

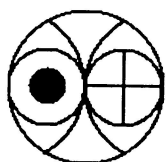
# **Isotopic and Geochemical Studies of the Lesser Himalayan Sedimentaries**

**by**  
**Sunil Kumar Singh**

*Thesis submitted to*  
*the Maharaja Sayajirao University of Baroda*  
*For the degree of*

**Doctor of Philosophy in Geology**

**February, 1999**



**Physical Research Laboratory**  
**Ahmedabad - 380 009, India**

## ABSTRACT

The role of silicate and carbonate weathering in contributing to the major cations and Sr isotope geochemistry of the headwaters of the Ganga-Ghaghara-Indus system is evaluated by making *new* chemical and isotopic measurements of Precambrian carbonates from the Lesser Himalaya and from the available data on silicates. Samples of Precambrian carbonate outcrops collected across the Lesser Himalaya have been analysed for their mineralogy, chemical composition and isotope ratios of Sr, O and C. Their Sr concentrations range from 20 to 363 ppm with  $^{87}\text{Sr}/^{86}\text{Sr}$  0.7064 to 0.8935,  $\delta^{18}\text{O}_{\text{PDB}}$  -1.4 to -12.8 ‰ and Mn 11 to 2036 ppm. The petrography of the samples, their low Sr concentrations and wide range of  $\delta^{18}\text{O}$  values are all suggestive of their postdepositional alteration.

Comparison of the  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr/Ca ratios among the carbonates and silicates from the Lesser Himalaya and 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. The results show that on the 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.

The silicate Sr component in these headwaters range from 2% to 100% with a mean of 40%. The calculation shows that only in few of the headwaters Sr balance would be achieved based on a two component, silicates and Precambrian carbonates, mixing. This indicates the need of a third end member. Tibetan/Tethyan carbonates, evaporites, phosphorites are the possible end member.

The second part of the thesis deals with the study of Re-Os isotope systematics in black shales from the Himalaya for determining the chronology and evaluating their potential to contribute to the steady increase in  $^{187}\text{Os}/^{186}\text{Os}$  of the oceans since past ~25 Ma. Towards this, chemical procedures and Negative Thermal Ion Mass Spectrometry techniques have been established for the precise measurements of Re-Os concentrations in environmental samples and the Os isotope composition in them for the first time in our laboratory. The precision of  $^{187}\text{Os}/^{186}\text{Os}$  ratios and Os concentration determination are

better than 1% ( $\pm 2\sigma_\mu$ ) and 2-3% ( $\pm 2\sigma$ ) respectively in a few tens to few hundreds of picograms of Os.

Re and Os abundances and Os isotope composition 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 black shales from the Maldeota and Durmala mines, collected ~15 m above the Krol-Tal (Pc-C) boundary, yield  $^{187}\text{Re}$ - $^{187}\text{Os}$  isochron ages of  $535 \pm 11$  Ma consistent with stratigraphy and those assigned 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  $^{187}\text{Re}$ - $^{187}\text{Os}$  age of  $839 \pm 138$  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. If the  $^{187}\text{Os}/^{186}\text{Os}$  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  $^{187}\text{Os}/^{186}\text{Os}$  would have to increase from 0.51 moles  $\text{y}^{-1}$  at 16 Ma ago to 830 moles  $\text{y}^{-1}$  at present. The present day flux would correspond to Os concentration of ~40  $\text{pg } \lambda^{-1}$  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  $^{186}\text{Os}$  flux to be constant over the past 16 Ma at 15.8 moles  $\text{y}^{-1}$  (calculated from available data for rivers), show that  $^{187}\text{Os}/^{186}\text{Os}$  in HTP rivers have to increase from 7.7 at 16 Ma ago to 40.5 at present to reconstruct the observed seawater  $^{187}\text{Os}/^{186}\text{Os}$  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  $^{187}\text{Os}/^{186}\text{Os}$  in black shales from the Lesser Himalaya though can meet the model requirements, the demands on them can be more easily accommodated if the  $^{187}\text{Os}/^{186}\text{Os}$  of HTP rivers is taken as 16.2 and that in all the other rivers as 11.0.

This study has brought the need (i) to look for other possible source(s) to balance the Sr budget in the head waters and (ii) more detailed study of black shales from the inner and outer belts to determine their chronology and inter-relation.

# Contents

List of tables	iv
List of figures	vi
Chapter 1 Introduction	1
1.1 Introduction	2
1.2 Objectives of this thesis	6
1.3 The outline of the thesis	7
Chapter 2 Materials & Methods	8
A Materials	9
2.1 Stratigraphy and lithology of the area	9
(i) Outer belt sedimentary sequence	9
(a) Blaini	11
(b) Infra-Krol	11
(c) Krol	13
(d) Tal	13
(ii) Paleaontological records of ages of the various formations	14
(iii) Inner belt sedimentary sequence	17
(a) Deoban	17
(b) Mandhali	19
(iv) Intercorrelation between inner and outer belt sedimentaries	19
B Method	22
2.2 Field sampling	23
(i) Black shales	23
(ii) Carbonates	25
(iii) River water	26

2.3	Powdering	26
2.4	Analytical Techniques	26
(i)	Re-Os measurement techniques	28
(a)	Re, Os standards, spikes and reagents	29
(b)	Os chemistry	31
(c)	Re Chemistry	34
(d)	Os and Re mass spectrometry	36
(e)	Procedural blanks	40
(f)	Precision and accuracy of Re and Os measurements	40
(ii)	Rb & Sr measurements	42
(iii)	O & C isotopes measurements	43
(iv)	Determination of elemental abundances	43
(a)	Sample preparation for elemental analysis	43
(b)	Atomic Absorption Spectrophotometry	44
(c)	Inductively Coupled Plasma-Atomic Emission Spectrophotometry	46
(d)	UV-visible Spectrophotometry	47
(e)	Inorganic, Organic carbon and nitrogen analysis	49
(f)	Anion measurements by ion chromatography	51
(v)	Mineralogical Studies	51
Chapter 3	Silicate and carbonate weathering in the Himalaya: Impact on major ion chemistry and $^{87}\text{Sr}/^{86}\text{Sr}$ of the Ganga Headwaters	52
3.1	Mineralogy, Chemical and Isotopic Compositions of the Precambrian carbonates	54
(i)	Mineralogy and Chemical Composition	54
(ii)	Oxygen and Carbon isotopes	64
(iii)	Sr isotope systematics	65

(iv)	Impact of carbonate weathering on $^{87}\text{Sr}/^{86}\text{Sr}$ of the Ganga-Ghaghara- Indus Headwaters	69
(v)	Sr contribution from Precambrian carbonates to the headwaters	70
3.2	Silicate and carbonate weathering in the Ganga-Ghaghara- Indus Basin	73
(i)	Major ion chemistry of the G-G-I source waters	73
(ii)	Silicate weathering: Contribution of cations to headwaters	85
(iii)	Carbonate (Ca+Mg) in the headwaters	89
(iv)	Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ of Ganga, Ghaghara and the Indus source waters	92
3.3	Silicate and carbonate chemical weathering rates in the Ganga source water basins	102
Chapter 4	Re-Os isotope systematics in black shales from the Lesser Himalaya: Their chronology and role in $^{187}\text{Os}/^{186}\text{Os}$ evolution of seawater	105
4.1	Samples	108
4.2	Org. C, N, Re, Os concentrations and $^{187}\text{Os}/^{186}\text{Os}$	109
4.3	Lesser Himalayan black shale chronology	114
(i)	Outer belt black shales	116
(ii)	Inner belt samples	122
(iii)	Os isotopic ratio of Early Cambrian seawater	123
4.4	Os isotopes in the Himalayan black shales and $^{187}\text{Os}/^{186}\text{Os}$ evolution of seawater	125
Chapter 5	Summary & Conclusions	139
5.1	Chemical and isotopic studies of the Lesser Himalayan Carbonates	140
5.2	Re-Os Studies on Black shales of the Lesser Himalaya	142
5.3	Future Study	145
	References	147

For Fulltext Please Contact:

[library@prl.res.in](mailto:library@prl.res.in)