Chemical and Isotopic Studies of Estuaries and the Ganga Basin Sediments

A THESIS

Submitted for the Award of Ph. D degree of

MOHANLAL SUKHADIA UNIVERSITY

In the

Faculty of Science

By

Waliur Rahaman

Under the Supervision of

Dr. Sunil Kumar Singh
ASSOCIATE PROFESSOR

Physical Research Laboratory,
Ahmedabad-380009, India.

MOHANLAL SUKHADIA UNIVERSITY
UDAIPUR

2010

DECLARATION

I, **Mr. Waliur Rahaman**, S/o Mr. Md. Jillar Rahaman, resident of B-4, PDF Qtrs, PRL residences, Navrangpura, Ahmedabad – 380009, hereby declare that the research work incorporated in the present thesis entitled "***Chemical and Isotopic studies of Estuaries and the Ganga Basin Sediments***" is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required. I solely own the responsibility for the originality of the entire content.

Date: 2nd August, 2010

(Waliur Rahaman)

Acknowledgements

This thesis is the destination of five years journey accompanied by sincere guidance, advice, support, wishes and encouragements from many individuals. I am thankful and indebted to all of them. I feel immense pleasure in writing this acknowledgement.

First of all, I express my deep sense of gratitude to my thesis guide, Dr. Sunil Kumar Singh. I am extremely privileged to work under his supervision. I am heartily thankful to my supervisor, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding of the subject. He taught me right from the fundamentals to the intricacies of geochemistry. He introduced me with the field of mass spectrometry and taught me how to produce good quality data and their interpretations. He gave me freedom to think independently and put my views strongly during any scientific discussions. His friendly nature has always made me comfortable while working in the lab. I have enjoyed working with him.

I am highly grateful to Prof. S. Krishnaswami for his suggestions, criticisms and discussion which were always fruitful and improved my scientific knowledge. He always gave me valuable inputs to produce good quality data and their interpretation in the best possible way, preparing manuscripts up to the finest level. I always feel extremely privileged and lucky to be fostered and nurtured by such great, world renowned geochemist. I am indebted to him for his constant encouragement, concern, advice, teaching and care.

I sincerely thank Prof. M.M. Sarin for his suggestions and support during all kind of laboratory activities. He has been always enthusiastic to provide me help and advice whenever I needed. I learned lot of instrumental techniques right from operations to circumvent the problems during measurements by ICP-AES, AAS.

I thank Prof. J. N. Goswami, the Director, Prof. Utpal Sarkar, Dean and Prof. A.K. Singhvi, former Dean, Physical Research Laboratory, for providing me all kind of necessary facilities and help to carry out my thesis work successfully. I thank all the academic committee members for reviewing my work time to time.

Sumanta, Shuchita, Lokesh, Brajesh, Sanjeev, Ram, Rohan and Arvind, my seniors Rohit, Shreyas, Ritesh, Morthekai, Sanat, Uma, Rajesh, Salman Bhai,, Golamnabi bhai, Jayant, Zeen and Mauryaji, and my juniors (Suratna, Rohit, Amjad, Arvind Singh, Naveen Chauhan, Rabiul, Neeraj, Ashish, Tapas, Sunil, Arun, Surichi, Moumita, Arvind Saxena, Chinmay, Iman, Patra, Suman, Ashok, Praveen, Anand, Sandeep, Srikant, Soumya, Subrata, Vimal, Yogita, Zulfikar and Arvind Rajpurohit). I thank all of them for making my stay very pleasant and enjoyable at PRL.

I owe my immense respect to Mrs. Renu Singh for her care and affection which makes me feel that I am an integral part of her family. I thank all the family members Mrs Krishnaswami (Nanda), Mrs Sarin, Mrs Bhushan (Sravani Di), Mrs Sudher and Mrs Rengarajan for nice and cheerful company during all the get togethers. My love and affection also remains for Markandeya, Manu and Golu, the youngsters of our family. I thank Mrs. Pauline Josheph for her help, care and support and help.

I am deeply grateful to my parents and family for their continuous support, wishes and encouragement. They have always stood by me in strong times and provided me support to complete my thesis. I also thank my in-laws for their sincere care and concern to my work.

I would like to thank Swati Dutta (Swati Di) for her help, care and moral support which really matters in my life.

Lastly, I offer my regards and extend my sincere thanks to all of those who supported me in any respect during the completion of my PhD thesis.

Abstract

This thesis addresses two primary objectives, to determine (i) paleo-erosion distribution over the Himalaya during the past ~100 ka and its relation to climate change and (ii) the factors regulating the abundance and distribution of redox sensitive elements U, Mo and Re and alkaline earth metals Ba, Sr and $^{87}Sr/^{86}Sr$ in selected Indian estuaries and their impact on the oceanic budgets of these elements and isotopes.

Sr-Nd isotopes and major element compositions of a ~50 m long sediment core from the Ganga plain show reduced erosion over the Higher Himalaya and lower intensity of chemical weathering during ~90, ~70, ~40 and ~20 ka coinciding with periods of precipitation minima and glacial maxima. This study underscores the strong coupling between climate and erosion. The $^{87}Sr/^{86}Sr$ of calcretes of various ages from the Ganga plain shows recent abrupt increase in riverine $^{87}Sr/^{86}Sr$ of the Ganga attributed to enhanced weathering in the Lesser Himalaya due to variability of monsoon and/or enhanced agricultural activities and deforestation.

Re is conservative in all the estuaries studied whereas Mo and U behave inconsistently; with significant removal in the Hooghly and the Mandovi estuaries most likely due to their uptake in mangrove swamps. Extrapolation of these results on a global scale indicates that mangrove swamps can act as an important sink of oceanic Mo. This study highlights the significance of anthropogenic Re and Mo supply to oceans; the Re flux from this source seems far in excess of its natural input in some of estuarine/coastal regions. Ba is non-conservative with additional inputs at low to mid-salinites in estuaries; elemental Sr is conservative, however, the distributions of $^{87}Sr/^{86}Sr$ in the estuaries seem to be impacted by supply from additional sources. If Submarine Ground Water Discharge (SGD) is the source of $^{87}Sr/^{86}Sr$, it offers a good tool to estimate SGD supply to estuaries.

Thus this study have brought out the coupling between erosion and climate in the Himalaya and the role of solute-particle interaction, SGD and uptake in mangroves in regulating the distribution and budget of suit of redox sensitive elements and alkaline earth in estuaries.

Key-words: Ganga, Himalaya, paleo-erosion, isotope, trace elements, estuary

Content

		Page
	List of Tables	**v**
	List of Figures	**vii**
Chapter 1	**Introduction**	**1-11**
1.1	Introduction	2
1.2	Objectives of the thesis	9
1.3	Outline of the thesis	10
Chapter 2	**Materials and Methods**	**12-56**
2.1	The Ganga Basin	13
2.1.1	General description of the basin	13
2.1.2	Core Locations in the Ganga plain	15
2.1.3	(a) Litho-Stratigraphy and facies of the cores	17
	(b) Chronology of the IITK and JP core	20
2.1.4	Sub-sampling of the cores for chemical and isotopic studies	22
2.2	Estuaries and coastal areas of the Arabian Sea and Bay of Bengal	23
2.2.1	Lithology, geohydrology and climate	24
2.2.2	Sampling from estuaries and coastal areas	27
2.3	Analytical techniques	29
2.3.1	Water analysis	30
	(a) Temperature, pH, electrical conductivity and salinity	30
	(b) Alkalinity and Major Ions	33
	(c) Sr and $^{87}Sr/^{86}Sr$ by TIMS	33
	d) Re, U, Mo and Ba measurements by ICP-MS	35
	i) Analysis of dissolved Rhenium	35
	ii) Analysis of dissolved U, Mo and Ba	41

	2.3.2	Analysis of Sediments	47
		(a) Major and trace elements	47
		(b) $CaCO_3$ and organic carbon	49
		(c) Sr and Nd isotope measurement in sediments	50
		(d) Carbon and Oxygen isotopes in carbonate nodules	55
Chapter 3		**Major & trace elements and Sr & Nd isotope compositions of the Ganga plain sediments: Implication to weathering intensity and erosion distribution over the Himalaya during past ~100 ka**	**57-79**
3.1		Introduction	58
3.2		Results	60
3.3		Discussion	63
	3.3.1	Temporal variation in the paleo-weathering intensity	63
	3.3.2	Erosion distribution over the Himalaya	69
3.4		Conclusions	79
Chapter 4		**Sr, C and O isotopes in carbonate nodules from the Ganga Plain: Variations in dissolved $^{87}Sr/^{86}Sr$ of the Ganga water during the past ~100 ka**	**80-102**
4.1		Introduction	81
4.2		Results	83
4.3		Discussion	87
	4.3.1	Petrography and major element composition	87
	4.3.2	How do faithfully these carbonates record riverine Sr isotope signature?	88
	4.3.3	Sr isotopic composition in carbonate	92
	4.3.4	Carbon and Oxygen isotope composition	95
	4.3.5	Recent abrupt rise in $^{87}Sr/^{86}Sr$ of the Ganga and its implications	100
4.4		Conclusions	101

Chapter 5			**Mo, U and Re in rivers and estuaries of India: Implications to geochemistry of redox sensitive elements and their marine budgets**	**103-145**
5.1			Introduction	104
5.2			Results and Discussion	106
	5.2.1		Dissolved Molybdenum, Uranium and Rhenium in rivers and other samples	110
		(a)	Molybdenum	111
		(b)	Uranium	112
		(c)	Rhenium	114
	5.2.2		Dissolved Mo, U and Re in estuaries	115
		(a)	Molybdenum	115
		(b)	Uranium	123
		(c)	Rhenium	124
5.3			Particulate Mo, U and Re in estuaries	126
5.4			Comparative behaviour of U, Mo and Re in estuaries	129
5.5			Removal of U and Mo in the Hooghly and the Mandovi estuaries	131
5.6			Mo, U and Re in the Gulf of Cambay	133
	5.6.1		Sources of high Mo and Re to Gulf of Cambay	134
		(a)	Natural supply of Mo and Re	134
		(b)	Anthropogenic supply of Mo and Re	135
5.7			Riverine fluxes of Mo and Re	137
5.8			Global oceanic budget of Mo and Re	140
5.9			Conclusions	143
Chapter 6			**Ba and Sr in Indian rivers and estuaries: Implications to geochemistry of alkaline earth metals and submarine groundwater discharge**	**146-173**
6.1			Introduction	147
6.2			Results and Discussion	149

	6.2.1	Dissolved Sr	152
	6.2.2	Dissolved Ba	155
	6.2.3	Particulate Ba, Sr and major elements in the Narmada estuary	158
	6.2.4	Behaviour of dissolved $^{87}Sr/^{86}Sr$ in estuaries	159
	6.2.5	Implication of quasi-conservative behaviour of Sr in estuaries	167
	6.2.6	Dissolved Ba in estuary	167
6.3		Conclusions	172
Chapter 7		**Synthesis and future perspective**	**174-181**
7.1		Paleo-erosion over the Himalaya	175
7.2		Reconstruction of dissolved $^{87}Sr/^{86}Sr$ of the paleo-Ganga and paleoclimate of the Ganga plain	176
7.3		Study of redox sensitive trace elements (Re, Mo and U) in estuary	177
7.4		Studies on alkaline earth metals Ba, Sr and $^{87}Sr/^{86}Sr$ in estuary	179
7.5		Scope of future research	180
		References	**182-209**
		List of Publications	**210-211**

List of Tables

Table	Content	Page
2.1	Details of river water, groundwater and mollusk	22
2.2	Lithological and hydrological details of Rivers	25
2.3	Sampling location, and Salinity, Conductivity, Temperature Alkalinity and pH in the estuarine waters	32
2.4	Salinity, Conductivity, Temperature and pH in the miscellaneous samples	32
2.5	Precision of dissolved Sr and $^{87}Sr/^{86}Sr$ measurements in estuary samples	35
2.6	Details of the two Re spikes	37
2.7	Calibration of laboratory Re standard against CRPG ^{185}Re spike	37
2.8	Calibration PRL ^{185}Re spike against laboratory standard	37
2.9	Blank analysis of Re	39
2.10a	Replicate analysis of dissolved Re in estuary samples	40
2.10b	Dissolved Re comparison between 0.2 and 0.45μ filtered	41
2.10c	Repeat analysis of Re in particulate phase	41
2.11	U and Mo in reference materials and in seawater from the Arabian Sea	43
2.12	Replicate analyses of dissolved U and Mo in estuary samples	44
2.13	Experiments for Ba measurements by standard addition method	46
2.14	Elemental analyses in USGS reference material W-1 and G-2	47
2.15	Replicate analyses of Sr, Nd and their isotope compositions in silicate phase of sediments	53
2.16	Replicate analysis of $^{87}Sr/^{86}Sr$ in carbonate phase	54
2.17	Blanks of Sr and Nd	54
2.18a	Analysis of our laboratory standard Mc. Marbel and Z-Carara carbonates to check accuracy of the measurements.	55

2.18b	Replicate analysis of $\delta^{13}C$ and $\delta^{18}O$ in carbonate nodules	56
3.1	Major element composition of bulk sediments of IITK Core	60-61
3.2	Sr, Nd isotope composition of silicate fraction of sediments of IITK core	62-63
3.3	Average ($\pm\sigma$) composition of Himalayan Crystallines and the Ganga Sediments	65
3.4	Comparison of CIA* of different lithologies and sediments from the Ganga system	66
3.5	$^{87}Sr/^{86}Sr$ and ε_{Nd} of various litho-units of the Ganga System	73
4.1	Elemental composition, $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ of carbonate nodules from IITK core	84
4.2	Sr isotope composition of carbonate nodules from Jagdishpur	85
4.3a	Sr isotope composition of miscellaneous samples from Kanpur	86
4.3b	Sr isotope composition of miscellaneous samples from Allahabad after the confluence of Yamuna	86
5.1	Dissolved Mo, U and Re in the Indian Estuaries.	108-110
5.2	Dissolved Mo, U and Re in miscellaneous samples	110
5.3	Properties of best fit lines and estimates of U, Mo and Re concentration at 0‰ and 35‰ salinity based on estuarine data	120
5.4	Re, Mo, U, organic carbon and Al in suspended and bed/bank sediments of the Narmada and Tapi estuaries.	127
5.5	Compilation of Mo in global rivers along with this study	138
5.6	Dissolved Re in global rivers measured in this study and available in the literature	139-140
6.1	Dissolved Ba and Sr concentrations and $^{87}Sr/^{86}Sr$ in the Narmada, Tapi, Mandovi and the Hooghly Estuaries	150-152
6.2	Ba, Sr and major elements abundances in particulate matter from the Narmada estuary during monsoon	158
6.3	Dissolved and particulate Ba characteristics in estuaries	169

List of Figures

Fig.	Content	Page
2.1	Sampling locations.	16
2.2	Litho-stratigraphy of the IITK core analyzed in this study.	18
2.3	Lithostratigraphy of JP core.	19
2.4	Age-depth models of the IITK core.	21
2.5	Location of the Hooghly, Narmada, Tapi, Mahi, Sabarmati and the Mandovi estuaries.	26
2.6	The Gulf of Cambay and the estuaries of the Narmada, Tapi, Mahi and the Sabarmati.	28
2.7	Calibration of three aliquots of known Re metal standard were calibrated using ^{185}Re spike of known concentration from CRPG, CNRS, Nancy, France.	38
2.8	Analysis of three aliquots of the same sample ranging from 20 to 55 g analysed for total Re.	39
2.9	Standard calibration of Mo and U in the ICP-MS.	42
2.10	Ba calibration using four standards of known strengths.	45
2.11	Ba measurement in estuary water samples by standard addition method.	46
2.12	Comparison of measured and reported elemental concentrations in W-1 and G-2 USGS reference standards.	48
2.13	Variations of $^{87}Sr/^{86}Sr$ in NBS-987 and $^{143}Nd/^{144}Nd$ in JNdi-1 with time.	52
3.1	Scatter plot of Al_2O_3/Na_2O and CIA* of sediments.	67
3.2	Temporal variations in chemical indices such as CIA*, Na_2O/Al_2O_3 and Na_2O/TiO_2.	68
3.3	Scatter plot of Sr and Nd isotope composition with their concentrations in the sediments.	70

3.4	Scatter plot of $^{87}Sr/^{86}Sr$ and ε_{Nd} with their Al content and CIA*.	71
3.5	$^{87}Sr/^{86}Sr$ vs ε_{Nd} of sediments.	72
3.6	Variation in Sr and Nd isotope composition of the sediments with depth.	74
3.7	Three-point running average of $^{87}Sr/^{86}Sr$ and ε_{Nd} of the sediments.	76
4.1	Petrography of some of the carbonate nodules based on Scanning Electron Microscope.	90
4.2 a, b	Scatter plot of Sr/Ca vs Mn and $^{87}Sr/^{86}Sr$ vs Mn/Sr of the carbonate nodules.	91
4.3	$^{87}Sr/^{86}Sr$ in carbonate phase of the nodules from the IITK profile.	92
4.4	Variations in $^{87}Sr/^{86}Sr$ of carbonate nodules with depth in JP profile.	93
4.5	(a) Scatter diagram of $\delta^{13}C$ and $\delta^{18}O$ in carbonate nodules from IITK profile. (b) Covariation plot of $\delta^{13}C$ and $\delta^{18}O$ of carbonates from different areas of the Ganga plain.	96
4.6	Variations in $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ with age of the carbonate nodules from IITK profile.	99
5.1	Alkalinity vs. salinity distribution in estuaries.	107
5.2	Molybdenum, Uranium and Rhenium vs. salinity plots in the Narmada estuary for monsoon and pre-monsoon seasons.	116
5.3	Mo, U and Re Vs. salinity in the Tapi estuary.	117
5.4	Mo, U and Re distribution in the Mandovi estuary.	118
5.5	Mo, U and Re in the Hooghly estuary.	119
5.6	Mo/Al, U/Al of suspended load vs. salinity in the Narmada estuary.	128
5.7	Scatter diagram of Mo, U and Re concentration in suspended matter of the Narmada versus their organic carbon abundance.	129
5.8	Mo/Re and U/Re vs. salinity distribution.	130

5.9	Histogram of dissolved Mo concentration of the global rivers based on reported data and from this study.	139
6.1	Dissolved Sr vs. salinity plots in the Narmada, Tapi and Mandovi estuaries from Arabian Sea.	154
6.2	Dissolved Ba-salinity profile in four estuaries.	156
6.3	Scatter plots of Ca/Al, Sr/Al and Ba/Al of suspended particulate matter with salinity in the Narmada estuary.	159
6.4	Plots of dissolved $^{87}Sr/^{86}Sr$ vs. 1/Sr concentration in estuaries.	161
6.5	Schematic of submarine groundwater discharge in to coastal regions.	163
6.6	Plot of $^{87}Sr/^{86}Sr$ vs. 1/Sr in the Narmada estuary.	164
6.7	Effective zero salinity end member concentration of Ba in different estuaries.	170