A summary of the thesis entitled

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The impact of Himalayan Orogeny on the chemical and isotopic evolution of the oceans and on the long-term global climate change has been a topic of considerable interest and debate among geochemists in recent times. It has been surmised that increased rates of vertical movements in the Himalaya-Tibet (H-T) coupled with monsoon climate would enhance chemical and physical erosion of the region and hence the flux of dissolved and particulate materials to the sea. Available data, indeed suggest that the contemporary chemical weathering rate in the drainage basins of many of the rivers of the H-T region are much higher than the global average. To learn more about the influence of the Himalayan Orogeny in contributing to global climate, it is necessary to quantify the silicate vs carbonate weathering in the region and their temporal variations. In this context, Sr isotopes have been considered as a proxy for silicate weathering.

It is well established that the $^{87}Sr/^{86}Sr$ of the oceans have been increasing since the Cenozoic. Recent studies of Sr isotopes in the rivers draining the Himalaya show that some of these, particularly the Ganga-Brahmaputra, are characterised by moderate Sr concentration and high $^{87}Sr/^{86}Sr$. This coupled with the general correspondence between the history of the uplift of the Himalaya with periods of increased $^{87}Sr/^{86}Sr$ change in the oceans have led to the suggestion that weathering in the Himalaya could account for a significant fraction of the increase in the $^{87}Sr/^{86}Sr$ of the oceans over the past ~40Ma. The source(s) for the high Sr concentration and high $^{87}Sr/^{86}Sr$ in the G-B system is controversial, both silicates and metamorphosed carbonates enriched in radiogenic Sr have been suggested as possible sources. Better understanding of the relative proportions of carbonate versus silicate weathering in contributing to the $^{87}Sr/^{86}Sr$ of the rivers is needed to assess the coupling between weathering and climate. The first part of the thesis deals with the role of carbonates from the Lesser Himalaya in contributing to the Sr concentration and isotopic composition of the G-B system.

Similar to Sr isotopes, the $^{187}Os/^{186}Os$ of the oceans also has been increasing since the Cenozoic. One of the hypotheses suggested to account for this increase is weathering in the Himalaya, particularly the black shales. Black shales are exposed in both the inner and outer belt of the Lesser Himalaya. The intercorrelation between them are dogged due to poor fossil control and further by complicated tectonic history. The absolute ages of these sequences are contentious. Presence of trace fossils and small shelly faunas in the phosphorite band of Tal Formation, a part of the outer Lesser Himalaya, though places this formation in the Cambrian age, absolute or radiometric ages for these formations are very sparse.

In recent years, the ^{187}Re-^{187}Os system has been shown to be a good chronological tool for determining the ages of organic rich sediments. Black shales are known to have high concentrations of Re. During their deposition Re and Os both get scavenged from seawater to the sediments and seawater Re overwhelms the detrital value. Therefore, use of ^{187}Re-^{187}Os pair in black shales could provide their depositional ages. The second part of the thesis pertains to the study of Re-Os systematics in the black shales of the Lesser Himalaya to explore the possibility of using the system as a chronometer and also to assess their potential in contributing to the Os isotope evolution of the oceans.

The Present Study

The primary goals of the present study are:

(i) to assess the role of carbonates from the Lesser Himalaya in contributing to the Sr isotopic systematics to the headwaters of the Ganga-Ghaghara-Indus.

(ii) to constrain the source(s) of major ions and Sr budget of these rivers. This exercise also provides estimates on the present day weathering rates, of silicates (SWR) and carbonates (CWR) in their drainage basins and the corresponding CO_2 consumption rates.

(iii) to establish the extraction and measurement techniques (N-TIMS) in the laboratory for Re-Os isotopic measurements in black shales and their components.

(iv) to determine the chronology of black shales from the inner and outer belts of the Lesser Himalaya using ^{187}Re-^{187}Os isotope pair.

(v) to measure Os isotopic composition of black shales from the Lesser Himalaya to evaluate their potential influence on the ^{187}Os/^{186}Os evolution of the oceans.

The high $^{87}Sr/^{86}Sr$ values of some carbonates having close association with silicates probably indicate migration of radiogenic Sr from silicates to 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 carbonates with low Sr content and high $^{87}Sr/^{86}Sr$.

(ii) Silicate and carbonate weathering and major ion Chemistry of the Ganga-Ghaghara-Indus (G-G-I) source waters

Main sources of the major ions to these rivers are silicates, carbonates and evaporites. Mass balance calculation shows that silicate Na and K account for 6%-36% of the total cations of these rivers and represent the minimum silicate weathering contribution as the process would also supply Ca and Mg to these rivers. Ca and Mg derived from silicate weathering is calculated based on the Ca and Mg concentration in the rivers and Ca/Na or Mg/Na in silicate end members. These end member values are fixed based on the data from (i) granites and gneisses from the Higher and Lesser Himalaya, (ii) Jola Gad, a small stream, flowing predominantly through silicate terrain, and (iii) soil profiles from the Lesser Himalaya. These calculations show that silicate Ca in the G-G-I source waters vary from 2%-61% of their total Ca with a mean of ~16%. Thus, on an average bulk of the Ca in these waters has to be from the weathering of carbonates and evaporites. The silicate Mg ranges 2% to 52% with an average of 21%. Similar to Ca, bulk of Mg in these waters is also derived from non-silicates, in this case carbonates. The total silicate cations (Na, K, Ca and Mg) to the G-G-I source waters ranged between 8%-67% and suggest that on an average 30% of the cations in these source waters is of silicate origin.

(iii) Silicate and carbonate weathering and Sr isotope composition of G-G-I source waters

The source(s) for the high $^{87}Sr/^{86}Sr$ is a topic of debate and includes weathering of granite/gneisses, metasediments and metamorphosed carbonates. The data obtained in this work provides a mean to assess the role of the Lesser Himalayan Precambrian carbonate outcrops in contributing to the present day major ions and Sr isotope budget of these rivers. These carbonates are the most extensive carbonate deposits in the Himalaya and are drained by the source waters of the G-G-I.

Comparison of the $^{87}Sr/^{86}Sr$ and Sr/Ca ratios of the carbonates and silicates from the Lesser Himalaya with those of 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 and that their Sr/Ca is same as the meam value measured in the Precambrian carbonates. The results show that on an 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.

Based on the approaches adopted for major ions, attempts have been made to calculate the Sr budget of these rivers. The silicate Sr in the source waters range between 2% to 100% of their Sr with a mean of 40%. It is borne out from the these 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 $^{87}Sr/^{86}Sr$. The calculation shows that only in few of the headwaters Sr balance could be achieved based on a two component, silicates and Precambrian carbonates, mixing. This indicates the need for a third end member. Tibetan/Tethyan carbonates, evaporites, phosphorites are the possible candidates for the third end members.

(iv) Silicate and carbonate chemical weathering rates in the Ganga source water basins and CO_2 consumption

The present day chemical weathering rates of silicates and carbonates in river basins are determined from the silicate and carbonate components of their major cations, silica concentration and data on their water fluxes and drainage area. The results show that in the Bhagirathi and the Alaknanda basins silicate weathering contributes to 35 and 26 wt% of cations. These, coupled with silica concentrations, yield values of 4-6 mm/ky of silicate weathering rates in these rivers, 3-6 times lower than carbonate weathering rates. The drainage basins of these rivers, thus, are getting weathered at a rate of ~25 mm/ky.

The CO_2 consumption rates for silicate weathering in the Bhagirathi and the Alaknanda basins (calculated assuming that silicates are weathered only by CO_2) are 4.1×10^5 and 3.6×10^5 mole/km^2/y. If this calculation is extended to the entire Ganga-Brahmaputra basins, the proportion of cations supplied via silicate weathering is estimated to be 37 wt% and the corresponding CO_2 consumption rates by silicate weathering would be 3.3×10^5 moles/km^2/y.

(2) Re - Os studies: Black Shales

(i) Standardisation of Re-Os chemistry and establishment of N-TIMS facility

The extraction and measurement techniques for Re-Os in black shales have been established following available methods. The Os and Re isotopic composition are measured by Negative Thermal Ionisation Mass Spectrometry (N-TIMS) technique at PRL. The mass spectrometer used in our studies is an indigenously built, 23 cm radius, 60° sector magnetic field, single focusing instrument equipped with a faraday cup collector. The polarities of the magnet and ion acceleration high voltages were reversed to suit the N-TIMS operation.

The Os from various geological samples was extracted by NiS fusion and purified by distillation and ion exchange methods. For the determination of Re concentrations, the samples were brought into solution by acid digestion after ashing them at 450°C. Re from the solution was purified by ion exchange chromatography. The procedural blanks for Re and Os are 3.5 ± 1.2 and 1.8 ± 1.6 pg g^{-1}, significantly lower than the signals from the black shale samples. The precision Os and Re concentration measurements are better than ~2-3% and that for Os isotopic measurements is better than ~1% ($2\sigma_\mu$).

(ii) Re-Os Studies in Black Shales of the Lesser Himalaya:

Studies of ^{187}Re-^{187}Os isotope systematics in black shales from the Lesser Himalaya is motivated by two major considerations. These are (i) determination of their chronology and its implications to the inter-correlation of the two existing sedimentary sequences, the inner and outer belts and (ii) assessment of their potential in contributing to the Os isotope evolution of the oceans since the Cenozoic.

Re and Os abundances and Os isotope systematics 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 organic carbon and nitrogen content of samples are in the range of 0.2 to 7.3% and 0.02 to 0.27% respectively. The Re and Os concentrations in these samples exhibit wide range, 0.2 to 264 ng g^{-1} and 0.02 to 13.5 ng g^{-1} respectively with a mean Re/Os of ~25. The black shales from the Maldeota and Durmala mines, collected ~15 m above the Krol-Tal (Pc-C) boundary, yield ^{187}Re-^{187}Os isochron ages of 554 ± 16 and 552 ± 22 Ma respectively. As the samples from both the mines are from the same stratigraphic sequence, plotting together they yield an age of 535 ± 11 Ma consistent with the age of ~544 Ma assigned based on U-Pb systematics 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 Re-Os age of 839 ± 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 and the available data on present day Os fluxes and their isotopic compositions from the various sources. If the ^{187}Os/^{186}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 ^{187}Os/^{186}Os would have to increase from 0.51 moles y^{-1} at 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 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 ^{186}Os flux to be constant over the past 16 Ma at 15.8 moles y^{-1} (calculated from available data for rivers), show that ^{187}Os/^{186}Os in HTP rivers have to increase from 7.7 at 16 Ma ago to 40.5 at present to reconstruct the observed seawater ^{187}Os/^{186}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 $^{187}Os/^{186}Os$ in black shales from the Lesser Himalaya though can meet the model requirements, the demands on them can be more easily accommodated if the $^{187}Os/^{186}Os$ of HTP rivers is taken as 16.2 and that in all the other rivers as 11.0.

The studies on Sr budget of the G-G-I source waters indicate the need for a third source to balance the Sr budget in these rivers. An area which needs further investigation is the chemical and isotopic studies of the Tibetan and the tertiary carbonates. The significance of vein calcites in contributing to the Sr isotope mass balance needs to be quantified. Also the values of different endmembers used in this thesis need better constraints for improving the Sr isotope balance calculations. Studies of minor streams and rivers flowing through a specific lithology may help in this direction.

More study is required on the inner belt black shales to validate their preliminary ages obtained by ^{187}Re-^{187}Os pair. 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 also provide large data set for evaluating the potential of these black shales in contributing to the $^{187}Os/^{186}Os$ of the oceans.