Chemical weathering in the river basins of the Himalaya, India

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Rivers transport weathered materials from land to the ocean. The chemistry of river waters is dictated by supply of various elements from both natural and anthropogenic sources. Among the natural sources, chemical weathering of the drainage basin is the dominant component, a process which consumes atmospheric CO_2. On timescales of millions of years, atmospheric CO_2 balance and hence global climate is influenced by chemical weathering process, silicate weathering in particular. The suggestion that silicate weathering in the Himalaya may be a driver of global cooling during the Cenezoic[1-3] has prompted many studies on rivers draining the Himalaya, especially the source waters of the Ganga–Brahmaputra. This article reviews some of these studies and presents the current thinking on this topic.

Keywords: Chemical weathering, Himalaya, CO_2 drawdown, Ganga–Brahmaputra, Deccan.

CONTINENTAL weathering and erosion are major components of the exogenic cycles of elements on the earth. Weathering breaks down rocks and the resulting dissolved and particulate materials are transported by rivers to the sea. Chemical weathering of rocks and minerals determines the flux of dissolved materials carried by rivers whereas physical weathering regulates the particulate transport. This makes the study of dissolved and particulate components of rivers important to characterize and quantify weathering and erosion. The study of chemical composition of river water is important not only for determining erosion rates, but also to learn about sources of elements to rivers, mineral weathering and elemental mobility and uptake of CO_2 during chemical weathering. In addition, information on river chemistry is essential to assess water quality for domestic, agricultural and industrial usage.

During the past 2–3 decades, many studies have been reported on the chemical and isotopic composition of Indian rivers[4-10]. Among the river basins studied, those from the Himalaya have received more attention mainly to elucidate the coupling between tectonics, weathering and climate. In recent years, there have also been studies of rivers draining the Deccan traps[11,12] to determine the role of their weathering in contributing to global riverine fluxes and atmosphere CO_2 draw-down. In this article, some of these issues, particu-

larly those pertaining to silicate weathering rates of Indian river basins, associated CO_2 consumption and factors influencing them are reviewed based on available data on major ion chemistry of selected rivers.

Data source

India has a number of rivers all of which are fed mainly by water from monsoon rains. In addition, the rivers draining the Himalaya receive water from glaciers/snow melt during summer. Table 1 summarizes physical characteristics of a few selected rivers from India[13,14]. The rivers in India drain a total area of $\sim 3.1 \times 10^6$ km^2 and annually discharge ~ 1650 km^3 of water. This translates into a mean run off of about 500 mm yr^{-1} for the entire India. The water discharge from India accounts for $\sim 4.5\%$ global river discharge. The pattern of monthly discharge of rivers mimics that of rainfall, with maximum for most rivers during July–August, coinciding with the peak of the more intense south-west monsoon rainfall (Figure 1). Some of the rivers draining the eastern and peninsular part of India also receive water from NE monsoon rains, their discharge therefore show effect of these rains as well (Figure 1).

Water chemistry

Sources of major ions to rivers

The chemistry of river water is dictated by a number of sources. These include:

Rain/precipitation. The primary source of water for rivers is rainfall and snow melt; which makes their composition an important component of river water chemistry. It is their chemistry which forms the base line for the evolution of river water composition. Rain water composition is location-dependent, near the coasts it is dominated by sea salt and in these regions the elemental ratios in rains are more similar to those in ocean. In inland regions, sea salt, continental dust, biogenic and anthropogenic inputs contribute to chemistry of rains. The relative significance of marine contribution to rain decreases with distance away from the coast and generally levels off to a constant low value inland. Na^+ and Cl^- are the dominant components of coastal rains, this changes to Ca^{+2}, HCO_3^- and SO_4^{-2} inland. Typical major ion

Table 1. Drainage area and water discharge of major rivers of India[10,11,13,14]

River	Station	Area (10^5 km^2)	Discharge (km^3 yr^{-1})
Ganga			
Ganga	Devprayag	0.20	22
Yamuna	Batamandi	0.10	11
Gomati	Nr. Confluence with Ganga	0.30	7
Chambal	Nr. Confluence with Yamuna	0.25	30
Betwa	Hamirpur	0.46	10
Ken	Nr. Confluence with Yamuna	0.28	11
Yamuna	Allahabad	3.66	93
Ghaghara	Nr. Confluence with Ganga	1.28	94
Son	Nr. Confluence with Ganga	0.71	32
Gandak	Nr. Confluence with Ganga	0.46	52
Kosi	Nr. Confluence with Ganga	0.75	62
Ganga	Farakka	9.35	380
Brahmaputra			
Tsangpo	Yangcun	6.36	29
Siang	Pasighat	2.46	200
Dibang	Sadeya	0.13	63
Lohit	Sadeya	0.24	60
Brahmaputra	Dibrugarh	3.23	323
Subansiri	Nr. Confluence with Brahmaputra	0.33	54
Burhi Dihing	Nr. Confluence with Brahmaputra	0.08	14
Jia Bhareli	Nr. Confluence with Brahmaputra	0.12	26
Dhansiri	Nr. Confluence with Brahmaputra	0.12	20
Kopili	Nr. Confluence with Brahmaputra	0.16	28
Manas	Nr. Confluence with Brahmaputra	0.38	32
Brahmaputra	Bahadurabad	6.30	670
Indus			
Jhelum	Mangla	0.35	28
Chenab	Merala	0.26	29
Beas	Mandi	0.18	16
Sutlej	Rupar	–	17
Indus	Thatta	11.65	197
Peninsular rivers			
Mahanadi	Mouth	1.42	67
Godavari	Rajamundri	3.13	105
Krishna	Vijayawada	2.59	68
Bhima	Raichur	0.77	13
Pennar	Nellore	0.55	3
Cauvery	Lower Anicut	0.88	21
Sabarmati	Mouth	0.22	3
Narmada	Bharuch	0.99	41
Tapi	Kathor	0.65	18

chemistry of rains over select regions in India is given in Table 2.

Chemical weathering in drainage basins. Chemical reactions occurring in the drainage basins are the primary source of solutes to rivers. These reactions are of two types:

(i)   *Dissolution reactions*

$$NaCl \rightarrow Na^+ + Cl^-, \tag{1}$$

$$CaSO_4 \rightarrow Ca^{+2} + SO_4^{-2}. \tag{2}$$

These reactions are congruent dissolution and can be important source of ions to rivers draining terrains containing evaporites and saline/alkaline soils.

(ii)   *Reactions requiring protons.* The most common source of protons (H$^+$) in rivers is carbonic acid generated by solution of CO_2 from atmosphere in rains and from soil gas in river waters. The partial pressure of CO_2 in soil gas is generally much higher than that of CO_2 in the atmosphere because of oxidation of biogenic matter in the upper layers of soil, as a result rivers derive most of their carbonic acid from this source. In regions where vegetation is sparse, such
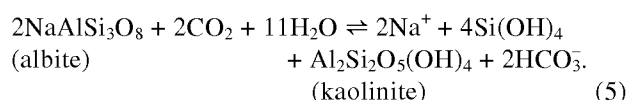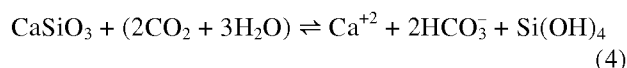
Table 2. Chemical composition of rain water over India

Location	μEq l^{-1}										Ref.
	Na	K	Mg	Ca	Cl	NO_3	SO_4	F	HCO_3	NH_4	
Coastal											
Goa	115	3	30	46	135	6	32	–	–	7	11
Chembur	96	28	57	175	141	–	421	5	–	117	34
Kalyan	103	26	39	93	112	31	108	6	–	21	34
Kalyan	147	6	48	130	134	66	110	–	–	14	35
Colaba	179	6	59	155	171	34	52	–	–	12	35
Alibag	220	5	64	133	236	9	36	–	–	8	35
Thumba	207	5.6	38	46	228	–	14	–	–	–	36
Bombay	115	3.6	24	36	138	–	10	–	–	–	36
Inland											
Pune	39	3	17	68	44	18	23	–	–	26	37
Silent valley (Nilgiris)	46	4	14	43	43	21	20	–	–	3	38
Hyderabad	40	36	20	119	47	10	32	–	22	13	39
Korba	21	4	43	183	32	25	213	5	–	15	34
Gopalpura (near Agra)	21	4	94	153	38	43	19	29	44	48	38
Dayalbagh	18.4	7.6	45.6	56.1	32	23	36	18	–	40	34
Delhi	82	44	70	134	140	67	90	–	–	26	34
Himalaya											
Nepal Himalaya	10	2	12	44	7	4	10	–	68	–	9
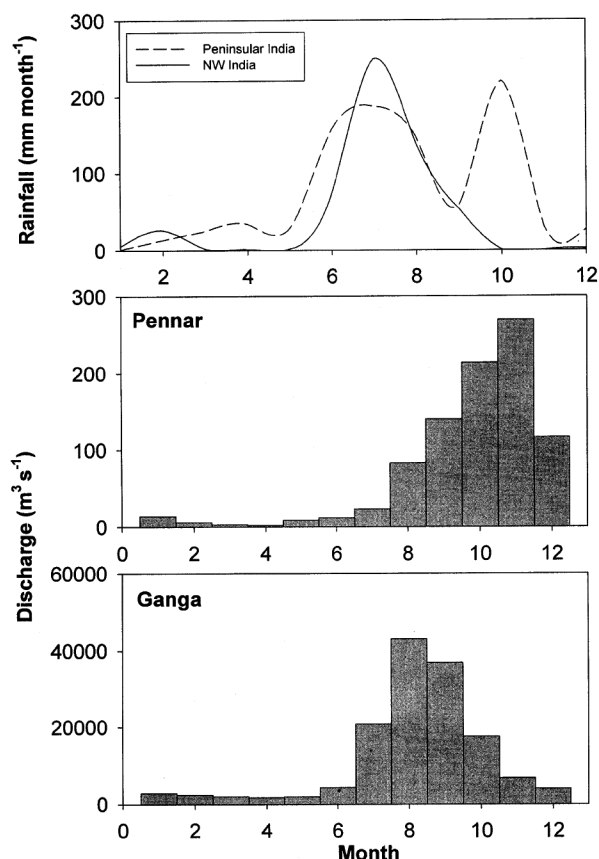
Figure 1. Monthly variations in rainfall and river discharge. In rainfall diagram the dashed line is for peninsular region, which experience both SW and NE monsoons and the solid line is for North–West region. Data from refs 13, 14, 42. Pennar river experiences NE monsoon and the Ganga SW monsoon. These discharges follow their rainfall patterns.

as bare mountains or glaciated areas, atmospheric contribution of CO_2 to carbonic acid could be dominant. Examples of weathering reactions involving carbonic acid are:

$$CaCO_3 + (CO_2 + H_2O) \rightleftharpoons Ca^{+2} + 2HCO_3^- \tag{3}$$

$$CaSiO_3 + (2CO_2 + 3H_2O) \rightleftharpoons Ca^{+2} + 2HCO_3^- + Si(OH)_4 \tag{4}$$

$$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \rightleftharpoons 2Na^+ + 4Si(OH)_4$$
(albite) $\quad + Al_2Si_2O_5(OH)_4 + 2HCO_3^-.$
(kaolinite) $\tag{5}$

Another source of protons for these reactions is sulphuric acid from the oxidation of pyrites
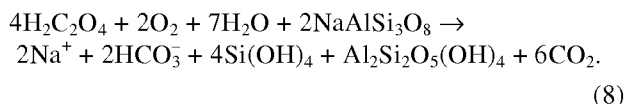
$$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8H_2SO_4. \tag{6}$$

The protons liberated from H_2SO_4 reacts with various minerals, yielding the corresponding cations and SO_4^{-2}. For example, weathering of albite by H_2SO_4 can be written as

$$2NaAlSi_3O_8 + H_2SO_4 + 9H_2O \rightarrow$$
$$2Na^+ + SO_4^{-2} + 4Si(OH)_4 + Al_2Si_2O_5(OH)_4. \tag{7}$$
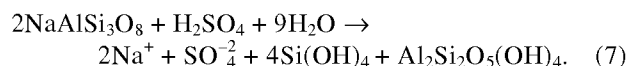
Pyrites are more common in organic-rich sediments and hence in river basins containing them H_2SO_4 can be an important source of H^+. In regions where there are abundant pyrites and other sulphides, there can be significant production of H_2SO_4. In such cases kaolinite and oxides of Fe (eqs (6) and (7)) would also react with H_2SO_4, producing other secondary minerals.

A third source of acids for chemical weathering is organic acids generated from partial oxidation of vegetation in the upper layers of soil. These include the humic and fulvic acids and others such as oxalic acid[15]. These acids weather rocks by solubilizing and complexing various elements including Fe and Al. These soluble complexes enter rivers and soil water. Many of these organic anions undergo oxidation in rivers to CO_2:

$$4H_2C_2O_4 + 2O_2 + 7H_2O + 2NaAlSi_3O_8 \rightarrow$$
$$2Na^+ + 2HCO_3^- + 4Si(OH)_4 + Al_2Si_2O_5(OH)_4 + 6CO_2.$$

$$(8)$$

The end products of reactions (5) and (8) are nearly the same, except for CO_2 produced from oxidation of oxalic acid in (8). Thus, from river water chemistry, it is sometimes difficult to quantitatively assess the role of organic acids in chemical weathering.

Weathering reactions mediated by acids can be both congruent dissolution (eq. (3)) and incongruent dissolution. Many silicate weathering reactions fall in the latter category, resulting in the formation of secondary solids such as clays and oxides of Fe/Al.

Anthropogenic input. Major ion abundances in rivers can be modified by anthropogenic inputs such as discharge of sewage, industrial and mining effluents, supply from fertilizers, etc. This input can be an important source for Na, Cl (NaCl in sewage, mining of sodium salts, solution of road salt, etc.), SO_4 (fertilizers, mining of pyrites, industrial wastes, atmospheric deposition from fossil fuel burning, etc.) and nutrients (nitrogen and phosphorus compounds, mainly from fertilizers). It is estimated that on average ~ 30% of Na, Cl, SO_4 and nutrients can be of anthropogenic origin[16], for individual rivers, however, the contribution from this source can be significantly different from the mean.

In addition, there can be two other potential suppliers of major elements to rivers. One is organic matter which during their growth incorporate elements such as N, P and K. Decay of organic matter can release these elements to rivers. Among these, the nutrients (N and P) are recycled and are generally reconverted to organic matter by plant uptake. Potassium, concentrated in plant leaves is from weathering of silicates.

Table 3. Sources of various dissolved elements

Element	Source
Na	Rain, halites, saline/alkaline soils, anthropogenic, silicate
K	Rain, silicates, biogenic, fertilizers
Ca	Silicates, carbonates, evaporites, fertilizers
Mg	Silicates, carbonates
HCO_3	Silicates, carbonate weathering, CO_2
Cl	Rain, halites, anthropogenic
SO_4	Rain, evaporites, pyrites, fertilizers
N species	Rain, fertilizers

Another supplier of major elements to rivers is springs/groundwaters. Many rivers receive water from springs and groundwater, particularly during lean stages of their flow. The primary source of major ions to spring and groundwaters is chemical weathering of aquifer rocks. The importance of springs/groundwater on the abundances of major ions in rivers, though is recognized, it is difficult to quantify. More recently, Ge has been used as a tracer[17] to estimate the water flow from springs to rivers in the Narayani basin of the Nepal Himalaya. Table 3 summarizes the various sources of major ions to rivers.

Rivers integrate the major ion contributions from the sources discussed above. Table 4 lists the chemical composition of select rivers. Several features are evident from the data. Total dissolved solids (TDS) show a range of over one order of magnitude, from 35 to 587 mg l^{-1}. These values are within the range recommended for potable water[18]. Among the various sources contributing major ions to rivers, supply from chemical weathering depends on the lithology of the basin. River basins, particularly those of medium and large size rivers, are multi-lithological comprising silicates/carbonates and lesser amounts of evaporites. Chemical weathering of river basins would supply major ions to so-
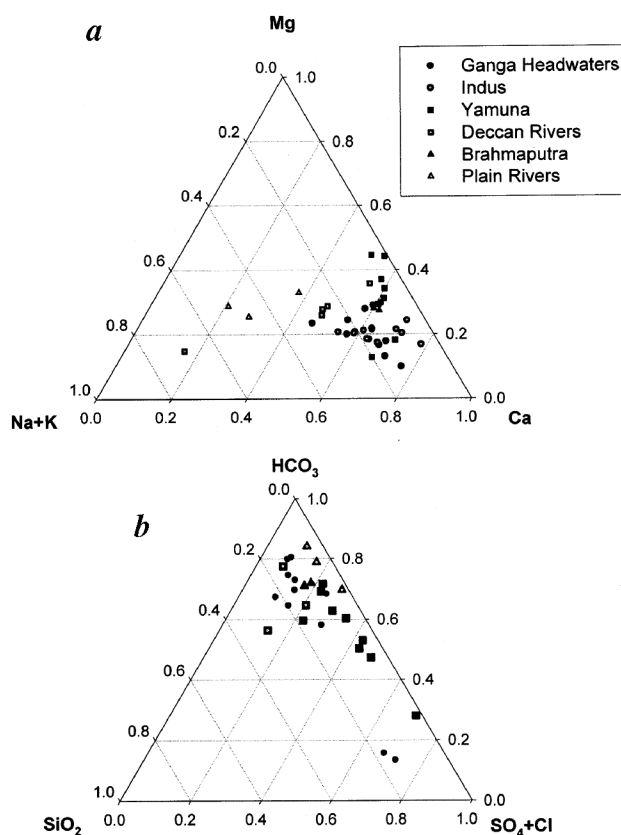
Figure 2. Ternary diagram for major cation and anion abundances in select Indian rivers. The cations cluster around Ca apex and the anions around HCO_3. The major ion abundances suggest predominance of carbonate weathering.

Table 4. Chemical composition of select Indian rivers

River	Location	Date	Na	K	Ca	Mg	F	Cl	NO₃	SO₄	HCO₃	Si	TDS (mg l⁻¹)	Ref.

Column header note: the μM label spans Na through Si.

River	Location	Date	Na	K	Ca	Mg	F	Cl	NO_3	SO_4	HCO_3	Si	TDS (mg l⁻¹)	Ref.
Ganga														
Bhagirathi	Gangotri	Apr–89	141	64	291	103	62	13	5	364	174	189	79	6
Kedarganga	Gangotri	Apr–89	98	83	373	93	36	6	11	460	174	194	91	6
Pilang gad	Pilang	Apr–89	68	34	179	52	38	11	15	46	427	131	52	6
Asiganga	Uttarkashi	Apr–89	42	51	229	60	19	9	19	45	543	102	59	6
Nagun gad	Nagun	Apr–89	249	29	555	190	–	30	–	69	1590	217	151	6
Seansu gad	Seansu	Apr–89	294	28	394	139	–	55	–	94	1144	254	123	6
Bhilangana	Ghuttu	Apr–89	89	46	288	54	26	13	14	120	524	122	69	6
Jola gad	Jola	Apr–89	184	31	160	82	42	45	–	24	601	197	67	6
Nailchami gad	Nailchami	Apr–89	132	61	388	187	16	56	4	33	1261	195	120	6
Balganga		Apr–89	119	36	310	108	37	27	–	47	853	170	88	6
Alaknanda	Badrinath	Oct–90	44	19	175	23	36	5	–	76	302	–	35	6
Ganga	Rishikesh	Apr–89	143	51	496	242	18	27	13	210	1241	126	136	6
Ganga	Arichaghat	Nov–83	614	84	923	410	–	175	–	–	2851	–	–	5
Indus														
Indus	Loma	Feb–92	452	34	522	200	–	210	–	128	1486	–	–	8
Sutlej	Salapar	Feb–92	84	82	622	193	–	25	–	306	1313	–	–	8
Beas	Hanogimata	Feb–92	48	25	148	39	–	29	–	50	347	–	–	8
Beas	Beas Kund	Feb–92	22	14	61	18	–	–	–	–	–	–	–	8
Chandra	Tandi	Feb–92	24	21	353	76	–	13	–	123	916	–	–	8
Bhaga	Tandi	Feb–92	28	19	332	114	–	11	–	187	594	–	–	8
Darcha	Darcha	Feb–92	24	20	189	54	–	7	–	117	322	–	–	8
Shyok	Sumur	Feb–92	341	68	567	197	–	249	–	144	1381	–	–	8
Tangstze	Tangstze	Feb–92	410	78	818	285	–	208	–	339	1833	–	–	8
Yamuna														
Yamuna	Batamandi	Oct–98	255	51	1019	497	8	60	35	333	2369	211	254	10
Yamuna	Hanuman chatti	Oct–98	67	56	388	100	16	30	14	113	780	92	88	10
Giri	Rampurmandi	Oct–98	259	49	1658	1065	10	48	58	1115	2834	231	399	10
Bata	Batamandi	Oct–98	275	42	954	460	7	77	39	395	1867	241	229	10
Tons	Mori	Oct–98	64	45	182	35	11	19	14	62	383	116	49	10
Tons	Kalsi	Oct–98	152	52	808	411	11	29	21	581	1395	186	202	10
Kemti fall	Near Mussorie	Oct–98	54	26	2520	2035		49	19	2913	2340	142	587	10
Aglar	Yamuna bridge	Oct–98	154	28	1099	957	10	39	28	1052	2115	217	318	10
Asan	Simla road bridge	Oct–98	330	46	1893	1080	11	225	164	975	3840	351	479	10
Deccan rivers														
Bhima	Near origin	Sep–02	174	10	182	110	–	133	19	5	585	309	75	11
Krishna	Panchaganga con.	Sep–02	484	20	454	270	–	287	39	90	1468	334	168	11
Mahanadi		Aug–81	257	–	225	123	–	286	–	–	–	97	–	40
Godavari			2957	59	350	325	–	–	–	–	–	271	–	41
Brahmaputra														
Brahmaputra	Dibrugarh	Apr–82	73	56	370	163	–	19	–	113	1021	172	107	5
Brahmaputra	Goalpara	Apr–82	80	46	318	148	–	29	–	99	884	118	92	5
Rivers in plains														
Gomati	Dobni	Mar–82	1149	99	794	695	–	258	–	255	3644	210	347	5
Chambal	Dholpur	Mar–82	1971	68	610	555	–	594	–	336	3095	83	333	5
Betwa	Hamirpur	Mar–82	2377	53	502	690	–	426	–	71	4238	237	388	5

lution from all these lithologies. In the Himalaya, high TDS are in rivers of the Yamuna system particularly in its lower reaches and in the rivers from the plains. Some of these samples also have high Cl and SO_4 indicative of major ion supply from weathering of evaporites, alkaline/saline soils and anthropogenic inputs[5,10]. Figure 2 a and b are ternary plots of cation and anion abundances in the rivers listed in Table 4. It is seen from Figure 2 a that most of the rivers from the Himalaya cluster around the Ca apex leaning

towards Mg. In the anion diagram (Figure 2 b) these data points are close to alkalinity apex and lie along a mixing line with Cl and SO_4. The distribution of data in Figure 2 is an indication that major ion abundances in these waters are dominated by carbonate weathering brought about mainly by CO_2. This inference is also attested from the Mg/Na–Ca/Na ratio plot (Figure 3). The three end members presented in Figure 3 are the oceanic end member, silicates and carbonates from the Himalaya[19]. The data show that, rain

water ratios fall along the mixing line between oceanic end member and carbonates, whereas the ratios of the rivers from the Himalaya follow silicate–carbonate mixing. The Ca/Na ratios of rivers can be affected by removal of Ca by calcite precipitation. Calcite supersaturation is common among many rivers from the Himalaya, especially in its lower reaches[20] and those from the plains. If this results in calcite precipitation, it would shift the Ca/Na data to the left of the mixing line. The observed scatter in Figure 3 seems to support such a removal process, however, it is difficult to confirm this removal because of uncertainties in the end member compositions.

Silicate weathering rates

Silicate weathering rate (SWR) per unit area is the riverine flux of dissolved major cations and silica derived from silicates in the basin

$$SWR = Q\Sigma(Na + K + Mg + Ca)_{sil} + SiO_2 = Q\{TDS(s)\},$$

where $(X)_{sil}$ is the dissolved riverine concentration of cations derived from silicate weathering and Q is the water discharge per unit area. To derive silicate weathering rates of river basins, it is necessary to extract the contributions of cations and silica from silicates to the measured major ion composition of rivers. This is one of the challenging problems in the determination of silicate weathering rates and associated CO_2 consumption. The estimation of $(X)_{sil}$ from the measured major ion abundances is model dependent and relies on the use of a suitable proxy. A common proxy is Na_{sil}, which is calculated as

Figure 3. Mg/Na and Ca/Na ratio plots for rain and river water samples. The rain samples follow the mixing trend between oceanic and carbonate end members. The rivers follow the silicate–carbonate mixing trend; points falling off the mixing line. This could be because of variability in end member compositions and/or precipitation of Ca as calcite.

$$Na_{sil} = Na_r - (Na_{rain} + Na_s),$$

where the subscripts sil, r, rain and s refer to silicate, river, rainwater and halite/salinealkaline soils/anthropogenic inputs. Na_{rain} is the rainwater concentration of Na, appropriately corrected for evapotranspiration. Often $(Na_{rain} + Na_s)$ is approximated as equal to measured Cl in rivers, Cl_r. This makes Na_{sil} equal to
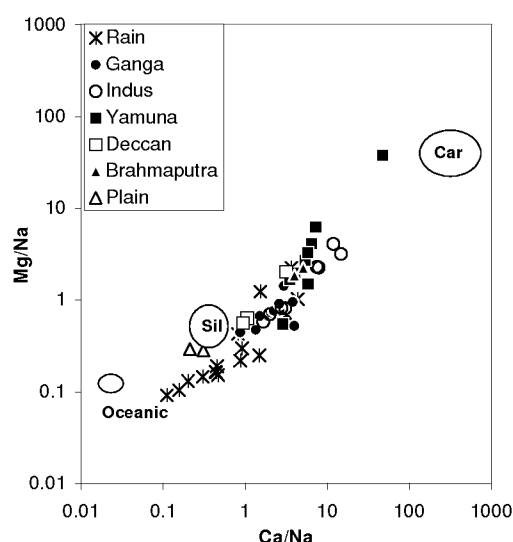
$$Na_{sil} \approx Na_r - Cl_r.$$

This approximation requires that Na_s is composed only of NaCl, the validity of which can be in doubt in basins with alkaline/saline soils and which receive anthropogenic inputs. In case of K, its dominant source is silicate weathering with minor supply from rains, therefore, K_{sil} can be calculated by subtracting the rainwater K contribution from measured values in rivers.
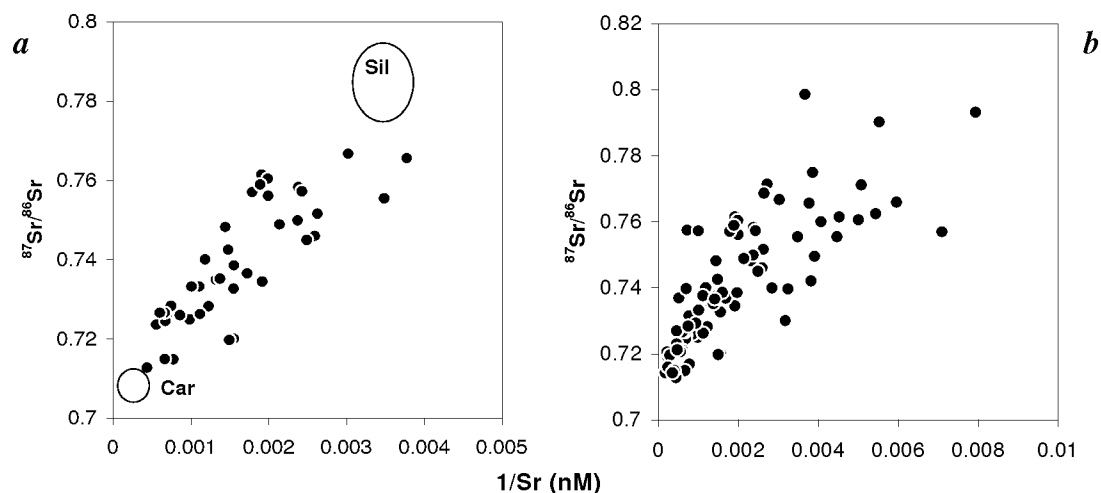
For Ca and Mg, their silicate components (Ca_{sil}, Mg_{sil}) are difficult to estimate as they have several sources (Table 3). Ca_{sil} and Mg_{sil}, therefore, are calculated assuming that they are released to rivers from silicates in the basin in a fixed proportion relative to Na. For the Himalayan rivers, the (Ca/Na) and (Mg/Na) ratios released to rivers is assumed to range from 0.2 to 1.0 and 0.3 respectively[19] based on their ratios in rocks, soil profiles and small streams predominantly draining silicates. The wide range in the Ca/Na ratio is because rocks of both the Higher and the Lesser Himalaya contribute Ca and Na to rivers draining them, the relative proportions of which are not well quantified. Further, the approaches used to derive the ratios also differ.

Another approach to derive contributions from various lithologies to the river water concentrations, is by the inversion method[21]. In this mixing equations are formulated for various elements w.r.t. Na and solved iteratively with an initial set of *a priori* parameters.

Sr isotopes, $^{87}Sr/^{86}Sr$, can also place constraints on silicate/carbonate weathering contributions to rivers. Carbonates and evaporites inherit their $^{87}Sr/^{86}Sr$ signatures from sea water from which they form. These values are in the range of 0.7070–0.7094 during the past[22] 500 Ma. The $^{87}Sr/^{86}Sr$ of silicates show very wide variations, depending on their Rb content and age. The granites and gneisses of the Himalaya are some of the highly radiogenic rocks in $^{87}Sr/^{86}Sr$. The Lesser Himalaya silicates have $^{87}Sr/^{86}Sr$ in the range of 0.78 to 0.90, whereas in the Higher Himalayan crystallines it varies between[23,24] 0.73 and 0.76. In contrast, the Deccan basalts are quite non-radiogenic and cluster around values[25] of ~ 0.706. Thus, rivers draining silicates of Lesser and Higher Himalaya are expected to have more radiogenic $^{87}Sr/^{86}Sr$ compared to those weathering carbonates, evaporites and Deccan basalts. The Sr concentration in rivers also reflects its abundance in silicates and carbonates/evaporites and the kinetics of their weathering. Generally, silicate weathering results in lower Sr and higher $^{87}Sr/^{86}Sr$ and carbonate/evaporite weathering in higher Sr and lower $^{87}Sr/^{86}Sr$. As

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Figure 4. Two end member mixing diagram for Sr in rivers from the Himalaya. *a*, Major rivers; *b*, Major rivers and tributaries. Larger scatter in (*b*) is a reflection of variability in $^{87}Sr/^{86}Sr$ values in the individual drainage basins. Data from refs 7, 8, 27.

Table 5. Silicate cations and silicate weathering rates

Rivers	Location	Area (10^3 km^2)	Discharge $(10^{12} \text{ l yr}^{-1})$	TDS(s) (mg l^{-1})	SWR $(\text{ton km}^{-2} \text{yr}^{-1})$	CO_2 draw-down $(10^5 \text{ moles km}^{-2} \text{yr}^{-1})$
Bhagirathi	Devprayag	7.8	8.3	14	15	4
Alaknanda	Bhagwan	11.8	14.1	9	10.2	4
Ganga	Rishikesh	19.6	22.4	11	12.9	4
Yamuna	Batamandi	9.6	10.8	25	26	5
Ganga–Brahmaputra	–	1555	1002	21	13.6	3
Krishna	Alamatti	36.3	17.3	30	14	–
West flowing rivers from Deccan	–	–	–	32	53	–
Deccan	–	500	–	–	–	4*

*For the entire Deccan[11].

the rivers integrate Sr contributions from both silicates and carbonates/evaporites, their data would fall on a mixing line if the end member compositions are unique. The $^{87}Sr/$ ^{86}Sr data for larger Himalayan rivers, indeed show an overall two component mixing trend (Figure 4 *a*). The trend, however, becomes less pronounced, as data from smaller tributaries are added to the plot (Figure 4 *b*). The increase in scatter reflects scatter in the end member $^{87}Sr/^{86}Sr$ values, particularly silicates, of the various basins.

The above simple interpretation of two-end member mixing is often challenged, especially for the Himalayan rivers, because of potential contributions from disseminated calcites and metamorphized carbonates (calc-silicates) which are shown to have highly radiogenic Sr isotope composition[26]. The impact of these sources on the Sr isotope budget of rivers draining the Himalaya are still debated[27,28]. Krishnaswami and Singh[29] have shown that in the Ganga head waters the source of high $^{87}Sr/^{86}Sr$ is silicate weathering, a similar conclusion has also been arrived by Bickle *et al.*[28] and Dalai *et al.*[27] for the Ganga and the Yamuna head waters.

Recently, HCO_3 and Mg concentrations in rivers have been used to derive silicate weathering rates of basalts[11,12]. The use of these proxies requires that they are supplied to rivers

only from silicate weathering, an assumption which may be violated if carbonate weathering is a source of dissolved inorganic carbon and Mg to these rivers. It is, however, demonstrated by Das *et al.*[11] that for Deccan basalts, Mg is a good proxy to derive basalt weathering rates, and that (Ca/Mg) and (Na/Mg) ratios released to rivers are roughly the same as in Deccan basalt, suggestive of near congruent weathering of these elements in basalts.

Table 5 presents TDS(s) in selected rivers and associated silicate weathering rates. The SWR for the head waters of the Ganga in the Himalaya (Bhagirathi, Alaknanda and Yamuna) is in the range of 10–25 tons $\text{km}^{-2} \text{yr}^{-1}$ (4–10 mm k yr^{-1}) The SWR for these rivers are factors of 2–5 higher than reported for world average attributable to enhanced weathering due to mountain uplift and monsoonal climate.

Factors influencing silicate weathering rates

A key issue in weathering studies is to understand the various factors especially the role of temperature in regulating weathering. This is because uptake of CO_2 by silicate weathering serves as negative feedback for atmospheric

CO_2. Weathering rate and temperature are related by the Arrhenius equation:

$$SWR = A\exp(-E_a/RT),$$

where E_a is the activation energy and T the temperature. Typical E_a for feldspars are in the range of 50–80 kJ/mol. For a temperature range of 20°C (10 to 30°C) and E_a of 60 kJ, the SWR change would be a factor of ~3. This difference in SWR should be measurable, if other factors remain nearly the same. Dalai et al.[10] observed a strong temperature dependence of SWR for the Yamuna tributaries in the Lesser Himalaya (Figure 5). Similarly, Dessert et al.[12] also reported temperature dependence for basalt weathering, based on a global database. In contrast, Edmond and Huh[30], based on geochemical data from large rivers at different latitudes, concluded that there is no discernible temperature dependence on weathering and that physical mechanisms of exposure and transport dominate weathering processes. Thus, at present, this is a controversial topic, resolution of which is compounded by the fact that in field studies several factors regulate the weathering rates making it difficult to critically assess the temperature dependence.

Runoff and physical erosion are the physical parameters which also contribute to enhanced chemical erosion[31,32]. Higher runoff and physical erosion helps in the transport of weathered materials and exposing fresh surfaces for weathering. Both these parameters, however, may be linked to temperature.

Lithology of the basins is another important variable determining the chemical weathering rate. Basalts are known to weather more rapidly than granites and gneisses[33]. However, the recent findings of Das et al.[11] that under favourable conditions granites/gneisses of the Himalaya weather at rates similar to that of Deccan basalts suggest that differ-ences in kinetics of weathering of these rock types can be compensated by other physical parameters.

Other factors such as vegetation, soil cover and frost shattering also contribute to variability in weathering rates in river basins. Thus, the dependence of weathering rates on a multitude of parameters continues to make the quantification of each of their roles a difficult issue. A focus of future research in continental weathering should be on this topic.

CO_2 consumption by silicate weathering

One of the goals of estimating the silicate cation abundances in rivers is to obtain CO_2 consumption rate by silicate weathering. Eqs (4) and (5) show that a definite relation exists between the CO_2 consumption and major ions released to rivers, for every equivalent of silicate cations released, one mole of CO_2 is consumed. Table 5 also lists the CO_2 uptake by some of the rivers in India. The results show that the head waters of the Ganga in the Himalaya consume 4×10^5 mole CO_2 km^{-2} yr^{-1}. This is a factor of ~3 higher than the global average CO_2 consumption by silicate weathering[31]. The uplift of the Himalaya, favourable monsoon climate, intense physical weathering all contribute to enhanced silicate weathering in this region and associated CO_2 consumption. Analogous to these basins in the Himalaya, weathering of Deccan basalts also have high CO_2 consumption rate, in the range of 0.5 to 10×10^5 moles km^{-2} yr^{-1}. These results demonstrate that under favourable conditions, both grainites/gneisses and basalts weather roughly at the same rates with similar rates of CO_2 consumption. This observation is significant in assessing the various factors influencing silicate weathering rates.

Summary

Chemical and isotopic studies of Indian rivers have taken major strides during the last 1–2 decades. These studies have generated high quality data, which have provided better quantification of chemical and silicate weathering rates of various basins, associated CO_2 consumption and factors contributing to their variations. Most of the conclusions, however, are based on limited sampling, particularly on temporal scales. More work needs to be done during peak discharge over several years to obtain weathering rates with less uncertainties. Another issue is the role of more easily weatherable minor lithologies in contributing to major ion chemistry and isotope systematics of the rivers. Developing suitable proxies to resolve this is important. The use of Re–Os, U isotopes, Ca, Mg isotopes to quantify erosion timescale, and weathering of organic rich sediments, silicates/carbonates should be informative.
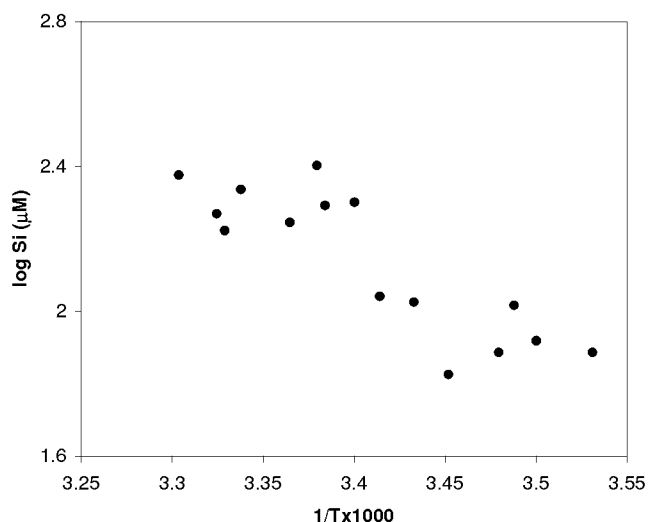
Figure 5. Arrhenius plot for Si in Yamuna tributaries[10]. The trend is suggestive of dependence of silicate weathering on temperature with an 'average' activation energy of 51 kJ mol^{-1}.

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