Isotope geochemistry of black shales and Recent marine sediments

A THESIS

Submitted for the Award of Ph. D degree of

MOHANLAL SUKHADIA UNIVERSITY

In the

Faculty of Science

by

Gyana Ranjan Tripathy



Under the Supervision of

Dr. Sunil Kumar Singh ASSOCIATE PROFESSOR

Physical Research Laboratory, Ahmedabad-380009, India.

DEPARTMENT OF GEOLOGY MOHANLAL SUKHADIA UNIVERSITY UDAIPUR

2011

DECLARATION

I, **Mr. Gyana Ranjan Tripathy**, S/o Mr. Uma Charan Tripathy, resident of A-4, PRL residences, Navrangpura, Ahmedabad – 380009, hereby declare that the research work incorporated in the present thesis entitled *"Isotope geochemistry of black shales and Recent marine 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:

(Gyana Ranjan Tripathy)

CERTIFICATE

I feel great pleasure in certifying that the thesis entitled "Isotope geochemistry of black shales and Recent Marine sediments" by Gyana Ranjan Tripathy under my guidance. He has completed the following requirements as per Ph.D. regulations of the University

(a) Course work as per the university rules

- (b) Residential requirements of the university
- (c) Presented his work in the departmental committee

(d) Published/accepted minimum of two research paper in a referred research journal.

I am satisfied with the analysis of data, interpretation of results and conclusions drawn.

I recommend the submission of thesis.

Date:

Name and designation of supervisor

Sunil Kumar Singh, Associate Professor

Countersigned by Head of the Department

Dedicated

To

My Parents,

Sri Uma Charan Tripathy L Smt. Monorama Tripathy

Acknowledgement

This thesis work would not have been possible without the help and support of many people. I sincerely thank all of them for their selfless cooperation.

Since my first day at PRL, Dr. Sunil Kumar Singh, my thesis supervisor, was always there to share his knowledge and expertise in geochemistry and instrumentation. He introduced me to the field of isotope geochemistry and mass spectrometry. Without him, my transition from physics to geochemistry would have been unexciting. He was very instrumental in educating me with every minute detail of isotope geochemistry, chemical processing of samples, working with TIMS, data analysis and interpretation. His friendly and informal nature helped me to boldly present my views during scientific discussions. I acknowledge him for providing me ample freedom to work and for his support and guidance.

I express my gratitude to Swami (Prof. S Krishnaswami) for his valuable comments and suggestions during this work. Discussions with him were always beneficial in my growth as a researcher. Scientific integrity, in-depth knowledge in geochemistry and his meticulous approach towards research makes him very special; it was truly an honor to be associated with such a great geochemist. His requirement for perfection in every aspect of science, although makes it tough to work with him, but has been very educative. I am immensely thankful to Prof. Swami for his valuable time and constructive views. I thank Prof. M M Sarin for his support and suggestion during my thesis work. His systematic approach towards scientific problems has been very encouraging and discussions with him, particularly on U-Th isotopic systematics, river water chemistry and instrumentation were very beneficial. I owe my sincere thanks to Prof. SVS Murthy for his guidance during my course work project.

I am extremely thankful to Prof. J. N. Goswami, the Director, Prof. Utpal Sarkar, Dean and Prof. S K Bhattacharya and A.K. Singhvi, former Dean, Physical Research Laboratory, for providing me support and facilities for my thesis work. I thank academic committee members for timely review of my work. Special thanks to Profs. R Ramesh, S K Gupta, Dr. D Banerjee for their informative lectures during course work. I am thankful to all members of the Chemistry Lab for their help and support during my thesis work. I thank Dr. Santosh K Rai for his guidance during chemical processing of samples and TIMS operation. I thank Dr. Ravi Bhushan for encouragement and support during my thesis. Working with him has always been a pleasure, whether on a cruise or during scientific discussions. I acknowledge the help of Dr. R Rengarajan for his co-operation and suggestions during my thesis work. Thanks to Sudheer for his help during geochemical analyses of river water samples. It's my pleasure to thank J P Bhavsar for his help and for providing a homely environment in the lab. I thank Rahaman, Kirpa, Ashwini, Timmy, Vineet, Satinder, Jayati, Srinivas and Prashant for their help and support. Discussion and support of my seniors, Tarun, Anirban and Neeraj was always helpful in my work. I duly acknowledge the help of Vishwanathan, Sneha, Komal and Shantaben.

I am thankful to Drs. J.S Ray, Navin Juyal, M.G. Yadava, Vinai K. Rai and Mr. A D Shukla for their reassurance towards my work. Thanks are also due to Drs. P. Sharma, R.D. Deshpande, Kuljeet Kaur, D. K. Rao, R.A Jani, D. Panda, Dibyendu Chakravarty, Som K. Sharma and Bhushit Vaishnav for their kind support. I am grateful for the instrumentation facility in Planex and to Durgaprasad, Jayesh and Narendra for his help during measurements. I thank Drs. Rajesh Agnihotri and Koushik Dutta for their help and support. I thank Dr. V Ramaswamy, Prof. H. Bhu and Prof. G J Chakrapani for their suggestions in our collaboration work. Discussions with Profs. A. Tarantola and P Gupta were very helpful during inverse modeling course at C-MMACS, Banglore. My sincere thanks to Drs. Subimal Deb, Sanat Kumar Das and Uma Das for their help in computer programming.

I am grateful to all the staff-members of Library, Computer Centre, Workshop, Administration, Dispensary, Maintenance section of PRL for their assistance and cooperation. Thanks to Bankim for fabricating Carius tube required for osmium chemistry.

The memorable moments of PRL tea-time, TV room, Volleyball and TT matches are pleasant and unforgettable. Thanks to my first friend at PRL, Lokesh for his care and support. I thank Naveen, Arvind, Bhavik, Sanjeev, Vishal, Anil, Kallol,

Pathak, Bindu and Charu for making my initial days of PRL joyful. I spent pleasant moments at PRL hostel with my close friends. Company of my batch-mates (Alok, Sumanto, Brajesh, Sumita, Bhatt, Tyagi, Shuchita, Harinder, Manan, Ram, Chandra Mohan (CM), Ayan, and Rohan), my seniors (Rajesh, Shreyas, Morthekai, Salman, Zeen, Mourya, Sunil, Amitavab, Sharma, Rohit, Ritesh, Satya, Antra, Vandana, Jayesh and Sasadhar) and my juniors (Arvind Saxena, Suratna, Rohit, Amjad, Chauhan, Rabiul, Neeraj, Ashish, Tapas, Sunil, Arun, Suruchi, Moumita, Chinmay, Iman, Patra, Suman, Ashok, Praveen, Bhaswar, Anand, Sandeep, Srikant, Soumya, Subrata, Vimal, Yogita, Prayakta, Pankaj, Zulfikar and Rajpurohit) made my stay pleasant and enjoyable at PRL.

I thank Mrs. Renu Singh for making me feel like part of her family. Thanks to Mrs. Krishnaswami, Mrs. Sarin, Mrs. Bhushan, Mrs. Rengarajan and Mrs. Sudheer for their care and nice get-togethers. My sincere thanks to Mrs. Pauline Josheph for her help, support and affection. Presence of Markandeya, Monu, Golu and Mahin always made me joyous. I thank Preeti and Reshma for their care, and of course for the delicious food.

I owe my sincere thanks to my brothers (Sarada Prasad, Simanchal, Biswa and Rashmi Ranjan) for extending every possible comfort and support to me during this work. I am deeply grateful to Satya and Sujata for their affection, encouragement, care and support. Thanks are due to Minati, Vijaya, Jyotchna for their faith and confidence on me. Love and affection to Sipra, Sambit, Smruti, Sriya, Srija, Bhabhani (Suraj) and Snigdha for making my life cheerful. Its my pleasure to thank Bini, Sudhansu, Sasank, Pinku and Raju; I really enjoyed every moment that I shared with them. I thank Swapn for his rational and mature suggestions. I would cherish his friendship forever.

Lastly, but most importantly, pranam to my parents (Sri Uma Charan Tripathy and Smt. Monorama Tripathy) for their love, care, affection and support during this work. It was their confidence that inspired me the most to complete this work, and hence, I take this opportunity to dedicate this thesis to them.

ABSTRACT

The focus of this thesis is on the applications of radiogenic isotopes of Os, Sr and Nd to determine chronologies of key sedimentary deposits in India and temporal variations in provenances of sediments from the Bay of Bengal (BoB). Black shales from the Vindhyan, Lesser Himalaya (LH) and Aravalli were analyzed for ¹⁸⁷Re-¹⁸⁷Os systematics to constrain their depositional ages and to assess their potential to track atmospheric oxygen evolution during the Proterozoic to Early Cambrian. These studies have provided precise depositional ages for the Vindhyan (Kaimur) and outer belt of LH, in contrast samples from the Aravalli and inner belt of LH show "open system" behavior of Re-Os due to the post-depositional alterations. The ¹⁸⁷Re-¹⁸⁷Os isochron of black shales from the Upper Vindhyan yield an age of 1196±41 Ma with an initial 187 Os/ 188 Os of 0.74±0.27. The shales lying just above the Pc-C boundary of the outer LH provided a Re-Os age of 541±4 Ma, in excellent agreement with U-Pb ages for the Pc-C boundary reported from other locations. Results suggest more intense reducing condition during their deposition with higher supply of mantle like Os. The initial ¹⁸⁷Os/¹⁸⁸Os obtained in this study along with those available in literature on the Proterozoic ocean show consistent trend of atmospheric oxygen, attesting to the potential of ¹⁸⁷Os/¹⁸⁸Os as a suitable proxy for paleo-oxygen record.

The Sr-Nd isotopes of sediments from a piston core from the western BoB indicate that their dominant supply from the Himalaya and Peninsular India. Temporal variations in the Sr-Nd isotopes suggest source variability in the past with relatively reduced contribution from the Himalaya during LGM indicating a strong erosion-climate link. Lower erosion over the Himalaya is due to lower southwest monsoon intensity and higher snow cover over the Higher Himalaya during LGM.

Efforts to characterize the chemical erosion pattern of the Ganga basin and to apportion the sources of solutes, inverse modeling of available literature data on elemental and Sr isotopic composition of the Ganga headwaters was carried out. These results show that on average ~25% of major cations are from silicates and balance from carbonates. The chemical erosion rates of the basin bring out the importance of lithology in controlling the erosion pattern.

Table of Contents

Pages

	List of Tab List of Figu			iv-v vi-vii
Chapter 1	Introduct	tion		1-13
•	1.1.	Introduction		1
	1.2.	Objectives of	the Thesis	11
	1.3.	Structure of t	he Thesis	12
Chapter 2	Materials and Methods			14-55
-	2.1.	Materials		15
		2.1.1.	Black Shales	15
		2.1.2.	Recent Marine Sediments	30
	2.2.	Analytical M	ethodology	34
			Osmium: Isotopes and	35
		2.2.1.	Geochemistry	55
		2.2.2.	Re and Os Spikes and Standards	36
		2.2.3.	Osmium Chemistry	38
		2.2.4.	Sr-Nd Isotope Analysis	47
		2.2.5.	Radiocarbon Chronology	49
		2.2.6.	Major and Trace elements	52
Chapter 3	and Early	y Cambrian Bla	s isotopic systematic of Precambrian ick Shales: Implications to their ages, ric oxygen evolution trend	56-97
	3.1.	Introduction	ne oxygen evolution trend	57
	3.2.	Vindhyan Su	pergroup	59
	0.21	3.2.1.	Re-Os Geochronology for Bijaigarh shales	62
		3.2.2.	Sedimentray Hiatus between Semri and Kaimur	68
	3.3.	Lesser Himal		69
		3.3.1.	Geochemistry of Black shales	73
		3.3.2.	Re-Os systematics	73
		3.3.3.	Re-Os isochrons	75
		3.3.4.	Oxic-anoxic conditions at Pc-C	78
	3.4.		boundary	82
	J.4.	Aravalli Supe	zigioup	02

		2 4 1	Geochemistry of Lower Aravalli	82
		3.4.1.	shales	84
	25	3.4.2.	Re-Os systematics of black shales	
	3.5.		d of Atmospheric Oxygen Level	89
	3.6.	Sr-Nd isotopes	of Black shales	94
Chapter 4			pic composition of the Bay of of Climate on Erosion	98-125
	4.1.	Introduction		99
	4.2.	Results		102
	4.3.	Discussions		108
		4.3.1.	$^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} of sources	108
		4.3.2.	Sr-Nd isotopes and CIA	111
			Temporal variations in erosion	114
		4.3.3.	pattern	114
		4.3.4.	Impact of climate on eroison	121
	4.4.	Conclusions		125
Chapter 5		l Erosion Rates of Model Approacl	f the Ganga Headwater Basins: An h	126-160
	5.1.	Introduction		127
	5.2.	The Ganga Bas	sin	129
		5.2.1.	Geology	129
		5.2.2.	Hydrology	130
		5.2.3.	Sources of Data	131
	5.3.	Chemistry and	⁸⁷ Sr/ ⁸⁶ Sr of Ganga Headwaters	132
	5.4.	Source Apportionment		135
		5.4.1.	Forward Model	136
		5.4.2.	Inverse Model	137
	5.5.	Source Apport	ionment	146
		5.5.1.	Sources of dissolved cations and Sr	146
		5.5.2.	Calcite Precipitation	149
		5.5.3.	Control of silicate weathering on ⁸⁷ Sr/ ⁸⁶ Sr	153
		5.5.4.	Erosion Rates	154
			Controling factors for chemical	
		5.5.5.	weathering Flux from the Himalaya to Ganga	157
		5.5.6.	mainstream	158
	5.6.	Conclusions		159

Chapter 6	Summary and Future Perspectives		161-167	
	6.1.	Ages of Black shales using Re-Os chronometer	162	
	6.2.	Provenance of sediments and Erosion-Climate Link	164	
	6.3.	Sources of river water solutes using inverse modeling	165	
	6.4.	Future Prespectives	165	
	Appende	x	168-174	
	References		175-206	
	List of Pu	iblications	207	

LISTS OF TABLES

Tables	Content	Page
2-1	Stratigraphic sequence of the Aravalli Supergroup with their chronology.	18
2-2	Sedimenatry sequence of the Vindhyan Supergroup.	21
2-3	Hydrological and geological details of rivers supplying sediments to the BoB.	31
2-4	Analytical techniques followed in this study.	34
2-5	Typical Re and Os elemental and isotopic composition in geological samples.	35
2-6	Calibration of Re Standard used in this study.	36
2-7	Calibration of Re spikes used in this study.	37
2-8	Calibration of osmium Spike used in this study.	38
2-9	Technical details of Isoprobe-T Negative-TIMS.	43
2-10	Repeat measurements of Re, Os and ¹⁸⁷ Os/ ¹⁸⁸ Os in black shales.	46
2-11	Procedural blank level for Re and Os measurements.	47
2-12	Reproducibility of Sr and Nd analysis.	48
2-13	Reproducibility of sedimentary carbon and nitrogen measurements.	50
2-14	Repeat measurements of major and trace elements.	51
2-15	Coefficient of variance for the analysis of different elements.	53
2-16	Measured values of the USGS G2 standard.	54
3-1	Radiometric ages for the sedimentary successions of the Vindhyan.	60
3-2	Re-Os isotopic systematics of the Bijaigarh shales.	63
3-3	Major elemental composition of black shales from the Lesser Himalaya.	71
3-4	Trace elemental composition of black shales from the Lesser Himalaya.	72
3-5	Re, Os and ¹⁸⁷ Os/ ¹⁸⁸ Os values of the black shales from the Lesser Himalaya.	74
3-6	Geochemistry of black shales from the Jhamarkotra formation.	83
3-7	Re, Os and ¹⁸⁷ Os/ ¹⁸⁸ Os of black shales from the Jhamarkotra formation.	84
3-8	Estimation of loss of Re for the Lower Aravalli shales.	88
3-9	Iinitial ¹⁸⁷ Os/ ¹⁸⁸ Os inferred from Re-Os ischrons of Precambrian black shales.	90
3-10	Sr, Nd and their isotope composition in silicate fraction of black shales.	93
4-1	Basin characteristics of rivers and their sedimentary Sr, Nd isotopes.	101
4-2	14 C ages of inorganic carbon from the core SK187/PC33.	102
4-3	Geochemical compositions of bulk sediments from the SK187/PC33.	102
4-4	Geochemistry of the BoB sediments and their riverine sources.	103
4-5	$CaCO_3$, C_{org} and total nitrogen content in the BoB sediments.	105
4-6	Magnetic susceptibility (MS) of sediments from the core SK187/PC33.	105

4-7	Sr, Nd concentrations and their isotope composition of the BoB sediments.	109
5-1	Silicate bed rock exposure area for the tributaries of the Ganga.	130
5-2	Sources of the data and details of the tributaries of the Ganga.	132
5-3	Results of inverse model used in this studyand that of Millot et al. (2003).	138
5-4	Sodium concentration in 0.1N HCl leach of Himalayan carbonates.	140
5-5	A-priori molar ratio for the various ends members.	142
5-6	A-posteriori results from the inverse model for of the Ganga tributaries.	143
5-7	Source apportionment for cations and Sr and silicate, carbonate erosion rates.	145
5-8	Results of inverse model with and without using Ca and alkalinity.	151
S1	Geochemical data of the Ganga headwaters along with source of data	168
S2	Results on sources of disolved solute obtained from inverse modeling	171

LISTS OF FIGURES

Figures	Content	Page
2.1	Locations from where black shales for this study are from.	16
2.2	Sampling location of black shales from the Aravalli Supergroup.	19
2.3	Geological distribution of the Vindhyan Supergroup.	24
2.4	Lithological startigraphy of the Lesser Himalaya.	25
2.5	Geological details of LH with sampling locations.	29
2.6	Wind and water circulation pattern over the BoB.	32
2.7	Location of the studied core SK187/PC33 in the BoB.	33
2.8	Flow chart showing Re-Os purification chemistry.	39
2.9	Dimension of carius tube used for Re-Os purification.	40
2.10	Micro-distillation procedure used to extract pure Os.	41
2.11	A typical spectrum of isotopes of OsO ₃ .	44
2.12	Measurement of ¹⁸⁷ Os/ ¹⁸⁸ Os of standard versus time.	45
2.13	Replicate analyses of geochemical compositions of sediments.	52
2.14	Measured vs. reported values for major elements of USGS-G2.	55
3.1	Re-Os isochron for the black shales from the Bijaigarh shales.	66
3.2	Re-Os isochron of black shales from Lower Tal.	75
3.3	Chronological information for the Krol-Lower Tal formation.	76
3.4	¹⁸⁷ Re/ ¹⁸⁸ Os- ¹⁸⁷ Os/ ¹⁸⁸ Os plot of the black shales from inner LH.	76
3.5	Histogram of Re-Os compositions of black shales from Aravalli.	85
3.6	¹⁸⁷ Re/ ¹⁸⁸ Os- ¹⁸⁷ Os/ ¹⁸⁸ Os plot of the Aravalli shales.	86
3.7	Compilation of temporal variation in seawater ¹⁸⁷ Os/ ¹⁸⁸ Os.	91
3.8	Plot of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ϵ_{Nd} of the black shales from India.	94
3.9	Mixing plot of Sr/Nd- ε_{Nd} of the Bijaigarh shales.	95
3.10	Mixing plot of Sr-Nd isotopes of the black shales from the LH.	97
4.1	Sample location of the sediment core SK187/PC33 in the BoB.	100
4.2	Depth profile of Sr and Nd isotopes of the BoB sediments.	110
4.3	$^{87}\text{Sr}/^{86}\text{Sr}$ vs. ϵ_{Nd} of the sediments from core SK187/PC33.	112
4.4	CIA and ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ (ϵ_{Nd}) of the sediments from the SK187/PC33.	113
4.5	Mixing plot of K/Al and Fe/Al of the BoB sediments.	117
4.6	Depth profiles of MS, Fe/Al and V/Al for BoB sediments.	118
4.7	Sr and Nd isotopic mixing plot for the SK187/PC33 sediments.	119

4.8	Temporal variation of of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ϵ_{Nd} of sediments from the BoB.	122
5.1	Geological map of the drainage basins of the Ganga and its tributaries.	131
5.2	Ternary diagram of the chemical composition of the Ganga headwaters.	133
5.3	Spatial variation of dissolved ⁸⁷ Sr/ ⁸⁶ Sr for the Ganga tributaries.	134
5.4	Reanalysis of Mackenzie river data using inverse model from this study.	139
5.5	Sensitivity test for the inverse model.	141
5.6	Bar diagram of contribution from different sources to dissolved cations.	147
5.7	Comparision of Cat _s (mM) obtained by the forward and inverse models.	148
5.8	Estimated loss of Ca with measured Ca/Sr of the Ganga.	152
5.9	The variation of 87 Sr/ 86 Sr vs. Cat _s in the Ganga headwaters.	154
5.10	Comparison of silicate and carbonate erosion rates in different tributaries.	156
5.11	Chemical erosion rates vs. the runoff for the Ganga tributaries.	157