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Diurnal hydrological controls and non-filtration effects on minor and trace elements in stream water draining the Qiyi Glacier, Qilian Mountain

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Diurnal minor and trace elements in glacial outflow water draining the Qiyi Glacier and associated hydrological controls as well as the filtration effects on water chemistry were examined. Results show that major ions, Li, Sr, and Ba are exported predominately as mobile monovalent or divalent ions and are controlled by hydrological variations over the diurnal cycle exhibiting an inverse concentration with discharge, suggesting that Li, Sr, and Ba can be used as tracers in subglacial hydrological investigations. Conversely, other elements (e.g. Fe, Al, and Cr) exhibit variations that are not strongly correlated with the discharge reflecting the physicochemical controls. The non-filtered operation appears not to strongly influence Sr and Ba, but has an effect on some elements such as Fe, Al, V, Ti, and Co, indicating that these changed elements are transported in particulate forms and thus their concentrations are highly dependent on particulate numbers in solutions. This implies that the immediate filtration after sampling is essential in hydrochemical studies at Alpine glacial basins due to subsequent mineral dissolution.

minor and trace elements, filtration, stream water, Qiyi Glacier, Qilian Mountain

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Glacial meltwater on Tibetan Plateau provides headwaters for some rivers that influence regional water availability and food security [1]. Meltwater chemistry enables us to understand the cryospheric influences on chemical denudation, biogeochemical cycling [2–4], and glacial ecosystems [5–7]. A few studies on minor and trace elements have been performed in Alpine glacial hydrological systems. At the Haut Glacier d'Arolla of Switzerland, some elements (e.g. Ba, Be, and Cd) exist primarily as monovalent or divalent cations, which are involved in interactions with suspended sediment surfaces. Some elements (e.g. Fe, Al, and Mn) are predominantly transported as colloids, which may remove other elements from solution by the co-precipitation reactions [8, 9]. The quantity and transport mode of minor and trace elements influence their bioavailability downstream of glacial headwater catchments, and their concentrations are influenced by (oxi)hydroxide precipitation and adsorption-desorption reactions with suspended sediment surfaces [8]. Minor and trace elements have potential in the so-lute-provenance and flow-routing studies, and their enrichment in meltwater has implications for downstream aquatic environments [8, 10–12]. The relationship between element concentration and discharge reflects the physicochemical controls, including sorption, oversaturation, and precipitation of other species [9, 10, 12]. Additionally, at the Wright Valley of the Antarctic, the element concentrations (e.g. Mn, Fe, and Ni) are lower than those in world's stream waters. Met-

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al uptake and exchange with particulate phases along the river serve as a buffer for the dissolved load [13]. At the Kuannersuit Kuussuat of the Greenland, a significant correlation exists between Fe, Al and Mg^{2+} , and significant effect of the sample filtration through 0.7 µm retention filters is not observed [14]. Under the Greenland ice sheet, the reactions of meltwater with proglacial sediments enhance Fe load, and Fe in shield bedrock is lower than that in crustal rocks. Fe can be used to give an estimate of global fluxes of Fe to coastal polar waters, and glacial water input of Fe to adjacent polar water is greatest around the Greenland where annual discharge is the highest. The biogeochemical weathering processes operating on the subglacial debris and suspended sediment are likely to be similar to those in other glacial catchments [15].

However, minor and trace elements in meltwater on Tibetan Plateau have not been examined, despite their importance as bio-limiting nutrients or toxic metals in freshwater, seawater, and other aqueous systems [16, 17], and their importance in downstream assessment of anthropogenic stream pollution [12, 18, 19]. Moreover, the immediate filtration after sampling sometimes was not satisfied probably owing to restricted field conditions, rigorous experiment demands or anthropogenic negligence [20-30]. This will affect meltwater chemistry due to the rates and magnitudes of post-mixing reactions-related variations in the size distribution of suspended sediment, suspended sediment load, physical process on glacier erosion and mineral surface properties, deposition and re-mobilization of suspended sediment, and proton availability [31]. In this study, we focus on the changes in chemical behavior of minor and trace elements in stream water draining the Qiyi Glacier over a diurnal cycle and associated hydrological controls as well as the effects of non-filtration after sampling on water chemistry. This study allows short-term diurnal variations in the export mode of minor and trace elements to be determined for the first time as well as the controls thereon to be assessed, and the non-filtration effects to be quantified as well.

1 Study area

The Qiyi Glacier (39.23°N, 97.76°E) is located at the northern slope of the Qilian Mountain, northeast of Tibetan Plateau (Figure 1). It is a cirque valley glacier with a length of 3.8 km and an area of 2.87 km², and its altitude ranges from 4300 to 5100 m [32]. The glacier was first investigated in 1958, and further studies were performed during 1975–1978, 1985–1988, and 2002–2003, including glacier mass balance, ice formation process, glacier flow, glacier thickness, and hydrology and meteorology [33]. The ELA shows an increasing trend, ascending 230 m during 1958–2008 and reaching 5131 m in 2006 [34], and annual

mass balance is -563 mm during 2001-2003 [33]. In the basin, the climate is dominated by westerly circulation, and is influenced occasionally by the Asian monsoon. Precipitation occurs mainly in summer, and the maximum precipitation zone is located at 4500 to 4700 m with annual precipitation of 485 mm during 2006-2008. Annual lapse rate of air temperature is on average 0.6°C/100 m in non-glacier area, and is slightly larger in summer and smaller in winter [34]. Field investigation shows that the glacier has lateral and terminal moraines. The bedrock in the basin consists largely of muscovite schist, hornblende schist, quartzite, siliceous rock, amphibolite, marble, and ferrous sulphide minerals [35], which contain more amounts of geochemically reactive quartz, illite and plagioclase, less amounts of potash feldspar, kaolinite, dolomite, chlorite and calcite, and trace amounts of montmorillonite, hematite, siderite and gypsum (Table 1).

2 Sampling and methodology

During the 2010 ablation season, stream water samples were collected bihourly ~500 m from glacier snout due to dispersed river channel between 18 and 19 August, and were immediately filtered through the 0.45 µm cellulose nitrate membranes using a Nalgene polysulphone filter unit and a manual vacuum pump. Each sample was separated between two pre-cleaned LDPE bottles containing as little air as possible. One was acidified with HNO3 for element analysis while the other was left unacidified for pH, electrical conductivity (EC), major ion and stable isotope analysis. Subsamples were not filtered to quantify, by comparison, the effects of non-filtered operation on water chemistry. All samples were kept at cool conditions in field, and then transported to the State Key Laboratory of Cryospheric Science, Chinese Academy of Sciences (CAS) and kept in a cold room at 4°C until analysis. The deposit samples were collected in polyethylene plastic bags at the glacier terminal, and then were transported to the Geochemistry Department of Test Center of Lanzhou Branch, CAS, for mineral composition analysis.



Figure 1 Map showing the Qiyi Glacier and meltwater sampling site.

 Table 1
 Mineral composition (%) of glacial deposits in the Qiyi Glacier basin ^{a)}

Samples	Montmorillonite	Illite	Gypsum	Kaolinite	Chlorite	Quartz	Potash feldspar	Plagioclase	Calcite	Dolomite	Siderite	Hematite	Pyrite
QL-S1	n.d.	10.2	n.d.	3.3	1.2	57.0	10.7	14.6	0.7	1.8	0.5	n.d.	n.d.
QL-S2	0.8	18.3	n.d.	2.5	1.1	48.7	6.1	17.2	2.4	2.7	0.2	n.d.	n.d.
QL-S3	1.3	18.3	n.d.	5.0	2.4	52.5	3.3	15.7	0.6	0.6	0.3	n.d.	n.d.
QL-S4	1.2	19.9	n.d.	3.8	1.4	54.6	6.7	10.5	1.1	0.5	0.3	n.d.	n.d.
QL-S5	1.0	17.7	0.1	2.3	1.3	48.2	10.6	16.9	0.5	1.1	0.3	n.d.	n.d.
QL-S6	1.1	13.7	n.d.	3.5	1.6	49.5	5.6	11.1	1.5	11.1	0.4	0.9	n.d.
QL-S7	0.8	10.9	n.d.	3.1	1.8	54.0	10.0	17.0	1.1	0.9	0.4	n.d.	n.d.
QL-S8	n.d.	14.5	n.d.	4.3	1.8	52.8	7.8	11.9	2.1	3.8	0.2	0.8	n.d.
Average		15.4		3.5	1.6	52.2	7.6	14.4	1.3	2.8	0.3		

a) n.d., Not detected in laboratory.

The pH and EC were determined by a PHSJ-3F meter and a DDSJ-308A meter respectively both with a precision of ±1%. δ^{18} O and δ D were determined by a Liquid-Water Isotope Analyzer (DLT 100, Los Gatos, USA) based on Off-axis Integrated Cavity Output Spectroscopy (OA-ICOS) with a ratio precision of $\pm 0.2\%$ and $\pm 0.6\%$, respectively. Cations and anions were analyzed by Dionex-600 and Dionex-2500 ion chromatographs respectively. The precision is $\pm 1\%$ for all measured ions. The HCO₃⁻ was determined by ion charge balance. All samples were acidifed with ultrapure HNO₃ (Merk, Germany) to reach a concentration of 1%, and then minor and trace elements were determined by an inductively coupled plasma sector-field mass spectrometer (ICP-SFMS, Finnigan MAT) one week later. External calibration method was used for quantification whereas Indium was added into all samples as an internal standard to compensate the sensitivity drift. The detection limits were determined by measuring 1% HNO₃ as blank solution ten times, and then were calculated as three times the standard deviation of ten measurements. The precision of the measurements in terms of relative standard deviation was obtained from one sample based on four consecutive measurements. Data quality was controlled by analyzing the standard reference material SLRS-4 (River Water Reference Material for Trace Metals, National Research Council Canada, Ottawa, Canada) to evaluate the accuracy of this method (Table 2). Good agreement between determined and certified values was observed for most measured elements. Mineral composition was determined by an X-radial diffraction (D/Max-IIIB) using a Cu butt, step-continual scanning with 4°/min of speed and tube 40 kV and 25 mA. Water stage at sampling site was monitored by a water gauge, and discharge was roughly estimated based on an empirical relationship between water stage and discharge established by Song et al. [36].

Principal component analysis (PCA) was performed on water chemistry using CANOCO 4.5 [37] to determine whether individual species were significantly controlled by discharge during a diurnal period. PCA was presented as a PCA of a correlation matrix, centered and standardized by individual species, where species are species concentrations, pH, EC and discharge. Speciation calculations were performed using PHREEQCi software with MINTEQ database [38] on immediately-filtered water. The software calculates the partitioning of minor and trace elements between inorganic species, which indicates geochemical mobility of species over a diurnal period, since the form of chemical species affects their affinity for the sorption-desorption reactions. Saturation indices (SI) of minerals in solution are calculated, where oversaturation suggests a mineral is likely to precipitate to maintain chemical equilibrium, and undersaturation suggests a mineral will dissolve in hydrological systems [38, 39].

3 Results

3.1 Diurnal discharge and water isotopes

Figure 2 shows variations in discharge, stable isotopes, pH and EC over a fine diurnal cycle, before which there are any precipitation events. Discharge straightly increases from 11:00 up to 19:00 and quickly decreases to 09:00 the following day (Figure 2(a)). δ^{18} O and δ D present increasing trends from 11:00–13:00 up to 23:00, and decreasing and fluctuation trends respectively to 09:00 the following day (Figure 2(b)), exhibiting two obviously conversion times at 13:00 and 23:00. Both pH and EC directly display decreases from 11:00–13:00 up to 19:00 and increases to 09:00 the following day (Figure 2(c)), exhibiting inverse variations with discharge, as confirmed by the PCA where pH and EC have direct opposite arrow direction to discharge, indicating a high negative correlation (Figure 3(a)).

3.2 Diurnal concentrations and fluxes

The concentrations of dissolved ions and elements in glacier ice, supraglacial and bulk meltwater are summarized in Table 2. HCO_3^- , Ca^{2+} and SO_4^{2-} are dominant ions in ice, supraglacial and bulk meltwater, with lesser quantities of NO_3^- and K⁺. The dominant elements in bulk meltwater are Sr, Ba, Al, Fe, and Mn, which are present at median

		Qiyi Glacier								Haut Glacier d'Arolla ^{b)}	World stream water ^{c)}		
	Median of glacier ice ^{a)} Supraglacial		Bulk meltwater $(\mu g L^{-1})$			Blank	Accuracy (µg L ⁻¹)		Precision	Detection	Median of	Median	
	$(\mu g L^{-1})$	meltwater ^{a)} ($\mu g L^{-1}$)	Max	Min	Median	S.D.	$(\mu g L^{-1})$	Found	Certified	% (±)	$(\mu g L^{-1})$	ter ($\mu g L^{-1}$)	$(\mu g L^{-1})$
$\delta^{18}{ m O}~(\% o)$			-10.02	-10.74	-10.32	0.2							
δD (%)			-58.10	-64.06	6-60.82	1.6							
pH		8.05	7.74	7.42	7.56	0.1						8.2	
$EC (\mu S cm^{-1})$		34	379	152	268	73							
Ca ²⁺	7984	6760	45464	17895	31024	9378						360	18000
Mg ²⁺	2070	625	11773	4467	8173	2415						35	4100
Na ⁺	552	645	2732	1680	2328	364						16	6100
K^+	146	95	818	347	568	142						10	2300
Cl	812	990	2159	868	1278	443						2.2	
NO_3^-	292	455	934	370	557	188						59	
SO_4^{2-}	738	1920	41320	12763	25020	10756						130	
HCO_3^-	33960	21230	155278	67359	110525	29219						290	
Li			1.441	0.567	0.959	0.260	0.014	0.47 ± 0.01	0.54 ± 0.07	2.5	0.0013	0.11	3
Sr			137.134	51.017	84.735	24.605	0.001	27.7±0.1	26.3±3.2	9.8	0.0003	18	70
Мо			0.286	0.206	0.254	0.021	0.009	0.218 ± 0.004	0.21 ± 0.02	1.4	0.0001		
Sb			0.020	0.015	0.016	0.002	0.002	0.246 ± 0.002	0.23 ± 0.04	3.3	0.0002		
Ва			56.411	16.784	32.100	11.426	0.002	13.1±0.1	12.2±0.6	9.8	0.0003	0.57	20
Al			73.049	3.288	6.145	19.479	0.127	57±1	54±4	3.1	0.0220	34	10
Ti			2.350	0.107	0.211	0.622		1.33 ± 0.04	1.46 ± 0.08	0.4	0.0055	9.4	3
V			0.205	0.011	0.019	0.054	0.001	0.34 ± 0.01	0.32 ± 0.03	3.9	0.0005		
Cr			0.448	0.056	0.094	0.104	0.002	0.32 ± 0.01	0.33 ± 0.02	16.8	0.0017	1.1	0.7
Mn			4.046	0.508	2.159	1.082	0.006	3.79 ± 0.03	3.37±0.18	0.7	0.0064	8.6	4
Fe			97.816	0.423	4.762	27.475	0.074	101±2	103±5	2.7	0.0360	250	40
Co			0.038	0.005	0.012	0.010	0.001	0.033±0.004	0.033±0.000	6.1	0.0004	0.07	0.1
Ni			0.222	0.083	0.098	0.041	0.010	0.76±0.04	0.67±0.08	6.8	0.0017	0.65	0.3
Cu			0.761	0.286	0.479	0.161	0.011	1.95 ± 0.07	1.81 ± 0.08	1.1	0.0015	0.23	0.3

 Table 2
 Immediately-filtered concentrations of dissolved elements together with pH, electrical conductivity (EC) and stable isotopes in glacier ice, input supraglacial and output meltwater

a) Values from Wu et al. [30]. Glacier ice is from 4350–4872 m a.s.l., and supraglacial meltwater is from 4337 and 4502 m a.s.l. b) Values from Mitchell and Brown [9]. Bulk meltwater is from 10:00–10:00, July 14 to 15, 1999. c) Values from Langmuir [40] and Reimann and de Caritat [41]. "Found" and "Certified" indicate the comparison of measured concentrations with its certified values. S.D.: Standard deviation.

concentrations ranging from 2 to 85 μ g L⁻¹, and the residual elements are below 1 μ g L⁻¹. Obviously, there is a significant solute acquisition as the dilute supraglacial and icemelt water are routed through subglacial hydrological system.

The immediately-filtered concentrations of dissolved ions and some elements are inversely related to discharge on diurnal timescale, which are clearest for major ions, Li, Sr and Ba (Figure 4(a)–(g), (j), and less clear for Mo and Cu (Figure 4(h), (s)). Results of PCA confirm that diurnal concentration variations of these species are controlled directly by diurnal discharge, as indicated by a direct opposite arrow direction to discharge, suggesting a high negative correlation (Figure 3(a)). However, diurnal concentration of other elements (e.g. Ni, Al, Ti, V, Cr, and Fe) is not clearly related to diurnal discharge, exhibiting apparently random changes over the diurnal cycle (Figure 4(k)–(n), (p)–(q)), as confirmed by the PCA where these species have a perpendicular arrow direction to discharge, indicating no correlation between diurnal concentration and discharge (Figure 3(a)). Whereas the concentrations of major ions and some elements are generally inverse or unrelated to discharge, the instantaneous fluxes (mg h⁻¹, derived from the product of concentration (μ g L⁻¹) multiplied by discharge (m³ s⁻¹) and extrapolated to an hourly flux) of immediately-filtered ions and elements generally increase linearly with discharge over the diurnal period, as shown by the relationship between the fluxes and discharge (Figure 5). Hence, the greatest instantaneous fluxes for most species are transported at 19:00 when the largest discharge is present (Figure 2(a)).

The comparison of element concentrations in immediately- and non-filtered meltwater is shown in Figure 6. This demonstrates that Sr and Ba in non-filtered meltwater appear to be broadly the same in immediately-filtered water, and Mo and Sb present higher or lower concentrations in non-filtered water than that in immediately-filtered water. Exceptions to this are Li, Cr, Mn, Ni and Cu, which exhibit higher concentrations, and Al, Ti, V, Fe and Co, which ex-



Figure 2 Diurnal variations of discharge (a), δ^{18} O and δ D (b), and pH and EC (c) in immediately-filtered meltwater.

hibit a significantly high concentration in non-filtered than immediately-filtered water (Figure 6). Moreover, PCA shows that Sb, Cu, Ti, V, Cr, Fe, Al and Co exhibit an inverse or no correlation with discharge in immediatelyfiltered water (Figure 3(a)), but in non-filtered meltwater they present positive relationships with discharge (Figure 3(b)), indicating that the non-filtered operation exerts large effects on these species. In detail, the increases of Fe (2556%), Al (968%), Ti (894%), V (694%), and Co (515%) at mean concentration are the largest in non-filtered than immediately-filtered water, and Mo (4%), Sr (5%), Sb (9%) and Ba (10%) are the smallest, compared to moderate increases of Ni (211%), Cr (179%), Mn (174%), Cu (87%) and Li (19%) (Figure 7).

3.3 Meltwater speciation and saturation state

The immediately-filtered concentration and fluxes of minor and trace elements do not account for the complex forms these elements may exist in (e.g. $Al(OH)_4^-$, $Fe(OH)_2^+$), which may influence their mobility and therefore their mode of export from the Qiyi Glacier basin. Speciation calculation performed using PHREEQCi software [38] on water



Figure 3 PCA of (a) immediately- and (b) non-filtered meltwater chemical composition. Similar arrow direction indicates species exhibit a positive correlation. Opposite arrow direction indicates species exhibit a negative correlation. Perpendicular arrow direction indicates species have no correlation. The percentage of data variation that each axis accounts for is indicated on plots.

samples from a diurnal period (Table 3) suggests that a mixture of soluble metal and non-metal ligand complexes and free monovalent and divalent ions characterize the distribution of metals in water. All dissolved redox sensitive elements (e.g. Cr, Cu, Fe, Mn, N, S) exist predominantly (>99%) in an oxidized state (e.g. Cr(6), Cu(2), Fe(3), Mn(2)). The alkali earth metals and alkali metals (e.g. Ca, Mg, Na, K, Li, Sr, Ba) exist primarily as uncomplex monovalent and divalent cations. Most remaining elements exist predominantly as hydroxyanions (e.g. Fe(OH)₂⁺, Al(OH)₄⁻),



Figure 4 Representative species concentrations in immediately-filtered meltwater versus discharge during a diurnal cycle.

Table 3 Aqueous speciation modeled by PHREEQCi software on immediately-filtered meltwater during a diurnal cycle

Elements (redox state) ^{a)}	Distribution of species ^{b)}			
Al	Al(OH) ₄ ⁻ (79%), Al(OH) ₃ (20%)			
Ba	Ba ²⁺			
С	HCO ₃ ⁻ (93%), H ₂ CO ₃ (5%), CaHCO ₃ ⁺ (1%)			
Ca	Ca ²⁺ (96%), CaSO ₄ (3%), CaHCO ₃ ⁺ (1%)			
Cr(6)	CrO ₄ ²⁻ (93%), HCrO ₄ ⁻ (7%)			
Cu(2)	Cu(OH) ₂ (62%), CuCO ₃ (32%), Cu ²⁺ (3%), CuHCO ₃ ⁺ (2%), CuOH ⁺ (1%)			
Fe(3)	Fe(OH) ₂ ⁺ (64%), Fe(OH) ₃ (26%), Fe(OH) ₄ ⁻ (10%)			
K	K^{+}			
Li	Li ⁺			
Mg	Mg ²⁺ (96%), MgSO ₄ (3%), MgHCO ₃ ⁺ (1%)			
Mn(2)	Mn ²⁺ (95%), MnSO ₄ (3%), MnHCO ₃ ⁺ (2%)			
N(5)	NO_3^-			
Na	Na^+			
Ni	NiCO ₃ (92%), Ni ²⁺ (6%), NiHCO ₃ ⁺ (1%), Ni(CO ₃) ₂ ²⁻ (1%)			
S(6)	SO ₄ ²⁻ (89%), CaSO ₄ (8%), MgSO ₄ (3%)			
Sb(5)	SbO ₃ -			
Sr	Sr ²⁺			
V(5)	H ₂ VO ₄ ⁻ (72%), HVO ₄ ²⁻ (28%)			

a) Values in parenthesis indicates dominant (>99%) redox state from average of all samples speciated. b) Main stable complexes listed (values in parentheses indicate moles of species as a percentage of the total moles of that element in solution. Only species values >1% are listed.

oxyanions (e.g. CrO_4^{2-} , $\text{H}_2\text{VO}_4^{-}$), or as uncharged hydroxides (e.g. $\text{Cu}(\text{OH})_2$). Ni occurs primarily as carbonate complexes (e.g. NiCO_3) (Table 3). Saturation index (SI) calculation indicates the oversaturation of a range of Al and Fe (oxi)hydroxides including Diaspore (AlOOH), Boehmite (AlOOH), Gibbsite (Al(OH)_3), Ferrihydrite (Fe(OH)_3), Hematite (Fe_2O_3), Maghemite (Fe_2O_3), Magnetite (Fe_3O_4), Goethite (FeOOH), Lepidocrocite (FeOOH), and the undersaturation of Mn (oxi)hydroxides including Manganite (MnOOH), Bixbyite (Mn_2O_3), Pyrolusite (MnO_2) and other compounds (Table 4).

4 Discussion

4.1 Diurnal controls on concentrations and fluxes

Discharge variations over the diurnal cycle (Figure 2(a)) clearly reflect the changes in surface ablation and associated changes in meltwater generation as well as the changes of sediment entrainment in subglacial environment [42]. Water

Table 4Mineral composition and saturation state modeled byPHREEQCi software on immediately-filtered meltwater during a diurnalcycle.

Mineral	Formula	Saturation index (SI)			
Gibbsite (C)	Al(OH) ₃	0.22			
Boehmite	Alooh	0.41			
Diaspore	Alooh	2.11			
Barite	$BaSO_4$	-0.47			
Calcite	CaCO ₃	-0.34			
Dolomite	CaMg(CO ₃) ₂	-0.99			
Gypsum	CaSO ₄ :2H ₂ O	-2.11			
Cupric ferrite	CuFe ₂ O ₄	12.07			
Cuprous ferrite	CuFeO ₂	11.73			
Fe(OH) _{2.7} Cl _{0.3}	Fe(OH) _{2.7} Cl _{0.3}	5.73			
Ferrihydrite	Fe(OH) ₃	1.4			
Hematite	Fe ₂ O ₃	16.59			
Maghemite	Fe ₂ O ₃	6.2			
Fe ₃ (OH) ₈	Fe ₃ (OH) ₈	0.12			
Magnetite	Fe ₃ O ₄	16.61			
Goethite	FeOOH	5.79			
Lepidocrocite	FeOOH	4.92			
Siderite	FeCO ₃	-2.38			
Alunite	KAl ₃ (SO ₄) ₂ (OH) ₆	-6.69			
Jarosite-K	KFe ₃ (SO ₄) ₂ (OH) ₆	-1.32			
Brucite	Mg(OH) ₂	-5.27			
Spinel	$MgAl_2O_4$	-6.84			
Mg-Ferrite	MgFe ₂ O ₄	7.34			
Bixbyite	Mn_2O_3	-12.17			
Pyrolusite	MnO_2	-10.69			
Manganite	MnOOH	-6.15			
Mirabilite	Na ₂ SO ₄ :10H ₂ O	-10.68			
Halite	NaCl	-10.05			
Jarosite-Na	NaFe ₃ (SO ₄) ₂ (OH) ₆	-4.08			
Retgersite	NiSO4:6H2O	-11.74			
Celestite	$SrSO_4$	-3.37			

isotope variations during the diurnal period probably reflect the changes in water sources (e.g. the ratio of snowmelt to icemelt) (Figure 2(b)), suggesting the availability of stable oxygen and hydrogen isotopes in hydrological investigation in glacial basins [31, 43]. Variations in pH and EC (Figure 2(c)) reflect the changes in discharge and sediment evacuation, and pH is closely associated with the physicochemical process. The dominance of HCO₃, Ca²⁺, SO₄²⁻, Sr, Ba, Al, Fe and Mn in glacier ice, supraglacial and bulk meltwater (Table 2) is intimately associated with the bedrock and mineralogy in the Qiyi Glacier basin. The enrichment of major ions between input and output water evidently resolute flects the liberation by the subglacial bio-geochemical weathering processes as surface meltwater is routed through the subglacial environment, as documented in other glacial basins [44-47]. Comparison suggests that the weathering of minerals (e.g. carbonation) in the basin may be stronger than in the Haut Glacier d'Arolla and World Stream Water, probably because of yearly-prevailing westerly jet and winter-influential polar air mass-associated cold-dry climate, and the Alpine river systems primarily fed by glacier meltwater derive much of their element loads in headwater region (Table 2). Hence, it is important to consider the timing and magnitude of element delivery to downstream river systems; however, element concentrations may not be sustained downstream owing to dilution, suspended sediment reactivity, sorption reactions, and co-precipitation of elements [8, 10].

The varying behavior of dissolved ions and elements (Figure 4) over the diurnal cycle reflects individual species sensitivity to diurnal change in hydrological controls (e.g. meltwater generation and routing, water-rock interaction time) or physicochemical controls (e.g. adsorption-desorption, precipitation, and co-precipitation) [9]. The remarkable inverse concentration-discharge relationship exhibited by immediately-filtered ions (e.g. Ca²⁺, Mg²⁺, SO₄²⁻) and elements (e.g. Li, Sr, Ba) over the diurnal cycle (Figure 4(a)-(g), (j)) and demonstrated by the PCA (Figure 3(a)) suggests the dominant hydrological control. The conceptual hydrological model shows that total bulk discharge consists of the quick-flow and delayed-flow components [3, 48]. The quick-flow component flows rapidly through a hydrological system predominantly in ice-walled conduits, limiting the potential for solute acquisition. The delayed-flow component transports meltwater slowly through a distributed hydrological system at ice-bedrock interface, encouraging the potential for solute acquisition. At minimum diurnal discharge, discharge is composed mainly of "delayed-flow" water from an inefficient distributed system, and then passes into a channelized system owing to high and low pressures in distributed and channelized system, respectively [49]. This promotes protracted and intimate contact with subglacial sediments, allowing more concentrated meltwater to evolve [31, 42]. Conversely, as discharge increases, meltwater is increasingly routed directly through



Figure 5 Representative species fluxes in immediately-filtered meltwater versus discharge during a diurnal cycle.

a channelized system [50], and solute is generated from the interaction of supraglacial meltwater and subglacial sediments [31, 42]. As more dilute water is routed into subglacial environment, the dilution of delayed-flow water and duration of water-sediment interaction declines and thus reduces the solute acquisition, resulting in lower concentrations. However, the unsystematic variations of many elements (e.g. Al, Ti, V, Cr, Fe, Co, Ni) (Figure 4(k)–(n), (p), (q)) exhibiting no correlation with discharge as confirmed by the PCA (Figure 3(a)) suggest that the dominant control is not the flow-routing and water residence time but probably the physicochemical control. Alternatively, the colloidal material containing these species passed through 0.45 μ m pore-size filters or the effects of inter-species variations

relative to ambient concentrations compromise the correlation between water residence time and species concentration. Some elements (Li, Sr, and Ba) are probably the most effective tracers in subglacial hydrological investigation although other elements are less effective (e.g. Fe, Mn, Co, Al, Ti, Cr) at the diurnal timescale. Moreover, the relationship between diurnal fluxes and discharge (Figure 5) suggests that the increases in magnitude of species fluxes are controlled by surface-melt driven increases in the magnitude of discharge over the diurnal period. Additionally, diurnal dynamics in the mode of species export from glacial headwater are initially controlled by the species geochemical mobility that dominates the species initial affinity for dissolved phase [9].



Figure 6 Immediately-filtered verse non-filtered element concentrations during a diurnal cycle.

The differences of element concentration between immediately- and non-filtered water (Figure 6) and their correlation with discharge (Figure 3) suggest that the non-filtration operation appears not to strongly influence the concentration of some elements (Sr, Ba), which can be attributed to the undersaturation of these species-related minerals (Table 4) and then the confined dissolution. Exceptions to this are Li, Mn, Cu, Cr and Ni that suffered moderate influences and Fe, Al, Ti, V and Co that suffered the largest influences due to oversaturation of these elements-related minerals (Table 4), which can be attributed to subsequent dissolution of silicate minerals (e.g. illite, plagioclase, montmorillonite (Table 1)) and possible dissolution of organic matter-related species. This suggests that elements showing high concentrations in non-filtered solutions are transported in particulate forms and thus their concentrations are highly dependent on particle numbers in solution, and the dissolution of suspended particulate-associated elements is easier and rapid. This implies that the immediate filtration after sampling is extremely important in the field for glacier hydrochemical studies. Moreover, the increase in maximum concentration of each element is the largest, and vice versa (Figure 7), indicating that the effects of non-filtered operation depend on original loadings of minor and trace elements, namely amount of suspended sediment in meltwater. Obviously, the effects of subsequent mineral dissolution on water chemistry are larger if samples are not filtered immediately after sampling in the field. This will profoundly attract more attentions from some scholars, and may help to correct previously late- or non-filtered water chemistry at Alpine glacial basins with similar geology and mineralogy condition.



Figure 7 Variation of element concentrations between immediately- and non-filtered meltwater. Variations (%) are determined by ([C2]-[C1])/[C1]×100, where [C1] and [C2] indicate immediately- and non-filtered element concentrations, respectively.

4.2 Chemical weathering

Water chemistry in an Alpine headwater basin is closely associated with bedrock mineralogy, solution geochemistry (e.g. pH, mineral saturation states, and sediment concentrations), and the evolution of subglacial hydrological system [3, 8, 10]. Dominant HCO₃⁻ and Ca²⁺ at the Qiyi Glacier catchment can be attributed to the equivalent-proportional dissolution of calcite and dolomite in subglacial hydrological system (eq. (1)). This is supported by measured and modeled mineral compositions (Table 1, Table 4), as confirmed by a significant correlation between HCO₃⁻ and Ca²⁺ (r=0.987, P<0.0001) and their mean molar ratios of 0.3 close to 0.4. Dominant SO_4^{2-} may be related primarily to the re-dissolution of subglacial gypsum precipitation (eq. (2)), which is confirmed by a significant correlation between SO_4^{2-} and Ca^{2+} (r=0.938, P<0.0001) and their mean molar ratio of 0.8 close to 1.0. Moreover, barite, alunite, jarosite-K, mirabilite, jarosite-Na, retgersite, celestite, and pyrite are also more or less responsible for SO_4^{2-} in meltwater (Table 4). Additionally, the primary control on dominant elements (Al, Fe) might be the combination of plagioclase dissolution coupled with illite surface weathering (eq. (3)), which is supported by measured dominant mineral composition (Table 1). Other dominant elements (Sr, Ba and Mn) can be attributed to the weathering of Celestite (SrSO₄), Barite (BaSO₄), Bixbyite (Mn₂O₃), Pyrolusite (MnO₂), and Manganite (MnOOH), which is supported by modeled mineral compositions (Table 4), reflecting the geochemical reactivity of ubiquitous minor and trace minerals that are widespread in the Qiyi Glacier basin.

$$\begin{aligned} & \text{CaCO}_{3(\text{calcite})} + \text{CaMg}(\text{CO}_{3})_{2(\text{dolomite})} + 2\text{CO}_{2} + 3\text{H}_{2}\text{O} \rightarrow 2\text{Ca}^{2+} + \\ & \text{Mg}^{2+} + 5\text{HCO}_{3^{-}} + \text{OH}^{-} & (1) \\ & \text{CaSO}_{4} \cdot 2\text{H}_{2}\text{O}_{(\text{gypsum})} \rightarrow \text{Ca}^{2+} + \text{SO}_{4}^{2-} + 2\text{H}_{2}\text{O} & (2) \\ & \text{Na}_{0.68}\text{Ca}_{0.32}\text{Al}_{1.32}\text{Si}_{2.68}\text{O}_{8(\text{plagioclase})} + \text{K}_{0.75}(\text{Al}_{1.75}\text{MgFe})[\text{Si}_{3.5}\text{Al}_{0.5} + \text{SO}_{3}^{-} +$$

 $\begin{array}{c} O_{10}](OH)_{2(illite)} + 4.07CO_2 + 0.375O_2 + 6.105H_2O \rightarrow 0.68Na^+ + 0.32\\ Ca^{2+} + 0.75K^+ + Mg^{2+} + 4.07HCO_3 + 2.61SiO_2 + Fe(OH)_3 \end{array}$

N

$$+1.785Al_2Si_2O_5(OH)_4$$
 (3)

Although specific sources of other species cannot be distinguished, results of speciation modeling provide useful predictions about their likely form in meltwater (Table 4). For example, Fe and Al (oxi)hydroxide oversaturation (Table 4) suggests that (oxi)hydroxide precipitates may form on surface of suspended sediments, and other species are also likely to be scavenged from solution by co-precipitation. This is supported by the common occurrence of Fe oxides as nano-particle spheres infilling surface pits at surface of aluminosilicate minerals exposed at surface of sediments [51]. The predominance of amorphous (oxi)hydroxides (Table 4) can be attributed to that there is insufficient time for thermodynamically stable crystalline (oxi)hydroxides to form [51]. Results of speciation modeling are also in support of species that are shown to be dominantly transported in dissolved phase, and that exhibit an inverse concentration with discharge including Li, Sr, Ba and major ions (Table 3). The alkali metals that are predicted to exist as monovalent or divalent cations and that possess low ionic potentials should also remain mobile and unabsorbed by solids (Table 3) [40, 52]. Temporal variations in pH may also explain complex changes of speciation and dominant species [9]. This complexity is particularly apparent when discharge and pH decreases on descending limb of diurnal hydrograph (Figure 2(a), (c)), most likely in response to reduction in suspended sediment concentration and reactive proton consumption sites on mineral surfaces [42, 48]. Changes in concentration of differently charged species are likely to cause complex sorption-desorption dynamics with charged mineral surfaces [52], and further account for a complex variation in species concentrations.

5 Conclusions

Diurnal dissolved major ion and minor and trace element concentrations in stream water draining an Alpine headwater basin were examined. Major ions, Li, Sr and Ba, exhibit an apparent inverse concentration with meltwater discharge over the diurnal period, which predominantly reflects the hydrological controls and indicates that these species, particularly Li, Sr and Ba, may be highly useful in hydrological investigations, at least on the diurnal timescale. However, the concentrations of most elements including Ni, Ti, Cr, V, Al, Fe, Co and Mn are not controlled by meltwater discharge variations during the diurnal period. Speciation modeling applied to meltwater suggests that these unsystematic temporal variations reflect the physicochemical controls including sorption, oversaturation and precipitation of Fe and Al (oxi)hydroxides and co-precipitation of other species. The not-immediate filtration after sampling appears not to strongly influence Sr and Ba, but has an effect on some elements such as Fe, Al, V, Ti and Co, which suggests that the immediate filtration after sampling is extremely essential in glacier hydrochemical studies.

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