

Chemical characterisation of meltwater draining from Gangotri Glacier, Garhwal Himalaya, India

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A detailed analytical study of major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (SO_4^{2-} , HCO_3^- , Cl^- , NO_3^-) of meltwater draining from Gangotri Glacier was carried out to understand major ion chemistry and to get an insight into geochemical weathering processes controlling hydrochemistry of the glacier. In the meltwater, the abundance order of cations and anions varied as follows: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ and $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^-$, respectively. Calcium and magnesium are dominant cations while sulphate and bicarbonate are dominant anions. Weathering of rocks is the dominant mechanism controlling the hydrochemistry of drainage basin. The relative high contribution of (Ca+Mg) to the total cations (TZ^+), high (Ca+Mg)/(Na+K) ratio (2.63) and low (Na+K)/ TZ^+ ratio (0.29) indicate the dominance of carbonate weathering as a major source for dissolved ions in the glacier meltwater. Sulphide oxidation and carbonation are the main proton supplying geochemical reactions controlling the rock weathering in the study area. Statistical analysis was done to identify various factors controlling the dissolved ionic strength of Gangotri Glacier meltwater.

1. Introduction

Glacierised areas present an ideal environment to study water–rock interaction, since chemical weathering rates are high and anthropogenic impacts are often minimal (Brown 2002). The Indian Himalayan region (27°–36°N and 72°–96°E) consists a total of 9575 glaciers (Raina and Srivastava 2008) covering an area of about 40,000 km². All three major river systems of north India, the Ganga, Brahmaputra and Indus originate from the Himalayan snow and ice fields. Himalaya is considered a geodynamically active area and is prone to violent crustal movements, which are responsible for seismicity and high erosion rates (Valdiya 1998). The growing demand for freshwater in downstream stretches and the geo-

logical setting has made the hydrochemical study of Himalayan glaciers highly imperative.

Solute in the meltwater is derived during the passage of meltwater through the sub-glacier channel at the rock-ice and meltwater interface (Trudgill 1986). The rate and mechanism responsible for dissolved ion release in the meltwater of glacier streams vary with lithology (Collins 1979a). Weathering of bedrock is likely to occur when water flows at the ice-rock interface. In glacial environment, proton (H^+) appears to be accountable for the weathering of rock-forming minerals. The carbon dioxide reacts with water and form the weak carbonic acid, which dissociates into H^+ and HCO_3^- . Sulphide oxidation is another mechanism, which is responsible for the production of hydrogen ions (Garrels and Mackenzie 1971). The

Keywords. Hydrochemistry; weathering; Gangotri Glacier; Himalaya.

hydrogen ions produced react with carbonate, silicate or aluminosilicate minerals, which result in release of cations, dissolved silica and clay minerals (Raiswell 1984).

Various studies on Alpine glaciers by Rainwater and Guy (1961); Beherens *et al* (1971); Lorrain and Souchez (1972); Collins (1978, 1979a, 1979b); Tranter and Raiswell (1991) and in Himalayan region by Singh *et al* (1998) and Ahmad and Hasnain (2001) have suggested two principal flow components, viz., water passing through subglacial channels in contact with the rock substrate and water running off rapidly through englacial channels without undergoing significant chemical change. These studies indicate the high rate of chemical weathering in glaciated regions resulting from long residence times of meltwater in contact with the bed rock. There are a few studies that deal with Gangotri Glacier meltwater such as Ahmad and Hasnain (2000) and Kumar *et al* (2009). But only very few studies including that of Trivedi *et al* (2010) discuss in detail the hydrochemical variability of the meltwater of the Gangotri Glacier. This particular study has been carried out in view of the lacunae in existing knowledge to give an insight into the chemical characteristics of meltwater and the factors controlling geochemical weathering processes operating in Gangotri Glacier.

2. Study area

The Gangotri Glacier located in the Uttarkashi district of Uttarakhand state is one of the largest Himalayan glaciers. This glacier is bound between $30^{\circ}43'22''$ – $30^{\circ}55'49''$ (lat.) and $79^{\circ}4'41''$ – $79^{\circ}16'34''$ (long.) and is classified as valley-type glacier (Naithani *et al* 2001). The Bhagirathi River originates from Gaumukh (meaning ‘mouth of cow’), the snout of the Gangotri Glacier. It is located at an elevation of about 4000 m.a.s.l. Although it is commonly known as Gangotri Glacier, in fact it is Gangotri Glacier System consisting of a cluster of many small and large glaciers. This system comprises three major glacier tributaries, namely, Kirti Glacier (length 11.05 km; area 33.14 km²), Raktvarn Glacier (length 15.90 km; area 55.30 km²) and Chaturangi Glacier (length 22.45 km; area 67.70 km²) with main Gangotri Glacier (length 30.20 km; area 86.32 km²) as the trunk part of the system (Singh *et al* 2011). Beside these three major glaciers, some other tributary glaciers of this area are directly draining into Gangotri Glacier; among them Swachand, Miandi, Sumeru and Ghanohim are important. Four other glaciers, which directly drain into the Bhagirathi River are Maitri, Meru, Bhrigupanth and Manda and the total glacierized area of the catchment is 258.56 km² (Naithani *et al* 2001). The sampling site was located about 1.5 km

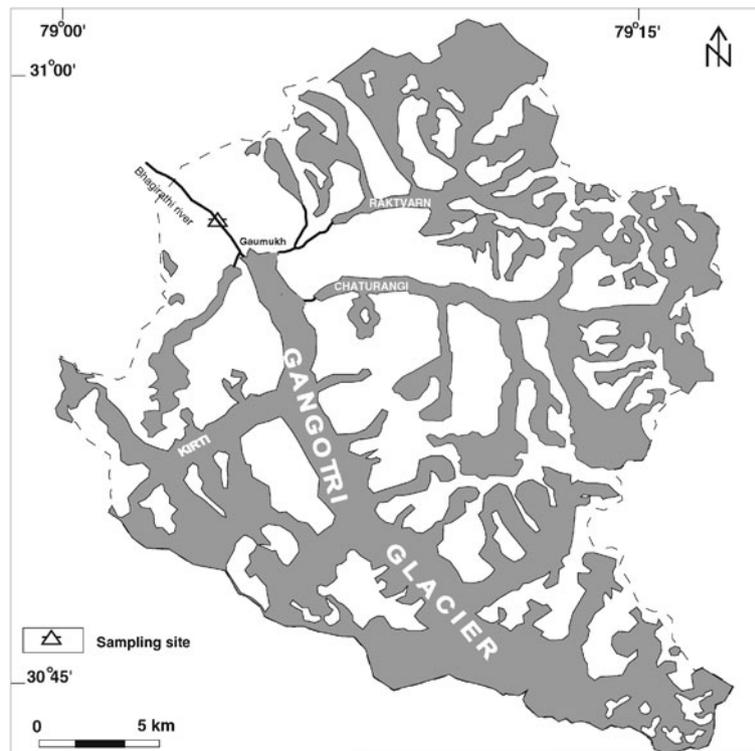


Figure 1. Map of the study area showing location of sampling site (modified after Singh *et al* 2011).

downstream from the snout of Gangotri Glacier at an elevation of about 3900 m.a.s.l (figure 1).

Geologically, the Gangotri Glacier System falls in the Central Crystalline Zone. From Gangotri further northeast, the mica schist, which is the dominant rock type above the Main Central Thrust (MCT) is retrograded in chlorite schist and intruded by hard and massive granite (Gangotri granite) (Kumar *et al* 2009). The Gangotri granite is one of the largest bodies of the Higher Himalayan Leucogranite belt located in the Garhwal Himalaya (Heim and Gansser 1939; Gansser 1964; Le Fort 1975; Yin 2006). It is exposed around the Gangotri Glacier region along the upper reaches of Bhagirathi River, including the peaks of Thalay Sagar (6904 m), Meru (6672 m), Shivling (6543 m), Bhagirathi (6856 m) and Bhrigupanth (6044 m) (Jowhar 2010). The Gangotri granite is fine grained (1–2 mm), composed of quartz + K-feldspar + plagioclase + tourmaline + muscovite \pm biotite (present only in the biotite-rich facies), \pm garnet (present only in the tourmaline-rich facies), \pm beryl, with apatite as the most abundant accessory mineral (Scaillet *et al* 1990; Jowhar 2010).

Granitic rocks of the Gangotri–Gaumukh area form a part of the Badrinath granitoid that has intrusive contact with the overlying and underlying metasedimentary rocks (Bassi 2004). However, detailed field investigations along the Gangotri Glacier and around the peaks of Bhagirathi, Meru, Shivling and Thalay Sagar have shown that regional, Barrovian facies metamorphic rocks underlie each leucogranite outlier (Searle *et al* 1999). Both CaSO_4 and MgSO_4 are found in Gaumukh–Gangotri shrine section. Sulphate minerals are normally expected to be associated with carbonate rocks, which are likely to have same packets, particularly when evaporites, such as, gypsum and anhydrite are present (Srivastava *et al* 2004). Several sulphide minerals like pyrite, chalcopyrite and arsenopyrites at the contact of quartz veinlets which traverses the country rocks are reported near the source area of Bhagirathi River (Bhatt 1963).

3. Materials and methods

Meltwater samples ($n=52$) draining from Gangotri Glacier were collected during the period from July to September 2007. The samples were collected two times a day, corresponding to diurnal low flow (0800 h) and high flow (1800 h). The samples were collected in prewashed polyethylene bottles of 300 ml capacity. Before collecting the samples, bottles were rinsed with the meltwater at the sampling site. The sample collection was done following the method suggested by Ostrem (1975).

Separate aliquots of the samples were removed to measure the electrical conductivity (EC) and pH in the field by using portable multiparameter meter (HACH-Sension 156). Bicarbonate was determined at the sampling site by acid titration method (APHA 2005). The samples were filtered through 0.45 μm Millipore membrane filters immediately after reaching the laboratory using vacuum filtration setup and stored at about 3°C during the period of analysis.

Dissolved silica analysis was carried out by molybdosilicate method (APHA 2005). Chloride concentration was determined by mercury (II) thiocyanate method (Florence and Farrar 1971). The turbidimetric method and brucine-sulphanilic acid method (APHA 2005) were used to measure the concentrations of sulphate and nitrate respectively. Major cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) were analysed by atomic absorption spectrophotometer (Shimadzu-AA-6800). Ca^{2+} and Mg^{2+} were determined in the absorbance mode and Na^+ and K^+ in the emission mode. The analytical precision for the measurement of major ions was better than $\pm 5\%$. TDS was calculated by summation of the masses of all the major dissolved constituents measured in each sample. Aquachem software was used for plotting the Piper diagram. Factor analysis for meltwater samples of the study area was carried out by Statistical Package for Social Sciences (SPSS); version – 10.5. Varimax rotation and principal component analysis were used for factor deriving and extraction respectively.

4. Results and discussion

4.1 Hydrochemistry

Chemical characteristics of meltwater draining from Gangotri Glacier is given in table 1. The charge balance errors determined by the formula $(\text{TZ}^+ - \text{TZ}^- / \text{TZ}^+ + \text{TZ}^- \times 100)$ were $<10\%$ and the ratio of TDS/EC was 0.63 ± 0.13 , confirming the reliability and quality of the analytical results. The average EC and pH values of meltwater of Gangotri Glacier were $81 \pm 5 \mu\text{S}/\text{cm}$ (69–92 $\mu\text{S}/\text{cm}$) and 7.2 ± 0.3 (6.2–7.7), respectively. These values are comparable to those reported in other available studies (Pandey *et al* 1999; Ahmad and Hasnain 2000) from the region. Sulphate was the dominant anion accounting 59.0% of the total anions. The average SO_4^{2-} concentration was $401 \pm 186 \mu\text{eq}/\text{l}$ (200–768 $\mu\text{eq}/\text{l}$) followed by HCO_3^- $266 \pm 27 \mu\text{eq}/\text{l}$ (210–314 $\mu\text{eq}/\text{l}$), Cl^- $11.2 \pm 11.0 \mu\text{eq}/\text{l}$ (1.4–66.2 $\mu\text{eq}/\text{l}$) and NO_3^- $1.9 \pm 1.0 \mu\text{eq}/\text{l}$ (0.0–3.2 $\mu\text{eq}/\text{l}$), respectively. In anionic abundance SO_4^{2-} was followed by HCO_3^- , Cl^- and NO_3^- accounting 39.1%, 1.6% and 0.3%

Table 1. Chemical characteristics of Gangotri Glacier meltwater.

Parameter	Max	Min	Average	SD
EC	92	69	81	5
pH	7.7	6.2	7.2	0.3
Ca ²⁺	343	102	206	76
Mg ²⁺	318	91	197	61
K ⁺	126	42	83	16
Na ⁺	128	45	75	16
SO ₄ ²⁻	768	200	401	186
HCO ₃ ⁻	314	210	266	27
Cl ⁻	66.2	1.4	11.2	11.0
NO ₃ ⁻	3.2	0.0	1.9	1.0
H ₄ SiO ₄	139	21	64	23
TZ ⁺	844	377	561	139
TZ ⁻	1020	459	681	174
TDS	73	35	51	12
(Ca+Mg)/TZ ⁺	0.83	0.53	0.71	0.08
(Na+K)/TZ ⁺	0.47	0.17	0.29	0.08
(Ca+Mg)/(Na+K)	4.99	1.14	2.63	0.95
Ca/Na	5.33	1.06	2.85	1.15
Mg/Na	5.37	1.00	2.76	1.01
HCO ₃ /Na	6.53	1.91	3.73	0.94
Na/Cl	54.1	1.2	13.5	11.2
K/Cl	61.3	1.5	14.9	12.7
TDS/EC	0.88	0.44	0.63	0.13
C ratio	0.61	0.23	0.43	0.13

Unit: Dissolved ions, TZ⁺; TZ⁻ in $\mu\text{eq/l}$; TDS in mg/l ; EC in $\mu\text{s/cm}$ and H₄SiO₄ in $\mu\text{mole/l}$.

of total anions, respectively. The average Ca²⁺ concentration was found to be $206 \pm 76 \mu\text{eq/l}$ (102–343 $\mu\text{eq/l}$) followed by Mg²⁺ $197 \pm 61 \mu\text{eq/l}$ (91–318 $\mu\text{eq/l}$), K⁺ $83 \pm 16 \mu\text{eq/l}$ (42–126 $\mu\text{eq/l}$) and Na⁺ $75 \pm 16 \mu\text{eq/l}$ (45–128 $\mu\text{eq/l}$). The cation chemistry indicates that Ca²⁺ and Mg²⁺ were the dominant cations, on an average constituting 36.7% and 35.1% of the total cations respec-

tively, followed by K⁺ (14.8%) and Na⁺ (13.3%). The average dissolved silica concentration in the Gangotri Glacier meltwater was recorded as $64 \pm 23 \mu\text{mole/l}$ (21–139 $\mu\text{mole/l}$).

4.2 Sources of dissolved ions

The chemical composition of glacier meltwater demonstrates that chemical weathering takes place beneath the glacier (Reynolds and Johnson 1972; Raiswell 1984). The release of dissolved ions to the glacier streams is governed by the rock–water interaction, bed rock mineralogy, weathering reactions, composition of atmospheric deposition and rate of water flow in the glacier catchment (Singh and Hasnain 1998). The hydrochemistry of reservoir is likely to be determined by mixing of two components from dissolution of carbonates and silicates and the relative significance of these two sources can be explained by cationic abundance and their ratios (Singh *et al* 2005). The scatter plot of (Ca+Mg) vs. TZ⁺ (figure 2a) shows that most of the points fall above 1:1 equiline with an average equivalent ratio of 0.71 ± 0.08 . The relatively high contribution of (Ca+Mg) to the total cations (TZ⁺) and high (Ca+Mg)/(Na+K) ratio (2.63 ± 0.95) indicate that carbonate weathering is a major source of dissolved ions in the meltwater of Gangotri Glacier, as reported by earlier researchers (Singh and Hasnain 1998; Pandey *et al* 1999; Kumar *et al* 2009). The scatter plot of Na+K/TZ⁺ (figure 2b) shows that all points fall above 1:1 equiline with a low ratio (0.29 ± 0.08), indicating a relatively low contribution of dissolved ions from silicate weathering, also reported by other researchers (Singh and Hasnain 2002; Kumar *et al* 2009). Na⁺, K⁺ and dissolved silica in the drainage basin are mainly derived from the weathering of silicate minerals, with clay minerals as

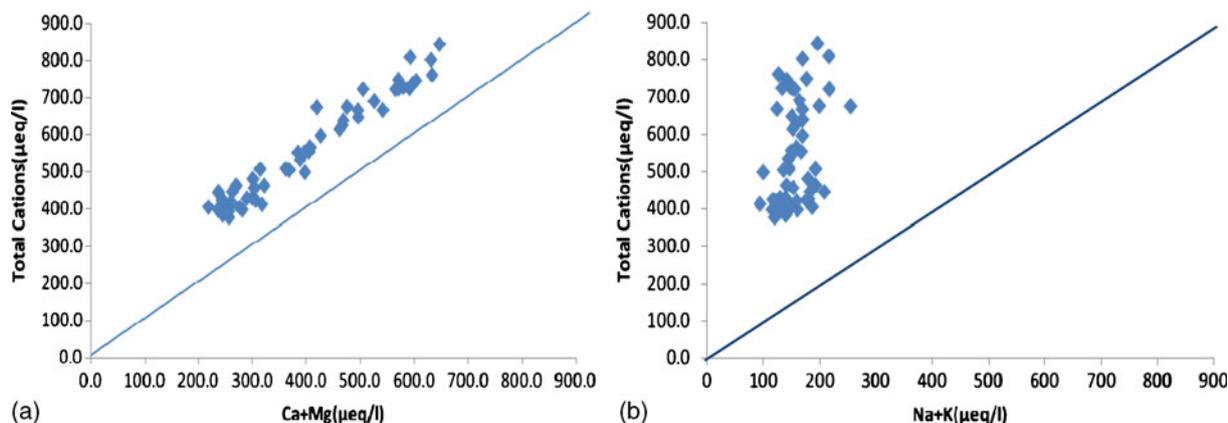


Figure 2. (a) Scatter plot between Ca+Mg and total cations (TZ⁺). (b) Scatter plot between Na+K and total cations (TZ⁺).

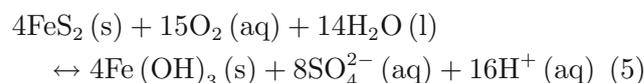
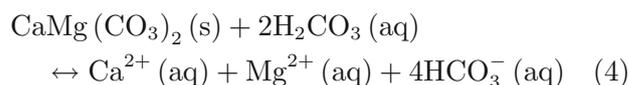
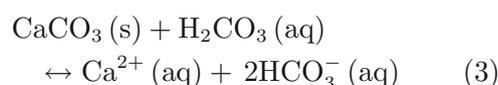
by-products. In the Ganga headwater, Na^+ and K^+ are mainly derived from igneous and metamorphic rocks of the Central Crystalline rocks. Micas, orthoclase (KAlSi_3O_8) and albite are common parental minerals for Na^+ and K^+ release in the Ganga headwater, which may react with water and carbonic acid and accumulate clay minerals in the sediments (Singh and Hasnain 2002).

Water draining carbonates show Ca^{2+} and Mg^{2+} dominated reservoirs and Ca/Na ratios close to 50, Mg/Na ratios close to 10 and HCO_3/Na ratios close to 120 (Negrel *et al* 1993; Meybeck 1986; Stallard 1980). The chemical composition assigned for silicate end member is $\text{Ca}/\text{Na} = 0.35 \pm 0.15$, $\text{Mg}/\text{Na} = 0.24 \pm 0.12$, and $\text{HCO}_3/\text{Na} = 2 \pm 1$ (Gaillardet *et al* 1999). The observed equivalent ratios of $\text{Ca}/\text{Na} = 2.85 \pm 1.15$, $\text{Mg}/\text{Na} = 2.76 \pm 1.01$ and $\text{HCO}_3/\text{Na} = 3.73 \pm 0.94$ in the meltwater of Gangotri Glacier are higher than those of meltwaters draining silicate lithology and much lower than those of waters draining carbonate lithology. These ratios indicate that chemical composition of the meltwater of Gangotri Glacier is influenced by carbonate weathering followed silicate weathering.

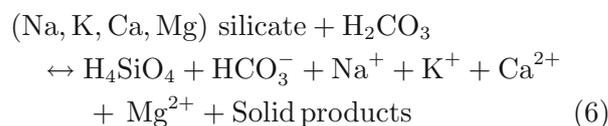
The scatter plot of $(\text{Ca}+\text{Mg})$ vs. $(\text{HCO}_3+\text{SO}_4)$ (figure 3a) shows good correlation throughout the range of data, though plotted points tend to fall above 1:1 equiline requiring a portion of the $(\text{HCO}_3+\text{SO}_4)$ to be balanced by cations ($\text{Na}+\text{K}$) from weathering of silicate rocks (Pandey *et al* 1999). The scatter plot of $(\text{Ca}+\text{Mg})$ vs. SO_4^{2-} (figure 3b) shows significant correlation between $(\text{Ca}+\text{Mg})$ and SO_4^{2-} ($r^2 = 0.93$) indicating that CaSO_4 and MgSO_4 contribute sulphate to the meltwater of Gangotri Glacier. The first possibility is that SO_4^{2-} content in the glacier melt could have acquired through dissolution of sulphate minerals (gypsum and anhydrite). The second possibility is that SO_4^{2-} has been derived through sulphide oxidation (equation 5) (Srivastava *et al* 2004). Trace amount of NO_3^- was also reported from the study area, indicating palatability of water. The NO_3^- in the monsoon season indicates possible influence of

atmospheric deposition associated with the acidic NO_3^- aerosol (Tranter *et al* 1993) coupled with possible contribution from anthropogenic activities in the sampling area.

The most important mechanism responsible for rock mineral weathering is acid hydrolysis (Raiswell 1984). In the bulk stream water, the relative proportions of HCO_3^- and SO_4^{2-} reflect the dominance of the two major sources of aqueous protons driving subglacial chemical weathering reactions (Raiswell 1984; Tranter *et al* 1993; Brown *et al* 1996).



The general reaction of weathering of silicate minerals with H_2CO_3 can be written as (Anshumali and Ramanathan 2007):



The relative importance of two major proton producing reactions – carbonation and sulphide oxidation can be evaluated on the basis of the C-ratio. Brown *et al* (1996) proposed estimation of C ratio ($\text{HCO}_3/\text{HCO}_3+\text{SO}_4$). If C ratio is 1.0, it indicates the significance of carbonation reaction involving acid hydrolysis and pure dissolution, consuming protons from atmospheric CO_2 (equations 1, 2 and

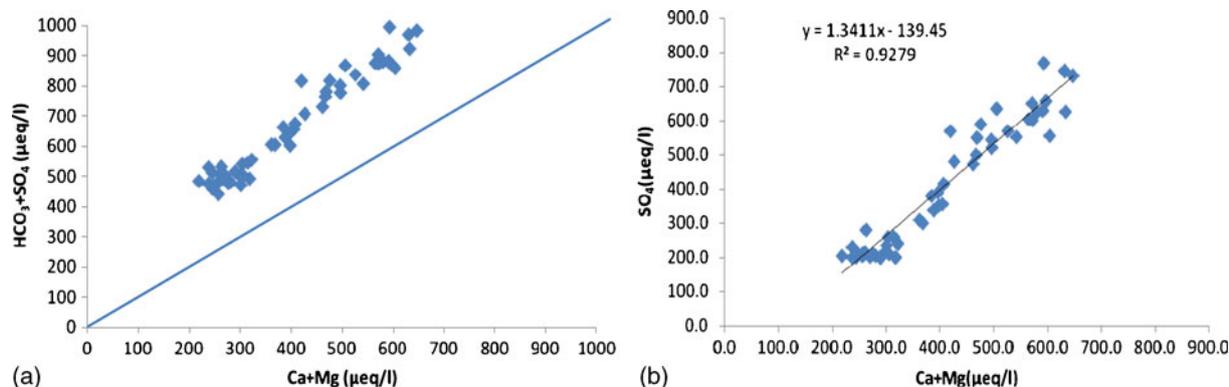


Figure 3. (a) Scatter plot between $\text{Ca}+\text{Mg}$ and HCO_3+SO_4 . (b) Scatter plot between $\text{Ca}+\text{Mg}$ and SO_4 .

3). Conversely if C ratio is 0.5, it suggests coupled reaction involving carbonate weathering and protons derived from oxidation of sulphide (equation 5). The average C-ratio for the meltwater of Gangotri Glacier is 0.43 ± 0.13 , which suggests that the major proton producing reaction is sulphide oxidation. The coupled reactions involving dissolution of CO_2 , carbonate dissolution and protons derived from sulphide mineral oxidation control the hydrochemistry of Gangotri Glacier. This ratio is similar to the results obtained for the nearby Dudu Glacier meltwater stream in Ganga head-water (Ahmad and Hasnain 2001).

Contribution of atmospheric input to the chemical composition of river water has been studied by many researchers (Biksham and Subramanian 1988; Meybeck 1983; Sarin *et al* 1989; Pandey *et al* 1999). The importance of atmospheric input for river water composition can also be determined by the ratio of ions to chloride. The scatter plot of (Na+K) vs. Cl^- (figure 4) shows that (Na+K) content is much higher than Cl^- and average Na+K/Cl ratio for the study area is significantly higher than expected from marine aerosols. The average equivalent ratios of $\text{Na}/\text{Cl} = 13.5 \pm 11.2$ and $\text{K}/\text{Cl} = 14.9 \pm 12.7$ are significantly higher than those of sea water (i.e., $\text{Na}/\text{Cl} = 1.0$ and $\text{K}/\text{Cl} = 0.2$ respectively). These ratios indicate relatively minor contribution from atmospheric precipitation to the observed dissolved ion budgets of the meltwater of Gangotri Glacier as reported by other researchers (Pandey *et al* 1999; Kumar *et al* 2009). Sarin *et al* (1992) estimated that atmospheric deposition may contribute up to 20% of Na^+ and K^+ and up to 5% of the Ca^{2+} , Mg^{2+} and SO_4^{2-} to the major ions chemistry of Ganga source water. The observed high ratios of Na/Cl and K/Cl may also be indicative of the contribution from salt dissolution from evaporites. But the observed high equivalent ratio of $\text{Mg}/\text{Na} = 2.76 \pm 1.01$ and low concentration of chloride along with less abundance of evaporites from the geological formation indicate that fraction of cations derived from

evaporites accompanying Cl^- is likely to be negligible (Pandey *et al* 1999). Thus the observations indicate the limited contribution of evaporite dissolution and atmospheric input in comparison to the contribution from rock weathering (carbonate and silicate) which is the major pathway controlling the hydrochemistry of the Gangotri Glacier.

Stability of minerals is an important way in which the approach to the equilibrium between natural water and clay minerals can be verified through thermodynamic data (Garrels and Christ 1965). The thermodynamic stability relationship plot of water chemistry in Na, K, Ca and Mg silicate system are given in figure 5. The pH-log H_4SiO_4 relation demonstrates that chemical composition of the meltwater of Gangotri Glacier falls in the region of kaolinite, implying that hydrochemistry favours kaolinite formation. X-Ray mineralogical studies of suspended sediment are to be carried out to support the above observation.

Meltwater evolution and relationship between water composition and rock type can be evaluated by plotting the concentrations of major cations and anions in the (Piper 1944) Tri-linear diagram. The Piper plot (figure 6) showed that majority of samples fell in the category of Ca- SO_4 type water. But a considerable number of samples also fell in Mg- SO_4 , Mg- HCO_3 and Ca- HCO_3 types of water. From Piper plot, it is clear that alkaline earth metals (Ca+Mg) are significantly higher than alkalis (Na+K) and strong acids (SO_4+Cl) dominated over weak acids (HCO_3+CO_3). This further confirms that carbonate weathering is the major source for the dissolved ions.

4.3 Effective CO_2 pressure

The effective CO_2 pressure or internal CO_2 pressure (Log pCO_2) has been estimated from pH values and HCO_3^- concentration. The pCO_2 of a solution reflects the rate at which CO_2 diffuses into or out of solution relative to the rate of other chemical weathering reactions (Raiswell 1984; Raiswell and Thomas 1984; Thomas and Raiswell 1984). The pCO_2 signature of meltwater can be used to characterize different glacial hydrological weathering environments (Sharp 1991; Wadham *et al* 1998). If pCO_2 of solutions are not equal to atmospheric pCO_2 ($10^{-3.5}$ atm), it can be said to be in disequilibrium with respect to the atmosphere. When the supply of protons is more than their consumption, then high pCO_2 conditions arise. CO_2 diffuses out from the solution, with the conversion of some HCO_3^- to CO_2 and loss of protons from solution. Low pCO_2 conditions arise when the demand of protons for chemical weathering is more than the rate of CO_2 diffusion

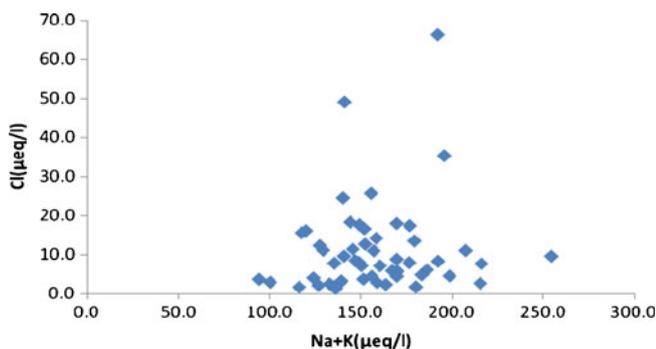


Figure 4. Scatter plot between Na+K and Cl.

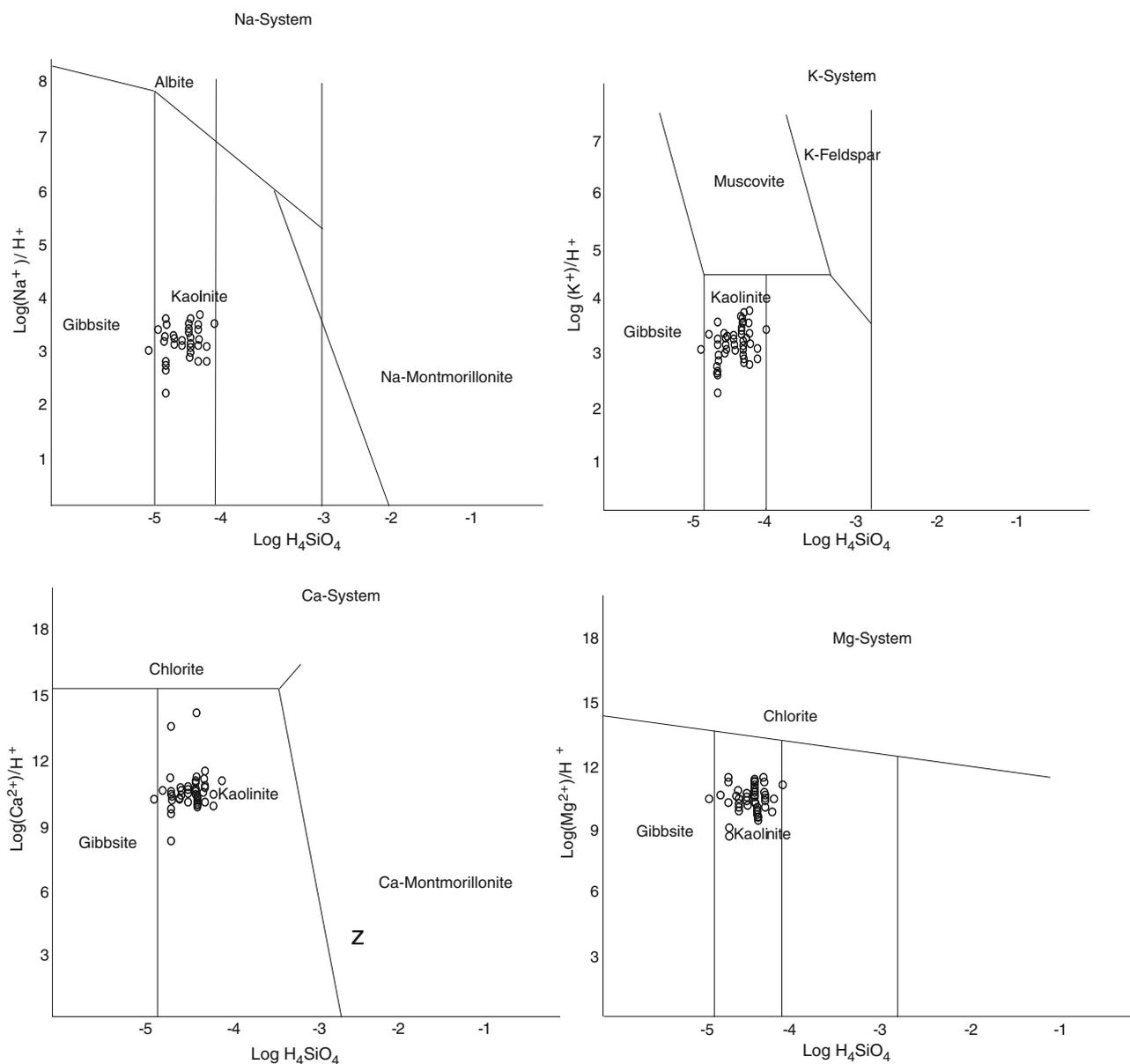


Figure 5. Stability diagram for Na, K, Ca and Mg silicate systems.

into solution (Wadham *et al* 1998). The average $p\text{CO}_2$ value for meltwater of Gangotri Glacier was slightly higher ($10^{-2.9}$) than the atmospheric value ($10^{-3.5}$) indicating open system weathering. This is a global trend that river water shows disequilibrium with the atmosphere (Garrels and Mackenzie 1971; Raymahasay 1986). The slightly higher values of $p\text{CO}_2$ could be explained by the relative higher rate of solubility in comparison to release of excess of CO_2 gas in a turbulent and low temperature environment (Stumm and Morgan 1970). The average $p\text{CO}_2$ value for this study area is comparable with the earlier reported value for Alaknanda River basin (Singh and Hasnain 1998). High $p\text{CO}_2$ values are likely to arise from the coupling of sulphide oxidation and carbonate dissolution (Wadham *et al* 1998).

4.4 Statistical analysis

Correlation analysis is a bivariate method commonly used to measure and establish the relationship between two variables. It is a statistical tool used to measure the degree of dependency of one variable to other. A parametric correlation analysis of measured parameter is given in table 2. Strong correlation was observed between Ca^{2+} and Mg^{2+} ($r^2 = 0.888$) and Na^+ and K^+ ($r^2 = 0.827$) indicating the same source, which may be carbonate and silicate weathering respectively. Good correlation was also observed between Ca^{2+} and SO_4^{2-} ($r^2 = 0.95$) and Mg^{2+} and SO_4^{2-} ($r^2 = 0.919$), probably resulting from dissolution of sulphate minerals, pyrite oxidation and secondary leaching of SO_4^{2-} from evaporites.

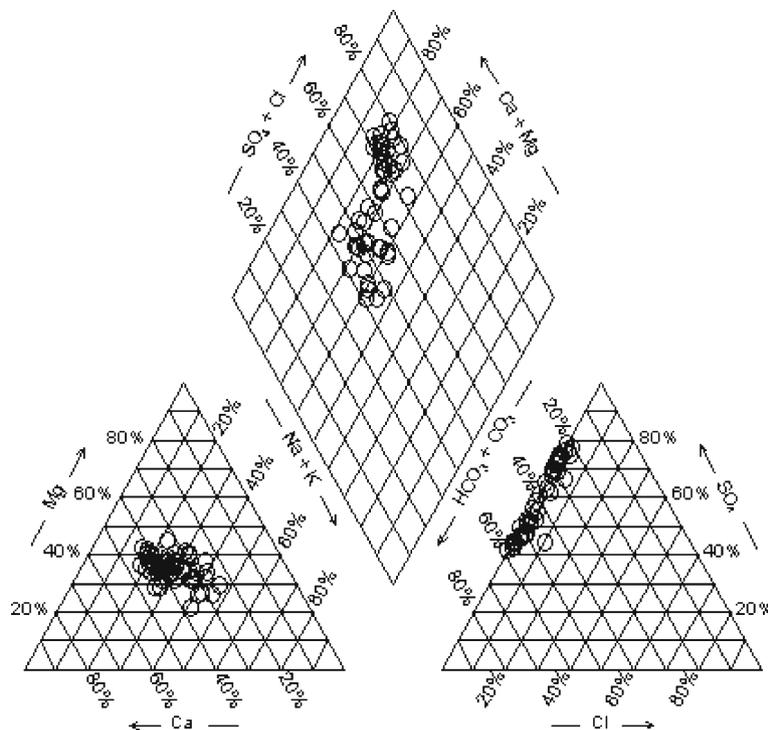


Figure 6. Piper plot for concentration of ions.

Factor analysis is an important statistical method used to explain observed relationships among numerous variables. The mode of factor analysis is R-mode or Q-mode. Factor analysis is termed R-mode when the concern is interrelationships among the variables and Q-mode when concern is the interrelationships between samples (Singh and Hasnain 2002). R-mode factor analysis was used to identify major factors controlling the hydrochemistry of Gangotri Glacier. Factor analysis results of meltwater of study area were given in table 3. When the corresponding eigenvalue is greater than 1, it is said to be significant contribution of factor. Three factors with an eigenvalue >1 were identified. These three factors explain about 68% of the total variance.

Factor 1 accounts for 38.2% variance in the dataset and shows high loading of H_4SiO_4 , SO_4^{2-} , Ca^{2+} and Mg^{2+} and negative loading of HCO_3^- . This factor explains contribution from carbonate/silicate weathering, sulphate mineral dissolution, carbonation and sulphide oxidation. HCO_3^- might have derived from carbonate dissolution, hence showing negative loading in comparison to Ca^{2+} , Mg^{2+} , Na^+ and K^+ . Factor 2 accounts for 17.6% variance in the dataset and shows strong loading of pH, Na^+ and K^+ . This factor describes contribution from weathering of silicate minerals. Factor 3 accounts for 12.2% variance in dataset and shows high loading of Cl^- . This factor represents contribution from evaporites and atmospheric precipitation.

Table 2. Correlation matrix of measured parameters in Gangotri Glacier meltwater.

	pH	H_4SiO_4	NO_3	Cl	HCO_3	SO_4	Na	K	Ca	Mg
pH	1.000									
H_4SiO_4	0.174	1.000								
NO_3	0.098	0.038	1.000							
Cl	0.062	0.131	0.126	1.000						
HCO_3	-0.139	-0.382	-0.147	0.048	1.000					
SO_4	0.038	0.637	0.126	0.022	-0.530	1.000				
Na	0.244	0.258	0.150	-0.002	-0.215	0.233	1.000			
K	0.243	0.296	0.066	0.246	-0.276	0.327	0.827	1.000		
Ca	-0.037	0.587	0.130	0.124	-0.393	0.950	0.070	0.181	1.000	
Mg	-0.030	0.567	0.060	0.031	-0.350	0.919	-0.029	0.072	0.888	1.000

Table 3. Principal and varimax rotated R-mode factor loading matrix.

Variables	Factor 1	Factor 2	Factor 3	Communalities
pH	–	0.602	–0.176	0.393
H ₄ SiO ₄	0.702	0.248	0.113	0.567
NO ₃	–	0.137	0.415	0.194
Cl	–	–	0.762	0.586
HCO ₃	–0.532	–0.330	0.123	0.407
SO ₄	0.977	0.117	–	0.977
Na	0.103	0.863	0.175	0.786
K	0.183	0.835	0.310	0.826
Ca	0.941	–	0.230	0.945
Mg	0.937	–0.125	–	0.893
Eigen value	4.590	2.107	1.466	
% of variance	38.247	17.556	12.218	
% of cumulative variance	38.247	55.802	68.02	

4.5 Temporal variation of the total dissolved solids (TDS)

Variations in the concentration of different ions with time are possibly due to different weathering intensities generating meltwater at different discharge values (Kumar *et al* 2009). There has been a marked temporal variation in the TDS of the meltwater draining from Gangotri Glacier. TDS was high in the mornings and reduced towards evenings (figure 7). The model of Rainwater and Guy (1961), Collins (1983), Kumar *et al* (2009), was used to explain the observed temporal variation in the TDS. In the morning, low supply of solar energy reduced the melting and dilution of subglacial water. The subglacial water produced at pressure melting point, has high ionic chemical enrichment as a result of high residence time and longer contact with the solute rich base. In the afternoon with an increase in insolation, englacial channels become active and large amount of supraglacial meltwaters become available for transportation so that

discharge is maximum in the evening, resulting in increased dilution of TDS.

4.6 Average chemical composition of Gangotri Glacier meltwater and comparison with other Himalayan glaciers' meltwater

The summary of chemical composition of meltwater draining from Gangotri Glacier and other selected Himalayan glaciers are given in table 4. The abundance of anions in the meltwaters of Kafni, Dokriani and Chhota Shigri glaciers varied as HCO₃[–] > SO₄^{2–} > Cl[–] while in Bagni Glacier it varied as SO₄^{2–} > HCO₃[–] > Cl[–]. In Dudu and Gangotri glacier meltwaters the abundance order was SO₄^{2–} > HCO₃[–] > NO₃[–] > Cl[–] and SO₄^{2–} > HCO₃[–] > Cl[–] > NO₃[–] respectively. The abundance of cations in the meltwaters of Dokriani and Gangotri glaciers varied as follows: Ca²⁺ > Mg²⁺ > K⁺ > Na⁺; whereas in Kafni and Chhota Shigri glaciers, it varied as Ca²⁺ > Mg²⁺ > Na⁺ > K⁺. In

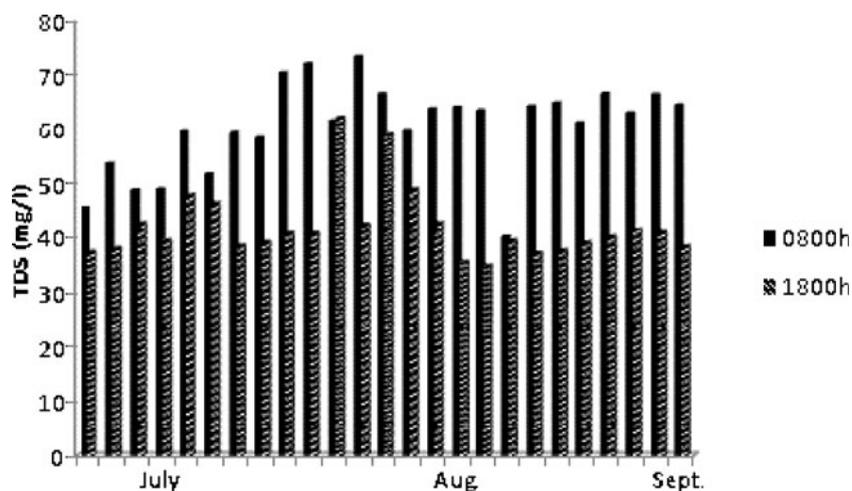


Figure 7. Temporal variation of the TDS in Gangotri Glacier meltwater.

Table 4. Average chemical composition of Gangotri Glacier meltwater and comparison with other Himalayan glacier meltwaters.

Glacier	EC	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	H ₄ SiO ₄	References
Kafni	89.2	7.2	587	165	65	31	623	76	35	–	28	Singh <i>et al</i> (1998)
Bagni	122	7.6	680	269	21	457	1557	1710	13.4	–	–	Ahmad and Hasnain (2000)
Dudu	31.9	6.3	91.1	6.5	42.7	24.6	52.3	85.4	5.0	14.9	36.0	Ahmad and Hasnain (2001)
Dokriani	48.2	7.0	271	100	64	116	625	406	16	–	–	Ahmad and Hasnain (2000)
Chhota Shigri	85.6	7.4	530	238	104	76	295	279	25	–	–	Sharma (2007)
Gangotri	81	7.2	206	197	75	83	266	401	11.2	1.9	64	Present study

Unit: Dissolved ions in µeq/l; EC in µs/cm and H₄SiO₄ in µmole/l.

Bagni and Dudu glacier meltwaters the abundance order was Ca²⁺ > K⁺ > Mg²⁺ > Na⁺ and Ca²⁺ > Na⁺ > K⁺ > Mg²⁺ respectively.

The average (Ca+Mg)/(Na+K) ratios for Kafni, Bagni, Dudu, Dokriani, Chhota Shigri and Gangotri glaciers are 8.00, 1.99, 1.40, 2.06, 4.27 and 2.63 which indicate the dominance of carbonate weathering as a major source of dissolved ions in the glacier basin, even when calcite is present in low concentrations (Raiswell 1984). The average (Na+K)/Cl ratios are 3.0, 35.7, 13.5, 11.3, 7.2 and 28.3 for Kafni, Bagni, Dudu, Dokriani, Chhota Shigri and Gangotri glaciers, respectively. These ratios are significantly higher than the expected from marine aerosols, suggesting little contribution from atmospheric input (Singh *et al* 1998; Ahmad and Hasnain 2000, 2001; Sharma 2007). Chemical characteristics of meltwater draining from different glaciers are in equilibrium with the bedrock terrain over which the glaciers flow (Meybeck 1981). Meltwater draining from Kafni Glacier shows high percentage of calcium and bicarbonate because of the presence of calcareous band and calc-silicate rocks in the glacier basin (Singh and Hasnain 1998). Whereas, meltwater draining from Bagni Glacier shows quite different characteristics with respect to other glacier meltwaters, because this glacier lies on Martoli Formation constituted of phyllite, which is responsible for high EC and high pH and exceptionally high potassium percentage in the meltwater (Ahmad and Hasnain 2000). Gangotri, Chhota Shigri, Bagni and Dokriani glaciers show high sulphate concentration, may be due to pyrite dissolution in the bed rock (Bhatt 1963; Sharma 2007). Another reason for high concentration of sulphate as compared to other ions in the meltwater of Gangotri Glacier may be dissolution of sulphate minerals (gypsum and anhydrite) (Srivastava *et al* 2004).

5. Conclusion

The Gangotri Glacier meltwater is alkaline in nature. Cationic abundance order is Ca²⁺ > Mg²⁺ > K⁺ > Na⁺, while anionic abundance order is

SO₄²⁻ > HCO₃⁻ > Cl⁻ > NO₃⁻. Calcium and magnesium are the dominant cations, while sulphate is dominant anion followed by bicarbonate. The high (Ca+Mg) *vs.* TZ⁺, (Ca+Mg)/(Na+K) ratios and low (Na+K)/TZ⁺ ratio indicate that chemical characteristics of meltwater draining from Gangotri Glacier System is largely controlled by carbonate weathering and partly controlled by silicate weathering. Coupled reactions involving sulphide oxidation and carbonation also seem to play a major role in controlling the solute acquisition process. Sulphide oxidation is the major proton producing reaction in the meltwater of Gangotri Glacier.

The equivalent ratios of Na/Cl and K/Cl are significantly higher than those of marine aerosols indicating minimal contribution from atmospheric precipitation to the dissolved ion budgets of the meltwater of Gangotri Glacier. Water types from Piper plots indicate the dominance of alkaline earth metals over the alkali metals and strong acids over weak acids in the meltwater. The average pCO₂ value for the meltwater of Gangotri Glacier is slightly higher than the atmospheric value indicating open system weathering and shows disequilibrium with respect to the atmosphere. The results of factor analysis indicate that carbonate/silicate weathering, sulphate mineral dissolution and sulphide oxidation along with atmospheric contribution regulate the major ion chemistry.

Acknowledgements

The authors are thankful to the Department of Science and Technology (DST), Govt. of India for funding the research project on Gangotri Glacier. The authors are also grateful to Jawaharlal Nehru University for providing the research facilities.

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