Summary of the Thesis entitled

Major ions, Stable isotopes, $^{87}Sr/^{86}Sr$ and Re in the headwaters of the Yamuna: Implications to chemical weathering in the Himalaya

Submitted to

The Maharaja Sayajirao University of Baroda,
Vadodara, India

For the degree of
Doctor of Philosophy in Geology

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December, 2001

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Introduction

Chemical weathering of silicate minerals in the continents serves as the primary sink for the atmospheric CO_2 on geologic time scales. It is suggested that the uplift of the Himalaya and associated monsoonal rainfall, rapid physical erosion, all contribute to enhanced chemical weathering of silicates which in turn results in increased consumption of atmospheric CO_2. This drawdown of atmospheric CO_2 has been invoked as a driver of the Global Cenozoic cooling (Raymo and Ruddiman, 1992). The enhanced chemical weathering has also been thought to influence the major ion and various trace metal budgets of the oceans. For example, the steady rise in $^{87}Sr/^{86}Sr$ and $^{187}Os/^{186}Os$ of the seawater through late Cenozoic has been ascribed to weathering of silicates and organic rich sediments in the Himalaya (Raymo and Ruddiman, 1992; Richter et al., 1992; Pegram et al., 1992). Similarly, weathering in the Himalaya has also been proposed to be controlling the marine uranium budget (Sarin et al., 1990). Indeed, the Sr isotope evolution of the oceans through the Cenozoic has been used as a supporting evidence in favour of enhanced silicate weathering in the Himalaya. This suggestion has become a controversy and the use of high radiogenic Sr isotopic composition in rivers as a proxy for silicate weathering has been questioned.

This thesis, through a detailed geochemical investigation of major ions, Sr, Ba, Re, stable isotopes (O and H) and $^{87}Sr/^{86}Sr$ in the river waters, sediments and various source rocks in the Yamuna catchment, the major tributary of the Ganga, focuses on assessing the influence of various lithologies on the solute budgets of the Yamuna River System (YRS) in the Himalaya and their influence on the marine geochemistry of selected elements and isotopes and their implications. The results provide estimates of the CO_2 consumption via silicate weathering in the catchment. In addition, the measurements made in this thesis allows to address some of the current debates such as the source(s) of high radiogenic Sr (^{87}Sr) in these rivers and role of black shale weathering on their Re and Os budgets.

Objectives of the Thesis

This thesis focuses on chemical weathering in the Yamuna River Basin in the Himalaya and addresses the following objectives.

1. To characterize chemical weathering in the Yamuna drainage basin and assess the sources controlling the solute budgets in the YRS.

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

To achieve the above goals, three field campaigns to the Yamuna were undertaken, covering three seasons, i.e. premonsoon, monsoon and postmonsoon. Water, sediment and rock samples were collected in these trips from near the source of the Yamuna at Hanuman Chatti to its outflow at the foothills of the Himalaya. These samples were analyzed for major ions, Sr, Ba, Re, stable isotopes ($\delta^{18}O$ and δD) and Sr isotopes ($^{87}Sr/^{86}Sr$).

Thesis outline

This thesis is divided into the following chapters:

Chapter 1 introduces the thesis by building a background on the current understanding on various aspects of chemical weathering in the Himalaya and associated controversies. The rationale and importance of studying the YRS are discussed.

Chapter 2 deals with the details of the samples analyzed along with a description of the geology and general geohydrology of the catchment. In addition, the chapter also includes methods and the analytical techniques used for sampling and analysis.

Chapter 3 presents and discusses the stable isotope data in the YRS in terms of source characterisation and 'altitude effect'. The results are compared with those in the Ganga, the Indus and the Gaula catchment and their implications are discussed.

Chapter 4 presents the results on major ions, Sr, Ba and $^{87}Sr/^{86}Sr$ in the river waters and bed sediments, discusses the relative contributions of cations from various lithologies to waters, dependence of chemical weathering on lithology and elevation. The sources of Sr in the YRS are assessed with special importance to its radiogenic isotope budget. An attempt is made to estimate CO_2 consumption via silicate weathering in the catchment and assess the significance of chemical weathering in the Himalaya in the global CO_2 drawdown.

Chapter 5 presents data and discussions on the dissolved Re in the YRS, its sources and fluxes from the Himalaya. The importance of black shales in contributing to the riverine budgets of dissolved Re, Os and U and atmospheric CO_2 is discussed.

Chapter 6 synthesizes the results and findings of the thesis on a regional and global context. It also outlines the scope of future research to better understand and resolve some of the issues resulting from this work.

Analytical Techniques

In the following the techniques used for measurements of various elemental and isotopic abundances of the samples are discussed briefly.

Major ions, Sr and Ba:

Na and K were measured by Atomic Absorption Spectrophotometry and Ca and Mg by ICP-AES for all samples. The sediment/rock samples were brought to complete solution by acid digestion prior to their analysis. The precision of the measurements is better than 5% for the major cations. Alkalinity in the water samples was measured by acid titration (manual as well as auto titration) with a precision of ~3%. Other anions (F, Cl, NO_3 and SO_4) were measured by ion chromatography. The overall precision of the anion measurements is better than 6%. Sr and Ba in the water samples were measured by ICP-AES coupled to an ultrasonic nebulizer, with precision of ~5%.

Stable isotopes:

The oxygen and hydrogen isotope measurements were carried out using a water equilibration system and GEO 20-20 mass spectrometer (PDZ Europa, U.K.). For oxygen and hydrogen isotopes, 1 ml of water sample was equilibrated with tank CO_2 (35°C, 12 hours) and tank H_2 (35 °C, 12 hours in presence of platinum catalyst) respectively and aliquots of equilibrated CO_2 and H_2 were cryogenically separated. The overall precision, based on repeat measurements of about a dozen samples, is ±0.1‰ for $\delta^{18}O$ and ±1‰ for δD.

Rhenium:

Re was measured by N-TIMS using ^{185}Re as the spike. For water, typically about 100g of filtered acidified sample was spiked with ^{185}Re and stored as such for at least 24 hours for sample-spike equilibration. The samples were then dried, digested with ultra pure HNO_3 and Re was extracted and purified using anion exchange in nitric acid medium. For granites and carbonates, the samples were brought to solution with ^{185}Re spike and Re extracted by ion exchange. Pure Re fractions from all these were measured by NTIMS (Creaser et al., 1991; Trivedi et al., 1999). The total Re blank in the present study is determined to be ~4 pg which in most of the samples is less than 5% of the measured Re signals, only in four of them (out of 60) the correction exceeded 10%. The precision of Re measurements, based on several repeat analyses, is better than 5%.

Strontium isotopes:

Sr isotopic abundance were measured in the water and rock samples by a triple collector TIMS (VG 354) at National Geophysical Research Institute, Hyderabad. Sr was separated from Rb and other matrix elements through ion exchange chromatography. Sr isotopic measurements were carried out both in single as well as triple collector mode. During the period of analysis SRM 987 standard was run a number of times with ^{87}Sr/^{86}Sr 0.710184±0.000006 (2σ, $n = 9$). Some samples were processed in replicate and analyzed for their isotopic abundance. Procedural blanks were run by processing the water collected at the sampling site and the reagents used for the sample processing. Few samples were run in duplicates and the measured ^{87}Sr/^{86}Sr were found to be within the analytical precision.

Results and Discussions

δD values in the Yamuna and its tributaries range from -41.7 to -72.0‰ and δ^{18}O from -6.2 to -10.3‰, the most depleted values being in the monsoon and high altitude samples. The spatial and temporal variations in the stable isotopic composition of the YRS waters are regulated by source composition, i.e. monsoon precipitation which in turn is dictated by 'amount effect', recycling of moisture in the region and evaporation of rain during fall. Further, mixing of snow/glacial melt with rainwater and mixing of rivers during their flow all contribute to the isotopic composition of these rivers. The 'altitude effect' in the Himalaya, derived from the YRS water isotopic compositions, is 0.11 ‰ per 100m. This varies among the river basins in the Himalaya and seems to be dictated by the 'amount effect'.

The YRS waters are mildly alkaline, with a wide range of TDS, ~32 to ~620 mg ℓ^{-1}. The Sr concentration and ^{87}Sr/^{86}Sr in the YRS range between 120-13,400 nM and 0.7142-0.7932 respectively. Catchment lithology exerts strong control on the abundances of major ions, Sr and Ba, and ^{87}Sr/^{86}Sr of the YRS waters. The streams in the lower reaches have higher TDS than those near the source region. This is caused by a number of factors, such as, the abundance of more easily weatherable rocks (carbonates and evaporites) in the lower reaches; higher temperature and vegetation. Carbonate weathering contributes dominantly to the major ion chemistry of the YRS, the estimated upper and lower limits of their contributions to the cations average ~70% and ~50% respectively. Silicates contribute, on average, ~25% to the YRS cation budgets. Sulphuric acid, generated via oxidation of pyrites, acts as an important agent of chemical weathering in the catchment.

Silicate contributions to the YRS Sr budget is in proportion to the silicate cations (~25%). $^{87}Sr/^{86}Sr$ show wide range, 0.7142 to 0.7932, with lower values typical of rivers in the lower reaches draining sedimentaries dominated by Precambrian carbonates and minor amounts of evaporites. The observation, that there is a strong correlation between silicate derived cations and $^{87}Sr/^{86}Sr$ and that rivers draining predominantly silicates have high $^{87}Sr/^{86}Sr$, suggest that silicate weathering regulates the high radiogenic Sr isotopic composition in these rivers. Precambrian carbonates, with lower Sr/Ca and $^{87}Sr/^{86}Sr$ than the YRS waters, is not a major component of Sr budget and high $^{87}Sr/^{86}Sr$ on a basin wide scale. On average, they can account for ~15% to the Sr of the YRS. Minor lithologies such as evaporites and phosphates, with relatively higher Sr concentrations and Sr/Ca also seem significant contributors to the YRS Sr budget. The high $^{87}Sr/^{86}Sr$ of the rivers, inherent from silicate weathering, is diluted by the Sr contributions from these lithologies, especially in the lower reaches. Vein-calcites occurring in granites can be an important source of Sr to the YRS, however, critical evaluation of their significance in influencing river water $^{87}Sr/^{86}Sr$ needs further detailed work on their Sr abundance and $^{87}Sr/^{86}Sr$.

Silicates and carbonates in the YRS basin contribute, on average, ~30% each, to the dissolved Ba in the YRS waters. They can be dominant contributors to the streams with low Ba concentrations. In the lower reaches, for tributaries with higher Ba, sources such as phosphorites have to be invoked.

The average dissolved Re concentrations in the YRS, 9.4 pM, is much higher than the reported global average, 2.1 pM. Estimations based on Re and major ion abundances in the crystallines and Precambrian carbonates show that, on average, they contribute insignificantly to the YRS dissolved Re budget. A very likely source for high Re in these waters is organic rich sediments such as black shales. Based on available data on Re in the black shales of the Lesser Himalaya, it has been estimated that Re from ~60 mg of black shales has to be released per liter of water to account for the measured average Re in the YRS. Currently no data is available on the distribution of organic rich sediments in the Yamuna catchment to determine if such requirement can be met. Using Re in rivers as an index of weathering of organic rich sediments, it has been shown that their weathering can account for the measured concentrations of dissolved Os and U in the rivers draining the Himalaya. The dissolved Re flux from the Ganga and the Yamuna in the Himalaya is disproportionately higher compared to their contributions to the global water discharge.

Silicates though contribute ~25% of cations and Sr to the YRS waters, and major source for radiogenic $^{87}Sr/^{86}Sr$, their weathering in the Yamuna basin in the Himalaya is not intense, as evident from the water and sediment chemistry. The chemical index of alteration in the YRS sediments is ~60. This is most likely caused by higher rate of physical weathering, about an order of magnitude more than chemical weathering rate. The rate of chemical weathering of carbonates in the Yamuna and Ganga basins in the Himalaya is about four times higher than the rate of silicate weathering.

The contemporary CO_2 consumption rates via silicate weathering in the Ganga and Yamuna basins in the Himalaya, $(2\text{-}7)\times10^5$ moles km^{-2} y^{-1}, are significantly higher than those reported for other major river basins in the world. Together, they account for ~0.1% of the global CO_2 consumption via silicate weathering compared to ~0.1% and ~0.03% of their contribution to the global water budget and drainage area. The CO_2 consumption via silicate weathering in the Ganga and the Yamuna basins in the Himalaya, is roughly balanced by the release of CO_2 by oxidation of organic rich sediments, estimated using dissolved Re as an index of their weathering.

This study brings out possible dependence of silicate weathering on temperature, supportive of the hypothesis that silicate weathering is dependent on climate. Using the major ion data (silicate Na and Si) in the river waters, activation energy for overall silicate weathering in the catchment has been estimated to be 50-75 kJ mol^{-1}.

The present work, based on a very comprehensive measurements of several chemical and isotopic species in the YRS waters and solid phases from drainage basins, has quantified contributions from various lithologies to riverine budgets of these elements and isotopes and has addressed to some of the issues of recent debate. Further, influence of lithology and temperature on chemical weathering of silicates has been demonstrated.

26|12