>Sr  $\approx 0.715$ ).

In this section attempts to establish a mass balance for Sr in the headwaters of the Ganga-Ghaghara-Indus system, based on contributions from silicates and carbonates, is presented. As evident, this is a difficult exercise as Ca and Sr in these waters have multiple sources with their own characteristic <sup>87</sup>Sr/<sup>86</sup>Sr. Our data and calculations show that silicate weathering exerts a more dominant control relative to carbonate weathering on the present day Sr mass balance and their <sup>87</sup>Sr/<sup>86</sup>Sr (Table 3.11) in the source waters of the Ganga, whereas in Kali & Sarju (of Ghaghara) and Sutlej (of Indus) the contributions from silicate and carbonate weathering to their Sr budget seem comparable.

## **3.3. SILICATE AND CARBONATE CHEMICAL WEATHERING RATES IN THE GANGA SOURCE WATER BASINS**

The present day chemical weathering rates of silicates and carbonates in river basins can be determined from the silicate and carbonate components of their major cations, silica concentration and data on their water fluxes and drainage areas. Among the source waters discussed in this study water flux data is available only for the Bhagirathi and the Alaknanda at Devprayag (Sarin *et al.*, 1992). The discharge of the Ganga at Rishikesh, a few tens of kilometers downstream of Devprayag is taken to be same as the sum of the discharges of the Bhagirathi and the Alaknanda which merge together at Devprayag to form the Ganga. The silicate weathering rates (SWR) are calculated by summing the Na, K, Mg and Ca contributions from silicate weathering and silica concentration (in units of mg/l); the carbonate weathering rates (CWR), from the carbonate Ca and Mg contributions and stoichiometric equivalent of carbonate. (The carbonate Ca and Mg are obtained by subtracting the silicate Ca and Mg from their measured concentrations in the rivers. As mentioned earlier, the carbonate Ca calculated this way would be an upper limit if Ca is also supplied to the waters via evaporite dissolution). The results show that in the Bhagirathi and the Alaknanda basins silicate weathering contributes to 35 and 26 wt% of cations (corresponding to 31% and 22% of cation charge). These, coupled with silica concentrations, yield values of 4-6 mm/ky for SWR in these river basins (Table 3.12); 3-6 times lower than the carbonate weathering rates (Krishnaswami *et al.*, 1998).

River	Discharge	Area	SWR		CWR		
	(10 <sup>12</sup> l/y)	$(10^3 \text{ km}^2)$					
			(a)	(b)	(a)	(b)	
Bhagirathi <sup>+</sup>	8.3	7.8	15.2	5.8	41.1	15.2	
Alaknanda <sup>+</sup>	14.1	11.8	10.2	3.9	63.2	23.4	
$\operatorname{Ganga}^+$	22.4	19.6	12.9	4.9	51.7	19.1	
G-B <sup>++</sup>	1002	1555	13.6	5.3	31.7	11.7	

 Table 3.12:
 Silicate and carbonate weathering rates\*

\* mean density for silicates and carbonates 2.6 and 2.7 gm cm<sup>-3</sup> respectively; (a) tons/km<sup>2</sup>/y; (b) mm/ky.

 $^{\star}$  calculated based on composition at Devprayag, Bhagwan and Rishikesh respectively.

<sup>++</sup> calculated for the entire basin based on composition at Patna and Goalpara (Sarin *et al.,* 1989).

The drainage basins of these rivers, thus, are getting chemically weathered at a rate of  $\sim 25 \text{ mm/ky}$ . (These weathering rate calculations are based on limited data both for discharge and the chemical composition of the rivers. More seasonally representative data for all these parameters, particularly the major ion chemistry of the rivers during their peak discharge, are required to obtain a better time averaged estimate of the weathering rates). Sarin et al (1992) had reported chemical denudation rates of  $\sim 50 \text{ mm/ky}$  for these

river basins, a factor of  $\sim 2$  higher than that calculated in this study. The difference between the two estimates is because the calculations of Sarin et al (1992) are based on the flux of total dissolved solids which include, in addition to cations, silica and carbonate from the chemical weathering of silicates and carbonates; contributions from the atmosphere (cyclic salts), alkalinity associated with silicate and carbonate weathering evaporite dissolution and/or pyrite oxidation. The contemporary silicate weathering rates of the Bhagirathi and the Alaknanda basins are comparable to those reported for other major world river basins, 1-7 mm/ky in the Guayana Shield (Edmond et al., 1995) and 0.2-8 mm/ky in the Amazon basins (Gailardet et al., 1997), and 1.3-2.4 mm/ky in the Congo (Gaillardet *et al.*, 1995). The CO<sub>2</sub> consumption rates for silicate weathering in the Bhagirathi and the Alaknanda basins (calculated assuming that silicates are weathered only by CO<sub>2</sub>) are  $4.1 \times 10^5$  and  $3.6 \times 10^5$  mole/km<sup>2</sup>/y. If this calculation is extended to the entire Ganga-Brahmaputra basin, the proportion of cations supplied via silicate weathering is estimated to be 37 wt% (34% of cation charge) and the corresponding  $CO_2$ consumption rates by silicate weathering would be  $3.3 \times 10^5$  moles/km<sup>2</sup>/y (using average composition of these waters at Patna and Goalpara, ref. Sarin et al., 1989). These estimates are likely to be on the higher side as (i) part of silicate weathering could be brought about by sulphuric acid from oxidation of pyrites and (ii) the assumption that chloride corrected Na is entirely of silicate origin may not be valid for the Ganga basin, which is known to have alkaline/saline soils in the plains (Sarin et al., 1989). Edmond and Huh (1997) estimated a CO<sub>2</sub> consumption rate of  $(1-3)\times 10^5$  moles/km<sup>2</sup>/y due to silicate weathering for the Himalayan collision zone.

It is apparent from the above preliminary calculations that the present day  $CO_2$  consumption by silicate weathering in the G-B basin is of the same order as those in other major river basins,  $0.2 \times 10^5$  to  $2.3 \times 10^5$ ;  $0.02 \times 10^5$  to  $0.8 \times 10^5$ ;  $0.1 \times 10^5$  to  $2.1 \times 10^5$  moles/km<sup>2</sup>/y in the Amazon (Gaillardet *et al.*, 1997), Congo (Gailardet *et al.*, 1995) and the Guyana (Edmond *et al.*, 1995) basins respectively. More precise estimates of  $CO_2$  consumption rates in the G-B basin need better constraints on the proportions of silicate weathering by  $CO_2$  and sulphuric acid and on the supply of various cations from silicates from the Higher and Lesser Himalaya and the plains.

Chapter 4

**Re-Os** isotope systematics in black shales from the Lesser Himalaya: Their Chronology and role in <sup>187</sup>Os/<sup>186</sup>Os evolution of seawater

In this chapter Re-Os isotope systematics in black shales from the Lesser Himalaya is discussed. Re-Os studies in these black shales have been done (i) to explore the possibility of providing chronology for the Krol belt and Tejam Group sediments of the outer and inner sequences of the Lesser Himalaya respectively and to test the various models given for their intercorrelation and (ii) to evaluate the role of these black shales in contributing radiogenic Os to rivers draining them and finally to the oceans. The ages of the sedimentary sequences in the Lesser Himalaya is a controversial topic. There is considerable debate on the ages of these sedimentary rocks either due to the paucity of fossil records or in the interpretation of available few fossils records. The Tal formation of the outer belt (Krol Belt) was initially assigned Permian age (Auden, 1937; Gansser, 1964) but now it is considered to be of Early Cambrian after the discoveries of small shelly and trace fossils of Cambrian origin (Azmi, 1983; Singh and Rai, 1983; Bhatt et al., 1985; Kumar et al., 1987). There are no radiometric ages for these rocks, except the one by Sharma et al., (1992) on the Lower Tal formation. In the absence of ages for the rocks from the inner and outer belts, attempts to inter-correlate them have been hampered.

The <sup>187</sup>Os/<sup>186</sup>Os of the oceans has been increasing with time since last ~50 Ma. This increase has been attributed to the intense weathering of the Himalaya (Pegram *et al.*, 1992; Ehrenbrink *et al.*, 1995; Turekian and Pegram 1997) particularly the organic matter rich black shales of the Lesser Himalaya. Black shales are known to contain high Re in them (Ravizza and Turekian, 1989) which over time decays to <sup>187</sup>Os making the Os isotope composition in them highly radiogenic. Weathering of such black shales could be an important source of radiogenic Os to the oceans.

As already discussed in Chapter 2 under the Stratigraphy and Lithology of the Area section, black shales occur in both the inner and outer sedimentary belts of the Lesser Himalaya as dispersed units (Gansser, 1964; Valdiya, 1980).

In the outer Lesser Himalaya, black shales are present in the Infra-Krol, Krol and Tal formations extending from Solan in the Himachal Himalaya to Nainital in the Kumaun Himalaya (Fig. 4.1). The black shales associated with the Infra-Krol and Upper Krol formations occur in and around Solan, Mussoorie, Garhwal and Nainital (Fig. 4.1). Black shales are generally more abundant in the Tal formation compared to Infra-Krol

and Krol formations. Prominent exposures of these black shales are around Mussoorie, Tehri-Garhwal and Solan

In the inner belt, black shale outcrops are reported (Rupke, 1974) at many locations between the rivers Beas (Himachal Himalaya) and the Kali (Kumaun Himalaya). These are dispersed in the drainage basins of Sutlej (Indus), Tons (Ganga), Sarju and Kali (Ghaghara) and are associated with the calcareous units of the Deoban, Shali and Mandhali formations.

As discussed earlier the stratigraphic correlation between the inner and outer sedimentary belts of the Lesser Himalaya is a topic of debate due to lack of sufficient data on their ages. The debate can be resolved if the chronology of black shales from these inner and outer belts are established. Efforts made in this work, to date the Maldeota and Durmala sections of the outer belt from the Mussoorie region and the inner belt outcrops from Simla is a step in this direction.

## **4.1 SAMPLES**

The samples analysed in this study (Fig. 4.1) are mainly from four regions, selected from various formations of the outer (Nainital, Mussoorie and Almora) and the inner belts (Simla) and were collected during three field campaigns in 1992, 1994 and in 1998. Samples adjacent to Nainital (Fig. 4.1) are from the Upper Krol formation whereas those from the Mussoorie region are from the lower Tal formation. The inner belt samples are from Simla area occurring in the Shali formation. The samples collected fall into two categories, (i) from outcrops to obtain spatial distribution of Os isotope ratios in the Lesser Himalaya. These were collected either from road cuts or from natural exposures and in most cases were sampled a few centimeters below their exposed surfaces to obtain better preserved samples. The samples ranged in colour from grey to black with many of them having laminations and pyrites in them. They were generally compact, however some of them, KU92-49, 50, 51 and UK94-51, 66 were friable. (ii) from the Durmala and Maldeota underground phosphorite mines, near Mussoorie, to explore the use of <sup>187</sup>Re-<sup>187</sup>Os isotope pair to date them. In the Mussoorie hills, a thick succession of Nagthat–Blaini–Infra-Krol–Krol and Tal formations are exposed which

represents the transition from the Proterozoic to the Lower Cambrian (Shanker *et al.*, 1993; see Chapter 2).

## 4.2 Org. C, N, Re, OS CONCENTRATIONS AND <sup>187</sup>Os/<sup>186</sup>Os

The concentrations of organic carbon, nitrogen, Re and Os and <sup>187</sup>Os/<sup>186</sup>Os in the black shale samples were measured by procedures outlined in Chapter 2. The results for the outcrop samples are given in Table 4.1, and those for the Maldeota and Durmala underground mine samples in Table 4.2. The Re and Os concentrations and <sup>187</sup>Os/<sup>186</sup>Os isotopic ratios given in Tables 4.1 and 4.2 are uncorrected for blank as they were considerably less than the sample values (Chapter 2).

The organic carbon and nitrogen content of the samples are in the range of 0.2 to 7.3 % and 0.02 to 0.27 % respectively (Tables 4.1, 4.2). The mean organic C in the mine and outcrop samples overlap within errors, however, the outcrop samples are characterised by lower organic C with many of them having <1%. In this work all these samples are considered as black shales, though there is some debate as to whether samples with <1% organic C can be included in this category (Arthur and Segeman, 1994; Meyer and Robb, 1996; Pasava *et al.*, 1996). The Re and Os concentrations in the samples show a wide range, 0.2-264 ng g<sup>-1</sup> and 0.02 to 13.5 ng g<sup>-1</sup>respectively (Tables 4.1, 4.2; Fig. 4.2). The outcrop samples generally have <20 ng Re g<sup>-1</sup> whereas those from the mines exhibit a wider range, with a significant number of samples having Re in excess of 50 ng g<sup>-1</sup>. The <sup>187</sup>Os/<sup>186</sup>Os also shows wide range 8.465 to 96.099, however, bulk of the samples have ratio between 10-30 (Fig. 4.2).

The covariation between Re and organic C and <sup>192</sup>Os and organic C are plotted in Fig. 4.3. The correlation coefficient between Re and organic carbon is 0.45 which increases to 0.59 if only samples with <20 ng Re g<sup>-1</sup> are considered. Similarly, the correlation coefficient for the <sup>192</sup>Os vs organic carbon is 0.24 which increases to 0.65 if only the samples having <1 ng g<sup>-1</sup> <sup>192</sup>Os are used for the regression. Plots of Re and <sup>192</sup>Os against nitrogen using it as the index of organic matter (Fig. 4.3) also give correlation coefficient which are similar to those derived based on the organic carbon data. The covariations of Re and <sup>192</sup>Os with organic carbon and nitrogen indicate their overall affinity with organic matter as observed by earlier workers (Ravizza and Turekian, 1989, 1992; Ravizza *et al.*, 1991; Colodner *et al.*, 1993).

Region &	Org. C	Ν	Os	Re	<sup>187</sup> Re/ <sup>186</sup> Os <sup>\$</sup>	<sup>187</sup> Os/ <sup>186</sup> Os <sup>\$</sup>				
Sample #	(% wt.)	) (% wt.)	$(ng g^{-1})$	$(ng g^{-1})$						
Outer Belt Samples										
Dehradun-Mu	ssoorie									
KU92-53*	1.62	0.02	0.83	16.9	$946 \pm 100$	$12.376 \pm 0.030$				
KU92-57	5.11	0.22	0.65	5.48	$425 \pm 13$	$18.608 \pm 0.176$				
UK94-51	2.98	0.12	4.13	-	-	$10.134 \pm 0.026$				
UK94-66	4.00	0.26	0.65	-	-	$22.447\pm0.178$				
UK94-52	0.76	0.04	0.05	0.52	$439 \pm 13$	$12.340 \pm 0.396$				
UK94-53	1.05	0.05	0.13	3.56	$1418 \pm 69$	$20.901 \pm 0.104$				
UK94-54	0.71	0.04	-	0.51	-	-				
UK94-55	0.54	0.04	0.04	0.35	$415\pm40$	$13.908 \pm 0.120$				
UK94-56	0.65	0.04	0.08	1.55	961 ± 69	$17.353 \pm 0.800$				
UK94-58	0.21	0.02	0.02	0.22	$524 \pm 71$	$14.263 \pm 0.400$				
Nainital										
KU92-51*	0.82	0.06	-	6.41	-	-				
KU92-50*	0.91	0.05	-	3.54	-	-				
KU92-49	0.91	0.06	0.08	5.18	$3713 \pm 290$	$29.820 \pm 0.458$				
Almora										
KU92-2	5.38	0.06	0.04	-	-	$8.465 \pm 0.452$				
KU92-6	5.85	0.03	0.51	-	-	$26.679 \pm 0.097$				
			Inner Bel	lt sampl	<u>es</u>					
Simla										
HP94-22*	3.95	0.27	0.18	13.1	$7216 \pm 1113$	$96.099 \pm 2.859$				
HP94-24	1.01	0.08	0.05	1.16	$1260\pm133$	$24.920\pm0.450$				
HP94-25	2.15	0.16	0.10	-	-	$74.336 \pm 3.366$				
HP94-26	0.67	0.12	0.05	0.87	867 ± 53	$17.757 \pm 0.212$				

Table 4.1: Re, Os abundances and Os isotopic composition of black shale outcrops from the Lesser Himalaya

\$ errors are  $\pm 2\sigma$  on the mean for <sup>187</sup>Os/<sup>186</sup>Os and  $\pm 2$  s.d. for <sup>187</sup>Re/<sup>186</sup>Os.

<sup>\*</sup> Re measurement by wet oxidation; others by ashing at 450°C followed by acid digestion (see Chapter 2).

Region &	Org. C	N	Os	Re <sup>+</sup>	<sup>187</sup> Re/ <sup>186</sup> Os	s <sup>* 187</sup> Os/ <sup>186</sup> Os <sup>*</sup>
Sample #	(% wt.	) (% wt.)	(ng g <sup>-1</sup> )	$(ng g^{-1})$		
Maldeota						
UK98-1	3.88	0.17	0.60	8.64 710	$0 \pm 23$ 15.	$373 \pm 0.093$
UK98-2	4.73	0.20	1.57	68.6 2564	$\pm 72$ 30.4	$490 \pm 0.164$
UK98-3	2.58	0.14	2.63	153 4340	$\pm 205$ 57.	$548 \pm 0.126$
UK98-4	1.01	0.16	0.17	3.16 945	$\pm 87$ 15.	$923 \pm 0.439$
UK98-8	4.87	0.18	0.42	5.37 628	$3 \pm 29$ 16.	$638 \pm 0.084$
UK98-9	5.04	0.19	0.40	5.10 612	$2 \pm 71$ 14.	$790 \pm 0.452$
UK98-11	4.69	0.17	0.57	13.4 1225	± 89 21.	$384 \pm 0.169$
KU92-56*	3.97	0.17	13.5	264 975	$\pm 32$ 18.	$002 \pm 0.134$
KU92-58*	4.57	0.20	0.79	18.8 1217	'±9 19.	864 ± 0.139
Durmala						
UK98-17	7.28	0.23	2.84	115 2373	± 106 31.	$853 \pm 0.179$
UK98-18	7.25	0.23	3.14	122 2249	$102 \pm 102 = 30.5$	$702 \pm 0.232$
UK98-19	3.06	0.14	0.34	7.22 1078	$3 \pm 42$ 19.	$271 \pm 0.180$
UK98-28	2.85	0.14	0.31	3.05 470	$\pm 15$ 14.	$450 \pm 0.155$
UK98-31	2.75	0.14	0.41	6.48 791	± 24 18.	$141 \pm 0.227$

Table 4.2: Re, Os and <sup>187</sup>Os/<sup>186</sup>Os in black shales from the Maldeota and Durmala mines

\$ errors are  $\pm 2\sigma$  on the mean for <sup>187</sup>Os/<sup>186</sup>Os and  $\pm 2$  s.d. for <sup>187</sup>Re/<sup>186</sup>Os.

+ all Re measurements by ashing at 450°C followed by acid digestion except where indicated.

\* Re measurements by wet oxidation. These two samples were not collected from the mine, but were picked up from the mined material outside.

In general, Re concentration, organic carbon and Re/Os (mean 25; range 8-73) in black shales from the Lesser Himalaya are lower than those reported for the Bakken, New Albany, Chattanooga (Ravizza and Turekian, 1989; Ravizza, 1991) and Canadian (Horan *et al.* 1994) black shales. The low organic carbon content of black shales from the Lesser Himalaya may be contributing to their low Re and Re/Os. Other possible



Fig. 4.2: Histograms of Re, Os concentrations and <sup>187</sup>Os/<sup>186</sup>Os in the Lesser Himalayan black shales.



Fig. 4.3: Covariation diagrams of <sup>192</sup>Os and Re with organic carbon and Nitrogen. Both <sup>192</sup>Os and Re show positive correlation with organic carbon and nitrogen.

Sample	Al	Fe	Mg	Ca	Na	K	Mn	Р	V	Cu	Re
KU92-49	12.86	2.93	1.54	0.09	0.29	6.28	38	282	167	7	5.18
KU92-50	11.57	2.59	1.26	0.02	0.11	5.21	46	193	121	14	3.54
KU92-51	10.62	3.86	2.79	1.37	0.22	5.51	598	321	72	44	6.41
KU92-53	0.47	0.30	0.45	0.92	0.15	0.30	100	493	136	23	16.9
KU92-56	6.47	2.49	2.08	4.68	0.21	3.14	213	10678	2643	101	264
KU92-57	7.77	4.84	1.18	1.46	1.38	3.37	207	943	118	60	5.48
KU92-58	7.82	4.52	1.17	0.12	1.33	2.13	192	658	59	66	18.8

 Table 4.3: Major and minor element data for black shales

All concentrations in % except for Mn, P, V and Cu which are in ppm and Re in ppb

explanations for this observation could be (i) water from which the black shales from the Lesser Himalaya were formed had lower Re and Re/Os (ii) loss of Re by weathering and mobilization. This seems an unlikely proposition considering the presence of fresh shining pyrites in many of them and considering that samples from the underground mines yield good isochrons with ages that are stratigraphically consistent (discussed below).

Major element composition for some of the black shales (Table 4.3) show that they are similar to shales except for the sample KU92-53, which is a chert, collected from the chert-phosphorite layer of the Tal formation. The covariations between Re vs P, V and Cu show positive correlations. The correlation coefficients between Re vs P, V and Cu are 0.997, 0.996 and 0.754 respectively which indicate the association of all these elements with organic matter.

### **4.3. LESSER HIMALAYAN BLACK SHALE CHRONOLOGY**

The chronology of black shales from the Maldeota and Durmala mines from the outer belt of the Tal formation and Shali formation of the inner belt are discussed in this section. The period of deposition of the various sedimentary sequences in the Lesser Himalaya, based on fossil records and the intercorrelation between them was summarised in Chapter 2.

Based on the lithological settings and fossil records, many workers have correlated the Inner and Outer belts of the Lesser Himalaya to understand their origin and tectonic settings. These were discussed in detail in Chapter 2 and the two models of correlation are briefly presented below. West (1939), Frank and Fuchs (1970) and Valdiya (1995) have correlated Deoban (Shali) formation of the inner belt to the Krol formation of the outer belt and Mandhali of the inner to the Tal of the outer belt based on the similarities in their lithologies and the formations underlying them. Mehr (1977) and Stocklin (1980) on the other hand based on structure and Shanker *et al.* (1993) based on the fossil records have suggested that the inner belt rocks are older than those of outer belts. Sharma *et al.*, (1992) have reported an age of 626±13 Ma for black shales from the chert-phosphorite unit of the lower Tal formation using Rb-Sr systematics. This unit is just above Krol-Tal boundary and about 10 m below the black shale band dated in this study using Re-Os.

Dating sedimentary rocks is difficult as the setting of radiometric clocks in them is not straightforward. The isotopic composition of sedimentary rocks often contain in them signatures of the rocks from which they are formed and thus serve more as tracers to tag the provinance from where they were derived, rather than as geochronometers. In addition, possible open system behaviour of both parent and daughter nuclides during weathering and burial diagenesis makes the application of the commonly used isotope pairs to date them difficult. In this context, Rb-Sr pair has met some success (Faure, 1986) when < 2  $\mu$ m clays are separated from sedimentary rocks and analysed for their Rb-Sr. Meaningful ages has been obtained using this technique for the sedimentary rocks (Gorokhov *et al.*, 1981).

More recently, Ravizza and Turekian (1989) demonstrated the potential of <sup>187</sup>Re-<sup>187</sup>Os isotope pair as a chronometer for black shales. Depositional enrichment of Re and Os in organic rich sediments sets the Re-Os system apart from other long-lived decay schemes and makes it a potentially viable tool for black shale geochronometry. Re and Os both are siderophilic and chalcophilic and are scavenged from seawater at the time of black shale deposition. The scavenged component of Re and Os generally overwhelms their detrital components.

<sup>187</sup>Re decays to <sup>187</sup>Os by beta decay with a decay constant of  $1.64 \times 10^{-11}$  y<sup>-1</sup> (Lindner *et al.*, 1989). The equation which describes the changes in the <sup>187</sup>Os/<sup>186</sup>Os ratio with time is given as

$$\left(\frac{{}^{187}\text{Os}}{{}^{186}\text{Os}}\right)_{t} = \left(\frac{{}^{187}\text{Os}}{{}^{186}\text{Os}}\right)_{o} + \left(\frac{{}^{187}\text{Re}}{{}^{186}\text{Os}}\right)_{t} \times \left(e^{\lambda t} - 1\right)$$

where,

$$\left(\frac{^{187}\text{Os}}{^{186}\text{Os}}\right)_t$$
 and  $\left(\frac{^{187}\text{Re}}{^{186}\text{Os}}\right)_t$  are the present day atomic ratios measured in the sample  $\left(\frac{^{187}\text{Os}}{^{186}\text{Os}}\right)_o$  is the atom ratio of the system at the time of closure.

 $\lambda$  is the decay constant of <sup>187</sup>Re.

In this context the time of closure designate the point in time after which neither Re nor Os are lost from or added to the system. To get a meaningful age, which corresponds to the time of deposition, following assumptions have to be valid:

- (i) initial <sup>187</sup>Os/<sup>186</sup>Os is homogeneous i.e. at the time of deposition <sup>187</sup>Os/<sup>186</sup>Os was uniform in the basin and
- (ii) the Re-Os system has remained closed since the time of closure, i.e. there is no gain or loss of Re-Os from the black shales since they were formed.

For a set of closed, coeval whole-rock samples with variable Re/Os ratios which are fulfilling above conditions, a plot of  $({}^{187}\text{Os}/{}^{186}\text{Os})_t$  vs  $({}^{187}\text{Re}/{}^{186}\text{Os})_t$  will yield a colinear array of points with slope of  $(e^{\lambda t}-1)$ . The array of points is known as an isochron. The amount of time which has been elapsed since the deposition of the rock can be calculated from the slope of the isochron and  $\lambda$ , the decay constant.

In this work, <sup>187</sup>Re-<sup>187</sup>Os isotope pair has been used to date the black shale samples from both the inner and the outer Lesser Himalaya.

#### (i) Outer belt black shales

In the outer Lesser Himalaya samples were collected for Re-Os chronology from two underground mines which are are at the two limbs of Mussoorie syncline, near Mussoorie. Rock phosphate is mined from these mines. Maldeota, one of these two mines is situated on the eastern limb whereas Durmala is on the western limb of the syncline. The lithological section of these mines has been already shown in Chapter 2. Above the chert-phosphorite unit of the Lower Tal formation is the black shales of argillaceous unit. Samples for Re-Os chronology were collected from this argillaceous layer (Fig. 4.4). In Maldeota, seven samples were collected from the same horizon (lateral distance of ~1km) at three different elevations in the direction of the bed strike. Two samples, KU92-56 and KU92-58, from the same horizon but are samples from an earlier sampling trip picked from the pile kept outside the mine. In Durmala, five samples were collected from the same horizon at two different locations separated by a distance of ~3-4 km. In hand



Fig. 4.4 Black shale samples collected in this study for chronology. The samples are ~10 m above the Krol-Tal boundary. Also shown is the age of black shale in the chert-phosphorite layer by Rb-Sr dating (Sharma *et al.*, 1992)

specimens, these mine samples are black and indistinguishable from each other. They were compact with thin laminations. Thin horizons rich in pyrite were common and in some cases small pyrite concretions were also encountered.

A total of 14 samples were analysed from the Maldeota and the Durmala mines for their Re, Os concentrations, <sup>187</sup>Os/<sup>186</sup>Os and organic carbon (Table 4.2; Singh *et al.*, 1999). The Organic carbon contents of the samples are in the range of 1.01% to 7.28%. The Re and Os concentrations in the samples show a wide range and vary from 3.05 to 264 and 0.17 to 13.5 ng g<sup>-1</sup> respectively. The age of the black shale formations from the Maldeota and Durmala mines can be determined from their <sup>187</sup>Os/<sup>186</sup>Os vs <sup>187</sup>Re/<sup>186</sup>Os plot if they satisfy the assumptions discussed earlier. With the data in Table 4.2 best-fit line is drawn following Williamson (1968) to derive their ages and initial ratio with associated errors (Singh *et al.*, 1999). This yield ages of 554  $\pm$  16 Ma and 552  $\pm$  22



Fig. 4.5: Isochron plot for black shales from Maldeota mine. The isochron age (t) obtained and initial <sup>187</sup>Os/<sup>186</sup>Os (R<sub>i</sub>) is given (Singh *et al.,* 1999).



Fig. 4.6: Isochron plot for black shales from the Durmala mine. The age is  $552 \pm 22$  Ma with an initial ratio of  $10.28 \pm 0.32$  (Singh *et al.*, 1999).

Ma ( $\pm 2\sigma$ ) for the Maldeota (Fig. 4.5) and the Durmala (Fig. 4.6) black shales (calculated using <sup>187</sup>Re decay constant of 1.64 × 10<sup>-11</sup> y<sup>-1</sup>, Lindner *et al.*, 1989) with initial <sup>187</sup>Os/<sup>186</sup>Os ratios of 9.16 ± 0.30 and 10.28 ± 0.32 ( $\pm 2\sigma$ ) respectively.

Since black shales from both the mines were collected from the same stratigraphic horizon and from same lithological settings as shown in Fig. 4.4, they can be plotted



Fig. 4.7: <sup>187</sup>Re-<sup>187</sup>Os isochron plot for data from both the mines, the Maldeota and Durmala. The pooled data yield an age of  $535 \pm 11$  Ma same within errors of those obtained for the individual mines (Singh *et al.*, 1999).

together. Pooling the data together (Fig. 4.7) gives an age of  $535 \pm 11$  Ma with an initial ratio of 9.81  $\pm$  0.20. All the isochron ages obtained for samples from both the underground mines and their pooled data are same within experimental uncertainties. In order to assess the influence of "mixing" in generating the isochron plot (Figs. 4.5-4.7) <sup>187</sup>Os/<sup>186</sup>Os were plotted against 1/<sup>192</sup>Os. The plots do not exhibit any systematic trend, ruling out the possibility of mixing as a cause for the observed isochron.

The Maldeota and Durmala mine samples are from the Lower Tal formation, ~15 m above the Upper Krol/Lower Tal (Pc-C) boundary (Fig. 4.4). The <sup>187</sup>Re-<sup>187</sup>Os isochron ages obtained for black shales in this study;  $535 \pm 11$  Ma is consistent with the Early Cambrian age assigned to the lower Tal formation based on the presence of trace fossils and microfauna in them (Azami, 1983; Singh and Rai, 1983). The Re-Os ages, however, are about 70 Ma younger than the Rb-Sr age of black shales from the chert-black shale layer collected from a location near the Maldeota mine (Sharma *et al.*, 1992). Their samples, occurring ~10 m below the black shale band dated in this study (Fig. 4.4), yield an age of  $626 \pm 13$  Ma.

Aharon et al. (1987) Shanker et al., (1993) have correlated the Lower Tal formation with the Tomotian stage of the stratotype section of Siberia based on fossil assemblages. U-Pb dating of zircons separated from volcanic braccia contained in the basal part of the Tommotian yield a maximum age of 534.6  $\pm$  0.4 Ma (Bowring *et al.*, 1993). In another section in the Olenek region Bowring et al. (1993) have reported an U-Pb age of 543.6  $\pm$  0.24 Ma for zircons from volcanic braccia occuring within the Nemakit-Daldynian Stage. Based on this age they have estimated an age of 544 Ma for Pc-C boundary. The chert member (with phosphorite) of the Lower Tal formation is also correlated with the Meishucunian Zone of South China (Fig. 4.8). Rb-Sr ages of black shales deposited just above the Pc-C boundary in the Meishucunian section, Yunnan province is 579.7  $\pm$  8.2 Ma (Xue 1984). Zhang *et al.* (1984) have reported Rb-Sr ages ranging between 569 to 602 Ma for samples collected just above the Pc-C boundary from various Chinese sections. Recent data from U-Pb isochrons from ash bands near marker B of Mishucunian section indicate a much younger age of  $525 \pm 7$  Ma (Compston *et al.*, 1992). It is seen from these comparisons that the Rb-Sr ages obtained for the Pc-C boundary are generally a few tens of million years older (569-626) than those based on U-Pb dating of zircons (520-545 Ma) separated from volcanic ash contained in the Early Cambrian sedimentary rocks in Canada, Morocco, China, Siberia and South Australia (Bowring et al. 1993; Brasier et al. 1994).

The Re-Os age of black shales analysed in this study,  $535 \pm 11$  Ma, deposited ~15 m above Pc-C boundary is consistent with these U-Pb ages of the Tommotian and

Mishucunian sections. The Re-Os chronology along with the available fossil records confirm the identity of Krol-Tal boundary as the Pc-C boundary.

#### (ii) Inner Belt Samples

Three black shale outcrop samples were analysed from the inner belt of the Lesser Himalaya for their Re, Os concentrations and <sup>187</sup>Os/<sup>186</sup>Os (Table 4.1). These samples were collected from road cuts. The data are plotted as an isochron in Fig. 4.9. The isochron age obtained from the slope of the line (Fig. 4.9) is  $839 \pm 138 (\pm 2\sigma)$  with an initial <sup>187</sup>Os/<sup>186</sup>Os ratio of  $5.98 \pm 2.28$ .



Fig. 4.9:  $^{187}$ Re- $^{187}$ Os isochron diagram for the inner belt black shales. The results yield an age of 839 ± 138 Ma, a few hundred million of years older than the outer belt samples. (Singh *et al.*, 1999).

These results seem to indicate that the inner belt samples are older than the outer belt (Maldeota and Durmala) samples; though the uncertainties associated with the age and the initial ratio of the former are large to make a critical assessment. More inner belt black shale samples have to be analysed to check on the preliminary results obtained in this study. If these preliminary results, however, are confirmed through more analysis then it would support the model proposed by Mehr (1977), Stocklin (1980) and Shanker *et al.*, (1993) that the inner belt samples were deposited much earlier than the outer belt and making the simple correlation based only on lithology questionable.

It is, however, noteworthy that even if the inner belt sequences (Deoban, Mandhali) are older than those of the outer belt (Krol-Tal) it is difficult from the available information to distinguish whether the outer belt sediments are allochthonus or autocthonus. Three scenerios are possible for their present occurrence in the inner and outer belts. (i) they are allochthonus i.e., they were deposited in the same basin above the Mandhali in the inner belt, but displaced southward along with the crystalline Klippe to the present position due to tectonic activities or (ii) they were deposited in the present location at the beginning or (iii) both the inner and outer belt were depositing in the same basin, but after the deposition of Mandhali, the basin got uplifted near the inner belt. Therefore, the sea regressed southward and deposition continued in the outer belt but stopped in inner belt (Sharma, 1998). A great deal more systematic geological surveying and regional large-scale mapping is needed to choose between these scenarios.

#### (iii) Os isotopic ratio of Early Cambrian seawater

It is established that the <sup>187</sup>Os/<sup>186</sup>Os of the seawater has been increasing with time through the Cenozoic (Pegram *et al.*, 1992, Ravizza, 1993, Ehrenbrink *et al.*, 1995; Turekian and Pegram, 1997; Reusch *et al.*, 1998). Information on longer-term variations in <sup>187</sup>Os/<sup>186</sup>Os of seawater, if any, has to be derived from samples deposited during various times in the past and which contain records of seawater Os in them. Black shales may satisfy these requirements as the Os concentration in them is generally dominated by seawater component and samples of different ages can be obtained. The initial <sup>187</sup>Os/<sup>186</sup>Os ratios obtained from the isochron plots of black shale Re-Os data is likely to be that of the seawater <sup>187</sup>Os/<sup>186</sup>Os of that time as most of the Os in them is derived from seawater. It is seen that the <sup>187</sup>Os/<sup>186</sup>Os of modern organic rich sediments is almost equal to the present day seawater value (Ravizza and Turekian, 1992). Thus by dating black shales of the various age groups, it should in principle be possible to obtain the <sup>187</sup>Os/<sup>186</sup>Os at the time of their deposition, which in turn can be used to reconstruct Os

evolution curve of ocean through the Phanerozoic and part of Proterozoic times. Uncertainties in the approach include (i) the possibility of inhomogeneous <sup>187</sup>Os/<sup>186</sup>Os ratio in the basin due to the local scavenging of Os or incomplete mixing of seawater, (ii) open system behavior of Re-Os system during later diagenesis and weathering resulting in the migration of Re and/or Os (Ravizza and Turekian, 1989) and (iii) contribution from detrital material, which can cause the <sup>187</sup>Os/<sup>186</sup>Os of black shales to be different from that of seawater from which they deposit.

The black shale samples from the Maldeota and Durmala mines are of Early Cambrian age. The <sup>187</sup>Os/<sup>186</sup>Os initial ratio obtained for these samples should be that of sea-water of that time, if Os in these black shales is derived almost entirely from it and if the seawater reservoir was well mixed. As the residence time of Os is much more than the mixing time of the ocean (Sharma *et al.*, 1997), it is very likely that the later condition is met. The average Os concentration in the black shale samples from the two mines is ~2 ng g<sup>-1</sup>, ~ 50 times higher than the average crustal value ~0.04 ng g<sup>-1</sup> (Esser, 1991; Shirey and Walker, 1998). Even the lowest Os measured in these samples, 0.17 ng g<sup>-1</sup> (Table 4.2) is a factor of ~4 higher than its crustal abundance. It is, therefore, very likely that the initial <sup>187</sup>Os/<sup>186</sup>Os ratio in many of these black shales is dominated by seawater component, however, in the low Os samples the influence of crustal component in determining the initial <sup>187</sup>Os/<sup>186</sup>Os could be important.

Ravizza (1991) reported initial ratios of  $13.1 \pm 1.6$  and  $6.4 \pm 3.0$  in black shales deposited  $354 \pm 14$  and  $358 \pm 47$  Ma ago. Sluggish ocean circulation and enhanced Os burial have been held responsible for such a large heterogeneity in the initial ratios of samples deposited at about the same time. Such large differences in the initial <sup>187</sup>Os/<sup>186</sup>Os ratio in samples deposited at about the same time raises doubt about their use to obtain <sup>187</sup>Os/<sup>186</sup>Os of seawater. Our results on the Maldeota and Durmala black shales deposited at ~535 Ma ago yield initial ratios 9.16 ± 0.3 and 10.3 ± 0.3 (Figs. 4.9 and 4.10) which are outside  $\pm 2\sigma$  errors.

The differences observed in the two initial Os isotopic ratios at 535 Ma may be due to the differences in the relative proportions of detrital and marine Os incorporated in the black shales during their formation. These results suggest the need to evolve suitable methods to correct for the detrital contribution which would enable the retrieval of the Os isotope composition of seawater at the time of their deposition from the black shale data. If the endmember composition of the detrital component and its contribution to the black shales can be obtained based on suitable elemental/isotopic proxies, it may be possible to derive seawater Os isotopic composition from the initial <sup>187</sup>Os/<sup>186</sup>Os of black shale based on two component mixing model. The problem may be compounded in case of sediments with low accumulation rate where extraterrestrial contribution of Os may become significant.

The value of  $9.81 \pm 0.20$  obtained in this study from the pooled data would seem to indicate that the seawater <sup>187</sup>Os/<sup>186</sup>Os was higher 535 Ma ago compared to the present day value of 8.7 (Sharma *et al.*, 1997), however, the interpretation of the data needs better constraints on the crustal contribition.

# **4.3.** OS ISOTOPES IN THE HIMALAYAN BLACK SHALES AND <sup>187</sup>OS/<sup>186</sup>OS EVOLUTION OF SEAWATER

The  ${}^{187}$ Os/ ${}^{186}$ Os of seawater is increasing with time since the Cenozoic (Pegram *et* al., 1992; Ravizza, 1993; Ehrenbrink et al., 1995; Turekian and Pegram, 1997). The Os isotopic composition of the seawater is determined by the mixing proportions of Os derived from three sources: (i) the mantle (hydrothermal supply and submarine basalt weathering) (ii) extraterrestrial and (iii) the currently eroding continental crust (Fig. 4.10). The first two sources have  ${}^{187}$ Os/ ${}^{186}$ Os of ~1 whereas the crustal source is far more radiogenic with <sup>187</sup>Os/<sup>186</sup>Os of 10-15 (Shirey and Walker, 1998). The available results on Os isotope evolution (op. cit.) show that at ~65 Ma it was as low as ~2 resulting from extraterrestrial impact which drastically decreased the sea water <sup>187</sup>Os/<sup>186</sup>Os. This steadily increased and reached a value of ~6 at about 30 Ma (Fig. 4.11). During the time interval of 28-16 Ma the seawater <sup>187</sup>Os/<sup>186</sup>Os was nearly constant. From 16 Ma to 1.5 Ma it increased from 6.2 to ~7.7 and then rapidly to the present day value of 8.7 (Fig. 4.11). The general increase of  ${}^{187}$ Os/ ${}^{186}$ Os in the ocean is similar to that observed for  ${}^{87}$ Sr/ ${}^{86}$ Sr (Pegram et al., 1992). The steady increase in the Sr isotope composition has been attributed to weathering and transport of radiogenic Sr from the Himalaya (Richter et al., 1992). Various evidences, such as high <sup>87</sup>Sr/<sup>86</sup>Sr in rivers draining the Himalaya, particularly in the Ganga-Brahmaputra, their moderate Sr concentration, the timing of <sup>87</sup>Sr/<sup>86</sup>Sr increase, all seem

to corroborate the suggestion, though there is some debate about the magnitude and sources of the contributions from the Himalaya to the <sup>87</sup>Sr/<sup>86</sup>Sr in ocean. Following the Sr analogy, and based on the timing and trend of <sup>187</sup>Os/<sup>186</sup>Os evolution in ocean, it was suggested (Pegram et al., 1992; Ehrenbrink et al., 1997; Turekian and Pegram, 1997) that the increase in the  ${}^{187}$ Os/ ${}^{186}$ Os since last ~50 Ma has resulted from intense continental weathering, particularly organic-rich ancient sediments of the Himalaya. Black shales generally contain high concentrations of both Re and Os with Re/Os ratios 10-20 times higher than average crustal materials (Ravizza and Turekian, 1989). As a result the <sup>187</sup>Os/<sup>186</sup>Os in old black shales become much higher than that in crustal silicates and their weathering can be significant source of Os isotopes to the sea. This coupled with intense weathering in the Himalaya make the black shales of the region a potential source of radiogenic Os to the ocean. More detailed analysis of Os isotope evolution (Ravizza, 1993; Ehrenbrink et al., 1995; Turekian and Pegram 1997) seem to indicate that, though, both <sup>187</sup>Os/<sup>186</sup>Os and <sup>87</sup>Sr/<sup>86</sup>Sr show steady increase during the past ~50 Ma, their evolutionary trend seem to be decoupled at different time segments, indicating that a common source for their oceanic increase during the past ~50 Ma, as was initially proposed may not be fully valid. For example, between 25 and 16 Ma <sup>87</sup>Sr/<sup>86</sup>Sr rises rapidly towards more radiogenic values whereas the Os isotopic composition remains essentially invariant. This lead Reusch et al. (1998) to suggest that weathering of New Guinea Arc and Australian continental margin could also be important in influencing the evolution of these isotope ratios in the ocean.

Detailed discussion and review on the various source (s) contributing to the Os isotope evolution of the ocean, though is beyond the scope of this thesis work, another possible source which can influence the difference in the Os and Sr isotope evolution of seawater is the intense weathering of Gangdese Batholith during the period of 25 to 16 Ma. The study of Indus fan in the northern Arabian Sea indicates that weathering in the western Himalaya was enhanced at ~25 Ma (Whitting and Karner, 1991). In the Southern Tibet, the Kailash conglomerate records the unroofing of the Gangdese batholith of (Copeland, 1997). The time of this deposition has been constrained to be Early Miocene (Copeland, 1997 and references therein) indicating rapid unroofing of Gandese batholith during that period. Copeland *et al.*(1987), based on the Ar-Ar study on the Gangdese

batholith infer that ~ 3 km thickness of the batholith eroded during 25-17 Ma. Isotopic data suggest a largely mantle source for the rocks of the Gangdese, with <30% of crustal contamination (Copeland, 1997 and references therein). The weathering of this batholith may contribute to the decoupling of Sr and Os isotope evolution druing 25-16 Ma as its weathering mostly supply mantle like Os ( ${}^{187}$ Os/ ${}^{186}$ Os  $\approx$  1) which would buffer the increase in oceanic  ${}^{187}$ Os/ ${}^{186}$ Os, whereas the weathering of granites and gneisses from the Higher Himalaya would continue to increase the  ${}^{87}$ Sr/ ${}^{86}$ Sr.

The ideal approach to test the importance of weathering in the Himalaya in contributing to the  ${}^{187}$ Os/ ${}^{186}$ Os is through measurements of the concentration of Os and its isotope composition in rivers draining the Himalaya. But till date there are no measurements of Os in Himalayan rivers. In the absence of such data from the Himalayan rivers, an indirect approach to check the hypothesis is through model calculations of Os flux and  ${}^{187}$ Os/ ${}^{186}$ Os required to account for the observed increase in marine  ${}^{187}$ Os/ ${}^{186}$ Os and whether such requirements can be met by weathering of black shales from the region as they are likely to be the major source of the Os to these Himalayan rivers (Singh *et al.*, 1999). This approach relies on the availability of data on the concentration of Os and its isotopic composition in black shales. Based on the Re-Os isotope analysis of black shales made in this study and models available in literature, their role in contributing to the temporal evolution of oceanic  ${}^{187}$ Os/ ${}^{186}$ Os has been assessed in the following section (Singh *et al.*, 1999).

Following the model of Richter *et al.* (1992) for oceanic Sr isotope evolution the balance equation for <sup>187</sup>Os and <sup>186</sup>Os in seawater can be written as:

$$\frac{d^{187}N}{dt} = \sum_{i}^{187} J_{i} - {}^{187} J_{o}$$
(4.1)

$$\frac{d^{186}N}{dt} = \sum_{i} {}^{186}J_{i} - {}^{186}J_{o}$$
(4.2)

where,

The Os isotopic ratio  $(R_s)$  of the ocean is

$$R_{s} = \frac{{}^{187}N}{{}^{186}N}$$
(4.3)

Substituting  ${}^{187}N=R_s {}^{186}N$  in Eqn. (4.1) yield:

$$R_{s} \frac{d(^{186}N)}{dt} + {}^{186}N \frac{dR_{s}}{dt} = \sum_{i} {}^{187}J_{i} - {}^{187}J_{o}$$
(4.4)

Subsituting  $\frac{d(^{186}N)}{dt}$  from Eqn. (4.2) in Eqn. (4.4) give:

$${}^{186}N\frac{dR_{s}}{dt} = \sum_{i}{}^{187}J_{i} - {}^{187}J_{o} - R_{s}\left(\sum_{i}{}^{186}J_{i} - {}^{186}J_{o}\right)$$
(4.5)

Eqn. (4.5) is simplified using following assumptions:

- (i) Os isotopes do not fractionate during their removal from the ocean, (hence,  ${}^{187}J_o = R_s {}^{186}J_o$ )
- (ii) The Os isotopic composition of different sources to the ocean can be characterised by an average value,  $R_{i}$  (thus,  ${}^{187}J_i = R_i {}^{186}J_i$ ). The value of  $R_i$  vary with time.

(iii) the total number of moles of <sup>186</sup>Os in the ocean (<sup>186</sup>N) is constant with time.This yield

$${}^{186}N\frac{dR_s}{dt} = \sum_i R_i {}^{186}J_i - R_s \sum_i {}^{186}J_i$$
(4.6)

Oceans receive Os isotopes principally from (i) rivers (dissolved and leachable) (ii) dissolution of extraterrestrial materials and (iii) hydrothermal sources and submarine weathering of basalts. The <sup>187</sup>Os/<sup>186</sup>Os of the ocean is controlled by the relative fluxes of <sup>186</sup>Os from these sources and the <sup>187</sup>Os/<sup>186</sup>Os of rivers as the <sup>187</sup>Os/<sup>186</sup>Os of the extraterrestrial and hydrothermal components can be considered invariant with time at ~1. Therefore, changes in the magnitude of any of these fluxes and/or <sup>187</sup>Os/<sup>186</sup>Os of rivers can cause variation in R<sub>s</sub>. Splitting the <sup>186</sup>J<sub>i</sub> term in equation (4.6) into the riverine (<sup>186</sup>J<sub>r</sub>) and the non-radiogenic cosmic/hydrothermal (<sup>186</sup>J<sub>nr</sub>) components, with their corresponding <sup>187</sup>Os/<sup>186</sup>Os, R<sub>r</sub> and R<sub>nr</sub> respectively, Eqn. (4.6) can be rewritten as:

$${}^{186}N\frac{dR_s}{dt} + R_s({}^{186}J_r + {}^{186}J_{nr}) = {}^{186}J_r R_r + {}^{186}J_{nr} R_{nr}$$
(4.7)


Fig. 4.11:  $^{187}\text{Os}/^{186}\text{Os}$  evolution of sea water during the past 25 Ma. Smooth line is drawn from the data of Ravizza, 1993 . The seawater  $^{187}\text{Os}/^{186}\text{Os}$  evolution can be devided into three segments 25-16 Ma (R<sub>s</sub>  $\approx$  6.2), 16-1.5 Ma (R<sub>s</sub> 6.2 to 7.7) and 1.5 Ma to present (R<sub>s</sub> 7.7 to 8.7)

The flux of <sup>187</sup>Os from rivers (<sup>186</sup>J<sub>r</sub>R<sub>r</sub>) would be governed by the intensity of weathering and the <sup>187</sup>Os/<sup>186</sup>Os of the drainage basin and any change in either or both of these can effect the riverine <sup>187</sup>Os flux and hence the oceanic <sup>187</sup>Os/<sup>186</sup>Os. Climate and tectonics are important in influencing the intensity of weathering and therefore the flux of Os transported to oceans. The degree of weathering also determines the proportion of Os isotopes contributed to rivers by various lithologies and hence the value of R<sub>r</sub>. The <sup>187</sup>Os/<sup>186</sup>Os of the basin can also vary because of radioactive ingrowth of <sup>187</sup>Os from the decay of <sup>187</sup>Re (Ravizza and Ehrinbrink, 1998). This can monotonically increase the <sup>187</sup>Os/<sup>186</sup>Os of the basin with time, the rate of change being dependent on its <sup>187</sup>Re/<sup>186</sup>Os abundance ratio. Tectonic processes can cause changes in the lithology of the drainage basin which in turn can also contribute to changes in its  $^{187}$ Os/ $^{186}$ Os.



Fig. 4.12 Rate of change of <sup>187</sup>Os/<sup>186</sup>Os in ocean.  $R_s$  has been increasing at a nearly constant rate of 0.1 Ma<sup>-1</sup> during the interval 16-1.5 Ma. And much more rapidly during the recent ~1.5 Ma (dR<sub>s</sub>/dt 0.68 Ma<sup>-1</sup>). Prior to 16 Ma it was constant at 6.2.

Available data (Pegram *et al.* 1992; Ravizza, 1993; Turekian and Pegram, 1997; Reusch *et al.* 1998) on the <sup>187</sup>Os/<sup>186</sup>Os of oceans show that its evolution during the past 25 Ma can be broadly divided into three segments (Fig. 4.11), it was nearly constant at 6.2 during 25-16 Ma, it increased uniformly from 6.2 to 7.7 between 16 Ma to 1.5 Ma with a slope of 0.10 Ma<sup>-1</sup> (Fig. 4.12) and far more rapidly during the recent 1.5 Ma at rate of 0.68 Ma<sup>-1</sup> (Fig. 4.12). The objective of this modelling exercise is to evaluate the changes required in <sup>186</sup>J<sub>r</sub> or R<sub>r</sub> to produce the measured temporal variations in R<sub>s</sub>. The approach followed is to obtain an estimate of the contemporary <sup>186</sup>J<sub>nr</sub> based on material balance considerations and using available data on N, R<sub>s</sub>, <sup>186</sup>J<sub>r</sub> and R<sub>r</sub> (Table 4.4).

## Table 4.4: Present day Os fluxes and isotopic ratios\*

$^{186}$ J <sub>r</sub>	= 15.8 moles $y^{-1}$ (total Os flux $\approx 1160$ moles $y^{-1}$ )
R <sub>r</sub>	= 11.0
<sup>186</sup> J <sub>nr</sub> **	= 4.72 moles $y^{-1}$ (total Os flux $\approx$ 300 moles $y^{-1}$ )
R <sub>nr</sub>	= 1
<sup>186</sup> N	= $3.1 \times 10^5$ moles (C <sub>s</sub> ≈ 16 fmoles kg <sup>-1</sup> )
R <sub>s</sub>	= 8.7

\* from Sharma and Wasserburg (1997) and Sharma *et al.,* (1997)

\*\* calculated from material balance considerations to produce present day  $R_s = 8.7$ .

Assuming that <sup>186</sup>J<sub>nr</sub> has remained the same at the present day value during the past 25 Ma, the changes required either in <sup>186</sup>J<sub>r</sub> or R<sub>r</sub> are calculated to account for the observed variations in R<sub>s</sub> (Fig. 4.11). There is very little data on the Os concentration and <sup>187</sup>Os/<sup>186</sup>Os of rivers. So far only results for four rivers are available in literature (Sharma and Wasserburg, 1997). The calculations that follow, assumes that the mean Os concentration and the <sup>187</sup>Os/<sup>186</sup>Os of these four rivers is representative of the present day global river (Table 4.4). The <sup>187</sup>Os/<sup>186</sup>Os of these rivers range between 8.8-14.4 (mean 11.0) and Os concentrations 2.6-8.6 pg kg<sup>-1</sup> (mean 5.9 pg kg<sup>-1</sup>). The mean <sup>187</sup>Os/<sup>186</sup>Os of 11.0 is quite similar to the value of 10.5 ± 0.5 reported by Esser and Turekian (1993) for <sup>187</sup>Os/<sup>186</sup>Os of erodable continental crust. The calculation has been done both for the global rivers and the Himalayan rivers.

## Case I. Temporal variations in $R_s$ is only due to change in $J_r$ ( $R_r$ is kept constant).

Using equation (4.7) and the available values for different parameters,  ${}^{186}J_r$  for the global rivers has been calculated with time. Figure 4.13 presents the changes in  ${}^{186}J_r$  with time required to produce the measured  ${}^{187}Os/{}^{186}Os$  variations in seawater keeping  $R_r$  constant at 11.0. The model shows that the global riverine flux of  ${}^{186}Os$ ,  ${}^{186}J_r$ , has to increase from 5.1 moles y<sup>-1</sup> 16 Ma ago to 9.5 moles y<sup>-1</sup> 1.5 Ma ago and more rapidly to

the present day value of 15.8 moles y<sup>-1</sup>. (for  $R_r = 11.0$ , this would translate to total Os flux of ~370 moles y<sup>-1</sup> at 16 Ma and 1160 moles y<sup>-1</sup> today). If enhanced weathering of black shales from the Himalaya accounts for this increase in <sup>186</sup>J<sub>r</sub>, as has been suggested (Pegram *et al.* 1992) the required variation in <sup>186</sup>J<sub>HTP</sub> with time would be as given in Fig. 4.14. This calculation has been made by splitting the river flux term in Eqn. 4.7 into two



Fig. 4.13: Temporal variations in total Os and <sup>186</sup>Os flux required from global rivers to reproduce the observed Os isotopic composition of seawater. The total Os flux required at 16, 10 and 1.5 Ma are given in parenthesis.

components, one representing the flux from HTP rivers  $(J_{HTP})$  and the second from all the other rivers,  $J_{rest}$ , (i.e. excluding those draining the HTP).

$${}^{186}N\frac{dR_{s}}{dt} + R_{s}\left({}^{186}J_{rest} + {}^{186}J_{HTP} + {}^{186}J_{nr}\right) = \left({}^{186}J_{HTP}R_{HTP} + {}^{186}J_{rest}R_{rest}\right) + {}^{186}J_{nr}R_{nr} \quad (4.8)$$

 $^{186}$ J<sub>rest</sub> and  $^{186}$ J<sub>HTP</sub> 16 Ma ago are taken to be 4.6 and 0.51 moles y<sup>-1</sup> respectively in proportion to their water discharge (HTP rivers make up ~10% of global river discharge. Taking Os flux via rivers in proportion to water discharge,  $^{186}$ J<sub>rest</sub> would be 4.6 moles y<sup>-1</sup>, 90% of the Os flux of 5.1 moles y<sup>-1</sup>16 Ma ago,). The results (Fig. 4.14) show that  $^{186}$ J<sub>HTP</sub>

has to increase from 0.51 to 4.9 moles y<sup>-1</sup> during 16 to 1.5 Ma and far more rapidly to 11.3 moles y<sup>-1</sup> today. The calculated present day <sup>186</sup>J<sub>HTP</sub> value of 11.3 moles y<sup>-1</sup> ( $\approx$  830 moles y<sup>-1</sup> total Os flux) would correspond to an Os concentration of ~40 pg  $\lambda^{-1}$  in these rivers. The average Os concentration in black shales from the Maldeota and Durmala mines is ~2 ng g<sup>-1</sup>. If this value is typical of Os concentration in black shales of the Himalaya, then to yield ~40 pg Os  $\lambda^{-1}$  of river water, it requires that Os from ~20 mg of



Fig. 4.14: Osmium flux required from HTP rivers if all the observed changes in oceanic <sup>187</sup>Os/<sup>186</sup>Os results from Os supply from the Himalayan-Tibetan-Plateau rivers. Calculation made by assuming that the <sup>187</sup>Os/<sup>186</sup>Os of the global (R<sub>rest</sub>) and the Himalayan rivers (R<sub>HTP</sub>) has remained constant at 11.0.

black shales has to be released per liter of river water. (if the highest concentration of 13.5 ng g<sup>-1</sup> measured in KU92-56, Table 4.2, is excluded from averaging, the mean Os in the mine samples would be  $\sim$ 1 ng g<sup>-1</sup> and Os from  $\sim$ 40 mg of black shale would have to be released per liter of river water). There is no data on the Os concentration of Himalayan rivers, however, there are some measurements of Re in the Ganges and the

Brahmaputra (Colodner *et al.* 1993). The Re concentration in these rivers at their mouth is 1-2 ng  $\lambda^{-1}$ . If all this Re is derived from black shales, with a concentration of ~60 ng g<sup>-1</sup> (mean of Maldeota and Durmala black shales) it would suggest that Re from ~15-30 mg of black shale is released per liter of river water, quite similar to that required to maintain the Os concentration of ~40 pg  $\lambda^{-1}$ . This seems to indicate that it may be possible for the rivers draining the Himalaya to acquire Os concentration of ~40 pg  $\lambda^{-1}$  through weathering of black shales and thus account for the temporal variations in R<sub>s</sub>.

Case II: Changes in  ${}^{187}Os/{}^{186}Os$  in seawater is only due to changes in  $R_r$  ( ${}^{186}J_r$  is constant).

These calculations (Eqn. 4.8), made by keeping <sup>186</sup>J<sub>r</sub> constant over 16 Ma at today's value of 15.8 moles y<sup>-1</sup> (Table 4.4), show that R<sub>r</sub> has to increase from 7.7 at 16 Ma to 9.7 at 1.5 Ma and to 11.0 at present (Fig. 4.15) to reproduce the observed variations in R<sub>s</sub>. If this entire increase has to result from HTP rivers, the corresponding change in their <sup>187</sup>Os/<sup>186</sup>Os with time has to be from 7.7 at 16 Ma ago to 27.1 at 1.5 Ma and 40.5 today (Fig. 4.16). In this calculation, <sup>186</sup>J<sub>rest</sub> is kept at today's value of 14.2 moles y<sup>-1</sup> (in proportion to water discharge; 90% of today's <sup>186</sup>Os flux, 15.8 moles y<sup>-1</sup>, Table 4.4) and R<sub>rest</sub> at 7.7, the ratio 16 Ma ago. The present day requirement of R<sub>HTP</sub>  $\approx$  40.5, though is within the range measured in this study for black shales from the underground mines, it is on the higher side of the mean ratio ~23 measured in them (only three out of 30 black shales analysed in this study had <sup>187</sup>Os/<sup>186</sup>Os in excess of 40.5) and those reported for leachable fraction of Ganga sediments 16.93 and 15.37 from Varanasi and Patna respectively (Pegram *et al.*, 1994).

Recently, Ravizza and Ehrenbrink (1998) have suggested an interesting possibility to bring about changes in  $R_s$ . Their model argues that bulk of the Os to the ocean is supplied via the weathering of organic rich sediments typically having <sup>187</sup>Re/<sup>186</sup>Os of ~6000. This high <sup>187</sup>Re/<sup>186</sup>Os would monotonically increase the <sup>187</sup>Os/<sup>186</sup>Os of the sediments due to radioactive decay of <sup>187</sup>Re, at a rate of 0.1 Ma<sup>-1</sup>. If the <sup>187</sup>Os/<sup>186</sup>Os of rivers draining these sediments also increase at the same rate, then it would account for a significant fraction of that required to produce the observed temporal variations in  $R_s$  during 16-1.5 Ma. If, however, the <sup>187</sup>Re/<sup>186</sup>Os of the sediments being weathered are

~1000-2000, similar to those measured in this study in black shales from the Lesser Himalaya, then the radiogenic ingrowth would be only a minor component contributing to the required increase in  $R_r$  (Fig. 4.15).



## Age (Ma)

Fig. 4.15: Changes required in riverine (global)  $^{187}$ Os/ $^{186}$ Os to reproduce the observed changes in seawater  $^{187}$ Os/ $^{186}$ Os during the past ~16 Ma. The calculation assumes that change in seawater  $^{187}$ Os/ $^{186}$ Os is only due to changes in riverine Os ratio. The numbers given in the parenthesis corresponds to values of R<sub>r</sub> at 16, 10, 1.5 Ma ago. The two dashed lines correspond to growth of  $^{187}$ Os/ $^{186}$ Os in the drainage basin over 16 Ma, for  $^{187}$ Re/ $^{186}$ Os = 6000 (typical of organic rich sediments; Ravizza and Ehrenbrink, 1998) and  $^{187}$ Re/ $^{186}$ Os = 1500 (typical of black shales measured in this study from the Lesser Himalaya).

In addition to the above calculations, it is possible to estimate the Os flux required from HTP rivers to yield present day value of  $R_s$  by changing both <sup>186</sup>J<sub>HTP</sub> and  $R_{HTP}$ . We use the mean of the reported (Pegram *et al.*, 1994) <sup>187</sup>Os/<sup>186</sup>Os in leachable component of the Ganga river sediments at Varanasi and Patna, 16.2, as representative of the HTP rivers at present, instead of 11.0 used in earlier calculations (case I). (the other values are <sup>186</sup>J<sub>rest</sub> = 4.6 moles y<sup>-1</sup> and  $R_{rest} = 11.0$ ). This yields a value for the present day <sup>186</sup>J<sub>HTP</sub> ~3.4 moles y<sup>-1</sup>, corresponding to an Os concentration of ~14 pg  $\lambda^{-1}$  in HTP rivers. This concentration can be more easily accommodated by weathering of black shales and also is well within the range of 3-25 pg kg<sup>-1</sup> for Os in rivers reported by Sharma and Wasserburg (1997) and Levasseur *et al.* (1998). The parametric values used in the calculation would make R<sub>r</sub> ~13, higher than the mean of the four river water values (Table 4.4); but within their range, 8.8-14.4 (Sharma and Wasserburg, 1997).

The rapid increase in  $R_s$  during the recent 1-2 Ma (Fig. 4.14), is difficult to be explained, eventhough the changes required in  $R_r$  and  $J_r$  to account for this have been calculated above. It is interesting to note that the sediment accumulation rate in the



Fig. 4.16: Required variations in <sup>187</sup>Os/<sup>186</sup>Os of HTP rivers if they account for the entire increase in seawater <sup>187</sup>Os/<sup>186</sup>Os during the past ~16 Ma. This calculation assumes <sup>186</sup>J<sub>rest</sub> = 14.2 moles y<sup>-1</sup> and R<sub>rest</sub> = 7.7, the values 16 Ma ago to be constant. The R<sub>HTP</sub> values at 16, 10, 5and 1.5 Ma are given in parenthesis.

Bengal Fan was about four times higher during the past ~1 Ma compared to that during 1-15 Ma (Cochran, 1990; Gartner, 1990). This enhanced sediment accumulation has been been attributed to intense weathering during Pliocene-Pleistocene glaciations and the direct dumping of river suspended material to continental slope due to lowering of sea level (Cochran, 1990). Studies on the fate of Os isotopes associated with river particles when they come in contact with seawater are too few to make any generalisation. Reisberg et al. (1997) based on studies of leachable and bulk Os in sediments from the Bengal Fan concluded that leachable Os from river suspended matter is released to seawater prior to their deposition on the seafloor and that it is an important source of Os to the oceans. They calculated that  $\sim 23$  % of the seawater increase can be accounted for by the release of Os from the sediments in the Bengal Fan. More recently, Porcelli et al. (1998) based on the distribution of dissolved Os in the Columbia river estuary reported that it exhibits an overall conservative behaviour, though signatures of its addition/removal are also evident in its distribution. The intense glacial weathering and large supply of river suspended matter directly to the slope regions may have a role to play in the rapid increase in  $R_s$  during the past ~1 Ma. Thus the enhanced amount of sediment supply from the Himalaya can provide higher leachable Os to the seawater and this leachable Os coupled with the dissolved phase can give rise to the present observed seawater Os isotope curve, however, it is difficult to quantify their significance at present.

It is important to mention here that all the above model calculations are based on the assumption that the Os flux to the oceans derived from cosmic/mantle materials have remained constant at today's value over the past ~25 Ma. The results of the calculations critically depend on the validity of this assumption.