

# Barium in Deccan Basalt Rivers: Its Abundance, Relative Mobility and Flux

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**Abstract.** The concentration of dissolved Ba in a number of rivers having their drainage almost entirely in Deccan Trap basalts has been measured. These results along with available data on the abundances of major elements in these waters, and on Ba and major elements in bed sediments of these rivers provide a measure of (i) the relative mobility of Ba during chemical weathering and erosion of basalts, particularly with respect to alkaline earths, Mg, Ca and Sr, and (ii) the flux of Ba out of the Deccan and its global significance. The concentration of dissolved Ba ranges from 8 to 105 nM. The average Ba/Mg\*, Ba/Ca\* and Ba/Sr (\* is concentration corrected for atmospheric contribution) in waters is lower than the corresponding mean ratios in Deccan basalts, though they overlap within errors. Majority of the water samples, however, have ratios less than that in basalts. These findings can be interpreted as a cumulative effect of limited release/mobility of Ba during chemical weathering and erosion of basalts and its reactive behaviour in waters which promote its association with clays and oxy-hydroxides of Fe. These results also indicate that during chemical erosion of Deccan basalts, Ba is the least mobile among the alkaline earth elements. The abundance of Ba in sediments and their Ba/Al ratios relative to basalts are consistent with the above conclusion. Ba/Mg and Ba/Ca ratios in water and in sediments from the same location are strongly correlated; however, the mean ratios in waters are far less than those in sediments. This is a result of limited Ba mobility, effectively 5–6 times lower than that of Mg. The annual flux of dissolved Ba out of the Deccan Traps is  $\sim 1 \times 10^7$  moles,  $\sim 0.2\%$  of its global riverine transport to oceans. The contribution of dissolved Ba from Deccan Traps, seem lower than its aerial coverage,  $\sim 0.5\%$  of the global drainage area; the potential causes for this could be the lower abundance of Ba in basalts relative to “average continental crust”, and its behaviour during chemical weathering and erosion.

**Key words:** barium, chemical weathering, Deccan basalts, dissolved flux, rivers

## 1. Introduction

Studies on the aqueous geochemistry of Ba have been motivated primarily by its application along with Ra, as a tracer for ocean circulation and mixing (Cochran, 1992) and as a tag to distinguish fluvial discharge to the sea (Guay and Falkner, 1998). In addition, the use of Ba as a proxy of paleoproductivity

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and paleocirculation of the oceans also depend on process regulating its geochemical cycle (Lea and Boyle, 1990; Dymond et al., 1992). Surveys of Ba in river-estuarine systems conducted to investigate its behaviour (Hanor and Chan, 1977; Edmond et al., 1978; Li and Chan, 1998; Carroll et al., 1993; Coffey et al., 1997; Guay and Falkner, 1998) and to fully exploit its application to track fluvial discharge to the sea (Guay and Falkner, 1998) show that Ba is non-conservative in estuaries due to its release from riverine particles to solution. A major outcome of these surveys is data on the concentration of dissolved Ba in rivers, however, these measurements are generally limited to river mouths as the focus of the studies were on estuaries. Thus, a cursory survey of literature shows the need for a more detailed investigation of an important component of the aqueous geochemistry of Ba, viz., its behaviour in fresh water systems, particularly that pertaining to its release from rocks and minerals during their chemical weathering and its subsequent transport through rivers. Guay and Falkner (1998) in their survey on Ba in estuaries of the Arctic rivers, attributed high concentrations of dissolved Ba in the Mackenzie river to its supply from Ba rich rocks in the basin. Dalai et al. (2002a) based on extensive measurements of Ba in water and sediments of the Yamuna river in the Himalaya, were able to apportion the contributions from silicates and carbonates in the basin to dissolved Ba abundance. Gaillardet et al. (1999) in their study of the geochemistry of river suspended sediments observed that Ba is systematically depleted in sediments relative to source rocks, consistent with the known mobility of elements during rock weathering. In addition, there are measurements of dissolved Ba in some of the major global rivers along with major and a few minor elements (Moore and Edmond, 1984; Dupre et al., 1996; Louvat and Allegre, 1997; Shiller, 1997). These results have provided insight into the relative behaviour of Ra–Ba, fluxes of Ba through rivers and its mobility during chemical weathering.

In this paper, the concentration of dissolved Ba and in bank sediments (Das and Krishnaswami, 2005) of the headwaters of the Krishna river system and in a number of small streams draining the Western Ghats are reported. The rivers sampled for this study are entirely from the Deccan Traps and therefore provide an understanding of the release and mobility of Ba during chemical weathering and erosion of basalts. Data for major and select trace elements in water and sediment samples analysed for Ba are available (Das et al., 2005a; Das and Krishnaswami, 2005) which allow the assessment of release and mobility of Ba relative to other elements, particularly the alkaline earths, Mg, Ca and Sr, during weathering of Deccan basalts. Further, the data also provide estimates of the dissolved and particulate fluxes of Ba from the Deccan Traps and their global significance.

## 2. Methodology

One of our ongoing programmes is the study of chemical weathering and erosion in the Deccan Traps (Das et al., 2005a) and in the Himalaya (Krishnaswami et al., 1999; Dalai et al., 2002b). These programmes address, among others, the relative mobility of various elements during chemical weathering, determination of silicate weathering rates and associated CO<sub>2</sub> consumption. The present study of Ba geochemistry in rivers draining the Deccan Traps also addresses some of these issues.

Samples for this study are from the headwaters of the Krishna river system, which comprises of the Krishna main stream, its tributaries and sub-tributaries and a few small rivers draining the Western Ghats into the Arabian Sea (Figure 1). All samples are from locations within the Deccan Trap basalts. The dominant source of dissolved cations in the samples is chemical weathering of basalts (Das et al., 2005a). The geo-hydrology of the Krishna river system and the west flowing Western Ghat (WFWG) rivers is discussed in Das et al. (2005a). Briefly, the Deccan Traps are in the west-central part of India, occupying an area of  $\sim 0.5 \times 10^6$  km<sup>2</sup> with an average thickness of  $\sim 750$  m. Tholeiitic basalts make up almost the entire lithology of the drainage basins of all the rivers sampled; these basalts consist mainly of plagioclase, pyroxenes and olivines (Mahoney, 1988; Sen, 2001) with trace calcites in some of them (Sukeshwala et al., 1972). In addition, there are reports of calcareous tufas in the upland Bhima and the Krishna basins and calcium carbonate in river sediments (Pawar et al., 1988; Das et al., 2005a). The soils of the region are dominated by black coloured vertisols with abundant laterites in the western coastal districts and in the Koyna river basin (Widdowson and Cox, 1996). There are also reports of occurrences of saline/alkaline soils in the basins of the Bhima and its tributaries (Bhargava and Bhattacharjee, 1982; NRSA, 1998). The source of water for these rivers is monsoon rainfall; as a result about 80% of the annual river discharge occurs during the southwest monsoon season (June–September). The river runoff is much higher for the rivers flowing west of the Western Ghats ( $\sim 1685$  mm year<sup>-1</sup>), compared to the rivers draining the rain shadow regions of the eastern side,  $\sim 463$  mm year<sup>-1</sup> (Das et al., 2005a).

The details of sampling locations and the various properties measured in the waters are given in Das et al. (2005a). Sampling was carried out during the monsoon seasons of 2001 and 2002; however, Ba concentration measurements were made only in samples of August 2002. Samples were collected from the Krishna mainstream, its tributaries and sub-tributaries and selected WFWG rivers (Figure 1). The water sampling was done from the mid-stream of rivers to avoid local heterogeneity and possible “near-bank” human influences. For major and trace element measurements, including Ba,  $\sim 1$  L samples were collected in high-density polyethylene bottles. Subsequently,

water samples were filtered through 0.4  $\mu\text{m}$  Nucleopore (within  $\sim 6$  h) and an aliquot ( $\sim 500$  ml) was acidified with high purity  $\text{HNO}_3$  to  $\text{pH} \sim 2$ , soon after filtration and stored in acid cleaned bottles. (The bottles were first soaked in dilute  $\text{HCl}$  for several hours, followed by distilled water and were thoroughly

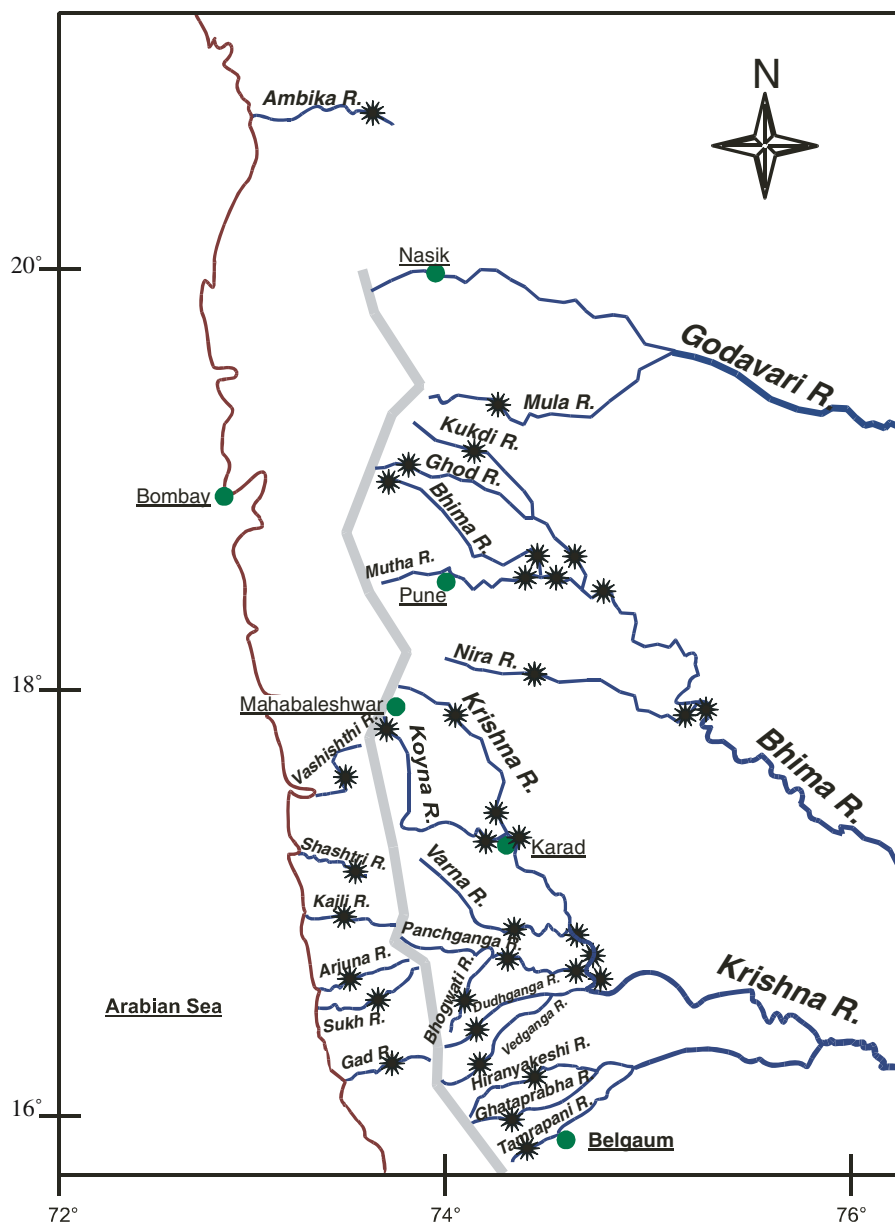


Figure 1. Sampling locations (\*), the water samples analysed for Ba were collected during monsoon of 2002. The Western Ghats is shown by a grey band parallel to western coast.

rinsed with filtered ambient river water). These samples were used for Ba and other trace element measurements. Bank sediments are from a previous collection, monsoon of 2001, these samples are, however, from the same locations as the water samples. Part of the sediments were dried, homogenized and powdered to  $< 100 \mu\text{m}$  size. A known weight of the powdered samples was brought to solution by acid digestion. Initially, the solids were digested repeatedly in HF to remove the silica, and then with a mixture of  $\text{HNO}_3$ –HCl to bring them to solution. Finally, they were made to known volume (in  $\sim 1 \text{ M HCl}$ ) and concentrations of various elements were measured in solution (Das and Krishnaswami, 2005).

Ba concentrations in river waters were measured using ICP-AES coupled to an ultrasonic nebulizer (Dalai and Sarin, 2002). Ba in sediment solutions was also measured by ICP-AES (Das and Krishnaswami, 2005). Calibration of the instrument was done with standard solutions made from analytical grade  $\text{Ba}(\text{NO}_3)_2$ . The accuracy of measurements, checked by analysing commercial standards (Merck) and with solutions of USGS standards (G-2), was better than  $\pm 5\%$ . The internal precision of the ICP-AES measurement, based on all samples covering the entire concentration range, average  $\pm 7\%$ .

### 3. Results and discussion

Das et al. (2005a) in their study of major ions in Deccan rivers showed that their abundances are determined by supply from basalt weathering, rainwater and saline/alkaline soils. Further, these authors, using dissolved Mg as a proxy for silicate (basalt) weathering determined the contribution of Ca and other major cations from basalts to rivers, and silicate weathering rates for the basin. These results suggested that the dominant source of dissolved major cations, particularly Mg, Ca, and Sr (Das et al., 2006) in these waters is chemical weathering of basalts. In light of these findings, it is expected that dissolved Ba in these rivers would also be of basalt origin. Dissolved Ba concentrations in the samples analysed are given in Table I. Also presented in this Table are  $\text{Mg}^*$ ,  $\text{Ca}^*$  and  $\text{Sr}$  concentrations (\* are concentrations corrected for atmospheric contributions; data from Das et al., 2005a,b). The geochemistry of major elements in water and in sediments and their implications to chemical weathering of Deccan basalts are discussed in Das et al. (2005a; Das and Krishnaswami, 2005). The focus of this manuscript, as mentioned earlier, is on the weathering geochemistry of Ba.

#### 3.1. DISSOLVED Ba AND ITS RELATION TO Mg, Ca AND Sr

The concentration of dissolved Ba in the waters analysed ranges from 8 to 105 nM (Table I, Figure 2). Of these, nine samples have concentration in

Table I. Concentration of dissolved Mg\*, Ca\*, Sr, Ba and TDS in Deccan Trap rivers

Sample code	River	Mg* ( $\mu\text{M}$ )	Ca* ( $\mu\text{M}$ )	Sr (nM)	Ba (nM)	TDS ( $\text{mg L}^{-1}$ )
<i>Krishna mainstream</i>						
KRS-1	Krishna	255	419	592	41	168
KRS-2	Krishna	191	294	567	47	114
KRS-3	Krishna	280	455	705	48	172
KRS-4	Krishna	360	610	797	46	225
KRS-5	Krishna	232	355	679	52	153
KRS-6	Krishna	563	868	1394	59	314
<i>Bhima mainstream</i>						
BHM-1	Bhima	95	147	378	34	75
BHM-3	Bhima	464	733	1029	96	307
BHM-4	Bhima	532	787	1239	105	337
<i>Tributaries of Bhima</i>						
GHOD-1	Ghod	325	575	907	56	202
MTH-1	Mutha	449	736	930	97	298
NIRA-1	Nira	626	637	1164	53	622
KUK-1	Kukdi	950	749	1583	34	428
<i>Tributaries of Krishna</i>						
KYN-1	Koyna	186	274	499	34	122
KYN-2	Koyna	44	46	164	9	40
VRN-1	Varna	170	262	352	35	114
PGN-1	Panchganga	110	173	368	46	81
PGN-2	Panchganga	123	177	346	53	84
GTP-1	Ghataprabha	37	39	148	28	34
HRN-1	Hiranyakeshi	39	36	134	23	34
TPN-1	Tamrapani	59	72	194	45	48
DDG-1	Dudhganga	153	254	322	27	100
VDG-1	Vedganga	95	137	301	33	71
BGW-1	Bhogwati	113	158	360	55	79
<i>West flowing western Ghat rivers</i>						
ARJ-1	Arjuna	116	144	206	18	80
GAD-1	Gad	99	130	210	19	75
SUKH-1	Sukh	115	140	204	18	77
KJL-1	Kajli	113	139	251	13	78
SHT-1	Shashtri	112	158	281	12	84
VAT-1	Vashishthi	127	174	225	14	88
<i>Others</i>						
AMB-1	Ambika	334	504	493	8	200
MULA-1	Mula	295	356	565	12	152

Mg\*, Ca\*, TDS data from Das et al. (2005a), Sr from Das et al. (2006).

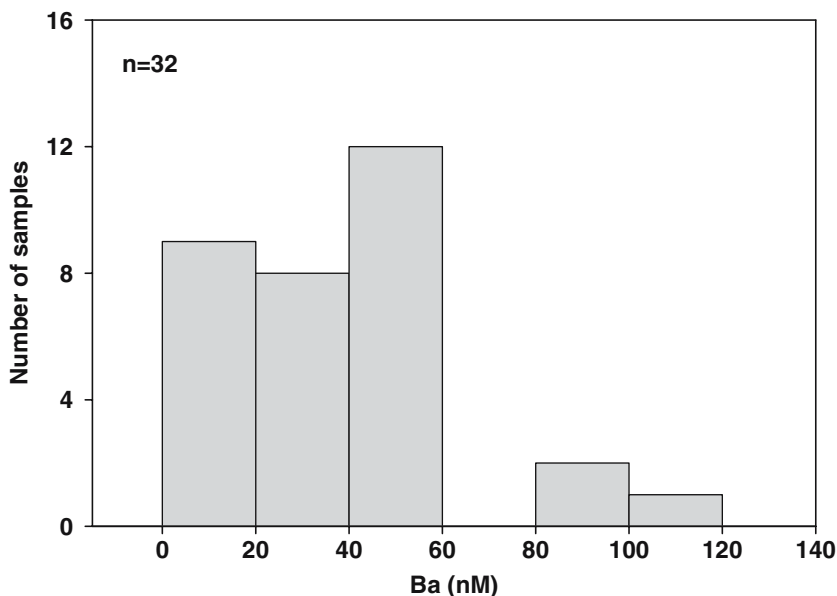


Figure 2. Frequency distribution of dissolved Ba in the samples. The range in Ba (8–105 nM) decrease to (8–59 nM) if samples suspected of having contributions from saline/alkaline soils, anthropogenic sources or supersaturation in calcite (i.e., samples with  $\text{Cl} > 300 \mu\text{M}$ , or  $\text{SO}_4 > 100 \mu\text{M}$  or  $\text{CSI} > 0$ ) are excluded.

excess of 50 nM (Table I), these are mainly from the Bhima, its tributaries (the Ghod, the Mutha and the Nira) and from the Krishna main stream. Some of these samples also have high TDS and dissolved Sr (Table I). If samples suspected of having inputs from saline/alkaline soils, anthropogenic sources and those which are supersaturated in calcite (samples with  $\text{Cl} > 300 \mu\text{M}$  or  $\text{SO}_4 > 100 \mu\text{M}$  or  $\text{CSI} > 0$ ; Das et al., 2005a) are excluded, the range in dissolved Ba narrows down to 8–59 nM ( $n = 24$ ). The low Ba samples are from the WFWG rivers and a few east flowing Krishna tributaries, these samples are also low in TDS and Sr. The abundance of dissolved Ba measured in this study in the Deccan rivers are much higher than those reported for the Reunion rivers (Louvart and Allegre, 1997), but are lower than that in the Amazon and Congo (Moore and Edmond, 1984; Gaillardet et al., 1995) and in rivers of the Yamuna system in the Himalaya (Dalai et al., 2002a).

The dependence of dissolved Ba concentration on  $\text{Mg}^*$  is shown in Figure 3, no systematic trend is evident from the data. Similar plot (not shown) with  $\text{Ca}^*$  almost replicate the scatter in Figure 3. This is not unexpected considering that  $\text{Ca}^*$  in these river waters vary with  $\text{Mg}^*$  in roughly constant proportion (Das et al., 2005a). A closer look at the scatter diagram (Figure 3) however, seem to show that the data fall in two groups, with

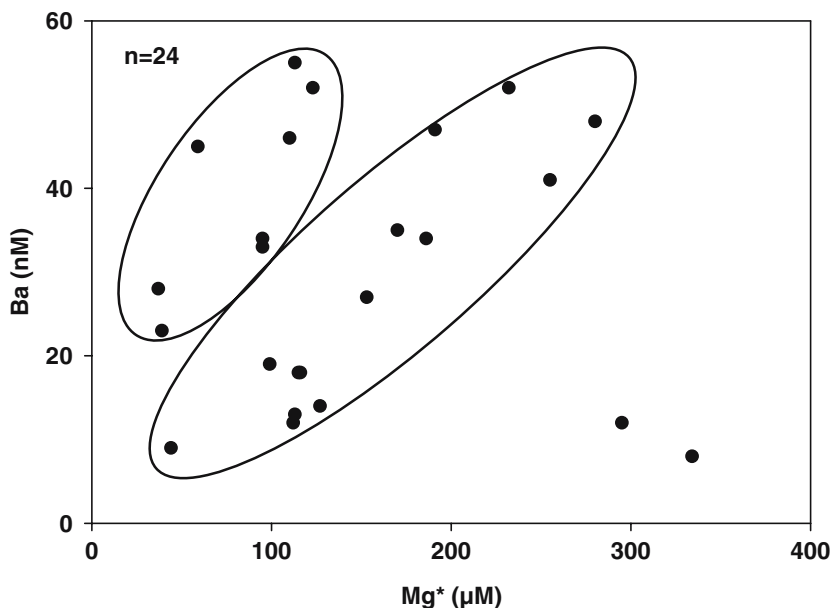


Figure 3. Scatter diagram of Ba with  $Mg^*$  ( $n=24$ ). The data seem to fall in two groups (enclosed in ellipses). The small Krishna tributaries seem to plot left to the trend set by fourteen others. The two outliers are from the northern most rivers, Ambika and Mula.  $Mg^*$  data from Das et al. (2005a).

discernable covariation between Ba and  $Mg^*$  within each group. One is a group of eight samples consisting mainly of small tributaries of the Krishna (Ghataprabha, Dudhganga and Panchganga and their tributaries all draining the south eastern side of the Western Ghats) with relatively low dissolved Mg ( $< 125 \mu M$ , Table I) and higher Ba/ $Mg^*$  ratio. The samples plot to the left of the trend set by a group of 14 rivers (two outliers in the plot are samples from the Ambika and the Mula rivers, the northern most rivers with very low Ba/ $Mg^*$ ). It is interesting to note that the ratios in water seem to reflect the Ba/Mg (Ba/Ca) of sediments (see later discussion). Ba– $Ca^*$  correlation also shows two similar groupings, this is expected as  $Ca^*$  and  $Mg^*$  are strongly correlated.

The scatter in Ba/ $Mg^*$  (Figure 3) is unlike the data for the Yamuna River System (Dalai et al., 2002a) in which Ba showed a much stronger correlation with  $Mg^*$ ,  $Ca^*$  and Si. The cause for this difference in the interrelation of Ba with major cations in these two river systems is unclear. Lithology of the drainage basins and their Ba/Mg (Ba/Ca) ratios may be some of the contributing factors. The Yamuna drains multi-lithologic terrains composed of a variety of silicates, carbonates and minor phases, unlike the rivers sampled in this study which flow by and large through a monolithologic terrain, the Deccan basalts. Available data (Subbarao et al., 2000) show that even among



the different Formations of the Deccan Traps through which the rivers sampled flow has a wide range of Ba/Mg (mol. ratio: 0.21–1.94; Figure 4). Lithology of the basins may also influence the chemical reactivity of dissolved Ba in river waters. Many of the Deccan basins sampled have clays and iron oxy-hydroxides rich laterites, which may be sequestering Ba from solution (Nesbitt et al., 1980) and thus contributing to the scatter in Figure 3. Studies of Ba in estuaries (e.g., Coffey et al., 1997; Dowling et al., 2003) show clear evidence of its reversible uptake in particulate phases, with its adsorption in fresh water system and its release in the seawater mixing zone. It has been shown that the adsorption–desorption process is a key component for Ba budget in river–ocean systems. Dowling et al. (2003), based on measurements of dissolved and adsorbed Ba in river water and sediments concluded that Ba is strongly adsorbed in river sediments. Further, these authors, to explain the strong correlation between dissolved Ba and Fe in groundwaters of the Bengal basin invoked a two step process, adsorption of Ba on FeOOH coatings in oxic river sediments, their burial and subsequent release of both Fe and Ba to groundwaters by microbial dissolution of FeOOH. All these

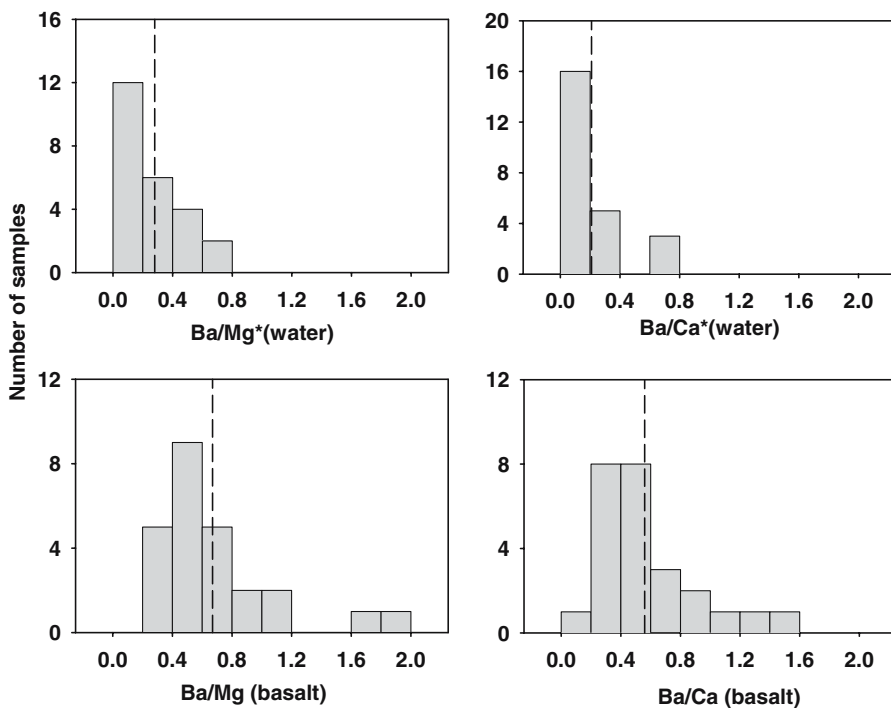


Figure 4. Frequency distribution of Ba/Mg and Ba/Ca ratios in waters and in basalts. The dotted lines are the respective average values. Majority of water samples have ratios lower than in basalts.

studies bring out the role of particulate phases in regulating dissolved Ba concentration in rivers.

The mean Ba/Mg\* (nM/ $\mu$ M, and hereafter) in waters (Cl < 300  $\mu$ M and SO<sub>4</sub> < 100  $\mu$ M) is  $0.28 \pm 0.21$  ( $n = 24$ , with half of the samples having values < 0.20; Figure 4), compared to the mean value of  $0.68 \pm 0.41$  in Deccan basalts ( $n = 25$ , with majority of the samples having values > 0.40; Figure 4). Similarly, the mean Ba/Ca\* (nM/ $\mu$ M, and hereafter) of waters is  $0.21 \pm 0.19$  (with  $\sim 70\%$  of the samples having ratios < 0.20), a factor of  $\sim 3$  lower than the Ba/Ca ratio in basalts ( $0.56 \pm 0.32$ ). The mean ratios though overlap within errors, the frequency distribution (Figure 4) of ratios shows an offset, with majority of the water samples having values less than that in basalts. The lower mean ratios in water and their offset in distribution relative to basalts seem to suggest that during chemical weathering of Deccan basalts either Ba is released to waters less efficiently relative to Mg and Ca and/or that after its release it is sequestered from the waters by various components of sediments. Either way, these results indicate that Ba is effectively less mobile than Mg and Ca during weathering and erosion of Deccan basalts. This is unlike Sr, which shows a near congruent release w.r.t. Mg and Ca (Das et al., 2006). This inference is also attested by the dissolved Ba/Sr ratios in waters. The mean Ba/Sr ratio in waters is  $\sim 0.1 \pm 0.05$ , compared to ratios of  $0.36 \pm 0.16$  in Deccan basalts. This can be understood in terms of limited mobility of Ba relative to Sr during chemical weathering and erosion of Deccan basalts. Thus, the ratios of dissolved concentrations of Ba relative Mg, Ca and Sr in Deccan rivers shows that Ba is the least mobile among these alkaline earth elements. The bed sediment data (discussed in next section) support this conclusion.

Compared to the dissolved Ba abundances in Deccan rivers, the rivers draining the Reunion basalts show much lower abundances of dissolved Ba in them. The dissolved Ba in the Reunion rivers ranges from 0.3–20 nM (average of  $\sim 3$  nM), an order of magnitude lower than that observed in the present study ( $\sim 40$  nM). Similarly, the Ba/Mg and Ba/Ca ratios in Reunion rivers are also an order of magnitude lower than the corresponding ratios in Deccan rivers. This is intriguing considering that the average Ba/Mg and Ba/Ca ratios in both Reunion and Deccan basalts are similar. The cause for this discrepancy though need further investigation, it reinforces the conclusion that the mobility of Ba during weathering and erosion of basalts is quite low among the various alkaline earth elements.

### 3.2. Ba IN BED SEDIMENTS

Ba concentration in river sediments range from 79 to 273  $\mu\text{g g}^{-1}$  (mean  $189 \pm 43 \mu\text{g g}^{-1}$ ; data from Das and Krishnaswami, 2005) within the spread

reported for the Deccan basalts,  $48\text{--}285 \mu\text{g g}^{-1}$  (mean  $133 \pm 60 \mu\text{g g}^{-1}$ , Subbarao et al., 2000). Ba distribution in sediments (Das and Krishnaswami, 2005) is presented in Figure 5a along with data for basalts (Figure 5c; Subbarao et al., 2000). The concentration of Ba in sediments and basalts, though overlap; there is an indication from its distribution (Figure 5a, c) that Ba is enriched in sediments relative to basalts. This can be explained in terms of cumulative effect of limited mobility of Ba and mass loss of parent rocks during chemical weathering. The release of Na, Mg, Ca and Si during weathering results in mass loss from parent basalts, whereas Ba, because of its limited mobility, is retained in the residual sediments. Both these processes cause enrichment in Ba concentration in sediments. The Ba/Al in sediments ( $\mu\text{g Ba}/\% \text{Al}$ ) vary between 12 and 40 with a mean of  $25 \pm 7$ . The mean in sediments seems to be marginally higher than the basalts ratio,  $18 \pm 8$ , though they overlap within the errors (Figure 5b, d). Considering that Ba is unlikely to be less mobile than Al during rock–water interactions, Ba/Al in bed sediments is expected to be equal to or less than that in parent basalt. The higher mean Ba/Al in bed sediments, therefore, can be a result of sequestration of Ba from solution by select sediment components such

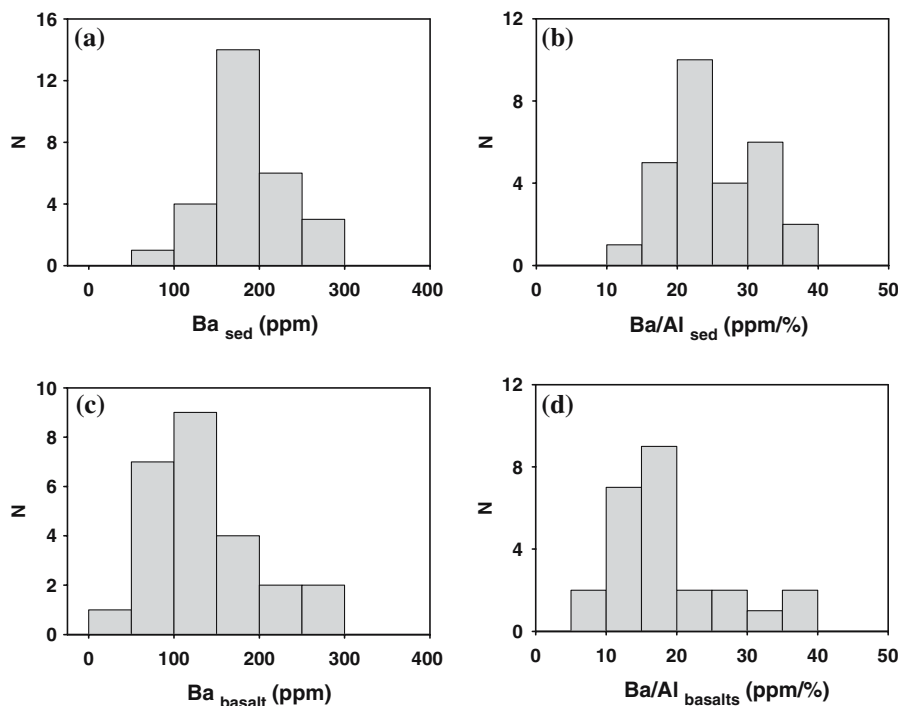


Figure 5. Frequency distribution of Ba concentration and Ba/Al in sediments and in basalts. Data from Das and Krishnaswami (2005) and Subbarao et al. (2000). The sediments seem to be marginally enriched in Ba.

as  $\text{CaCO}_3$ . Some of the sediments analysed, especially those from the Bhima and its tributaries, have significant  $\text{CaCO}_3$  in them (Das and Krishnaswami, 2005). Many of these sediments also have  $\text{Ba}/\text{Al} > 25$ . Excluding sediments with  $> 0.5$  wt%  $\text{CaCO}_3$ , yields an average value of  $21 \pm 5$  for the mean  $\text{Ba}/\text{Al}$ , nearly the same as the mean basalt ratio. These findings, similar (or marginally higher) concentration of Ba in sediments and basalts with similar mean  $\text{Ba}/\text{Al}$  ratios, lend support to the conclusion arrived earlier based on dissolved Ba data that the mobility of Ba is limited during weathering and erosion of basalts. The inference draws further support from the observation that average  $\text{Ba}/\text{Mg}$  and  $\text{Ba}/\text{Ca}_{\text{sil}}$  ratios in sediments are also higher than that in basalts ( $\text{Ca}_{\text{sil}}$  is silicate-Ca concentration. This is calculated by subtracting from the measured Ca, the Ca contribution from carbonates. All carbonate measured in sediments is assumed to be  $\text{CaCO}_3$ , Das and Krishnaswami, 2005).

The high  $\text{Ba}/\text{Mg}$  and  $\text{Ba}/\text{Ca}_{\text{sil}}$  values in sediments tend towards the ratios reported for laterites from the Deccan Traps (Widdowson and Gunnell, 2004). The increase in  $\text{Ba}/\text{Mg}$  and  $\text{Ba}/\text{Ca}_{\text{sil}}$  in bed sediments, starting with the basalt ratio (Figure 6a, b), results from preferential mobility of Mg and Ca over Ba during chemical erosion of basalts. Dalai et al. (2002a) in their study of the Yamuna River System in the Himalaya observed that Ba is less mobile than Na, a conclusion similar to that reached in this study regarding the mobility of Ba in Deccan basalts. Gaillardet et al. (1999) in their study of the geochemistry of major global rivers, observed that the weathering index of Ba is much lower than that for Na, conforming to the conclusion of limited mobility of Ba during chemical weathering and erosion. The restricted mobility of Ba can be because of its association with weathering resistant minerals and/or due to its sequestration in sediments by various components such as clays, oxy-hydroxides of Fe, and carbonates. The strong correlation of Ba with K in these bed sediments (Das and Krishnaswami, 2005) suggests that the association of Ba with weathering resistant K minerals (Wedepohl, 1972; Nesbitt et al., 1980; Dalai et al., 2002a) is an important factor contributing to its limited mobility.

Figure 6a, b are plots of  $\text{Ba}/\text{Mg}$  and  $\text{Ba}/\text{Ca}$  in water against the corresponding ratios in bed sediments. The data show strong correlation. It is tempting to interpret this correlation by suggesting that Ba is released to waters along with Mg (Ca) from bed sediments in a constant proportion to their abundances. Such an interpretation requires bed sediments to be the source of these elements to river waters and that the effects of differences, if any, in spatial and temporal scales over which Ba, Mg and Ca concentrations in water and sediments are integrated, is not significant. The slope of the best fit line of Ba–Mg plot suggests that  $(\text{Ba}/\text{Mg})_{\text{water}}$  is  $\sim 0.15 (\text{Ba}/\text{Mg})_{\text{sed}}$  or that the average effective mobility of Ba from source materials (basalts and

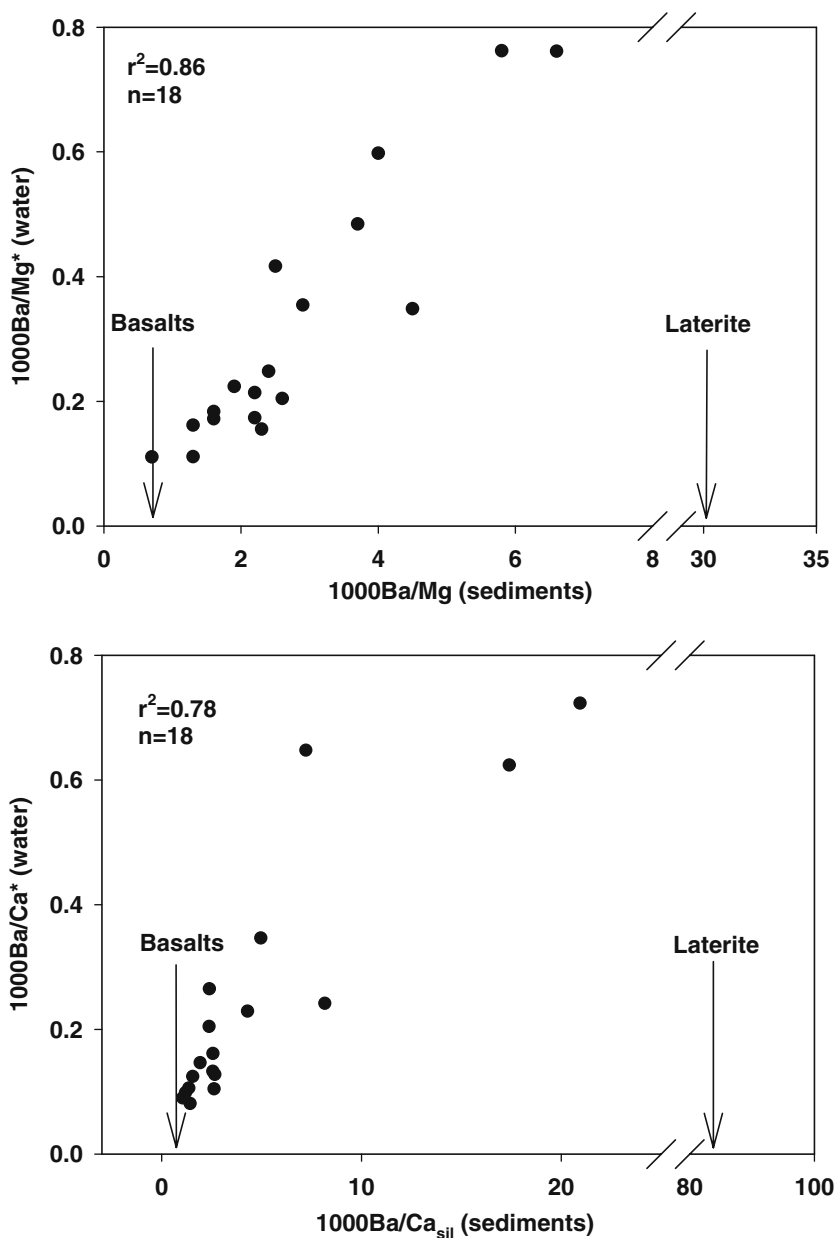


Figure 6. Ratio (molar) plots of 1000 Ba/Mg and 1000 Ba/Ca in waters with corresponding ratios in sediments (water samples which have  $\text{Cl} < 300 \mu\text{M}$ , or  $\text{SO}_4 < 100 \mu\text{M}$  or  $\text{CSI} < 0$  only are plotted). The data show a strong linear trend. The average ratios in Deccan basalts and in laterites of the region are also shown.

bed sediments) to water is about 0.15 times that of Mg. The properties of Ba, which contribute to its restricted mobility, viz., incongruent release w.r.t. major elements and/or its reactivity in river water, limits its use as a proxy of silicate weathering.

### 3.3. DISSOLVED FLUX OF Ba

Ba concentration in Krishna River near its outflow from the Deccan Traps (KRS-2) is 47 nM. Using this as typical of Deccan Rivers, an annual runoff of 46 cm year<sup>-1</sup>, and Deccan area of  $5 \times 10^5$  km<sup>2</sup> yield a value of  $\sim 1 \times 10^7$  moles year<sup>-1</sup> for the dissolved flux of Ba out of the Deccan Traps. This compares with the flux of  $5.4 \times 10^6$  moles year<sup>-1</sup> from the Yamuna and the Ganga together at the foothills of the Himalaya (Dalai et al., 2002a). The lower flux from the Ganga and the Yamuna is because the calculations have been made for their headwaters in the Himalaya, which have about an order of magnitude lower drainage area and discharge, compared to that of the entire Deccan.

The concentration of dissolved Ba in some of the major global rivers along with the data for the Krishna measured in this study are given in Table II. For the Ganga–Brahmaputra, in addition to the value listed in Table II (Carroll et al., 1993), concentrations of 110 and 131 nM have also been reported (Moore, 1997). The data of the Yenisey, Ob and Lena rivers are for samples of near zero salinity collected in 1994 (Guay and Falkner, 1998). The rivers listed in Table II account for about a third of global water discharge. This compilation shows that the dissolved Ba concentration varies over an

Table II. Dissolved Ba in major world rivers and those draining Deccan

River	Discharge (10 <sup>15</sup> L year <sup>-1</sup> )	Ba (nM)	Flux (10 <sup>8</sup> moles year <sup>-1</sup> )	References
Amazon	5.7	150	8.6	Gaillardet et al. (1997)
Congo	1.35	143	1.9	Dupre et al. (1996)
Orinocco	1.2	68	0.8	Edmond et al. (1996)
Mississippi	0.53	450	3.6	Shiller (1997)
Ganga–Brahmaputra	1.0	157	1.6	Carroll et al. (1993)
Mackenzie	0.31	425	1.3	Guay and Falkner (1998)
Yenisey	0.62	106	0.7	Guay and Falkner (1998)
Ob	0.4	102	0.4	Guay and Falkner (1998)
Lena	0.53	73	1.4	Guay and Falkner (1998)
Deccan Traps	0.23	47	0.1	Present study

Based on area of  $\sim 5 \times 10^5$  km<sup>2</sup> and annual runoff of 46 cm. Ba concentration is of KRS-2.

order of magnitude, with lowest value for the Krishna, and highest for the Mississippi. The discharge weighted dissolved Ba concentration of rivers listed in Table II is  $\sim 153$  nM. Using this value as the mean concentration for the global river, the dissolved global river Ba flux can be estimated to be  $\sim 0.5 \times 10^{10}$  moles year<sup>-1</sup>. In addition to this dissolved flux entering the coastal ocean, there will also be supply of Ba from desorption of river particulate matter (Hanor and Chan, 1977; Edmond et al., 1978; Coffey et al., 1997; Guay and Falkner, 1998) and submarine ground water discharge (Moore, 1997; Shaw et al., 1998). The flux estimates show that the dissolved Ba flux from the Deccan corresponds to  $\sim 0.2\%$  of the global riverine dissolved Ba flux. This contribution seems to be a factor of  $\sim 2$  lower than the fractional area of Deccan ( $\sim 0.5\%$ ) relative to global drainage area. This result though need to be confirmed by better constraining the Deccan and global river fluxes, it gives an indication that chemical weathering of Deccan basalts may be contributing disproportionately lower flux of dissolved Ba to oceans relative to their aerial coverage. This could be due to a combination of factors such as the lower abundance of Ba in basalts [ $\sim 130$  ppm; Subbarao et al. (2000)] compared to the range in its average crustal abundance, 250–390 ppm (Taylor and McLennan, 1985, 1995; Rudnick and Fountain, 1995), and the aqueous geochemical behaviour of Ba in basaltic terrains.

#### 4. Summary

Measurements of Ba in river waters draining the Deccan Traps have been carried out to determine its relative mobility during chemical erosion and the processes affecting it. The mean Ba/Mg and Ba/Ca ratios in waters seem to be factors of 2–3 lower than that in Deccan basalts. A similar difference is also observed for Ba/Sr ratios. These results suggest that Ba is less mobile relative to other alkaline earths during chemical erosion of Deccan basalts. Available data on Ba/Mg and Ba/Ca<sub>sil</sub> ratios in sediments from the same location of these rivers also support this conclusion. The lower mobility of Ba can be a result of its association with weathering resistant minerals in basalts and/or sequestration of dissolved Ba by clays and, oxy-hydroxides of Fe in sediments. Support for the former comes from the reported strong correlation of Ba and K in these river sediments, and for the latter from the presence of clays and Fe rich laterites in them. The annual dissolved flux of Ba calculated assuming that the concentration measured in this study are typical of the region from the entire Deccan, is  $\sim 1 \times 10^7$  moles,  $\sim 0.2\%$  of global riverine dissolved Ba flux. More results though are needed to confirm this, the data obtained in this study seem to indicate that the contribution of Deccan is a factor of  $\sim 2$  lower than that expected from its aerial coverage. The lower

abundance of Ba in basalts relative to that in average continental crust may be a factor contributing to this.

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