Chapter 5

Summary & Conclusions

This chapter summarises the salient results of this thesis and present the conclusions drawn from them. Primary focus of this thesis has been to understand the importance of weathering of the Lesser Himalayan sedimentaries, **the carbonates and black shales**, in contributing to the evolution of Sr and Os isotope composition of seawater since the Cenozoic. Further, attempts have been made to date black shale deposits from the inner and outer Lesser Himalaya using ^{187}Re-^{187}Os isotope pair and thereby help in understanding the correlation between these sedimentary units. In the following, the isotopic and chemical studies on the Lesser Himalayan carbonates are summarised first, which is followed by the summary and conclusions of the Re-Os study on black shales.

5.1. CHEMICAL AND ISOTOPIC STUDIES OF THE LESSER HIMALAYAN CARBONATES

Identifying the source(s) for the highly radiogenic Sr isotope composition and cations in the Ganga-Brahmaputra-Indus source waters is important to assess the role of weathering in the Himalaya in global climate change. The ^{87}Sr/^{86}Sr of silicates (granites, gneisses and sedimentaries) in the drainage basins of these rivers are known to be quite radiogenic and are capable of supplying adequate quantities of Sr with high ^{87}Sr/^{86}Sr to these rivers. The dominance of carbonate weathering in the major ion chemistry of the headwaters, however, has led to the suggestion that metamorphosed carbonates in these basins could be enriched in ^{87}Sr/^{86}Sr and could also serve as a source for the high ^{87}Sr/^{86}Sr in rivers. In this study, the later possibility has been assessed through a detailed chemical and isotopic investigation of the Precambrian carbonate outcrops, the largest carbonate exposures across the Lesser Himalaya. The results show that these Pc-C carbonates are predominantly dolomites with Sr concentration 20 to 363 ppm and ^{87}Sr/^{86}Sr 0.7064 to 0.8935. The Sr isotopic composition though shows a wide range, most of them have ^{87}Sr/^{86}Sr <0.72.

The mean (Sr/Ca) ratio in the source waters (1.41±0.69 nmol/μmol), is about an order of magnitude higher than the mean in the Pc-C carbonates (0.20±0.15 nmol/μmol). The ^{87}Sr/^{86}Sr of most of the carbonates are <0.720, significantly less than those reported in several of the source waters, (which are generally >0.730). The average carbonate Sr in these rivers, calculated assuming *all* the Ca in them to be of carbonate origin, is only ~18%. This itself is an upper limit, as part of the Ca in the waters is derived from silicates and evaporites. The results thus suggest that on a basin wide scale these Precambrian carbonates are unlikely to be a major contributor to the present day high ^{87}Sr/^{86}Sr in the source waters, however, they may represent a significant source for particular streams, for example, for those flowing through the inner belt carbonates with high ^{87}Sr/^{86}Sr.

This study also addresses to the contributions of silicate and carbonate weathering to the present day major ion chemistry, Sr abundance and ^{87}Sr/^{86}Sr of the source waters of the Ganga, Ghaghara and the Indus and the contemporary chemical weathering rates of their drainage basins. Many of the major rivers of these source waters though originate in the Higher Himalaya (e.g. Bhagirathi, Alaknanda, Ramganga, Sarju) a significant fraction of their drainage and those of their tributaries lie in the Lesser Himalaya. This coupled with the more favourable conditions for weathering in the Lesser Himalaya would make this region a major contributor to the dissolved load of these rivers.

The contributions from various sources (atmospheric supply, evaporite dissolution, carbonate and silicate weathering) to the major cation and Sr budget of the source waters of the G-G-I have been estimated from available data on the major ion ratios in the river waters and in the various end members. The salient features of these calculations are

(i) About 30% (molar) of (Na+K+Mg+Ca) in these waters is of silicate origin (range 8%-67%). Among the major rivers of the source waters, the Bhilangna and the Bhagirathi waters have the highest contribution of cations from silicate weathering, ~40%.

(ii) The silicate Sr component in these source waters vary widely ranging from 2-100%, with a mean of ~40%. In many of them the Sr contribution from silicates to the present day Sr budget is more than that from Precambrian carbonate outcrops of the Lesser Himalaya, exceptions being some of the tributaries of the Indus and Ghaghara where both are comparable. The high ^{87}Sr/^{86}Sr of the source waters is coupled to silicate weathering in the basin as evidenced from its positive correlation with the silicate component of cations in the waters.

(iii) The calculation also show that only in a few of the headwaters Sr balance would achieved based on two component mixing, silicates and Precambrian carbonates. Property plots of $^{87}Sr/^{86}Sr$ and Ca/Sr in the source waters reveal the need to have a third end member (in addition to silicates and Precambrian carbonates) to explain the data. This third member is characterised by $^{87}Sr/^{86}Sr$ and Ca/Sr of ~0.715 and ~0.2 (μmole/nmole). Tibetan/Tethyan carbonates, evaporites, phosphates could be the third source, however data on their Ca/Sr abundances and $^{87}Sr/^{86}Sr$ are needed to confirm this. Further, the role of vein calcites and detrital carbonates in contributing to the Sr isotope budget of the headwaters, particularly in the Higher Himalaya warrants further study.

(iv) The present day silicate and carbonate chemical weathering rates, in the Bhagirathi and the Alaknanda basins are in the range of 4-6 mm/ky and 15-23 mm/ky respectively, calculated assuming that only silicates and carbonates contribute to Ca and Mg in these waters. The present day CO_2 consumption rates in the G-B basin by silicate weathering is $\sim 3\times10^5$ mole/km^2/y, same order as those reported for other major river basins. The role of sulphuric acid from pyrite oxidation in contributing to silicate weathering need to be better constrained to obtain more precise estimate of weathering rates and CO_2 consumption rates. Study of sulphur isotopes in dissolved sulphate of rivers may help resolve the contribution of pyrite oxidation to the sulphate budget of the rivers.

5.2. Re-Os STUDIES ON BLACK SHALES OF THE LESSER HIMALAYA

Re-Os isotopic studies in black shales from the Lesser Himalaya have been done to (i) determine their chronology. Towards this, samples from the Tal formation of the outer and the Shali formation of the inner belt were analysed and (ii) evaluate the impact of weathering of these black shales in contributing to the $^{187}Os/^{186}Os$ evolution of the oceans.

To achieve these goals, chemical procedures for the extraction and purification of subnanogram to nanogram levels of Re and Os from a few grams of environmental samples and for their measurement using Negative Thermal Ionisation Mass

Spectrometry were established, based on available procedures, as a part of this thesis work. The precision of $^{187}Os/^{186}Os$ determination (± 2σ) in Os loads of a few tens to hundreds of picograms extracted from black shale samples is better than ~1% (error on the mean). The precision of Os concentration determination (± 2 s.d. within runs) is typically 2-3%. The procedural blanks for Os averaged 1.8 ± 1.6 pg and that for Re 3.5 ± 1.2 pg.

Following the establishment of chemical procedures and measurement techniques, Re, Os concentrations and $^{187}Os/^{186}Os$ have been measured in a suite of black shale samples from the inner and outer belts of the Lesser Himalaya alongwith their chemical composition ($CaCO_3$, C_{org}, major and minor elements). Samples from the Maldeota and Durmala mines, for which detailed lithologs and stratigraphy were available, were selected for chronological work. In addition, a reconnaissance survey of Os isotope composition in black shale outcrops from the inner and outer belt sediments were made to evaluate the role of their weathering on the seawater $^{187}Os/^{186}Os$ evolution. The results show that the Os concentration in these black shales varies from 0.02 ng g^{-1} to 13.5 ng g^{-1} and $^{187}Os/^{186}Os$ of 8.5 to 96.1. The Re concentration also shows a considerable range, from 0.22 ng g^{-1} to 264 ng g^{-1}.

The Re-Os isochron ages of black shales from the Maldeota and Durmala underground mines of the outer belt of the Lesser Himalaya are 554 ± 16 Ma and 552 ± 22 Ma respectively, indistinguishable from each other within experimental uncertainties. Plotted together, as they are from the same stratigarphic section, they yield an age of 535 ± 11 Ma with an initial $^{187}Os/^{186}Os$ ratio of 9.81 ± 0.20. The ages of these samples, occuring ~15 m above the Krol-Tal (Pc-C) boundary, are consistent with the Pc-C boundary age of ~544 Ma reported from other locations based on U-Pb measurements in zircons. The Re-Os age, however, is a few tens of millions of years younger than the reported Rb-Sr age (626 ± 13 Ma) of black shales collected from the chert-phosphorite layer occuring ~10 m below the black shale bed sampled in this study. Preliminary data on the ^{187}Re-^{187}Os systematics from inner belt samples yield an isochron age of 839 ± 138 with an initial ratio of 5.98 ± 2.28. This would suggest that the inner belt sediments are older than those from the outer belt by a few hundred millions of years and that the suggested correlations between the Deoban formation of the inner to the Krol formation of the outer and the Mandhali of the inner to the Tal of outer need to reassessed. More measurements on the inner belt samples are required to confirm the preliminary ages obtained in this study.

Initial $^{187}Os/^{186}Os$ isotopic ratios obtained from the Re-Os isochrons of black shales provide a means to study the seawater $^{187}Os/^{186}Os$ evolution over thr distant past. The initial ratio, 9.81 ± 0.20, derived from the combined data of the Maldeota and Durmala mines if taken to represent the $^{187}Os/^{186}Os$ of the ocean at the time of their deposition, ~535 Ma, it would suggest that $^{187}Os/^{186}Os$ of the Early Cambrian seawater was higher than the today's value of 8.7. This inference critically depends on the assumption that the measured Os in the black shales is almost entirely of marine origin.

Based on a simple budget model, the temporal changes in either the Os flux from the HTP rivers or their $^{187}Os/^{186}Os$ to produce the observed variations in seawater $^{187}Os/^{186}Os$ over the past ~25 Ma was calculated. The results show that

(i) if the present day $^{187}Os/^{186}Os$ of HTP rivers is the same as other global rivers (11.0), the Os flux from HTP rivers has to increase from 37 moles y^{-1} 16 Ma ago to ~830 moles y^{-1} at present. The present day flux would correspond to Os concentration of ~40 pg ℓ^{-1} in the HTP rivers. Such a concentration can be sustained if Os from ~20 mg of black shales with Os concentration of ~2ng g^{-1}, similar to that measured in this study in the Maldeota and Durmala samples, is released per liter of HTP river waters. If the $^{187}Os/^{186}Os$ of HTP rivers is ~16.2, (reported in the leachable fraction of the Ganga sediments) and all the other rivers 11.0, then the present day Os concentration in these waters would have to be ~14 pg ℓ^{-1}. There are no data on the Os concentration and $^{187}Os/^{186}Os$ in HTP rivers, but the model derived concentrations are similar to those reported for elsewhere in the world rivers (Sharma and Wasserburg, 1997; Levasseur et al., 1998).

(ii) A similar calculation made to assess the temporal variations in $^{187}Os/^{186}Os$ of HTP rivers (keeping the Os flux from rivers constant at the present day value) to sustain the measured $^{187}Os/^{186}Os$ in the oceans show that it has to increase from 7.7 at 16 Ma to 40.5 at present. The present day value though, is within the range measured in this study in black shales, it is much higher than their mean value of ~23 and that reported in the leachable fraction of the Ganga sediments.

These calculations support the suggestion (Pegram et al., 1992; Ehrenbrink, 1995; Turekian and Pegram, 1997) that weathering of black shales from the Himalaya can be a dominant source of Os to the oceans to produce the observed variations in its $^{187}Os/^{186}Os$ over the past ~16 Ma. The model predictions need to be tested through direct measurements of Os isotope systematics in the HTP rivers.

5.3. Future Study

The work in this thesis has led to the conclusion that silicate weathering is an important source for the high $^{87}Sr/^{86}Sr$ in many of the source waters of the Ganga, Ghaghara and Indus and that the Precambrian carbonates are not a major contributor on a basin wide scale. The results also have brought to light the difficulties in making a balance for Sr in many of the source waters based on a two component system, silicates and Precambrian Carbonates. An area which needs further investigation is the chemical and isotopic studies of the Tibetan carbonates and the Tertiary carbonates present in the drainage basins of the headwaters of the Ghaghara and Indus. Equally important is to search for a methodology to quantify the Ca and Sr derived from evaporites to these headwaters. Sulphur isotopes may help in this regard. While the study was in progress, it was reported that vein calcites present in silicates could be an important source for the radiogenic Sr in the rivers. The significance of this component in contributing to the Sr isotope mass balance need to be quantified. The budget calculations made in this study depends on the composition used for the various endmembers. The values of these parameters were derived in this thesis using various approaches, however, better constraints on these would help in improving the Sr isotope balance calculations. Studies of minor streams and rivers flowing through a specific lithology may help in this direction. In this context, the reliability of mild acid leaching experiments to derive endmember composition of carbonates from its admixture with silicates needs to be evaluated.

Preliminary results of ^{187}Re-^{187}Os on inner belt black shales show that they are older than the outer belt samples. There is a need to assess these results through more analysis of the inner belt samples. Further, the ^{187}Re-^{187}Os pair can be used to date black shales from Nepal and Arunachal Pradesh to look for east-west correlations among the various sedimentary units of the Lesser Himalaya. This exercise will provide a larger data base for $^{187}Os/^{186}Os$ across the Lesser Himalaya and thus help in evaluating the role of these black shales on the seawater Os isotope evolution. Thus, measurements of Os concentrations and $^{187}Os/^{186}Os$ in black shales across the Himalaya including the Tertiary deposits of Spiti Valley and Karakoram would help in better assessing their contribution to the present day seawater Os. A more direct approach to assess the problem would be measurements of Os concentration and its isotopic composition in the Himalayan rivers.