Chapter 5

Dissolved Rhenium in the Yamuna River System: Black shale weathering and its role on riverine trace metal budgets

5.1 INTRODUCTION

The surficial geochemistry of Re plays a significant role in determining the utility of the Re-Os system for dating. The application of ^{187}Re-^{187}Os pair as a chronometer to date sedimentary formations and igneous rocks is getting increasingly recognized (Ravizza and Turekian, 1989; Allegre et al., 1999; Singh et al., 1999). Despite its low crustal abundance, Re has relatively high concentration in seawater (Anbar et al., 1992) due to the solubility of perrhenate (ReO_4^-) anion in oxidizing environments. From seawater, Re is removed via scavenging under suboxic-anoxic conditions leading to its strong enrichment in organic rich marine sediments. Since ^{187}Re, more abundant of the two isotopes of Re, decays to ^{187}Os, organic rich sediments such as black shales serve as an important crustal reservoir for radiogenic ^{187}Os. These sediments, being reduced in nature, are prone to oxidative weathering in aqueous oxic environments. Hence weathering of these sediments would release both Re and ^{187}Os to solution. Therefore, drainage basins abundant in organic rich sediments are potential sources of Re and radiogenic Os to the oceans. The ^{187}Os/^{188}Os of seawater shows a steady rise since last ~40 my to present (Pegram et al, 1992; Ravizza, 1993; Peucker-Ehrenbrink et al., 1995; Turekian and Pegram, 1997). The timing of the increase coupled with the knowledge of presence of black shales in the Himalaya (Valdiya, 1980) led to the suggestion that their weathering is an important driver in determining the steady increase of seawater ^{187}Os/^{188}Os through Cenozoic (Pegram et al., 1992). The validity of this suggestion though being debated, it has been found that rivers draining the Himalaya have Os isotopic composition generally more radiogenic compared to other major world rivers (Levasseur et al., 1999; Sharma et al., 1999). The ^{187}Os/^{188}Os of rivers is determined by the Re/Os ratios and age of the basins drained by them. Relatively higher ^{187}Os/^{188}Os in rivers can result if they drain basins with high Re/Os such as those containing organic rich sediments. Considering that weathering of these sediments by oxic river waters would also release Re to solution as perrhenate oxyanion (Brookins, 1986; Koide et al., 1986), the concentration of Re in such rivers are expected to be relatively high. Hence data on the abundance of Re in river waters in the Himalaya can aid not only in constraining their sources but also provide better understanding of the comparative geochemistry of Re and Os during weathering.

Knowledge of the sources of Re in river waters and understanding its geochemical behaviour in surficial weathering environment also has implications to the use of ^{187}Re-^{187}Os isotope pair for geochronology. The application of this pair for age determination requires, among other conditions, closed system behavior of both Re and Os in the rock/sediment system to be dated (Ravizza and Turekian, 1989; Raviza et al., 1991; Allegre et al., 1999; Cohen et al., 1999; Singh et al., 1999; Peucker-Ehrenbrink and Hannigan, 2000). Studies of Re in rivers is one approach to learn about the extent of its mobility from various rock types during surficial weathering and its possible consequences to Re-Os chronometry.

Some of these considerations, coupled with the availability of high sensitive measuring techniques such as the ID-NTIMS and ICP-MS which have considerably improved the precision and accuracy of Re determinations (Anbar et al., 1992; Colodner et al., 1993a,b) have contributed to recent studies of Re in natural waters. Colodner et al. (1993b) in their reconnaissance study of the geochemical cycle of Re observed that rivers draining black shales, such as those in the Venezuelan Andes, have higher dissolved Re concentrations. Hodge et al. (1996), on the other hand, proposed carbonates to be an important source of Re to groundwaters based on their observation that Re/Mo/U ratios in groundwaters from Palaeozoic carbonate aquifers in the southern Great Basin, USA and seawater are quite similar. This finding led them to suggest quantitative uptake of these trace elements from seawater by carbonates during their precipitation and their subsequent release to groundwater during dissolution.

This chapter presents and discusses Re abundances in the Yamuna and many of its major as well as a number of minor tributaries in the Himalaya. For comparison, a few samples from the Ganga collected at Rishikesh at the base of the Himalaya were also analyzed for Re. In addition, Re has been measured in various source rocks from the catchment, such as carbonates and granites, and a few groundwaters percolating through a phosphorite-black shale-carbonate sequence in a phosphorite mine in the Lesser Himalaya. This work, which forms the first comprehensive study on the geochemistry of Re in a river system in the Himalaya, aims at (i) determining dissolved Re flux from the Yamuna and the Ganga at their outflow at the foothills of the Himalaya, an important data set to assess the role of weathering in the Himalaya in contributing to Re budget of the oceans, (ii) delineating the source(s) of dissolved Re to these rivers based on Re in granites, carbonates and those available in literature for black shales in the Lesser Himalaya (Singh et al., 1999) (iii) understanding the implications and influence of weathering of organic rich sediments such as black shales on the riverine trace metal (Re, Os and U) budgets and global carbon cycle, using dissolved Re in rivers as a proxy.

5.2 RESULTS AND DISCUSSION

The concentration of dissolved Re in the Yamuna and its tributaries are given in Table 5.1 and Re abundances in granites collected from the YRS catchment and the Precambrian carbonates from the Lesser Himalaya in Table 5.2.

Table 5.1 Dissolved Re in the Yamuna River System, the Ganga and mine waters.

Code[a)]	**River**	**Location**	**Season[b)]**	**SO_4 (µM)**	**Re[c)] (pM)**	**ΣCat* (mg ℓ^{-1})**	**TDS* (mg ℓ^{-1})**
Yamuna mainstream							
RW98-16	Yamuna	Hanuman Chatti	PM	113	5.3±0.2	20.7	88
RW98-20	Yamuna	D. of Paligad Bridge	PM	100	4.6±0.1	21.2	93
RW98-25	Yamuna	Barkot	PM	76	5.4±0.4	22.2	100
RW98-22	Yamuna	U. of Naugaon	PM	76	4.1±0.2	23.0	103
RW98-15	Yamuna	U. of Barni Gad's confluence	PM	72	3.5±0.1	27.2	124
RW98-14	Yamuna	D. of Barni Gad's confluence	PM	63	3.7±0.2	28.8	136
RW98-12	Yamuna	D. of Nainbag	PM	66	3.6±0.1	27.1	125
RW98-9	Yamuna	D. of Aglar's confluence	PM	220	5.6±0.4	34.9	157
RW99-51	Yamuna	D. of Aglar's confluence	M	40	1.7±0.1	17.7	85
RW98-6	Yamuna	U. of Ton's confluence	PM	216	5.9±0.2	37.1	168
RW99-64	Yamuna	U. of Ton's confluence	M	154	4.2±0.2	31.2	140
RW99-31	Yamuna	D. of Ton's confluence	S	405	7.9±0.1	39.5	172
RW99-53	Yamuna	D. of Ton's confluence	M	93	3.5±0.1	19.4	102
RW98-1	Yamuna	Rampur Mandi, Paonta sahib	PM	101	6.2±0.2	26.8	117
RW99-58	Yamuna	Rampur Mandi, Paonta sahib	M	100	4.9±0.1	24.2	109
RW98-4	Yamuna	D. of Bata's confluence	PM	333	14.6±0.3	58.7	254
RW99-55	Yamuna	D. of Bata's confluence	M	288	14.1±0.4	51.3	274
RW98-33	Yamuna	Yamuna Nagar, Saharanpur	PM	268	10.0±0.2	53.4	236
RW99-7	Yamuna	Yamuna Nagar, Saharanpur	S	321	15.0±0.2	55.8	262
RW99-54	Yamuna	Yamuna Nagar, Saharanpur	M	192	7.7±0.2	28.2	151
Tributaries							
RW98-17	Jharjhar Gad	Hanuman Chatti-Barkot Road	PM	27	2.7±0.1	11.5	51
RW98-18	Didar Gad	Hanuman Chatti-Barkot Road	PM	11	0.50±0.02	6.1	32
RW98-19	Pali Gad	Pali Gad Bridge	PM	61	3.9±0.2	21.6	94
RW98-13	Barni Gad	Kuwa	PM	27	4.8±0.1	44.8	200
RW98-21	Kamola	Between Naugaon and Pirola	PM	32	1.7±0.2	30.9	142

RW98-24	Gamra Gad	Near the bridge over it	PM	26	1.5±0.1	32.1	153
RW98-26	Godu Gad	Purola-Mori Road	PM	19	2.7±0.2	10.2	53
RW98-27	Tons	Mori	PM	62	7.0±0.4	10.7	49
RW98-28	Tons	D. of Mori	PM	58	5.7±0.5	11.1	50
RW98-29	Tons	Tiuni	PM	62	5.4±0.7	12.8	60
RW98-31	Shej Khad	Minas	PM	159	18.7±0.8	37.8	166
RW98-30	Tons	Minas	PM	100	10.8±0.6	24.0	107
RW98-5	Amlawa	Kalsi-Chakrata Road	PM	127	5.1±0.2	39.4	181
RW99-62	Amlawa	Kalsi-Chakrata Road	M	150	4.6±0.2	40.7	184
RW98-32	Tons	Kalsi, U. of confluence	PM	581	9.7±0.2	46.9	202
RW99-29	Tons	Kalsi, U. of confluence	S	777	10.4±0.4	46.9	197
RW99-63	Tons	Kalsi, U. of confluence	M	340	7.7±0.2	34.1	146
RW98-7	Kemti Fall	Dehradun-Mussourie Road	PM	2913	23.8±0.4	151	587
RW98-8	Aglar	Upstream of Yamuna Bridge	PM	1052	18.9±0.9	70.6	318
RW99-52	Aglar	Upstream of Yamuna Bridge	M	1139	17.9±0.6	70.8	328
RW98-2	Giri	Rampur Mandi	PM	1115	33.3±0.5	98.6	399
RW99-3	Giri	Rampur Mandi	S	2046	35.7±1.2	119	547
RW99-57	Giri	Rampur Mandi	M	881	24.9±0.6	80.3	348
RW98-3	Bata	Bata Mandi	PM	395	17.8±0.2	54.7	229
RW99-56	Bata	Bata Mandi	M	386	17.8±0.3	59.3	274
RW98-10	*Tons*	*Tons Pol*, Dehradun	PM	1226	10.7±0.4	87.9	384
RW99-65	*Tons*	*Tons Pol*, Dehradun	M	707	8.0±0.1	76.8	320
RW98-11	Asan	Simla Road Bridge	PM	975	5.7±0.3	104	479
RW99-61	Asan	Simla Road Bridge	M	822	5.9±0.1	101	461
RW99-60	Spring	Shahashradhara	M	15400	16.1±0.2	640	2412
Ganga							
RW98-34	Ganga	Rishikesh	PM	165	6.7±0.2	26.0	117
RW99-6	Ganga	Rishikesh	S	204	7.9±0.1	25.5	115
RW99-59	Ganga	Rishikesh	M	145	5.3±0.2	22.0	99
Mine Waters and Misc. samples							
RW99-8	Bandal	Near Maldeota	S	909	32.2±2.3	82.9	366
MW-1		Maldeota mines	S	4123	61.9±0.9	n.m.	n.m.
MW-2		Maldeota mines	S	4750	7.5±0.3	n.m.	n.m.
MW-3		Maldeota mines	S	2571	111±1	n.m.	n.m.
MW-4		Maldeota mines	S	6854	86.9±1.2	n.m.	n.m.

[a]RW - river water, MW - mine water. [b]S = summer, M = monsoon, PM = post-monsoon. U: upstream, D: downstream. [c]Re values are blank corrected, errors are ±2σ. ΣCat* = (Na*+K+Mg+Ca), Na* is Na corrected for chloride, major ion data from Table 4.1. n.m.: not measured.

In rivers, dissolved Re varies by about two orders of magnitude, during the three periods, from 0.5 to 35.7 pM (Table 5.1; Fig. 5.1), with an average of 9.4 pM (~1.8 ng ℓ^{-1}). This compares well with the discharge weighted Re concentration, 8.9 pM, in the Yamuna at Saharanpur suggesting that the Yamuna mainstream receives Re and water roughly in the same proportion till it flows at at the fothills. The average Re in the Yamuna system and in the Yamuna and the Ganga samples at Batamandi and Rishikesh respectively, near the foothills of the Himalaya, is significantly higher than the global average value of 2.1 pM, reported by Colodner et al. (1993b; their average value of 2.3 pM is reduced by 10% to correct for spike calibration, Colodner et al., 1995). Re concentrations of the Ganga water at Rishikesh varied between 5.3 to 7.9 pM during the three seasons, compared to ~14 pM for the Yamuna at Batamandi (downstream of Bata's confluence), both at the foothills of the Himalaya. Re concentration of the Ganga at Rishikesh is marginally lower than the value of 8.2 pM reported near its out flow at Aricha Ghat, Bangladesh (before the confluence of the Ganga and the Brahmaputra, data corrected for spike calibration Colodner et al., 1993b, 1995).

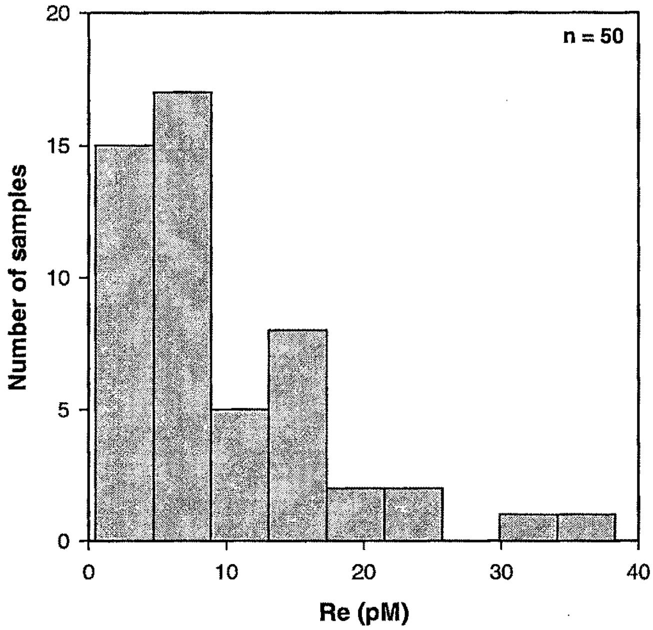

Fig. 5.1 Frequency distribution of dissolved Re in the Yamuna and its tributaries. The concentrations range from 0.5 to 35.7 pM with an average of 9.4 pM.

Dissolved Re concentrations show a significant positive correlation with ΣCations* (Fig. 5.2) and total dissolved solids (TDS) in these rivers albeit with some scatter (ΣCations* = Na*+K+Ca+Mg, where Na* is Na corrected for cyclic component). This is also reflected in the seasonal variations in the Re abundances. The waters collected during June (summer) often have both higher TDS and Re concentrations than those collected during October (post-monsoon) and September (monsoon) periods. Considering that the Yamuna and its tributaries drain different sub-basins with their own characteristic lithology and hence (Re/major ion) ratios, such a scatter is not unexpected. For example, the tributaries sampled in and around the foothills of the Himalaya have, in general, higher Re than the streams flowing in the upper reaches probably because of more widespread occurrences of organic rich sedimentary rocks in their drainage basins. Another contributing factor for the scatter in Fig. 5.2 could be seasonal variations in Re/ΣCations*. The intensity of weathering of different lithologies in the drainage basin and hence Re/ΣCations* of the rivers could be season dependent. It is also observed that Re/ΣCations* in the Tons and its tributaries are generally higher than those in the Yamuna and its tributaries.

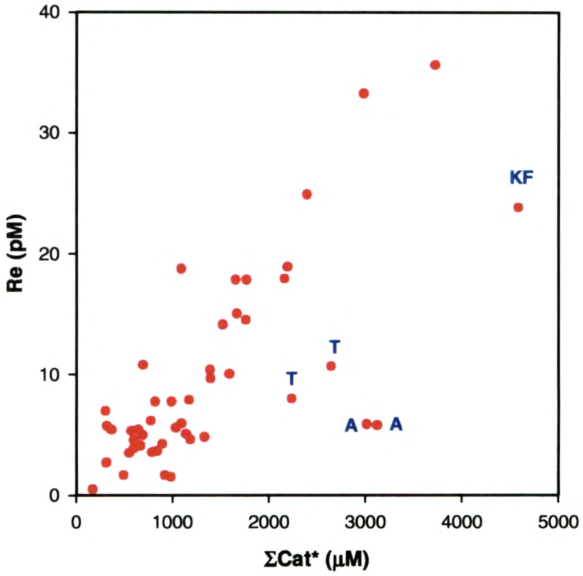

Fig. 5.2 Scatter diagram of Re vs. ΣCations in the water samples analyzed (excluding Shahashradhara sample). ΣCations* = Na*+K+Ca+Mg. The data show a strong positive correlation (r = 0.90, p<0.005) suggesting that Re and (Na*+K+Mg+Ca) are released to the rivers in roughly the same proportion along its entire stretch. Regression analysis excludes Kempti Fall (KF), Tons at Dehradun (T), and Asan (A) rivers which fall far outside the trend set by other rivers.*

The strong positive correlation between Re and ΣCations* (Fig. 5.2) is an indication that both of them are released to the rivers in roughly the same proportion throughout the drainage basin. Samples from the Kempti Fall, the Asan river, and the *Tons* at Dehradun (Table 5.1) plot significantly away from the trend set by the bulk of the samples (Fig. 5.2). The ΣCations* of these streams seem to have a significant evaporite component (Chapter 4) which may be contributing to their low (Re/ΣCations*) ratios. The observation, that the Shahashradhara sample (RW99-60, Table 5.1) having the highest SO_4 concentration, 15.4 mM has only ~16 pM Re, attests to the idea that evaporites are not a significant source of Re (Colodner et al., 1993b). The regression line (Fig. 5.2, r = 0.90) plotted through the data (excluding Kempti Fall, Asan, and *Tons* at Dehradun,) yields a (Re/ΣCations*) slope of ~9.9 pM mM^{-1} (~60 pg Re mg^{-1} ΣCations*). The implications of this, in determining the source of Re to these river waters, are discussed in the following sections.

5.2.1 Sources of dissolved Re in the YRS

(i) Re contribution from Crystallines

Granites and granodiorites, as already mentioned in Chapter 2 (Chapter 2, section 2.1.1), constitute a significant proportion of the Yamuna catchment particularly in its higher reaches. Previous studies (Pierson-Wickmann et al., 2000) have reported Re concentrations ranging from 26 to ~1430 pg g^{-1} (geometric mean ~270 pg g^{-1}) in granites and gneisses from the Central Nepal Himalaya. Peucker-Ehrenbrink and Blum (1998) reported Re concentrations for two samples of Precambrian granitoid rocks (gneiss) from Wyoming, 109 and 55 pg g^{-1}. In the present study, analysis of four granites from the Yamuna catchment yielded 14 to 46 pg g^{-1} of Re (Table 5.2).

The average Re in these four samples is about an order of magnitude lower than the mean Re in granites and gneisses from Nepal Himalaya, however, a critical comparison may not be appropriate considering that the samples analyzed are few and from different locations. If, however, this difference is indeed valid, then their conditions of formation and their mineralogical composition may be contributing to it. Taking a value of 50 pg g^{-1} Re for granites, (close to the maximum concentration measured in samples from the Yamuna catchment, Table 5.2), it can be estimated that about ~35 grams of them would have to be dissolved /leached per liter of Yamuna water to yield the average dissolved Re of 1.8 ng ℓ^{-1}. This requirement, as discussed below, is very difficult to be met either through congruent dissolution of crystallines or preferential release of Re from them.

Table 5.2 Re abundances in granites and Precambrian carbonates from the Himalaya

Granites[a]	**Re**	**Re/Na**		**Re/ΣCat**	
	pg g^{-1}	**pg mg^{-1}**	**pM mM^{-1}**	**pg mg^{-1}**	**pM mM^{-1}**
GR98-1(A)	45.8±1.9	1.25	0.154	0.69	0.103
GR98-1(B)	41.6±2.7	—	—	—	—
GR98-2	26.9±2.8	0.65	0.080	0.29	0.045
GR99-1	17.4±1.7	0.50	0.062	0.20	0.032
GR99-2	13.7±1.7	0.38	0.047	0.16	0.025
Mean	***26±14***	***0.7±0.4***	***0.09±0.05***	***0.3±0.2***	***0.05±0.04***

Carbonates[b]	**Re**	**Re/Ca**		**Re/Ca+Mg**	
	pg g^{-1}	**pg mg^{-1}**	**pM mM^{-1}**	**pg mg^{-1}**	**pM mM^{-1}**
KU92-9 (D)	54.0±5.1	0.32	0.069	0.21	0.037
KU92-43 (D)	30.4±0.9	0.24	0.052	0.16	0.027
KU92-48 (D)	35.6±1.0	0.17	0.037	0.11	0.018
HP94-42 (C)	~0	~0	~0	~0	~0
UK94-77 (D)	225±3	1.07	0.230	0.68	0.118
UK94-45 (C)	5.0±3.5	0.01	0.002	0.01	0.003
UK94-50 (C,D)	35.9±2.1	0.10	0.022	0.09	0.019
UK95-23 (D)	29.7±0.2	0.13	0.028	0.09	0.015
Mean	***52±72***	***0.26±0.34***	***0.06±0.07***	***0.17±0.21***	***0.03±0.04***

[a]Collected in and around Hanuman Chatti. [b] Samples and their Ca, Mg data from Singh et al. (1998), C: calcite, D: dolomite. (A) and (B) are duplicates.

Another approach to gauge the role of crystallines in contributing to dissolved Re is from the Re-ΣCations* scatter plot (Fig. 5.2). The slope of the Re-ΣCations* regression line, as mentioned earlier, is ~9.9 pM/mM. This is more than two orders of magnitude higher than the [Re/(Na+K+Mg+Ca)] ratio in crystallines ~0.05 pM mM^{-1} (0.3 pg mg^{-1}, Table 5.2). Comparison of these two ratios and the calculations to follow, suggest that crystallines can account only for a small fraction of dissolved Re in the YRS, if Re and (Na+K+Mg+Ca) from them are released to the rivers in the same proportion as their abundance. Using the mean Re/(Na+K+Mg+Ca) in granites 0.3 pg mg^{-1} (Table 5.2) and ΣCat* in the YRS rivers, it is estimated that silicates can contribute ~2 to 45 pg ℓ^{-1} Re (mean: ~13 pg ℓ^{-1}) to these rivers. This estimate, based on the assumption that *all* dissolved major cations are derived from crystallines, would be an *upper limit* as a significant fraction of Ca and Mg in these waters is from carbonates and/or evaporites (Chapter 4). Therefore, to obtain a more realistic estimate of Re contribution from the crystallines, calculation was done using Na as an index of silicate weathering. Comparison of Re/Na ratio in crystallines with Re/Na* in rivers reinforces our earlier inference that weathering of crystallines is not an important source of Re to the Yamuna waters (Fig. 5.3). The Re contribution to the YRS waters, based on their Na* content and the mean Re/Na ratio in crystallines, ~0.09 pM mM^{-1} (~0.7 pg mg^{-1}, Table 5.2) is in the range of ~0.1 to 4 pg ℓ^{-1} (mean: ~2 pg ℓ^{-1}). This estimate is based on the assumption that Re and Na are supplied from silicates to the rivers in the same proportion as their abundances. The estimated contribution accounts for less than one percent of the mean dissolved Re in the Yamuna system. This conclusion would be valid even if a much higher average Re concentration is used for the crystallines, ~270 pg g^{-1} (geometric mean of the values reported by Pierson-Wickmann et al., 2000).

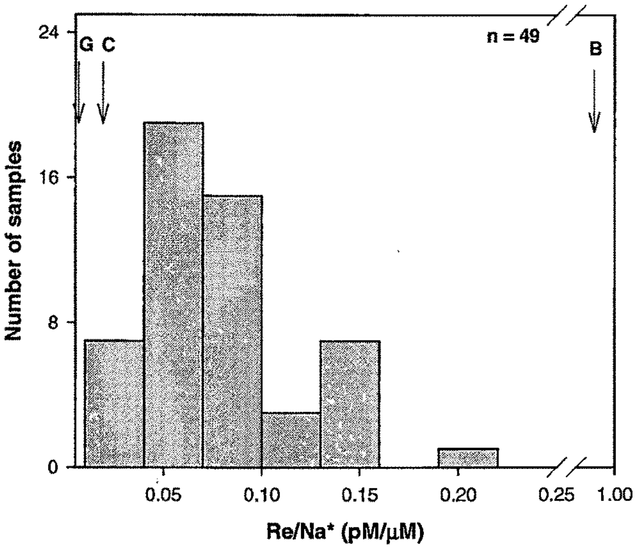

Fig. 5.3 Frequency distribution of Re/Na in the water samples. The ratio varies between 0.01 to 0.21 pM/μM with a mean of 0.08. Typical ratios for granites from the Yamuna catchment (G), Precambrian carbonates (C) and Black shales from the Lesser Himalaya (B) are also shown. Data for Kempti Fall is not plotted.*

The role of preferential release of Re to solution from crystallines is more difficult to assess. One approach is to assume that all the suspended matter in the Yamuna system is derived from crystallines and that all Re in them is released to solution during weathering. Both these assumptions may be quite exaggerated (cf. Peucker-Ehrenbrink and Blum, 1998), however, the estimates based on them can place useful constraints. Using a suspended matter concentration of ~2 g ℓ^{-1} (Subramanian and Dalavi, 1978; Hay, 1998) and assuming them to be derived entirely from crystallines with 50 pg g^{-1} Re in them, the maximum Re supply would be ~100 pg $\ell^{-1}$of Re, only a few percent of the average Re abundance in these rivers. This contribution may increase by a factor of ~2 if the recent estimate of Galy and France-Lanord (2001) on the total erosion in the Himalaya is considered. Their results suggest that the contribution of bed load and flood plain deposition is comparable to the sum of suspended and dissolved loads. A similar conclusion is also borne out for the Ganga at Rishikesh if the granites analyzed in this work (Table 5.2) are taken to be representative of its catchment. Calculation of the impact of preferential release of Re from suspended matter for individual rivers and streams has not been attempted due to non availability of suspended/bed load data.

Thus, if granites analyzed in this study (Table 5.2) are typical of the crystallines of the Yamuna and the Ganga catchments in the Himalaya, then the present results show that on an average these lithologies can make only a minor contribution to the dissolved Re budgets of the Yamuna and the Ganga rivers on a basin wide scale. However, for rivers with low Re (e.g. Didar Gad, 0.1 ng ℓ^{-1}, Table 5.1) the contribution by preferential leaching can become significant if they have suspended matter concentrations comparable to those of the Yamuna and if a large fraction of their Re can be mobilized. The later requirement, as already discussed, may be difficult to comply.

The strong positive correlation between Re and ΣCations* in the Yamuna system (Fig. 5.2) is intriguing in light of the above calculations and conclusions and suggests the need for a source with significantly higher Re/(Na + K + Mg + Ca) or Re/Na compared to those in the granites of the Yamuna catchment (Table 5.2). Pierson-Wickmann et al. (2000) reported one gneiss sample with ~1430 pg g^{-1} Re from Nepal Himalaya. Such Re rich crystallines or organic rich sediments, which are known to be abundant in Re, could fit in the requirement (see later section on black shales). More analysis of Re in crystallines is necessary to assess the distribution of Re rich granites and gneisses in the Yamuna and the Ganga catchments and to determine if they are abundant and typical. From the data available at present, however, the crystallines seem to be only a minor source of dissolved Re to the Yamuna and Ganga waters in the Himalaya.

(ii) Re contribution from Precambrian Carbonates

Precambrian carbonates (calcites and dolomites), occurring in the drainage basins of the headwaters of the Yamuna and the Ganga in the Lesser Himalaya, significantly influence their water chemistry, contributing bulk of the total cations in them (Sarin et al., 1989; Chapter 4). Dissolved Re shows positive correlation with Ca and alkalinity, which dominate the cation and anion budgets in the YRS respectively. The regression line through the data points (excluding the *Tons* at Dehradun and the Asan, which fall far away from the line) has a slope ~0.019 pM Re/μM Ca with r^2 = 0.79 (Fig. 5.4). It is tempting to infer, from this observation, that major source of Ca (carbonates) might also be contributing significantly to the dissolved Re of these waters. To test this, Re was measured in the Precambrian carbonates of the Lesser Himalaya.

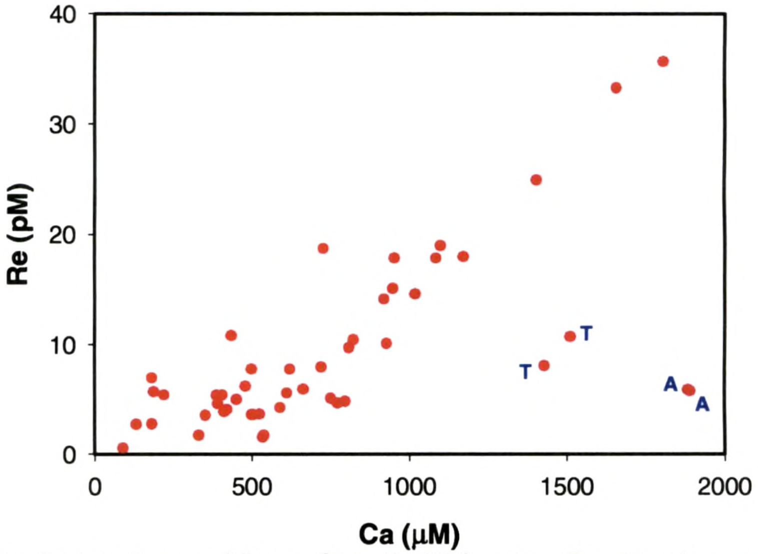

Fig. 5.4 Scatter diagram of Re vs. Ca in the YRS waters. The data show a strong positive correlation (r^2 = 0.79). Regression analysis excludes Tons at Dehradun (T), and Asan (A) rivers which fall outside the trend set by other rivers.

The Re abundances in the Precambrian carbonate outcrops from the Lesser Himalaya (both calcites and dolomites), based on the analysis of nitric acid *leach* of eight samples vary from ~0 to 225 pg g^{-1} with an average of 52 pg g^{-1} (Table 5.2). Pierson-Wickman et al. (2000) reported values of 187, 273 and 1160 pg g^{-1} Re for three *whole rock* limestone/marble samples from the Nepal Himalaya. These values are higher than those measured in this study. This can be because of a variety of reasons, such as difference in leach vs. whole rock concentrations, the extent and nature of metamorphism of carbonates and abundance of Re rich phases in them. Among the samples analyzed (Table 5.2), the two calcites have the lowest Re, ≤5 pg g^{-1}. If data in Table 5.2 can be considered typical of calcites and dolomites, then it would suggest that dolomites incorporate in them measurable quantities of Re during their formation or that they contain minor amounts of Re rich phases such as organic matter. The Re concentrations of these samples do not seem to show any discernible trend with their $^{87}Sr/^{86}Sr$, the Re content of the sample KU92-43 with a high $^{87}Sr/^{86}Sr$, 0.8786 (Singh et al., 1998) is very similar to other samples with lower $^{87}Sr/^{86}Sr$. This is an indication that metamorphic alteration of these carbonates may not have caused substantial modification of their Re abundances. Using the highest measured concentration, 225 pg g^{-1} as typical of Re in these carbonates, it can be estimated that on an average, Re from ~8 grams of them needs to be supplied per liter of Yamuna waters to give rise to the average 1.8 ng $\ell^{-1}$of dissolved Re. As in the case of crystallines discussed above, this requirement is also almost impossible to comply with. Using Ca+Mg in the YRS waters (Table 4.1, Chapter 4) and Re/(Ca+Mg) in the Pc carbonates (Table 5.2), their contribution to the dissolved Re can be estimated. This estimate assumes (i) all Ca and Mg in the waters are derived from carbonates, (ii) Re, Ca and Mg are released to the waters in the same ratio as their abundances and (iii) once supplied to the rivers, Re, Ca and Mg behave conservatively. Using the maximum value of Re/(Ca+Mg), 0.12 pM mM^{-1} (0.7 pg mg^{-1}, Table 5.2), it is estimated that carbonates can contribute ~3 to 105 pg ℓ^{-1} (with a mean ~30 pg ℓ^{-1}) to the YRS waters, less than 2% of their average Re concentration. A similar conclusion also results for Re in the Ganga at Rishikesh. As the carbonate content of suspended matter is quite low (between 0.1 to 7 % in the bed load of Yamuna, Table 4.2) its selective leaching is also unlikely to be a significant source of dissolved Re to the waters. Assuming that the suspended and bed load in the YRS waters (~4 g ℓ^{-1}) have 5% carbonates with 225 pg g^{-1} Re in them (the maximum Re in the carbonates analyzed, Table 5.2) and all Re is leached from them, it is estimated that carbonates account for ~45 pg ℓ^{-1}, <3 % of the average dissolved Re. The slope of the regression line in the Ca-Re plot (Fig. 5.4), ~0.019 pM Re/μM Ca, is more than two orders of magnitude higher than the average Re/Ca in the Precambrian carbonates, $\sim 5\times10^{-5}$ pM/μM, attesting to the earlier estimates that these carbonates play only a minor role in contributing to dissolved Re in the YRS streams/rivers. Thus, it is evident from the present study that Precambrian carbonates of the Lesser Himalaya are not a major contributor to the Re budget of the Yamuna River System. If, however, there are wide spread occurrences of carbonates with high Re abundance (such as the limestone with 1160 pg g^{-1}, Pierson-Wickmann et al., 2000) in the Yamuna and the Ganga catchments, their leaching can contribute significantly to the dissolved Re in these rivers.

Hodge et al. (1996), based on the similarity in Re/Mo/U ratios in groundwater draining carbonate aquifers from Southern Great Basin, USA and that in seawater, suggested that these elements are sequestered quantitatively by carbonates during their precipitation from seawater and are subsequently released to groundwater during their weathering. The results obtained in this study, on the Re abundances in Precambrian calcites and dolomites of the Lesser Himalaya and in rivers draining them, lead to the conclusion that at least for these rivers such carbonates are not a significant source of Re. The average Re/Ca in the Precambrian carbonates analyzed in this study (~0.05 pM/mM, this is obtained by taking the ratio of average Re in the carbonates analyzed in this study given in Table 5.2, 52 pg g^{-1} and average Ca in the Pc carbonates, 24.3%, Singh et al., 1998) and that in calcareous oozes (Colodner et al., 1993b) from the major ocean basins (~0.025 pM/mM) is nearly two orders of magnitude lower than that in seawater ~4 pM/mM. This coupled with the observation that burial of Re in suboxic and reducing marine sediments is its primary sink in the ocean (Colodner et al., 1993b; Morford and Emerson, 1999; Crusius and Thomson, 2000), points out the need to re-evaluate the suggestion that Re is quantitatively scavenged by carbonates during their precipitation from seawater and that they form an important source of Re to groundwaters (Hodge et al., 1996).

(iii) Re contribution from organic rich sediments

The hypothesis that weathering of black shales can be an important source of dissolved Re to rivers comes from the work of Colodner et al. (1993b). Their hypothesis is based on the observations of high Re concentrations in some of the tributaries of the Orinoco draining black shales and bituminous limestones and the strong correlation between Re and SO_4 in the waters. The knowledge that Re is highly enriched in black shales relative to its crustal abundance (Ravizza and Turekian, 1989) and that these organic rich sediments are more easily weatherable further supports their suggestion.

In the present study, there is evidence of the dominant role of weathering of black shales and other organic rich sediments in contributing dissolved Re to the headwaters of the Yamuna and the Ganga in the Himalaya. Firstly, there are reports of exposures of greyish black and black shales in the Lesser Himalaya (Valdiya, 1980) and association of carbonaceous matter with the crystallines and carbonates (Gansser, 1964; Valdiya, 1980) many of which form part of the drainage basins of the Giri, the Aglar and the Bata, tributaries of the Yamuna. These rivers have dissolved Re concentrations about a factor of 2-4 higher (Table 5.1) than the average for the YRS. The river Bandal draining black shale deposits near Maldeota mines has Re as high as 32.2 pM (Table 5.1).

The black shales in the Lesser Himalaya have Re concentrations spanning a wide range, 0.2 to 264 ng g^{-1} (Table 5.3, Singh et al., 1999 had designated all shale samples they analyzed as black shales, though some of them had C_{org} <1% wt. The same convention is also followed here). Among these samples, those from the underground mines, which are better preserved, have higher Re (3.1 to 264 ng g^{-1}) and C_{org} (1 to 7.3% wt.), compared to surface outcrops (Re: 0.2 to 16.9 ng g^{-1} and C_{org}: 0.2 to 5.9% wt.) indicating that Re and C_{org} are lost during weathering. This inference is also supported by more recent results of Peucker-Ehrenbrink and Hannigan (2000) on Re abundances in black shale weathering profiles from Utica Shale, Quebec.

Table 5.3. C_{org}, Re, Os and U in black shales from the Lesser Himalaya[a]

Element		Outcrop		Mine		All samples
	n	range	n	range	n	(X/Re)[b]
C_{org} (wt %)	19	0.21 - 5.85	14	1.01 - 7.28	26	~2×10^7
Re (ng g^{-1})	14	0.22 -16.9	14	3.05 - 264	28	—
Os (ng g^{-1})	16	0.02 - 4.13	14	0.17 - 13.5	25	0.05
U (µg g^{-1})	—	—	8	16.6 - 94.8	8	1900

[a] C_{org}, Re and Os, from Singh (1999), U this study, n = number of samples. [b] working ratio used in calculations, C_{org}/Re is molar ratio, Os/Re and U/Re in ng ng^{-1}.

The mobility of Re during weathering is also borne out from the analysis of water percolating through the phosphorite-blackshale-carbonate layers of Maldeota mines, near Dehradun, (MW-1—MW-4, Table 5.1). Three of the four mine waters have dissolved Re factors of 2-3 higher than the maximum river water Re concentrations measured in this study (Table 5.1) with the highest value ~21 ng ℓ^{-1} (111 pM). All these data provide evidence that black shales can release high concentrations of Re to waters draining them. Since black shales (and other organic rich sediments) are generally associated with pyrites, their oxidative weathering produces sulfuric acid that attacks these shales as well as other rocks associated with them releasing SO_4 and a host of cations to waters. Hence Re, SO_4 and the cations released to waters from weathering of such sediments is very likely to show a positive correlation with each other (Colodner et al., 1993b). Indeed, a significant correlation between Re and SO_4 in these waters has been observed (Fig. 5.5) supporting the idea that black shales are an important source of dissolved Re to these rivers (Fig. 5.5 is a log-log plot of Re as SO_4 concentrations range over two to three orders of magnitude). It is seen from Fig. 5.5 that the data of three of the four mine water samples are also consistent with the trend of Yamuna waters. Statistical analysis of the data in Fig. 5.5 yields a correlation coefficient of 0.84 (n = 53) which becomes 0.83 if the four mine waters are excluded. The scatter in Fig. 5.5 probably results from supply of SO_4 to the waters from evaporite dissolution (Chapter 4) and/or the presence of multiple end members with different Re/SO_4 ratios. The wide range in Re/SO_4 of mine waters (Table 5.1) is an indication for the

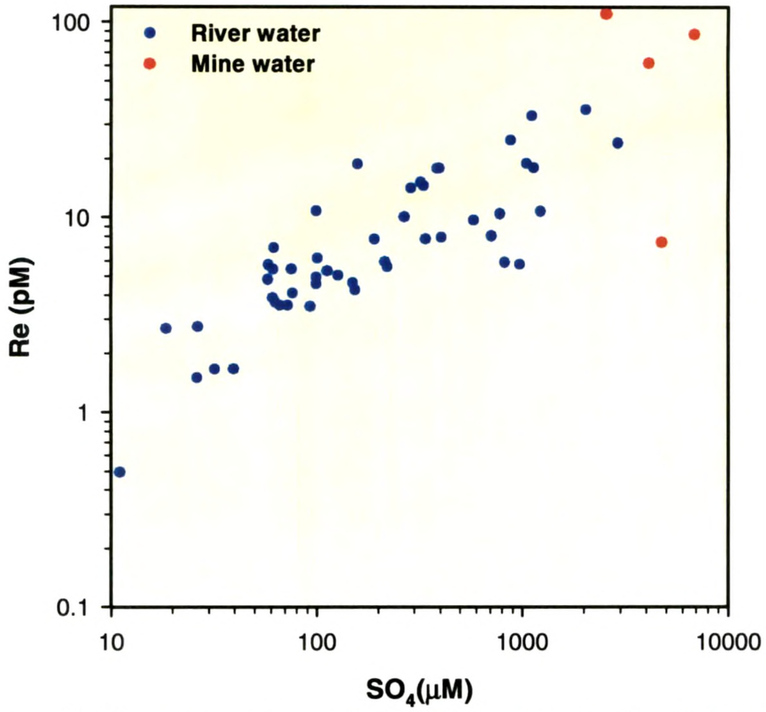

Fig. 5.5 Re-SO_4 scatter plot on log-log scale. Data for the YRS (excluding Shahashradhara sample) and mine waters are presented. Three of the four mine waters analyzed also fall in the trend set by the YRS data. The significant correlation ($r = 0.84$, $p < 0.005$) between Re and SO_4 supports the hypothesis that black shale weathering is a major source for dissolved Re to these waters.

occurrence of various end members and/or dilution effect caused by mixing with SO_4 from evaporites. As mentioned earlier, Re also shows positive correlation with Ca and alkalinity. This suggests that sulphuric acid released via pyrite oxidation weathers, in addition to black shales, carbonates associated with them with a consequent release of Re, Ca, SO_4 and alkalinity to waters. But Ca and alkalinity when normalized with SO_4 show a negative correlation with Re suggesting that very little dissolved Re is associated with Ca and alkalinity released via dissolution of carbonates by carbonic acid (hence not associated with SO_4).

An important consideration in assessing the role of black shales and other carbonaceous sediments as a major source of Re to the Yamuna waters is their volumetric abundance and distribution in their drainage basins. The occurrence of black shales and carbonaceous sediments, though, are reported in the Lesser Himalaya (Gansser, 1964; Valdiya, 1980), there is no quantitative data on their areal coverage, abundances and distribution in the river basins. The paucity of such data makes it difficult to attest the inference drawn earlier, based on geochemical evidences, that these sediments are a major supplier of Re to the Yamuna waters. The geochemical data, however, allow us to make rough estimates on the quantity of organic rich sediments that needs to be weathered to account for the measured dissolved Re in the Yamuna waters. The average Re concentration in black shales in the Lesser Himalaya, based on both the outcrop and underground mine samples, is ~30 ng g^{-1} (Singh et al., 1999). Taking this as the typical Re concentration in black shales of the Yamuna basin, it can be estimated that on an average all Re from ~60 mg black shales will have to be released per liter of river water to yield 1.8 ng ℓ^{-1} Re. If Re is mobilized preferentially and the weathered black shales are added to the particulate load of the rivers, it would make up 1-2 % of the total abundance of their suspended and bed loads. These calculations are based on the assumption that *all* Re from the black shales be released to rivers and hence the estimates of black shales required to account for the dissolved Re in the YRS are *lower limits*. These estimates require that black shales occur at least at levels of a few percent in the drainage basin. The available data, as mentioned earlier, is not sufficient to determine if they occur in such abundance. Pierson-Wickmann et al. (2000) in attempting to balance Os isotope composition in river bedloads from the Nepal Himalaya also came to the conclusion that the abundance of black shales in the catchment has to be at a few percent level, a requirement which they indicate may be difficult to comply with. Further, to explain the strong positive correlation between Re and ΣCations* (Fig. 5.2) it would require that black shales and other reducing sediments be dispersed throughout the drainage basin such that both Re and ΣCations* are released to rivers in roughly the same proportion along their entire stretch in the Himalaya.

In addition to black shales, other reducing sediments and Re rich phases (e.g. sulfides) could also serve as source(s) to dissolved Re. In this context, recent studies of Re in mildly reducing suboxic sediments show that they are a dominant sink for Re in the oceans (Morford and Emerson, 1999; Crusius and Thomson, 2000). The role of such sediments in contributing to the Re budgets of rivers in the Himalaya needs to be assessed. It is also interesting to note that even at Hanuman Chatti, near the origin of the Yamuna, where the predominant lithology is of granitic-granodioritic composition, the Yamuna water has Re concentration as high as 1 ng ℓ^{-1} (Table 5.1). Calculations based on Re in granites (Table 5.2) do not allow such high Re concentrations to be achieved from their weathering and suggest the need of Re rich phases. There are reports of organic matter associated with these rocks (Valdiya, 1980) and sulphide mineralization at places upstream of Hanuman Chatti (Jaireth et al., 1982), either or both of which may be contributing Re to these waters, however, their analysis is required to verify such a speculation. Silicates of sedimentary origin and with widespread occurrence in the YRS basin, could be another possible source of dissolved Re to the rivers. This speculation results from higher abundance of organic matter in such sediments. There is no data available on Re abundances in them.

The role of crystallines, Precambrian carbonates and black shales in determining the composition and Re abundances of the Yamuna System is summarized in the Ca/Na* vs. Re/Na* plot (Fig. 5.7). The plot also presents the average Ca/Na and Re/Na ratios of these lithologies from the Lesser Himalaya (Table 5.4).

Considering that bulk of the drainage of the YRS lies in the Lesser Himalaya, for mixing calculations the average abundances of Ca and Na in the Lesser Himalaya crystallines have been used. Ca/Na ratio in the LH crystallines (R_1) is calculated to be 0.34 μM μM^{-1} (Table 5.4).

Table 5.4 Ca, Na and Re abundances in various lithologies from the Lesser Himalaya

End member	Ca (% wt)	Na (% wt)	Re (pg g^{-1})	Ca/Na (μM/μM)	Re/Na (pM/μM)
LH Crystallines	1.04	1.76	26	0.34	0.0002
Pc Carbonates	24	0.03	52	460	0.02
LH Black shales	0.67	0.58	30000	0.68	0.66

[$R_1 = \frac{\bar{C}_{Ca}}{\bar{C}_{Na}}$ where $\bar{C}_{Ca}$ and $\bar{C}_{Na}$ are average Ca and Na concentrations in the LH crystallines (1.04% wt. and 1.76% wt. respectively). This value is different from the average Ca/Na ratio for LH crystallines reported by Krishnaswami et al. (1999), 0.46±0.28 as they had calculated the ratio (R_2) as: $R_2 = \Sigma R/N$ where R is the (Ca/Na) ratios in the individual samples and N is the number of samples for which the data was compiled. Similarly, the difference in the Re/Na in the LH crystallines, listed in Table 5.4 and in Table 5.2, is due to the difference in approach and database used for calculations. The Re/Na in Table 5.4, 0.0002 pM μM^{-1}, is the ratio of average Re in granites analyzed in this study and average Na for the LH crystallines whereas that in Table 5.2, ~0.0001 pM μM^{-1}, is the average of the Re/Na in the individual four granite samples]. In the calculations made for the plots in Fig. 5.7, Re in LH crystallines and Pc carbonates are from present study, Na and Ca in the Precambrian carbonates are from Mazumdar (1996) and Singh et al. (1998) and all the black shale data from Singh (1999).

The ratios of concentrations of elements C_1 and C_2 in a mixture of two components (1 & 2) were calculated as:

$$\left(\frac{C_1}{C_2}\right)_{mix} = \frac{X_{comp1}C_{1,comp1} + X_{comp2}C_{1,comp2}}{X_{comp1}C_{2,comp1} + X_{comp2}C_{2,comp2}}$$

where $C_{1,comp1}$ and $C_{1,\ comp2}$ are the concentrations of element C_1 in component 1 and component 2 respectively, $C_{2,comp1}$ and $C_{2,\ comp2}$ are the concentrations of element C_2 in component 1 and component 2 respectively, X is the mixing proportion so that X_{comp1} and X_{comp2} add to 100%. In the first step, such mixing calculations were performed for elements (Re, Ca and Na) in the mixtures with various proportions of two components, crystallines and Pc carbonates. From these calculations, it is seen that Ca/Na* in the waters is by and large a mixture of ~40-70% Precambrian carbonate end member with the balance from an end member having LH crystalline composition. (Fig. 5.6).Hence in the next step, these two different mixtures, were fixed as components to which various proportions of black shales were added using the above equation.

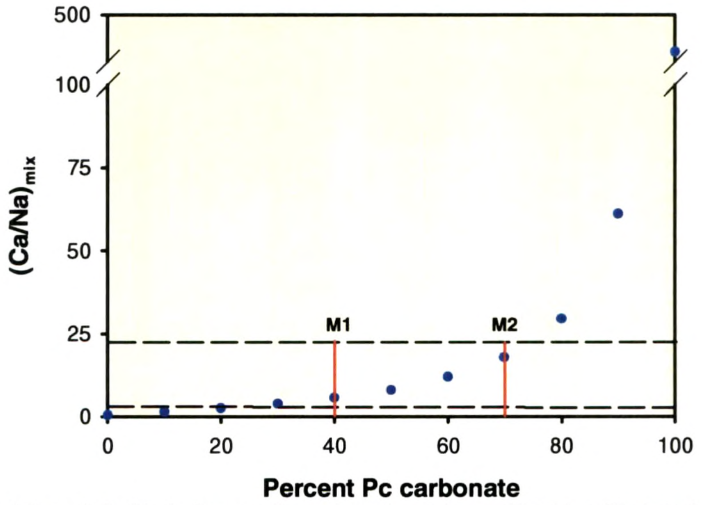

Fig. 5.6 Variation of Ca/Na in the granite-carbonate mixtures. The blue filled circles represent the mixture proportions with their Ca/Na, the horizontal dashed lines mark the limits for Ca/Na in the YRS waters. It is seen that Ca/Na in bulk of the water samples can be explained by a mixture of 40% carbonate+60% crystalline (M1) and 70% carbonate+30% crystalline (M2).

The Re/Na* in these carbonate-crystalline mixtures is only ~5×10^{-4} about two orders of magnitude lower than those measured in river waters, ~5×10^{-2}. Addition of 10-30% of an end member having Re/Na as in LH black shales, to this carbonate-crystalline mixture would yield Re/Na* values similar to the measured ratios in waters (Fig. 5.7). Thus it is seen that several percent contribution from black shale end member is required to reproduce the Re/Na* measured in the Yamuna and the Ganga waters. These estimates rely on the assumption that Ca/Na and Re/Na are released to waters from the crystallines, carbonates and black shales in the same ratio as their abundances. Considering that Re is a redox sensitive element and that in reducing sediments it may be associated with organic matter (Peucker-Ehrenbrink and Hannigan 2000; Crusius and Thomson, 2000) it is possible that during weathering Re is more rapidly and readily lost compared to Na. If, for example, the Re/Na released to the waters from black shale weathering is five times their abundance ratio, then the proportion of black shales required to match the measured ranges of Re/Na in the YRS reduces to ~1-5% (Fig. 5.8). Thus it is seen that to account for measured Re abundances and

Re/Na ratios in the YRS, several percent contributions from black shales/organic rich sediments are required. Currently available data on these lithologies are insufficient to determine if such a requirement can be met.

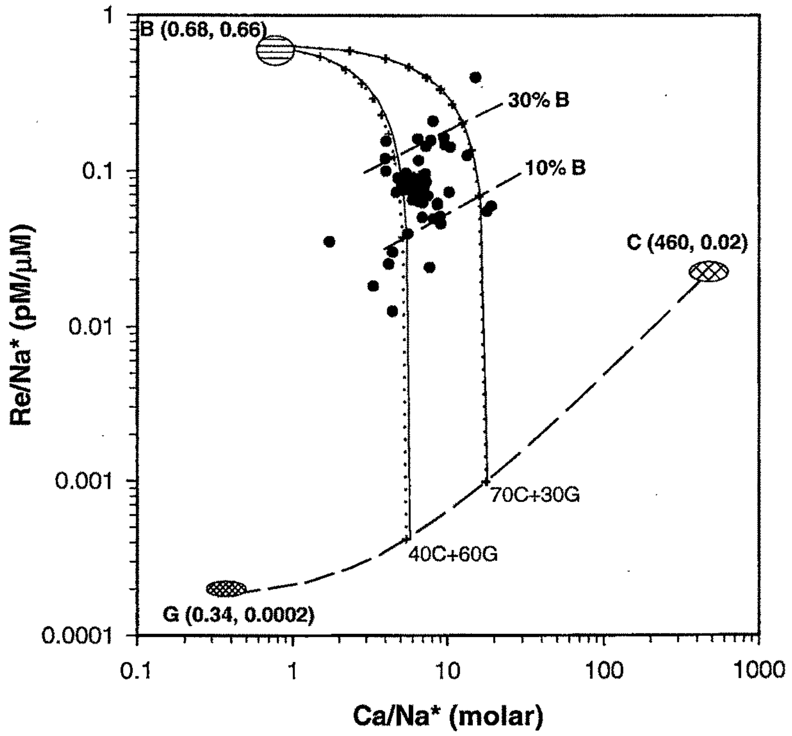

Fig.5.7 Re/Na vs Ca/Na* plot for the waters analyzed. The points plot within the mixing space bound by the three end members; crystallines (G), Precambrian carbonates (C) and LH black shales (B). The dotted evolution line calculated on the basis that Ca/Na and Re/Na are released to waters in the same ratio as their abundances in the three end members. The Ca/Na* in the waters is governed by and large by mixing between crystallines and carbonates, whereas Re/Na* is predominantly controlled by contribution from black shales. The solid line represents the evolution in which the Ca/Na ratio released to the waters from the granites is twice their abundance ratio. The proximity of the solid and dotted lines is an indication that the Ca/Na in the granite-carbonate mixture is not significantly affected by the preferential release of Ca (over Na) from granites.*

Data on Re/Na and Ca/Na in streams draining monolithologic units and/or laboratory leaching experiments with various rock types would help in better constraining the sources of dissolved Re of rivers.

This study reveals that organic rich sediments such as black shales could be a major source of dissolved Re to the river waters and hence "closed system" assumption required for their chronology by Re-Os systematics may not be satisfied in all cases. Therefore, to achieve a valid Re-Os isochron, it is necessary to ensure the "pristine" character of the rock samples to be dated. Open system behavior of Re and Os involving their differential mobility, owing to their different geochemistry in the natural oxic environment, may yield isochron ages different than the true depositional ages of the sediments. That differential mobility of Re and Os from black shales during weathering can disturb the Re-Os isochron was borne out from the studies of Peucker-Ehrenbrink and Hannigan (2000) and Jaffe et al. (2000).

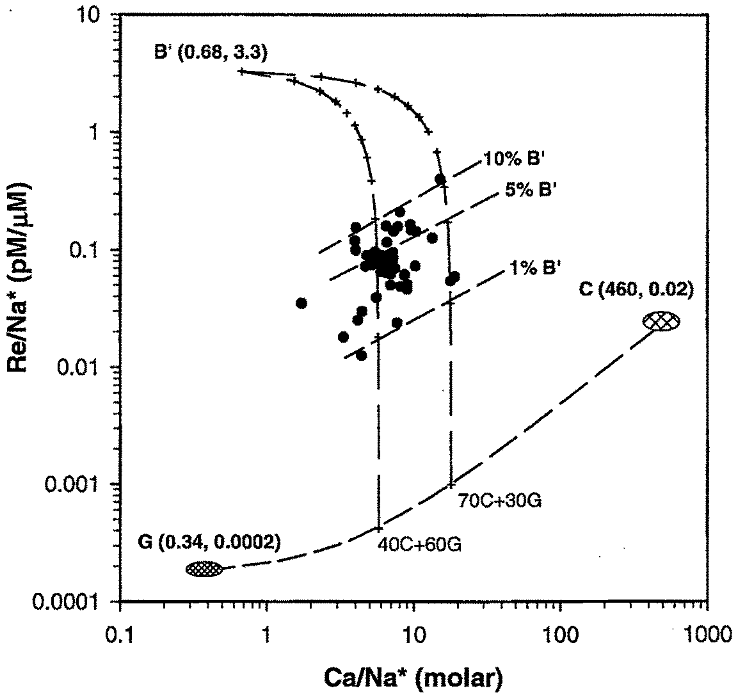

Fig. 5.8 Three end member mixing diagram as in Fig. 5.7. Mixing calculations done by assuming preferential release of Re over Na from the black shales, the Re/Na in solution being five times their abundance ratio. It is seen that the proportion of black shales needed to explain the Re/Na in the river waters reduces to 1 to 5% from 10 to 30% (Fig. 5.7).*

5.2.2 Re Flux from the Yamuna and the Ganga basins

The dissolved Re fluxes from the Yamuna and the Ganga at the foothills of the Himalaya have been determined from the data in Table 5.1. These calculations, based on Re concentrations in September (peak flow), yield ~150 and ~100 moles y^{-1} Re from the Yamuna at Batamandi and Saharanpur respectively and 120 moles y^{-1} from the Ganga at Rishikesh. [These values differ from the earlier reported values of Dalai et al. (2000) for two reasons. Firstly, the fluxes of the Yamuna and the Ganga in Dalai et al. (2000) are presented in reverse order; they should have been reported as 200 and 120 moles y^{-1} instead of 120 and

200 moles y^{-1} as given. The value of ~200 moles y^{-1} from the Yamuna basin is based on its Re concentration at Batamandi and water discharge at Okhla-Delhi (13.7×10^{12} ℓ y^{-1})]. The Yamuna (at Batamandi) and the Ganga (at Rishikesh) together contribute 270 moles Re per year at their outflow at the foothills of the Himalaya (Table 5.5). This constitutes ~0.4% of global Re flux (Colodner et al., 1993b), about thrice their contribution to the global water discharge (~0.1%). The flux calculation also shows that Re is released from the catchment of these rivers in the Himalaya at a rate of ~6-16 mmoles km^{-2} y^{-1}, an order of magnitude higher than the global average (Table 5.5).

Table 5.5 Re fluxes from the Yamuna and the Ganga at the base of the Himalaya

River	Location	Discharge (10^{12} ℓ)	Area (10^3 km^2)	Re (pM)	Flux (moles y^{-1})	Flux (mmoles km^{-2} y^{-1})
Yamuna[a)]	Batamandi	10.8	9.6	14.1	150	16
Ganga	Rishikesh	22.4	19.6	5.3	120	6
Ganga[b)]	Aricha Ghat	450	975	8.2	3700	4
Global[b)]		36000	101000	2.1	75000	0.7

[a)] based on Re of sample RW99-55 (Table 5.1) and discharge at Tajewala, few tens of kilometers downstream of Batamandi. [b)] Re concentrations for Ganga at Aricha Ghat and Global average from Colodner et al. (1993b)

It is important to note that the dissolved Re concentration in the Ganga at Rishikesh, 5.3-7.9 pM, is similar to that in the Ganga at Aricha Ghat before its confluence, 8.2 pM (Colodner et al., 1993b). This would suggest that other tributaries joining the Ganga after it drains past the Himalaya at Rishikesh add Re and water in the same proportion as they are at Rishikesh.

These estimates of Re flux from the Yamuna and the Ganga at the foothills of the Himalaya is disproportionately high compared to their contribution to water discharge. The available data for the Ganga at Aricha Ghat also shows a similar trend. The impact of this impact on a global scale is not pronounced as the drainage area and water discharge of these rivers are only a small fraction of the global value. However, if all Himalayan rivers exhibit a trend similar to that of the Ganga, then supply from these rivers could be a major component of the Re budget of the global rivers. Sarin et al. (1990) reported that the weathering rate of uranium in the Himalaya is about a factor of ten higher than the global average. Similarly, based on Os abundances in the Ganga waters (Levasseur et al., 1999) it can be estimated that Os is released by weathering from the Himalaya at a rate of about three times the global average. These estimates show that chemical weathering in the Yamuna and the Ganga basins liberates Re, Os and U in amounts disproportionately higher than their contribution to global water discharge and drainage area.

In the previous sections it was discussed that black shales exert dominant control on the Re budgets of the Yamuna and the Ganga rivers. This makes it possible to use Re a proxy to estimate the quantity of black shales being weathered in the Yamuna and Ganga basins. Based on the Re flux (Table 5.5) and using 30 ng g^{-1} Re as an average, it is estimated that ~$(6\text{-}9)\times10^{8}$ kg of black shales are being weathered annually in the Yamuna and the Ganga basins in the Himalaya. This estimate assumes that all Re in rivers is from the black shales. If a part of Re is from other sources, then the quantity of black shales weathered would be lower than that calculated above.

5.2.3 Black shale weathering: Implications to riverine trace metal budgets and carbon cycle

Black shales, in addition to Re, are abundant in carbon, PGE and redox sensitive metals such as V, U and Mo (Horan et al., 1994; Peucker-Ehrenbrink and Hannigan 2000). Their oxidative weathering can also release these elements and CO_2 in addition to Re to the river waters draining them (Petsch et al., 2000; Peucker-Ehrenbrink and Hannigan 2000). We have evaluated the influence of black shale weathering on the budgets of some of these elements in the Yamuna and the Ganga rivers based on available data on Re, Os and U in rivers and Re, Os, U and organic carbon in black shales (Table 5.3, Singh et al., 1999). These calculations assume that all Re in the YRS are of black shale origin.

The Os/Re weight ratios in black shale samples from the outcrops and under ground mines overlap with each other and center around a value of 0.05±0.03 (Singh et al., 1999). If Re and Os are supplied to rivers in the same ratio as their abundance in black shales, then it can be estimated from Os/Re in them and Re content of the Ganga at Rishikesh (1.0 ng ℓ^{-1}, Table 5.1) that black shales would contribute about 20-80 pg of Os per liter of water. This estimate is significantly higher than the Os measured in the Ganga water at Rishikesh (6.2 pg ℓ^{-1}, Levasseur et al., 1999) indicating that black shale weathering can account for the dissolved Os levels in the Ganga. It is also interesting to note that the estimated Os value is similar to the desorbable Os concentration, as determined by leaching the Ganga bed sediments at Patna (30 pg ℓ^{-1}, Pegram et al., 1994). The Os/Re in the Ganga at Rishikesh and at Rajashahi (based on Os data of Levasseur et al., 1999 and Re from present study and Colodner et al., 1993b) is ~0.006, an order of magnitude lower than those in the Lesser Himalayan black shales. This would suggest that Os is less mobile than Re during weathering of black shales and/or that the Os released is removed by scavenging on to the sediment surfaces by Fe-Mn oxyhydroxides. The geochemical behaviour of Re, i.e. inertness and stability of ReO_4^- in oxygenated aqueous environment (Koide et al., 1986; Colodner et al., 1993b) and the particle reactivity of Os (Williams et al., 1997; Levasseur et al., 2000) would favour the latter hypothesis, that it is removed from dissolved phase to particulates to explain the low Os/Re in rivers. The presence of significant desorbable component of Os in river sediments further attests to this hypothesis (Pegram et al., 1994; Pierson-Wickmann et al., 2000). The available data on Os and Re abundances in black shale weathering profiles show evidence for differential mobility of Re and Os (Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2000). It is, however, difficult to assess from these results whether Re is more mobile than Os or vice versa. The results of Peucker-Ehrenbrink and Hannigan (2000) show that in three of the four profiles Os is lost from black shales more than Re during weathering whereas the data of Jaffe et al. (2000) indicate that Re is more mobile than Os. More importantly, it is borne out from the above calculations that even if the Os mobility from black shales during weathering is lower than that for Re it may still account for the reported dissolved Os concentration in the Ganga. Ganga water at Rishikesh has higher radiogenic Os isotopic composition of ($^{187}Os/^{188}Os = 2.65$, Levasseur et al., 1999) compared to other major rivers. Black shales from outcrops and the mines in the Lesser Himalaya have $^{187}Os/^{188}Os$, 1.02-11.5 (Singh et al., 1999), with many of the samples having values much higher than 2.65. Crystallines (granites and gneisses) from the Central Nepal Himalaya have been reported to have $^{187}Os/^{188}Os \leq 1.63$ (Pierson-Wickmann et al., 2000). These observations support the hypothesis that black shales, with much higher Os concentrations and $^{187}Os/^{188}Os$ than other lithologies, can be a major contributor to the Os budget and its high radiogenic isotopic composition in rivers draining the Himalaya.

Using the available data, it is possible to place an upper limit of Os contribution from silicates. The average Os in seven granite/gneiss samples reported by Pierson-Wickmann et al. (2000) is ~8 pg g^{-1}. Assuming this as representative for the granites in the Yamuna catchment and using the average ΣCations* in the YRS waters, ~40 mg ℓ^{-1}, it can be estimated that silicates (with Σcations ~80 mg g^{-1}) contribute ~4 pg of Os per liter of these waters. This estimate is based on the assumptions that all the cations in the river waters are of silicate origin and that Os and the cations are released to water in the same proportion as their abundances in silicates. Considering that bulk of the cations in these waters is derived from carbonates and/or evaporites, this estimate is an *upper limit*.

Following the approach similar to that adopted for Os, it can be estimated from the average U/Re of ~1900 in black shales (Table 5.3) and dissolved Re of ~1.8 ng ℓ^{-1}, that their weathering can contribute on an average ~3 μg $\ell^{-1}$of U to the rivers. The estimated uranium concentration is very similar to the values reported for some of these rivers and the Ganga headwaters (Sarin et al., 1990, 1992b) indicating that black shales can be a significant source of dissolved uranium to them. The significant correlation between U and ΣCations* in the Ganga waters prompted Sarin et al. (1990, 1992b) to suggest that weathering of silicates and uraniferous minerals could be important source(s) of U to these waters. Colodner et al. (1993b), though proposed carbonaceous shales as a possible source for U and Re in these waters, they also suggested that there could be additional sources for U as the U/Re in the Ganga-Brahmaputra were much higher than those in typical organic rich sediments. Analysis of a few black shales from the Lesser Himalaya shows that U/Re (wt. ratio) are ~200 to 30000 with an average of ~1900 (Table 5.3) which is very similar to those found in the river waters. Using the lowest U/Re ratio ~200, a *lower limit* of U contribution from black shales to river waters, can be estimated to be ~0.4 μg ℓ^{-1}. This is ~20% of the average river water U in the Ganga and the Indus headwaters, ~1.7 μg ℓ^{-1} (Sarin et al., 1992b; Pande et al., 1994). The average U/Re in the black shales, ~1900 (U data from Sarin et al., 1990) is much higher than that in the Yamuna waters in Saharanpur, ~1350 suggesting that all U in the water can be contributed from black shales if U and Re are released in the same proportion as their abundances. These calculations show that organic rich sediments in the catchment can be a candidate for contributing to high uranium to the rivers draining the Himalaya.

In addition to the discussion on the trace elements presented above, another important aspect of black shale weathering is the fate of organic carbon in them. Petsch et al. (2000), based on a study of black shale weathering profiles, proposed that the rate of black shale weathering is controlled by the rate of physical erosion and their subsequent exposure to oxygenated surface waters. In the Himalaya, black shale weathering rate is expected to be high since the basin is dominated by physical erosion resulting from steep gradients and intense precipitation (rain and snow melt) throughout the year. The C_{org}/Re molar ratio in the black shales in the Lesser Himalaya range between (0.23-24) $\times 10^{7}$ (Singh et al., 1999). Using a typical value of 2×10^{7} for C_{org}/Re (Table 5.3) it can be estimated that ~$(1\text{-}3)\times 10^{5}$ moles km^{-2} y^{-1} of CO_2 would be released from them in the Ganga and the Yamuna basins in the Himalaya (Table 5.6).

Table 5.6 Uptake and release of CO_2 in the Yamuna and the Ganga basins in the Himalaya.

River	Area (10^3 km^2)	Discharge (10^{12} ℓ)	Re Flux[a)]	CO_2 flux (moles km^{-2} y^{-1})[b)]	
				Uptake	Release
Ganga	19.6	22.4	6	$(2\text{-}4)\times 10^{5}$	1.2×10^{5}
Yamuna	9.6	10.8	16	$(4\text{-}7)\times 10^{5}$	3.1×10^{5}

[a)] Re flux in units of mmoles km^{-2} y^{-1}. [b)] uptake is the CO_2 consumption due to silicate weathering and release is the flux of CO_2 from black shale weathering.

This calculation assumes (i) dissolved Re in rivers can be used as an index to derive the quantity of the black shales being weathered and (ii) all organic carbon in the black shales is oxidized to CO_2 during weathering. Study on chemical weathering of black shales (Petsch et al., 2000) shows that they lose between 60 to 100% of their original organic matter during weathering. The fate of weathered organic matter is not yet well known though it is assumed to be oxidized to CO_2. Experimental study on coal weathering (Chang and Berner, 1999) shows that not all the coal is oxidized to CO_2, rather the organic carbon is transformed into basically three forms, (i) oxidation of C_{org} to CO_2, (ii) production of solid oxidation products such as humic substances and (iii) dissolved organic carbon (DOC) in rivers. Petsch et al. (2000) observed that organic matter in the black shales is extremely labile when exposed to O_2-rich surface waters and they are rapidly removed from the outcrops by an as yet undetermined mechanism likely associated with slow oxidation followed by rapid cleavage, dissolution and advection (as either $CO_{2(aq)}$ or dissolved organic matter). Quantification of the relative amounts these various forms of organic matter, during their weathering in the surficial aqueous environments, remains uncertain. Our estimate of CO_2 release via oxidation of organic matter, however, is an upper limit as it assumes that *all* C_{org} is oxidized to CO_2. Such estimations (Table 5.6) show that the amount of CO_2 release from the Yamuna basin is about a factor of 2-3 more than that from the Ganga (Table 5.6). [This value is higher than the preliminary estimate reported in Dalai et al. (2000) the cause for the increase being higher C_{org}/Re used in the present calculation]. In the chapter 4, based on various approaches, CO_2 consumption rates via silicate weathering in the YRS and Ganga basins have been estimated to be (4-7)$\times 10^5$ moles km^{-2} y^{-1} and (2-4)$\times 10^5$ moles km^{-2} y^{-1} respectively (Table 5.6). Comparison of the estimates of CO_2 release and consumption rates suggests that CO_2 release rate via black shale oxidation can roughly balance the CO_2 consumption via silicate weathering in the river basins in the southern slopes of the Himalaya (Table 5.6).

5.3 CONCLUSIONS

The focus of this work has been to assess the importance of black shale (organic rich sediments) weathering in contributing to dissolved Re in the YRS and the Ganga and its impact on the budgets of a few other elements; Os, U and C. This has been done through (a) systematic study of dissolved Re in the YRS and the Ganga, (b) measurements of Re abundances in granites and Precambrian carbonates, some of the major lithologies of their drainage basins and (c) the use of available data on Re and other elements in black shales from the Lesser Himalaya and information on its behaviour during weathering. The following observations and conclusions result from this study:

(i) The average dissolved Re in the YRS is 9.4 pM (~1.8 ng ℓ^{-1}), significantly higher than the reported global average river water concentration of 2.1 pM (Colodner et al., 1993b). Re in the Yamuna and the Ganga collected at Batamandi and Rishikesh, locations near the foothills of the Himalaya are also factor about 6 and 3 higher than the global average. The fluxes of dissolved Re from the Yamuna (at Batamandi) and the Ganga (at Rishikesh) are 150 and 120 moles y^{-1} respectively. These fluxes translate to Re weathering rate of ~1 to ~3 g km^{-2} y^{-1}, an order of magnitude higher than the global average of ~0.1 g km^{-2} y^{-1} (Colodner et al., 1993b). These results suggest that dissolved Re flux from the Yamuna and the Ganga are disproportionately high compared to their water discharge and drainage area. The impact of such high Re mobilization in the basins of these rivers, however, is not pronounced on the global riverine Re fluxes as the water discharge of the Yamuna and the Ganga at the foothills of the Himalaya is only ~0.1% of the global discharge.

(ii) The Re abundances in the granites of the Yamuna basin and Precambrian carbonates average ~26 and ~52 pg g^{-1} respectively. Calculations using Re/element ratios, ΣCations* and (Ca+Mg) abundances in river waters to estimate the contribution of Re from these lithologies show that the Re concentrations in them are too low to make a significant impact on the dissolved Re budget of these rivers on a basin wide scale.

(iii) The significant correlation between Re and SO_4 in waters and higher Re in rivers flowing through known black shale occurrences and ground waters dripping through black shale - phosphorite - carbonate layers all favour the idea that black shales could be a major source of Re to these waters. Further, the strong correlation between ΣCations* and Re in these waters require that both these are supplied to the YRS along its entire stretch in roughly the same proportion. An important consideration to decide if black shales can be a dominant source for dissolved Re in the YRS and the Ganga is their abundance and distribution in the drainage basins. The concentration of 1.8 ng ℓ^{-1} in the YRS requires that on average Re from at least ~60 mg black shales be released per liter of water. This is a few percent of the suspended and bed loads in these rivers. The available data is too sparse to determine if this requirement can be met.

(iv) Using dissolved Re as an index, it is shown that the reported concentrations of Os and U in these rivers can be supplied via black shale weathering if all these metals are released to water in the same proportion as their abundance. Extension of these calculations to C_{org} in black shales shows that if it is oxidized entirely to CO_2, its flux released to waters/atmosphere in the Yamuna and the Ganga basins in the Himalaya is similar to its consumption via silicate weathering.