

The hydrochemistry of Bayelva, a high Arctic proglacial stream in Svalbard

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Abstract

Major ion, silica and pH data from a high Arctic proglacial stream network are examined. Factor analysis shows that the major controls upon hydrochemistry in the basin include snowpack solute elution, rapid alteration of minerals via surface reactions and slow, incongruent silicate dissolution. The importance of chemical weathering is found to increase downstream at the expense of solute acquisition from the transient snowpack. Data from a series of snow pits show that snowpack solute elution is characterised by the preferential elution of SO_4^{2-} . Evidence for the preferential elution of NO_3^- is equivocal. However, NO_3^- levels in proglacial runoff may be enhanced by the leaching of cryotic soils later in the ablation season.

Chemical weathering is dominated by calcite dissolution at high elevations and a combination of calcite and dolomite dissolution in the downstream proglacial environment. Silicate weathering at high elevations is characterised by the enrichment of K^+ relative to Si. Concentrated active layer soil waters show less enrichment of K^+ and constitute a potentially important source of dissolved silica to the river system. Na^+ is also produced by silicate weathering, but its mobility is believed to be largely governed by ion exchange with Ca^{2+} early in the ablation season.

All chemical weathering environments are characterised by high $p(\text{CO}_2)$ due to either respiration within the soil or, at higher elevations within the catchment, H^+ provision from acid aerosol and sulphide oxidation. However, rates of sulphide oxidation are limited because the cold-based thermal regime of the glaciers effectively prevents access of meltwaters to freshly comminuted sub-glacial sulphide minerals. The restricted sub-glacial weathering therefore means that ice marginal and proglacial environments are the most important zones of solute acquisition by meltwaters, causing significant enrichment of major ions, silica and dissolved CO_2 within only a short distance of the contemporary ice margin. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Meltwater chemistry; Chemical weathering; Snowpack elution; Glacier hydrology; Svalbard

1. Introduction

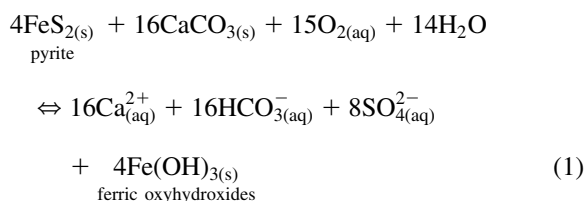
The chemical composition of glacial meltwaters has received significant attention over the last 25 years. Initial interests lay in the use of proglacial hydrochemical data to elucidate drainage pathways

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through glaciers (e.g. Collins, 1977; Oerter et al., 1980) and to compute solute fluxes for the estimation of chemical weathering rates (e.g. Reynolds and Johnson, 1972; Eyles et al., 1982; Collins, 1983). More recent work has documented the composition of different flow paths through (largely temperate) glaciers in much greater detail (e.g. Lamb et al., 1995; Tranter et al., 1997) and has also presented data from more remote Arctic (e.g. Hasholt and Hagedorn, 2001; Hodgkins et al., 1997; Skidmore and Sharp, 1999; Wadham et al., 1998), sub-arctic (Gíslason et al., 1996; Theakstone and Knudsen, 1998) and Himalayan (e.g. Hasnain and Thayyen, 1996, 1999; Hodson et al., in review) study sites. Hodson et al. (2000) argued that the acquisition of data from the remote study sites is particularly important, as the efficacy of chemical weathering in glacier basins can now be assessed over a broader spatial framework than that afforded by earlier syntheses, which presented data mostly from temperate glacier basins in the European Alps and North America (Anderson et al., 1997; Hallet et al., 1996).

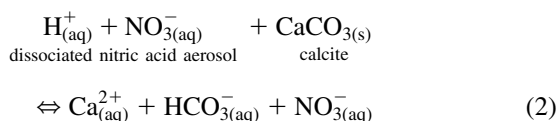
The above studies have shown that solute in glacial runoff is principally derived from atmospheric deposition and rock–water interactions, which mostly take place in sub-glacial and ice marginal environments (Tranter et al., 1993; Fairchild et al., 1999a). Most recent work has given emphasis to rock–water interactions and it is now widely believed that acid hydrolysis reactions dominate chemical weathering in glacier basins (Raiswell, 1984; Tranter et al., 1993; Brown et al., 1996). Interestingly, one such reaction, namely the coupling of sulphide oxidation and carbonate dissolution (see Eq. (1)), has been found to operate consistently across a broad range of glaciated environments with a multitude of rock types (e.g. Anderson et al., 1999; Hasnain and Thayyen, 1999; Hodgkins et al., 1997; Raiswell and Thomas, 1984; Tranter et al., 1996; Wadham et al., 1998).



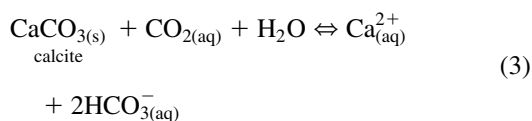
Eq. (1) shows that this reaction causes the

$\text{SO}_4^{2-}/\text{HCO}_3^{-}$ ratio to tend towards 1 when $\mu\text{Eq l}^{-1}$ concentrations are used. In many studies, however, the $\text{SO}_4^{2-}/\text{HCO}_3^{-}$ ratio of proglacial meltwaters is <1 , suggesting that, under certain conditions, a further source of HCO_3^{-} must exist. Several researchers have argued that the additional source of HCO_3^{-} is one or a number of the following:

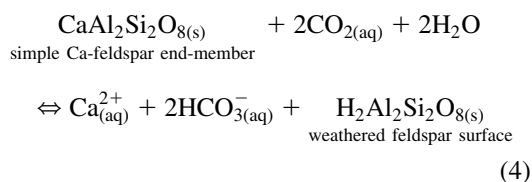
(i) neutralisation of snowpack acid aerosol by carbonates, for example,



(ii) carbonation reactions, which sequester atmospheric CO_2 , for example, carbonation of carbonates:



carbonation of silicates:



Other potential HCO_3^{-} sources include the oxidation of organic carbon, which may be mediated by microbial activity; or the simple hydrolysis of carbonate minerals, which is only likely to supply HCO_3^{-} in the early stages of rock–water contact (Raiswell, 1984; Tranter et al., 1997; Brown et al., 1996; Fairchild et al., 1994).

Like carbonate dissolution, the chemical weathering of silicate and aluminosilicate minerals has also been shown to indicate broadly consistent characteristics in a variety of different glacier basins. In particular, high crustal K^{+} concentrations and low dissolved silica concentrations appear to be typical for glacial runoff (see Anderson et al., 1997; Axtmann and Stallard, 1995; Hodson et al., 2000). This has been

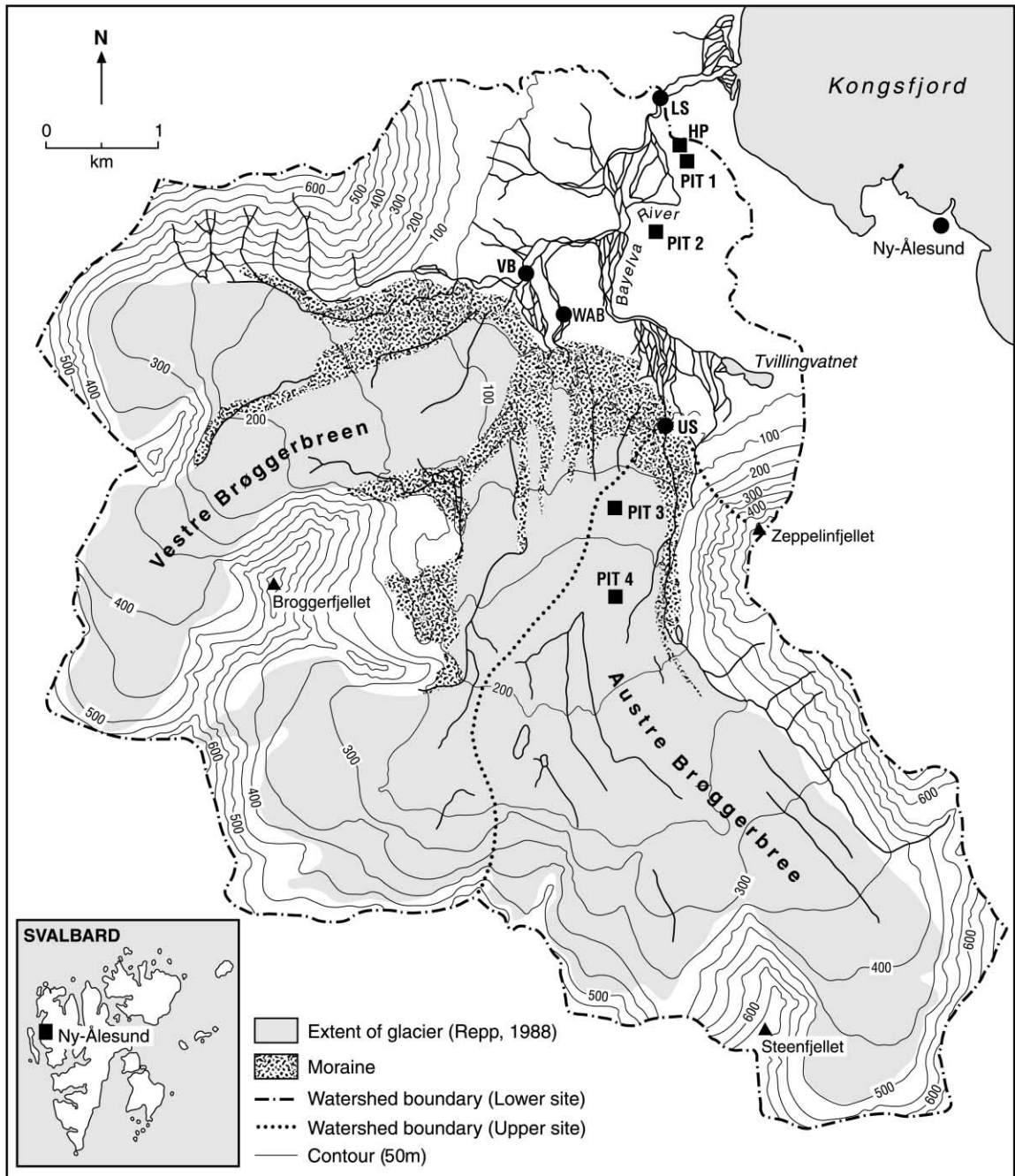


Fig. 1. The Bayelva catchment and the various sampling and gauging stations visited during the 1991 and 1992 ablation seasons. 'US' denotes the Upper Site, 'LS' denotes the Lower Site, 'HP' denotes the hillslope sampling plot (where overland flow and soil water samples were collected), 'VB' denotes the Vestre Brøggerbreen sampling site and 'WAB' denotes the sampling site for the western Austre Brøggerbreen meltwaters. The four snow pits are denoted by 'Pit 1–4', respectively.

attributed to leaching of K^+ from glacially comminuted K-feldspars, which are sensitive to the high rates of mineral disaggregation that the physical weathering environment of glaciated basins favours (Axtmann and Stallard, 1995; Anderson et al., 1997). The effect may also be enhanced relative to other types of fluvial basin by minimal sequestration of K^+ by plants in glacierised environments.

The purpose of this paper is to test the above conceptual framework of solute acquisition for a maritime high Arctic, glaciated catchment by analysing data collected from the Bayelva basin in Svalbard during the 1991 and 1992 ablation season. The basin is particularly important, as it is adjacent to the Ny Ålesund International Research Facility, representing one of the principal sites for field monitoring in the European high Arctic. Specifically, this paper examines the composition of the snowpack, snowmelt, icemelt, proglacial soil waters and bulk runoff in order to determine the principal controls upon meltwater composition at various points within the entire basin. In doing so, this paper develops from earlier studies in the basin (see Tranter et al., 1994, 1996) by giving more emphasis to the role of the downstream proglacial region, an environment that has been greatly neglected in recent research (Malard et al., 1999).

2. Field site

The Bayelva catchment, located at $\sim 79^\circ\text{N}$, 12°E in the Svalbard archipelago, contains two glaciers, Austre Brøggerbreen (11.7 km^2 of permanent ice and snow) and Vestre Brøggerbreen (VB) (5.3 km^2 ; Fig. 1). The hydrological and meteorological characteristics of the basin are well known and described by Bogen (1991, 1996), Hagen et al. (1991), Hagen and Lefauconnier (1995), Hodson et al. (1998a,b) and Repp (1978). These studies show that the specific annual runoff from the entire catchment (estimated at the Lower Site, see Fig. 1) is between 0.6 and 1.2 m a^{-1} , whilst the mean sediment yield is approximately $570 \text{ t km}^{-2} \text{ a}^{-1}$.

Of the two glaciers within the Bayelva catchment, Austre Brøggerbreen has received particular research attention. This glacier has been shown to have a strongly negative mass balance since monitoring

began in 1966 (Lefauconnier and Hagen, 1992; Washington et al., 2001). The thermal structure is dominated by sub-freezing ice temperatures because the glacier is thin ($<150 \text{ m}$) and there is no accumulation of temperate ice in the upper accumulation area of the glacier (Hagen et al., 1991; Björnsson et al., 1996). Due to the glacier thermal regime, meltwaters are predominantly routed through supraglacial, englacial and lateral channels (Hodson et al., 1998a; Tranter et al., 1996). Dye and salt injections into a major moulin in the ablation area indicate that parts of the englacial system are very efficient, having throughflow velocities as high as $0.4 \text{ m}^3 \text{ s}^{-1}$ during July and August (Hagen et al., 1991). Repeated dye injections over the course of several years have also shown remarkable consistency in the throughflow times of the englacial system from year to year (Vatne, unpublished data). Most meltwaters leave the glacier via large lateral channels to which reactive, fine sediments are supplied by mass wasting of ice-cored moraines (Hodson et al., 1998b; Hodson and Ferguson, 1999).

Although much less is known of VB, it is also believed to be dominated by a cold ice thermal structure. Lateral channels may be observed to convey supraglacial runoff directly to the proglacial region and only minimal contact between meltwaters and the glacier bed occurs near the glacier margin. VB is also retreating from its Little Ice Age moraines, suggesting that this glacier also has had a negative mass balance in recent years.

The basin is largely underlain by Permian, Carboniferous and Tertiary sedimentary rocks, including sandstones, shales, dolomites and limestones (Hjelle, 1993). In addition, Proterozoic basement rocks, including quartzites and phyllites exist in the mountains of the southern and south-eastern parts of the catchment. Carbonates dominate the bedrock in the western and northern parts of the catchment, where younger sandstones are also present (Orvin, 1934). Older red sandstones are also present, especially in the Austre Brøggerbreen sub-basin. Soils exist beyond the Little Ice Age moraines (Fig. 1) and they are colonised by *Dryas* and *Salix* communities. The active layer of these soils develops to depths in excess of 1 m in most parts of the proglacial region and strong spatial variations in soil moisture content are typical (Colin Lloyd, personal communication, 1999).

3. Monitoring and analytical methodology

3.1. Streamflow gauging

Streamflow gauging was undertaken at two sites (Fig. 1). The Upper Site had a catchment area of $\sim 9.8 \text{ km}^2$, of which 70% was occupied by the eastern parts of Austre Brøggerbreen. The Lower Site was the Norwegian Water Resources and Energy Administration (NVE) gauging station, some 2.5 km downstream from the Upper Site. Here, the catchment area is $\sim 32 \text{ km}^2$ and 54% glacierised. Runoff to the Lower Site is therefore received from both glaciers, Austre Brøggerbreen and VB, and also from the proglacial soils and sandur plain.

At both sites, hourly records of discharge, electrical conductivity and water temperature were derived by averaging 1 (discharge) or 10 min (conductivity and temperature) records. Errors in the discharge estimates were $\sim 5\%$ at the Lower Site (Pettersson, 1991) and $\sim 10\%$ at the Upper Site (Hodson, 1994). The electrical conductivity values were temperature-corrected (see Hodson et al., 1998a) and then converted to estimates of total dissolved (ionic) solutes (TDSi) using the major ion data (see Hodson, 1999). Errors in the TDSi estimates are typically 10%. Further details of the hydrological monitoring undertaken at the two gauging stations are given by Hodson et al. (1998a).

Discharge, TDSi and water temperature were monitored at the Lower Site between Days 178 and 226 in 1991, and Days 175 and 215 in 1992. The corresponding monitoring intervals at the Upper Site were Days 183–226 and 175–215 during 1991 and 1992, respectively. Both monitoring periods extended from the early phases of snowmelt until the snowline had receded close to its seasonal altitudinal limit on the glacier surface between 400 and 500 m altitude. Hydrochemical sampling began earlier than streamflow gauging, starting on Days 176 and 164 in 1991 and 1992, respectively, and continuing until the cessation of continuous monitoring at the Upper and Lower Sites.

3.2. Hydrochemical sampling

Concentrations of major cations, major anions and silica, along with pH, were determined for all melt-

water samples collected from the Upper and Lower Sites. In addition, snow samples and supraglacial runoff samples were collected from Austre Brøggerbreen and analysed for the same solutes (except pH). Several meltwater samples were also collected from the western margin of Austre Brøggerbreen (WAB), VB and a small hillslope plot (HP) established near the Lower Site (Fig. 1). Here soil waters were collected throughout the 1992 monitoring period at two points on a hillslope transect where soil moisture and temperature data were also collected. Overland flow was also sampled between the two soil-moisture sampling sites.

During 1991, samples were collected twice daily and approximately once daily at the Lower and Upper Sites, respectively, until Day 199. Thereafter, twice-daily samples were collected at each site every 2 days. This sampling strategy was then continued throughout the 1992 monitoring period. The times of sample collection were designed to coincide with the discharge maximum and minimum during 1991 (e.g. 1800 and 1000 h at the Lower Site). However, since data from the first monitoring period revealed the presence of long lags between the TDSi series and the discharge series, the time of sample collection was changed to 03:00 and 15:00 h at the Upper Site and 05:00 and 17:00 h at the Lower Site during 1992.

Stream samples were taken by hand using a pre-rinsed 500 ml polyethylene bottle and vacuum filtered immediately through a $0.45 \mu\text{m}$ filter membrane. All filter units and sample bottles were rinsed three times with either sample or filtrate. Duplicate and replicate sampling was conducted periodically to check for contamination from the sample apparatus and bottles. A separate sample bottle for pH and HCO_3^- analyses was used and filled completely in order to prevent degassing. The snow samples were collected at four locations (see Fig. 1) which were revisited between four and seven times throughout the 1992 ablation season (between Days 160 and 178). An aluminium spade was used to dig the snow pits from which three to five samples were taken at regular intervals down the profile (depending on the snow depth) and stored in plastic bags. When the snow depth was $< 40 \text{ cm}$, a bulk sample was collected from the entire profile. Separate samples of basal slush were also taken from every snow pit. The snow was allowed to thaw

Table 1
 Summary statistics of the major ion, pH and Si data from the principal sampling sites. Mean values are presented followed by the standard deviation (in parenthesis) and the number of observations. 'VB' denotes the Vestre Brøggerbreen sampling site and 'WAB' denotes the western Austre Brøggerbreen sampling site (see Fig. 1 for locations). For the hillslope sampling site, 'soil water' denotes samples collected by suction sampling, whilst 'soil Qs' denotes overland flow

Site	Ca ²⁺ (μEq l ⁻¹)	Mg ²⁺ (μEq l ⁻¹)	Na ⁺ (μEq l ⁻¹)	K ⁺ (μEq l ⁻¹)	Cl ⁻ (μEq l ⁻¹)	NO ₃ ⁻ (μEq l ⁻¹)	SO ₄ ²⁻ (μEq l ⁻¹)	HCO ₃ ⁻ (μEq l ⁻¹)	SiO ₂ (mg l ⁻¹)	pH
Lower, 1991	520 (130) 51	170 (54) 59	98 (66) 61	8.8 (2.2) 59	120 (87) 64	1.6 (2.2) 61	60 (27) 68	620 (67) 68	0.26 (0.10) 67	7.03 (0.19) 69
Lower, 1992	400 (60) 47	120 (22) 47	83 (90) 47	6.8 (1.2) 47	110 (120) 49	1.4 (2.4) 49	42 (21) 49	530 (92) 49	0.21 (0.06) 41	7.00 (0.17) 48
Upper, 1991	240 (50) 29	81 (30) 28	110 (110) 28	6.7 (1.9) 30	130 (130) 32	2.4 (3.6) 33	42 (23) 32	300 (70) 31	0.14 (0.07) 29	6.84 (0.20) 30
Upper, 1992	170 (60) 43	70 (42) 49	100 (130) 44	5.9 (1.4) 48	140 (170) 50	3.0 (4.8) 50	38 (40) 49	230 (40) 50	0.12 (0.05) 42	6.92 (0.22) 50
Snow, 1992	25 (41) 49	34 (53) 45	90 (110) 49	4.5 (4.9) 49	110 (160) 47	1.5 (2.3) 46	18 (35) 47	11 (18) 7	0.0 (0.0) 5	–
Supraglacial	38 (43) 9	18 (14) 9	29 (14) 9	1.5 (1.7) 9	35 (19) 9	0.72 (0.90) 9	10 (7.0) 9	68 (52) 9	0.038 (0.074) 8	6.37 (0.55) 9
Soil water	2700 (810) 8	1700 (500) 9	180 (20) 9	31 (8.3) 8	120 (22) 8	19 (10) 9	240 (16) 9	4100 (1500) 6	3.3 (1.1) 8	7.38 (0.19) 6
Soil Qs	550 (300) 8	360 (180) 8	190 (271) 8	13 (2.4) 8	88 (20) 8	1.5 (1.7) 8	59 (36) 8	870 (490) 7	0.63 (0.14) 6	–
VB	520 (31) 3	130 (23) 3	42 (26) 3	5.3 (1.2) 3	48 (35) 3	0.56 (0.49) 3	32 (7.2) 3	630 (12) 3	0.23 (0.06) 3	7.2 (0.07) 3
WAB	510 (83) 7	130 (28) 7	38 (16) 7	8.1 (2.4) 7	44 (17) 6	0.79 (0.77) 6	27 (9.3) 6	660 (75) 7	0.24 (0.10) 7	7.13 (0.06) 7

completely at room temperature and then filtered in the manner described above.

Soil water samples were collected using ceramic falling-head soil moisture suction samplers inserted 30 cm into the active layer at the beginning of the 1992 field season. Samples were drawn with 80 cbar of soil moisture pressure over a period of 24 h. The influence of the falling suction head and the interaction of the sampler with the soil are likely to have a significant effect upon the solute concentrations determined during this study (see Anderson, 1986). These problems mean that our data only represent tentative indicators of the composition of active layer soil waters.

3.3. Analytical methods

The analytical methodology adopted in the present study is described by Tranter et al. (1996). This involved the following methodology for each determinant:

1. pH: Measurement was undertaken within 10 days of sample collection using an Orion SA250 portable meter with a Ross combination electrode, low ionic strength adjustors and a procedure after McQuaker et al. (1983). Duplicate and replicate tests indicated precision errors of ± 0.2 pH units and negligible changes during storage.
2. HCO_3^- : Samples were titrated using ~ 1 mmol HCl (standardised on return from fieldwork) and BDH 4.5 indicator within 10 days of sample collection. A correction was employed to account for the amount of acid required to acidify the sample and indicator to pH 4.5. Precision errors were $\pm 3\%$.
3. *Major cations*: Emission mode atomic absorption spectroscopy was used for Na^+ and K^+ , whilst absorption mode was used for Ca^{2+} and Mg^{2+} . Chemical interferences and ionisation were overcome using $\text{La}(\text{Cl})_3$ and CsCl , respectively, whilst sample acidification prior to analysis with 1 ml concentrated HNO_3 was used to release any cations adsorbed to the bottle surfaces. Precision errors were $\leq 5\%$ for all cations except K^+ , where precision errors were $\pm 10\%$ for concentrations $\geq 8 \mu\text{Eq l}^{-1}$ and $\pm 20\%$ for concentrations $\leq 8 \mu\text{Eq l}^{-1}$.
4. *Major anions* (except HCO_3^-): A Dionex 4000I ion

chromatograph was used to determine Cl^- , NO_3^- and SO_4^{2-} in all samples. Precision errors for SO_4^{2-} and Cl^- were $< 4\%$. NO_3^- precision errors were typically up to 20%, although at concentrations $< 2 \mu\text{Eq l}^{-1}$, NO_3^- precision errors were as high as 50% (Tranter et al., 1996).

5. *Dissolved silica*: Si was determined using flow injection analysis with a FIAstar 5023 spectrometer and using the molybdosilic acid method (see Wadham et al., 1998). Precision error estimates were $\leq 5\%$.

4. Results

4.1. Major ion and Si data

Table 1 shows high concentrations of Ca^{2+} relative to other cations for all samples except snow. Mg^{2+} is typically the next most abundant cation, and concentrations of Mg^{2+} are highest relative to Ca^{2+} in concentrated soil waters and dilute samples from the glacier surface (snow and supraglacial streams). Concentrations of HCO_3^- are high relative to the other anions, except in the snowpack, where Cl^- is the dominant anion. SO_4^{2-} concentrations are low compared with HCO_3^- in all cases ($\text{SO}_4^{2-}/\text{HCO}_3^-$ ratios are always < 0.2), as are NO_3^- concentrations, which only exceed levels of $20 \mu\text{Eq l}^{-1}$ in soil water samples. Si is virtually absent from snow and supraglacial samples. Otherwise Si is present in mean concentrations between 0.1 and 0.3 mg l^{-1} at all sites except the soil water sampling site, where the mean concentrations exceed 3 mg l^{-1} . Table 1 shows that the average pH of virtually all samples is circum-neutral.

Fig. 2 shows that the 1991 monitoring season began with high flows at the Lower Site, followed by a strong flow recession between Days 178 and 196. This was caused by proglacial drainage following an outburst flood which occurred immediately after monitoring began. The flow recession was later punctuated by a rainstorm, causing high flows on Day 182, after which low air temperatures caused the flow recession to continue (see Hodson et al., 1998a). Upper Site records are sparse during this early phase of monitoring in 1991, although low flows were

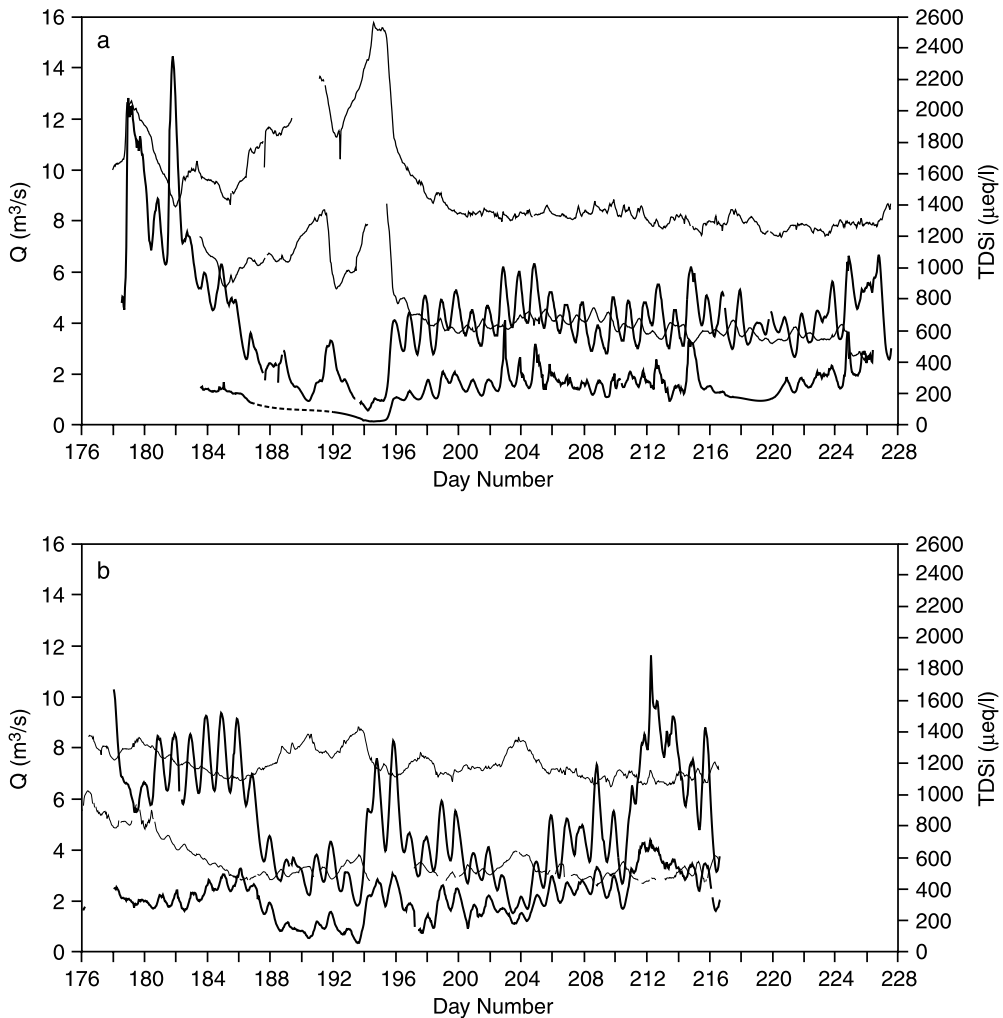


Fig. 2. Time series observations of discharge (thick line) and total dissolved (ionic) solids (thin line) for the (a) 1991 and (b) 1992 monitoring seasons. During 1991, a cubic spline curve has been used to interpolate periods of missing discharge data (Day 187–194, 1991, Upper Site). For each pair of lines, the Lower Site data are always the upper series on the graph.

known to have occurred because the outburst flood was not routed via this site. After Day 196 significant diurnal variations occurred at both the Upper and Lower Sites. However, diurnal variations in TDSi were muted throughout the entire ablation season. These ablation-season TDSi dynamics also occurred during 1992, because a period of high discharges and TDSi levels was followed by a flow recession which lasted until Day 193. Diurnal variations in discharge were more significant throughout the 1992 monitoring period at both the Upper and Lower Sites although

again, this was only accompanied by muted diurnal variations in TDSi.

4.2. Multivariate factor analysis

Temporal mode factor analysis (FA: see Davies et al., 1993) was employed to assist the interpretation of data collected at the Upper and Lower Sites. This method is often used to reduce the dimensionality of hydrochemical data sets from eight or more separate variables to a smaller number (usually three or four)

Table 2

Details of the factor loadings produced after factor analysis and Varimax rotation procedures. Factor loadings whose modulus values are less than 0.3 are excluded to improve clarity. The percentage of the total variance within the data set explained by the individual factors (% Var) and the four factors combined (% total) are also given. Weak factor loadings (see text for explanation) are given in italics

	Upper Site factor			Lower Site factor			West Site factor			
	1U	2U	3U	1L	2L	3L	1W	2W	3W	4W
Na ⁺	0.99				0.98			0.94		
Cl ⁻	0.99				0.98			0.95		
NO ₃ ⁻	0.99				0.92					-0.98
SO ₄ ²⁻	0.94			0.76	0.56		0.90			
K ⁺	0.79	0.41		0.83	0.43		0.95			
Mg ²⁺	0.86	0.43		0.93			0.95			
HCO ₃ ⁻		0.97		0.87			0.90	-0.39		
Ca ²⁺		0.89		0.88			0.88	-0.42		
Si			0.95	0.46		0.89	0.96		-0.93	
% Var	59	25	12	50	39	6	49	25	12	11
% Total			96			95				96

of underlying ‘factors’. Temporal mode analysis may then be used to identify controls upon stream chemistry over the course of episodic, seasonal and/or longer-term variations (e.g. Davies et al., 1993; Evans et al., 1996; Miller and Drever, 1977; Reid et al., 1981; Richards et al., 1996).

Temporal mode FA was applied to the major ion and Si data only. The FA was originally performed using data from both monitoring seasons combined and produced three orthogonal factors at the Upper and Lower Sites that accounted for $\geq 95\%$ of the data set variance in both cases. Subsequent factors were then omitted on account of the low proportion of data variance, which they explained (after Evans et al., 1996). These three factors were then rotated using the Varimax procedure in order to ease their interpretation (see Johnston, 1978). A repeat analysis was then undertaken which checked for consistency in the composition of the separate factors from year to year. It was then found that the analysis of the bulked data sets produced identical factors to the separated data and thus only the former are discussed below.

Since Hodson et al. (1998a,b) have shown that differences between the Upper and Lower Site data yield insights into the processes which may be occurring in the intervening proglacial environment, the difference in the individual ionic mass balances at the Upper and Lower Sites in 1992 was used to construct a third data set which was also subjected to FA (and which in this case produced four factors).

Data from 1991 were not used to construct this additional data set because the sampling strategy adopted produced few days when samples were taken at both the Upper and Lower Sites. Conceptually, this new data set represents a combination of net solute acquisition by runoff draining parts of the catchment not served by the Upper Site (i.e. the proglacial region, the WAB Site and the VB Site: Fig. 1), as well as solute acquisition from post-mixing reactions and error. Since the catchment area to this intermediate site largely lies in the western parts of the Bayelva watershed, these data will hereafter be referred to as the ‘West Site’. Fig. 1 shows that waters draining the higher elevations of this West Site pass through the WAB Site (6.2 km² with 3.7 km² (62%) covered by Austre Brøggerbreen) and the VB Site (8.3 km² with 5.3 km² (63%) covered by VB). Importantly, the sandur and the vegetated parts of the proglacial region form a far greater proportion of the West Site catchment area (21%) compared with the Lower Site (13%).

4.3. Description of the orthogonal factors

Table 2 shows the Varimax factor loadings produced from the full data sets at each site. The suffixes ‘U’, ‘L’ and ‘W’ are used to denote the Upper, Lower and West Site factors, respectively. At each site, the factors are ranked according to the proportion of the total (data set) variance which they

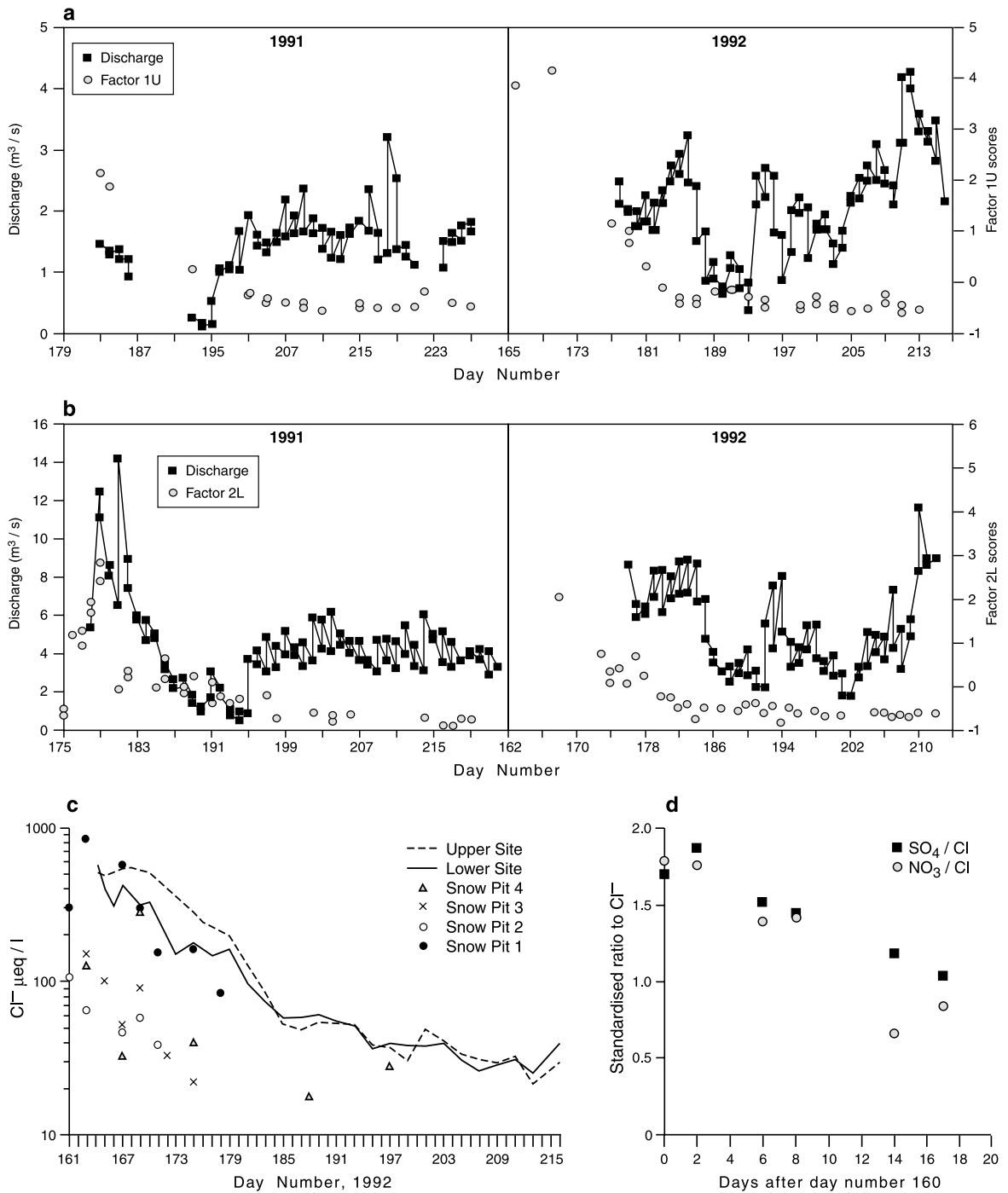


Fig. 3. (a) Time series of discharge and Factor 1U scores at the Upper Site; (b) discharge and Factor 2L scores at the Lower Site; (c) Cl⁻ concentrations in the basal snow melt and runoff samples; and (d) SO₄²⁻/Cl⁻ and NO₃⁻/Cl⁻ ratios in basal snowmelt at Snow Pit 4. The ratios have been standardised relative to the mean ratios of the first snowpack survey.

explain. In the following discussion, we also define how strongly each solute species is associated with separate factors by using the terminology of ‘weak’, ‘moderate’ and ‘strong’ according to whether the modulus of the individual factor loadings in Table 2 lies within the range 0.0–0.39, 0.4–0.75 and 0.76–1.0, respectively (after Evans et al., 1996).

The analysis produced three factors, which are broadly similar at the Upper, Lower and West Sites. Factor 1U is characterised by strong loadings from Na^+ , Cl^- , NO_3^- , SO_4^{2-} , K^+ and Mg^{2+} and represents the majority (59%) of variance in the Upper Site data set. This factor is also present as Factor 2L at the Lower Site, although Mg^{2+} is absent and SO_4^{2-} and K^+ only show moderate loadings. The composition of Factors 1U and 2L is therefore strongly indicative of marine and atmospheric aerosol, particularly due to the strong loadings of Cl^- and NO_3^- in both cases (Goto-Azuma et al., 1993; Hodgkins and Tranter, 1998; Semb et al., 1984). Factor 2W is also indicative of marine aerosol, although NO_3^- is absent.

Factor 2U explains 25% of the total variance in the Upper Site data set and is characterised by strong loadings from HCO_3^- and Ca^{2+} , as well as moderate loadings from Mg^{2+} and K^+ . The composition of Factor 2U is therefore indicative of crustal rock weathering within the catchment area to the Upper Site. Factors 1L and 1W, the dominant factors to emerge from the Lower Site and West Site analyses, are also similar to Factor 2U, except that Mg^{2+} , K^+ and SO_4^{2-} have strong loadings (SO_4^{2-} is absent from Factor 2U) and Si is also present.

Factors 3U and 3L and 3W are all characterised by strong, independent loadings from Si. Since biological Si sequestration is likely to be minimal in the rapid and turbid glacial streams, these factors are most likely to indicate the incongruent dissolution of silicates, possibly within ground waters.

Factor 4W is characterised by a strong loading from NO_3^- alone and makes an important contribution to West Site data variance (11%). This suggests that proglacial nutrient dynamics are not simply governed by snowpack elution.

5. Discussions

The preceding factor analysis suggests that the

hydrochemistry of the Bayelva catchment is principally governed by three broad categories of processes: (1) snowpack solute release; (2) rapid mineral surface reactions; and (3) slow, incongruent silicate dissolution. These three processes therefore form the basis of the following discussion.

5.1. Snowpack solute release

Fig. 3(a) and (b) shows discharge and Factor 1U and Factor 2L time series for the two monitoring seasons. A rapid, quasi-exponential decline in the factor scores is observable which begins early in the ablation season. These characteristics are typically reported in nival basins (e.g. Johannessen and Henriksen, 1978) and indicate that the elution of snowpack solutes, rather than simple dilution, is the most important control upon snowpack solute transport at the Upper and Lower Sites. This is supported by Fig. 3(c), which shows that concentrations of Cl^- at the base of the four snow pit sites also decline in a quasi-exponential manner at the beginning of the ablation season. Fig. 3(c) therefore suggests that snowpack solute elution occurs simultaneously across the entire catchment (certainly at elevations less than 300 m). Fig. 3(a)–(c) also suggests that only limited storage of the concentrated, early season snowmelt occurs in the basin. For this reason, Cl^- concentrations do not increase significantly during flow recessions at either the Upper or the Lower Sites (e.g. Days 185–195 in 1991 and Days 187–193 in 1992), suggesting that snowmelt supply to delayed flow pathways at the glacier bed is restricted. Tranter et al. (1996) argued that the severely limited distribution of temperate glacier ice at the glacier bed is a major reason for the absence of such storage.

Previous studies of snowmelt hydrochemistry have given particular emphasis to the preferential elution of NO_3^- and SO_4^{2-} from snowpacks undergoing melt and its potential to depress the pH of snowmelt runoff (Brimblecombe et al., 1985; Johannessen and Henriksen, 1978; Tranter et al., 1996). To date, however, preferential elution in high Arctic snowpacks of pristine or near pristine condition has received little attention (e.g. Goto-Azuma et al., 1993). Since preferential elution usually favours anions in the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ (e.g. Brimblecombe et al., 1985), the ratios of NO_3^- and SO_4^{2-} to Cl^- were examined in

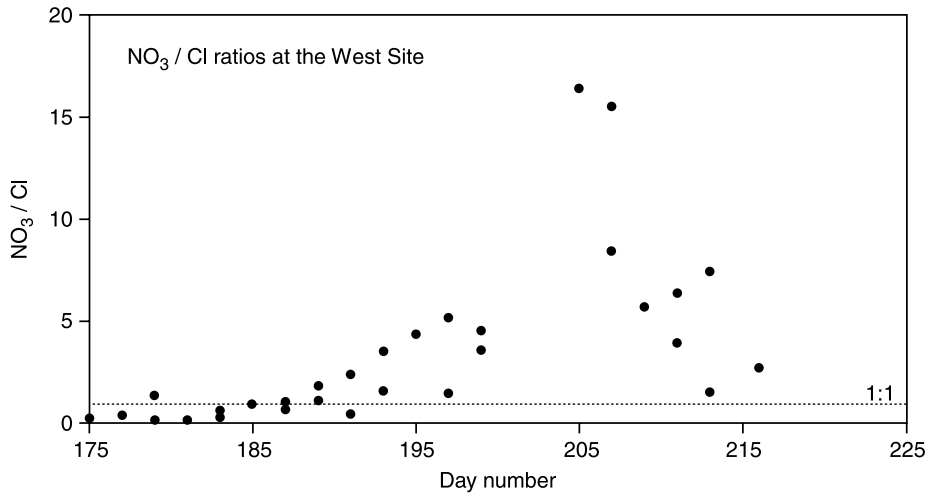


Fig. 4. $\text{NO}_3^-/\text{Cl}^-$ ratios at the West Site in 1992. The ratios have been standardised relative to the mean $\text{NO}_3^-/\text{Cl}^-$ ratio of the entire snow pit data set.

the basal snow pit samples collected during Days 161–178. Basal snow pit (slush) samples were inspected because it was assumed that basal snowmelt best identifies the ionic composition of recent melt percolating down through the overlying snowpack (Goto-Azuma et al., 1993). Another assumption was that no additional source or sink of either SO_4^{2-} or NO_3^- existed within the snowpack. Preferential elution was considered to have been effective if the ratios in basal melt were initially high relative to the mean snowpack ratios of the first survey, and thereafter showed a significant decline throughout the course of ablation. Fig. 3(d) shows an example where both these criteria were met at Snow Pit 1. Here the ratios have been standardised relative to the ratios first observed in the initial bulk snowpack survey.

Changes in the ratios depicted by Fig. 3(D) were best described by linear regression relationships of the form

$$\text{snowmelt} \text{SO}_4^{2-}/\text{Cl}^- = -0.05(\text{Day No.}) + 1.8 \quad (5)$$

and

$$\text{snowmelt} \text{NO}_3^-/\text{Cl}^- = -0.07(\text{Day No.}) + 1.9 \quad (6)$$

where ‘Day No.’ represents the number days after Day 160, 1992. The slope and intercepts of Eqs. (5) and (6) were significant at $p \leq 0.001$ whilst the coefficients of determination were 0.93 and 0.91, respectively.

Significant ($p \leq 0.05$) linear relationships of the form depicted by Eqs. (5) and (6) were found at all snow pit sites with respect to their basal $\text{snowmelt} \text{SO}_4^{2-}/\text{Cl}^-$ ratios. However, such a trend was only found at the lowest elevation site (Snow Pit 1) with respect to the $\text{snowmelt} \text{NO}_3^-/\text{Cl}^-$ ratios (Fig. 3(d)). Hence, our findings suggest that preferential elution of SO_4^{2-} is likely to have been widespread across the catchment and most probably contributed to the SO_4^{2-} content of runoff at the Upper and Lower Sites during the early stages of the monitoring period (e.g. before Day 190). However, since no evidence for pH depression at either of these two sites is evident when the pH time series are scrutinised before Day 190 (Hodson, 1994), it is likely that any acidic SO_4^{2-} aerosol eluted from the snowpack is quickly neutralised by an abundance of reactive particles on the glacier surface and at its margins.

For NO_3^- , our data suggest that preferential elution was not widespread in the Bayelva basin and so it is unlikely to have enhanced the NO_3^- content of the proglacial river. However, our results for NO_3^- may simply reflect the poor precision of NO_3^- detection at low concentrations and/or biological processes within the snowpack and its underlying substrate (e.g. Jones and Deblois, 1987). Such biologically mediated processes may also have already been identified during the preceding factor analysis because NO_3^- loaded strongly onto a separate and highly significant

fourth factor at the West Site (Factor 4W). Fig. 4 shows the $\text{NO}_3^-/\text{Cl}^-$ ratios of the West Site data during 1992. Again, the ratios have been standardised relative to those observed in bulk snow and so the values >1 after Day 190 clearly show that the West Site runoff became progressively enriched in NO_3^- relative to Cl^- during the latter stages of the ablation period. This trend cannot be explained by preferential elution (see Fig. 3(D)) and so it is likely that an additional NO_3^- supply exists within the West Site catchment area. Table 1 shows that nitrification in soils might be responsible because markedly greater NO_3^- concentrations were found in soil waters relative to concentrations at either the Upper Site or the Lower Site. The mean values of the overland flow samples were low, however (Table 1). This is because overland flow was initially Hortonian (due to the absence of an active layer early in the monitoring period) and so the NO_3^- content was also low and reflected the elution of an old snowpack lying further upslope (Hodson, 1994). It is therefore interesting to note that, later in the ablation period, saturation return flow was initiated on the hillslope and NO_3^- concentrations in overland flow rose significantly to values of $\sim 3.7 \mu\text{Eq l}^{-1}$ after leaving the active layer. We therefore believe that nitrification within the developing active layer progressively enriches the NO_3^- content of proglacial runoff following the onset of ground thaw. The latter stages of the ablation season are likely to be particularly favourable for such a soil N input because several authors have observed a direct relationship between drier soils and higher nitrification rates in the soils of Arctic (Gersper et al., 1980; Chapin, 1996) and Alpine (Jaeger et al., 1993) environments. Further, Chapin (1996) has reported nitrification rates of between 6.6 and 53 $\text{mg NO}_3^- \text{N m}^{-2} \text{d}^{-1}$ in a comparable high Arctic, carbonate bedrock site to the present study. If such rates of nitrification operate in the vegetated parts of the Bayelva catchment ($\sim 3.1 \text{ km}^2$ of the West Site), then a soil NO_3^- pool is available for leaching to the proglacial channel which is more than four orders of magnitude greater than the entire flux of NO_3^- through the Lower Site.

5.2. Crustal solute acquisition

The dominant factor to emerge from the Lower Site analysis (Factor 1L) had a composition which

reflected the acquisition of solute from crustal sources via chemical weathering. At the Upper Site, the significance of the factor with a similar crustally derived composition was usurped by the acquisition of solute from the snowpack lying at higher elevations within the catchment (Factor 1U). This suggests that the downstream chemical evolution of the Bayelva river is increasingly dominated by solute acquisition from rock weathering reactions, as has been observed in similar environments elsewhere (e.g. Caine and Thurman, 1990). The following sections therefore examine which chemical weathering reactions furnish solute in the higher, glacierised sub-catchments of the Bayelva basin (i.e. the Upper, WAB and VB Sites in Fig. 1) and then consider which processes govern their downstream evolution as they pass through the proglacial region. In order to do so, we have used standard marine ratios to Cl^- (after Holland, 1978) to remove the marine contributions of major ions from our data set. Hereafter, the prefix ‘*’ is used to denote these ions in their crustal provenance category. Additionally, concentrations of SO_4^{2-} in runoff were corrected for acid aerosol in the snowpack. This was done using a fixed $\text{snowmelt SO}_4^{2-}/\text{Cl}^-$ ratio set at 0.118, the mean ratio of the entire snow data set. Clearly, this method does not account for the preferential elution of $\text{snowmelt SO}_4^{2-}$ described in Section 5.1, suggesting that early season $^*\text{SO}_4^{2-}$ may be overestimated. However, using the variable $\text{snowmelt SO}_4^{2-}/\text{Cl}^-$ ratios observed at the base of Snow Pits 1–4, we found that overestimation of $^*\text{SO}_4^{2-}$ was negligible after Day 175 in 1992 (a period missing in the 1991 data set) and that no impact upon the temporal variability of $^*\text{SO}_4^{2-}$ in runoff was observable (see also Tranter et al., 1996).

5.3. Chemical weathering in the glacierised Upper, WAB and VB Sites

Fig. 5 shows the crustal ion, Si and discharge data for the Upper Site during 1991 and 1992. Virtually all ions show a decline in concentration throughout the ablation season, particularly during 1992. This simple trend suggests that the leaching of glacial debris in the early stages of the ablation season produces runoff, which is most concentrated in crustally derived ions. A significant exception to this trend involves the 1991 flow recession (Days 178–198), when the concentration of most ions (excluding $^*\text{Na}^+$)

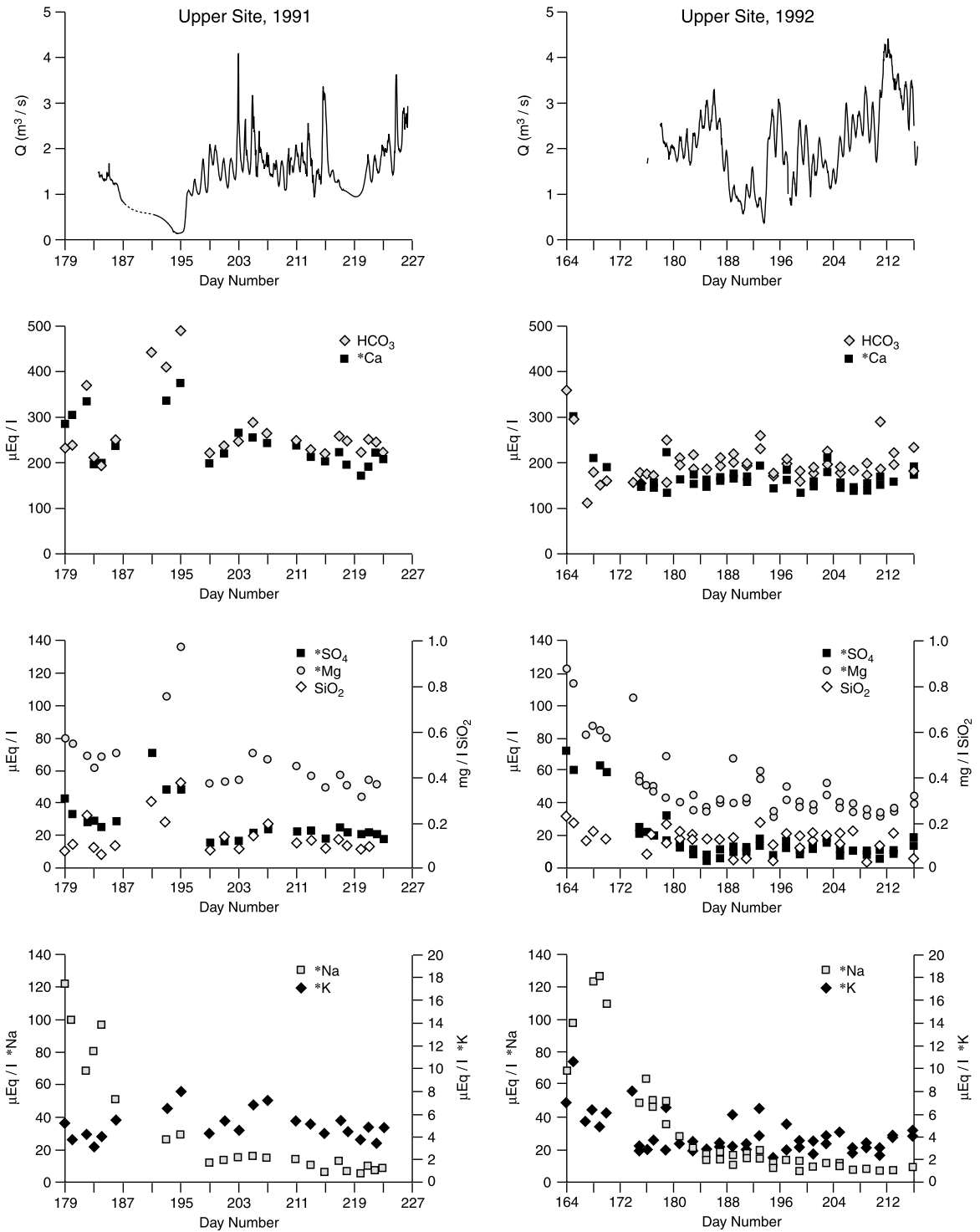


Fig. 5. Discharge, concentrations of all crustal ions (denoted by ‘*’) and silica in Upper Site meltwaters during 1991 and 1992.

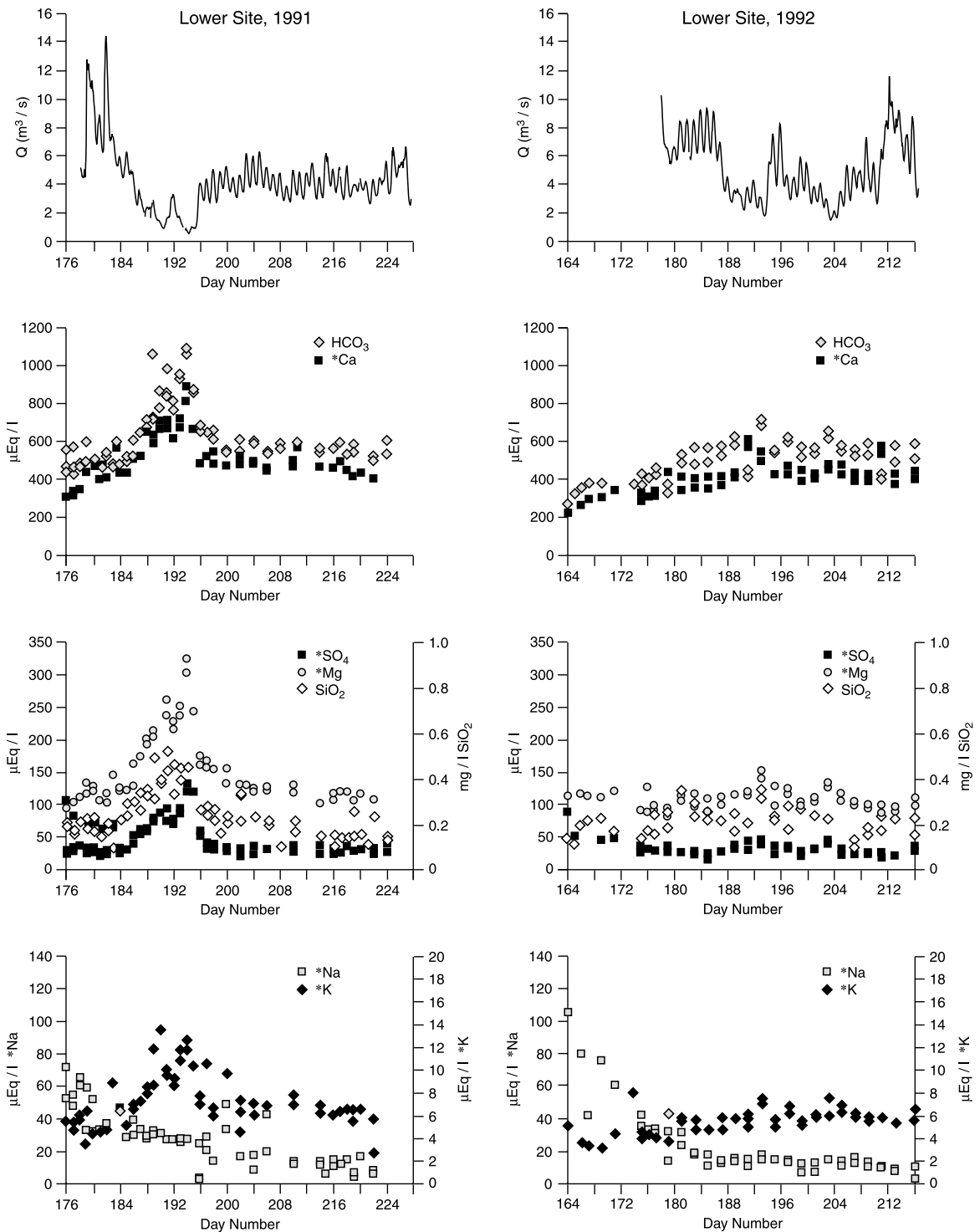


Fig. 6. Discharge, concentrations of all crustal ions (denoted by ‘*’) and silica in Lower Site meltwaters during 1991 and 1992.

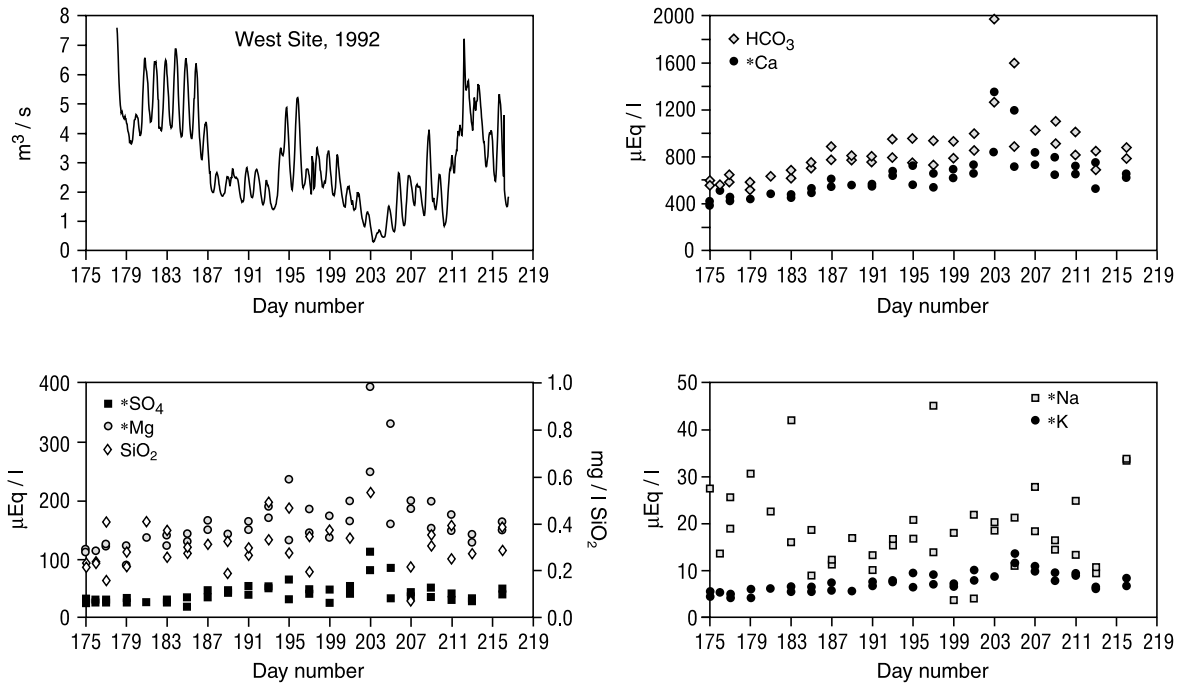


Fig. 7. Discharge, concentrations of all crustal ions (denoted by '*') and silica in West Site meltwaters during 1992.

increased significantly. From Fig. 5 it is also clear that $^*Ca^{2+}$ and HCO_3^- dominate the crustal ions with a $^*Ca^{2+}/HCO_3^-$ ratio close to unity when equivalent concentrations are used. Similar ratios characterise samples from the WAB and VB Sites, suggesting that carbonation reactions involving calcite and either atmospheric CO_2 (Eq. (3)) or organic C are the most important chemical weathering process in the glacierised parts of the Bayelva basin. Carbonation of Ca-silicates may also produce such a ratio (Eq. (4)), but the low solubility of these minerals and the relative abundance of calcite in the catchment mean that this reaction is likely to be relatively unimportant. Coupled sulphide oxidation–carbonate dissolution (Eq. (1)), which is widely reported to dominate the composition of sub-glacial meltwaters (Tranter et al., 1993) cannot produce a $^*Ca^{2+}/HCO_3^-$ ratio of 1 unless dolomite weathering is important. This is not believed to be the case because the slopes of regression relationships between $^*Ca^{2+}$ and $^*Mg^{2+}$ produce $^*Ca^{2+}/^*Mg^{2+}$ ratios of 3.4 and 4.0 using Upper Site data and pooled WAB and VB Site data, respectively. Table 1 suggests that the calcite carbonation is largely occurring in ice-marginal environments as Ca^{2+} and

HCO_3^- concentrations in the supraglacial streams and snow cannot account for the downstream concentrations observed at the Upper Site. Further, calcite dissolution in dilute supraglacial meltwaters is more likely to be achieved by simple hydrolysis and the neutralisation of snowmelt acid aerosol (Fairchild et al., 1994; Tranter et al., 1993).

The absence of $^*SO_4^{2-}$ from Factor 2U, and the $^*Ca^{2+}/HCO_3^-$ ratio close to unity therefore indicate that coupled sulphide oxidation–carbonate dissolution (Eq. (1)) is insignificant in the Upper Site catchment. However, Fig. 5 shows that $^*SO_4^{2-}$ is in fact present at the Upper Site, but the concentrations are low ($\sim 5\text{--}15 \mu\text{Eq l}^{-1}$ after Day 185) and can account for $\leq 10\%$ of the HCO_3^- at the Upper Site (the proportion is $\sim 8\%$ at the WAB and VB Sites). Sulphide oxidation therefore appears to be severely restricted compared to other glacier studies (e.g. Tranter et al., 1993; Wadham et al., 1998). This is due to either sulphide-deficient local rock types or the absence of a renewable source of freshly comminuted sulphide minerals (e.g. at the glacier bed) for oxidation by meltwaters. Since black, sulphide-rich veins are observable in younger cherts and sandstones

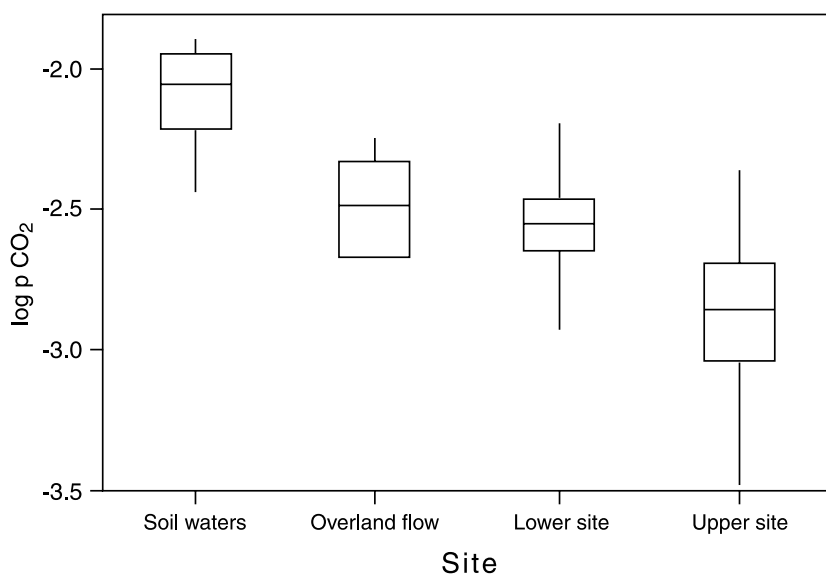


Fig. 8. Box-whisker plots showing $\log_{10} p(\text{CO}_2)$ values for soil waters, overland flow and runoff at the Upper and Lower Sites. The West Site is excluded due to uncertainty in the mass balance calculations used when estimating West Site pH.

~200 m upstream of the Upper Site, we favour the latter hypothesis. Further, sulphide oxidation exerts a fundamental control on the composition of sub-glacial meltwaters draining an adjacent glacier basin (Midre Lovenbreen: see Hodson and Tranter, 1999). This new evidence therefore adds further support to Tranter et al.'s (1996) assertion that sub-freezing ice temperatures restrict the access of Upper Site meltwaters to potentially reactive mineral surfaces at the glacier bed.

The remaining crustal ions in Fig. 5 and a small proportion of the HCO_3^- may be largely explained by the carbonation of silicate minerals in the Upper Site catchment. This produces $^*\text{K}^+$ and $^*\text{Na}^+$ concentrations between 2 and $10 \mu\text{Eq l}^{-1}$ and 130 and $15 \mu\text{Eq l}^{-1}$, respectively. The high $^*\text{Na}^+$ concentrations mean that its absence from Factor 2U is confusing and so an explanation is sought later in the paper.

5.4. Chemical weathering and the downstream evolution of glacial meltwaters

Figs. 6 and 7 show the crustal ion, Si and discharge data for the Lower Site and the West Site, respectively. Both figures show that much more concentrated runoff is present at these downstream sites

when compared to their upstream counterparts described in Section 5.3. Also, unlike Upper Site data depicted in Fig. 5, the concentrations of many crustal ions do not decrease throughout the ablation season. For example, concentrations of $^*\text{Ca}^{2+}$, $^*\text{Mg}^{2+}$ and HCO_3^- at the West Site clearly increase throughout the observation period (Fig. 7). Further differences include lower $^*\text{Ca}^{2+}/\text{HCO}_3^-$ ratios in the Lower Site and West Site data relative to the Upper Site (the corresponding ratios are 0.68, 0.79 and 0.88, respectively, if defined using regression relationships). The excess HCO_3^- relative to $^*\text{Ca}^{2+}$ is probably a consequence of dolomite weathering because $^*\text{Mg}^{2+}$ concentrations are significantly higher at both the Lower and West Sites and can account for virtually all the remaining HCO_3^- via carbonation. Table 1 suggests that proglacial soils favour the dolomite weathering to the greatest degree because concentrated waters are present. The $^*\text{Ca}^{2+}/^*\text{Mg}^{2+}$ ratio of the soil and overland flow waters is also low (1.6) compared with upstream sites described in Section 5.3 (≥ 3.4) and the downstream Lower Site (2.2). Further, the low solubility of dolomite relative to calcite suggests that extended rock–water contact (compared to that afforded by ice-marginal environments) is required in order for the observed

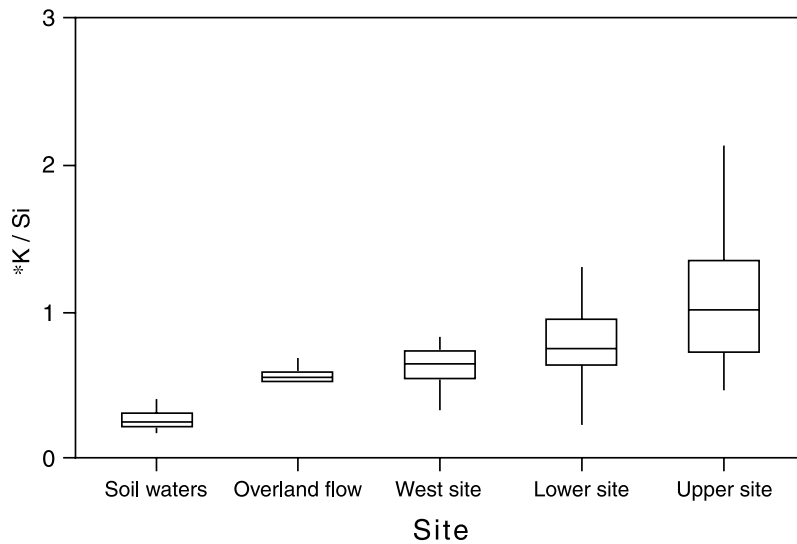


Fig. 9. Box-whisker plots showing $*K^+/Si$ ratios (derived from molar concentrations) for soil waters, overland flow and runoff at the Upper, Lower and West Sites.

downstream enrichment of $*Mg^{2+}$ to occur. Development of the active layer clearly has the potential to provide such conditions, particularly at the end of the ablation season, when active layer depths are at a maximum. Chemical weathering in the developing active layer also has the potential to explain the progressive increases in $*Ca^{2+}$, $*Mg^{2+}$ and HCO_3^- in Fig. 7 provided that concentrated soil waters are leached into the main river network. Leaching by snowmelt may be less effective than rainfall later in the summer because low snowpack water equivalents, thick basal icing layers and negligible active layer depths are typical across the entire proglacial region at the beginning of the ablation season (Hodson, 1994).

In addition to extended rock–water contact times, high soil-water $p(CO_2)$ conditions may also enhance chemical weathering within the active layer. Fig. 8 shows logarithmically transformed $p(CO_2)$ estimates for the soil waters, overland flow and meltwaters from the Upper and Lower Sites during 1992. The $p(CO_2)$ estimates were derived using the expression

$$p(CO_2) = (HCO_3^-)(H^+)/K_1K_H$$

where K_1 and K_H are coefficients of $10^{-6.58}$ and $10^{-1.12}$ at $0^\circ C$ (Garrels and Christ, 1965).

The $p(CO_2)$ of a sample is a reflection of the rate at

which CO_2 diffuses into or out of solution relative to the rate of chemical weathering reactions and microbial processes. It is a useful concept in glacier hydrochemistry because glacierised environments have the potential to reduce $p(CO_2)$ by either promoting high weathering rates (e.g. Eq. (4)) or by reducing the exchange of CO_2 between the atmosphere and meltwaters in sub-glacial environments (Raiswell, 1984). High $p(CO_2)$ meltwaters may also be observed in glacial meltwaters, which is often due to an additional H^+ supply (e.g. sulphide oxidation and/or snowpack acid aerosol) that causes CO_2 to attempt to diffuse out of solution (Tranter et al., 1993). Fig. 8 suggests that these processes are effective in the Upper Site catchment since high $p(CO_2)$ conditions relative to the atmosphere ($\sim 10^{-3.5}$ at.) characterise all meltwaters sampled there. However, soil and overland flow samples have even greater $p(CO_2)$. This may be most likely due to the microbial respiration within the active layer, as has been observed in the upper horizons of soils elsewhere in Svalbard (Pecher, 1994). However, it is possible that solute rejection during freezing within the active layer may also contribute to the high $p(CO_2)$ of the soil water solutions.

The $p(CO_2)$ of Lower Site samples are elevated with respect to the Upper Site samples, indicating

that runoff equilibration with the atmosphere is clearly not possible during its short transit through the proglacial stream network (~1–3 h; Hodson et al., 1998a). Since sulphide oxidation is limited and the elution of acid ions from the snowpack is only likely to persist at high elevations within the catchment, the increase in Lower Site $p(\text{CO}_2)$ relative to the Upper Site is most likely due to active layer soil waters mixing with glacial runoff in the proglacial plain. Overall, Fig. 8 therefore provides further evidence that chemical weathering is important within the active layer and that mixing between soil waters and glacial meltwaters is an important characteristic of the downstream evolution of bulk runoff.

5.5. Silicate weathering characteristics

Factors 3U, 3L and 3W all indicate that Si dynamics differ from those of other silicate weathering products (e.g. $^*\text{K}^+$ and $^*\text{Na}^+$). A possible reason for this is that the stoichiometry of silicate weathering is unusual in glacierised basins. For example, Anderson et al. (1997) and Hodson et al. (2000) have reported that the molar ratios of $^*\text{K}^+/\text{Si}$ are typically high (~1) in glacial meltwaters when compared with global mean silicate weathering data (e.g. Holland, 1978). This is believed to partly reflect the sensitivity of K-feldspar dissolution to mechanical disaggregation (Blum and Erel, 1997; Hoch et al., 1999). However, deduction of silicate weathering stoichiometry from field data is fraught with uncertainty. Fig. 9 shows this point; high $^*\text{K}^+/\text{Si}$ ratios (~1) exist at the Upper Site, whilst significantly lower ratios exist within runoff at the Lower Site, the West Site and the hillslope sampling plot (soil waters and overland flow). This suggests that glacial meltwaters have high $^*\text{K}^+/\text{Si}$ ratios inherited from short-term contact with glacially disaggregated minerals and then mix with downstream soil waters which have low $^*\text{K}^+/\text{Si}$ ratios inherited from more 'complete' silicate weathering in longer residence time active layer soils. However, an alternative explanation is that the low $^*\text{K}^+/\text{Si}$ ratios of the active layer end member are simply due to $^*\text{K}^+$ sequestration by plants and clays. Testing these hypotheses is clearly not simple because the processes involved are intricately linked. For example, plants are responsible for stabilizing slopes that would otherwise be subjected to

more intense cryoturbation and mineral disaggregation. Despite these problems, the different $^*\text{K}^+/\text{Si}$ ratios depicted by Fig. 9, coupled with the high concentration of Si in soil waters (see Table 1) are significant because they show that leaching of the active layer also has the capacity to enhance the downstream Si content of bulk runoff.

5.6. Ion exchange as a potential control upon $^*\text{Na}^+$ dynamics

The dynamics of $^*\text{Na}^+$ at the Upper and Lower Sites clearly differ from other crustally derived solutes because concentrations show little change during flow recessions and generally decrease throughout the ablation season. Inspection of the snow pit data does not indicate that preferential elution of Na^+ occurs and so alternative explanation is required.

Eyles et al. (1982) found that as much as 72% of the total Na^+ transported by meltwaters in the Berendon catchment (Canada) was adsorbed onto sediment surfaces. It is therefore possible that an ion exchange mechanism may be responsible for its unusual seasonal dynamics. This is because Na^+ present on adsorption surfaces may be readily displaced by other (usually divalent) cations due to the selective adsorption characteristics of cations in low ionic strength solutions (Freeze and Cherry, 1979). For this reason, exchange of Ca^{2+} in solution for adsorbed Na^+ has already been argued to occur in glacial till aquifers of North America (Freeze and Cherry, 1979) and within a sediment layer beneath Finsterwalderbreen, a Svalbard glacier (Wadham et al., 1998). Fairchild et al. (1999b) have also commented upon the ion exchange capacity of proglacial suspended sediments in the carbonate-dominated Glacier de Tsanfleuron basin, Switzerland.

A simple test of the ion exchange capacity of artificially crushed bedrock and of suspended sediments collected from the Upper Site was therefore undertaken. Ion exchange capacities were determined by leaching suspended sediment samples and sieved rock powders with an ammonium acetate solution buffered to pH 7 using acetic acid (after Lorraine and Souchez, 1972). Crushed limestone was excluded from the tests because calcite dissolution at pH 7 could not be avoided. Table 3 summarises the cation concentrations of the leachate solutions following

Table 3

Ion exchange capacities (IEC) for ground rock flour and proglacial suspended sediments. The composition of the exchangeable cation pool is also shown

Sediment sample	Na ⁺ (%)	K ⁺ (%)	Mg ²⁺ (%)	Ca ²⁺ (%)	Ca ²⁺ /Na ⁺	IEC (mEq/100 g)	Exchangeable Na ⁺ (mEq/100 g)
<i>Finsterwalderbreen; Wadham et al. (1998)</i>							
Proglacial sediment	1.0	1.0	7.0	91	91	8.2	8.2
Shale	6.0	2.0	27	64	11	10	60
Sandstone	7.0	11	34	49	7	6.0	42
<i>This study</i>							
Proglacial sediment	0.7	0.9	8.3	90	130	5.6	3.9
Shale	3.2	6.0	17	74	23	4.2	13
Red sandstone	18	23	22	37	2.1	0.39	7.0
Phyllite	2.6	6.6	8.0	83	32	5.0	13
Phyllite/Schist	2.9	18	11	68	24	3.7	11

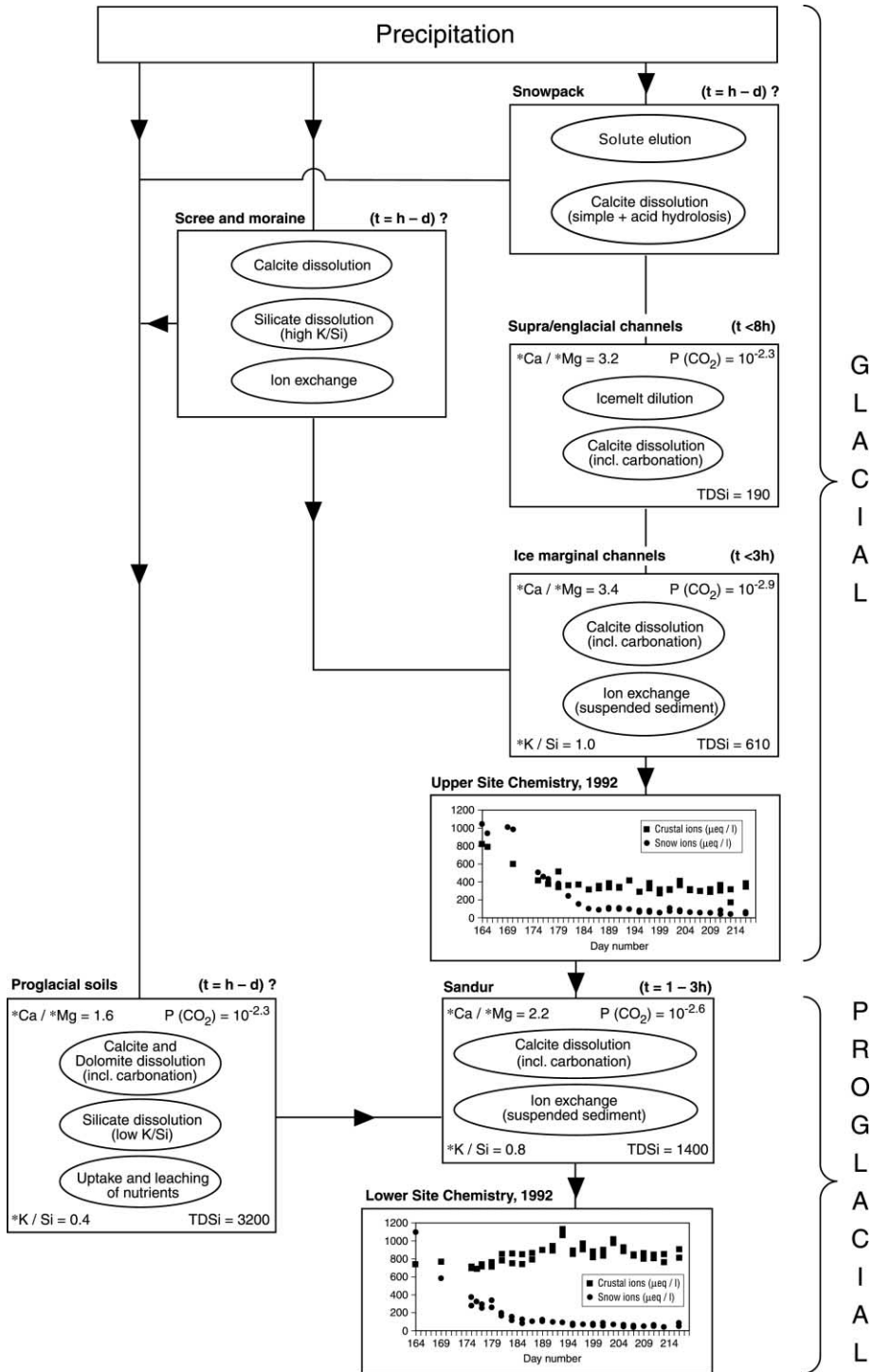
their analysis using the methods reported in Section 3. For comparison, data are also presented from Finsterwalderbreen, a glacier basin which lies ~180 km south of the Bayelva catchment (after Wadham et al., 1998). For both glacier basins, the proglacial sediment leachates show a high Ca²⁺ content and a significant ion exchange capacity relative to all crushed bedrock samples. However, some of the Ca²⁺ may be attributable to calcite dissolution during the experiments. It is therefore important to note that the quantity of exchangeable Na⁺ per 100 g sediment is also low for Upper Site suspended sediment (3.9 mEq/100 g) relative to the crushed bedrock samples (7–13 mEq/100 g). These data therefore tentatively suggest that Ca²⁺ release following calcite dissolution may induce the rejection of Na⁺ from ion exchange sites on suspended sediment surfaces. However, this argument does not explain why the widespread rejection of ²²Na⁺ only occurs in the early stages of the ablation season. We believe this is achieved by shifting suspended sediment source areas in the Upper Site catchment (see Hodson et al., 1998b). This is because the lateral moraines, which are the first to be exposed to the ground thaw, are composed of red sandstone debris that quickly creates slurries and supplies sediments to the stream via mass movement. These moraines soon stabilise

after drying and sediment source areas migrate upstream to parts of the catchment where other rock types are present (Hodson et al., 1998b). Hence, it is the cessation of fresh inputs of red sandstone material that we believe causes Na⁺ rejection from ion exchange sites to decrease throughout the ablation season. Other rock types are less favourable because they have a lower proportion of exchange sites occupied by Na⁺ (Table 3) and/or they are arguably more important sources of suspended sediment in the latter stages of the ablation period. This speculation, along with the observations of Eyles et al. (1982), Lorraine and Souchez (1972), Wadham et al. (1998) and Fairchild et al. (1999b) therefore suggests that ion exchange processes in glacial meltwaters require detailed assessment.

6. Summary and conclusions

Major ion, silica and pH data have been presented from a high Arctic proglacial river system in Svalbard. Factor analysis of these data suggests that the major controls upon hydrochemistry in the basin include snowpack solute elution, rapid mineral surface weathering and slow, incongruent silicate dissolution. A descriptive model showing the operation

Fig. 10. A descriptive model showing the principal solute processes (ellipses) occurring at the various locations (boxes) within the Bayelva watershed. All data are derived from $\mu\text{Eq l}^{-1}$ units except $p(\text{CO}_2)$ (atm) and the ²²K/Si ratio (a molar ratio). An indication of the meltwater residence time in each box is given which is derived from dye tracing and other hydrological studies conducted within the basin (Hagen et al., 1991; Hodson, 1994; Hodson et al., 1998a; Vatne, unpublished data).



of these processes at various points within the catchment is shown in Fig. 10. Rain and snowmelt produce water, dissolved gases and acid aerosol for chemical weathering reactions within the entire basin. Where rock–water contact is of limited duration (i.e. within the snowpack and supraglacial channels), calcite dissolution is the principal weathering reaction. However, where more intimate and prolonged contact is offered, silicate weathering increases in significance, producing high K^+/Si ratios in the upper parts of the catchment and low K^+/Si ratios in proglacial soils. Proglacial soils are also the locus of enhanced dolomite dissolution. Short residence time channels at the glacier margins and in the proglacial sandur have high-suspended sediment concentrations relative to supraglacial channels. This enables further calcite dissolution via carbonation and also ion exchange processes to occur.

Combination of the above processes produces dilute runoff at the Upper Site in which concentrations of crustally derived solutes effectively decline following the leaching of sediments and moraines early in the ablation season. However, combination of all solute processes shown in Fig. 10 produce a more concentrated time series of crustally derived solutes with the opposite trend at the Lower Site, demonstrating increasing solute supply from the active layer throughout the runoff season. Since snowpack elution occurs across the entire catchment, it is therefore the hydrology and chemical weathering processes of the active layer that dominate the downstream evolution of glacial meltwater composition. In addition, microbial processes enable NO_3^- and high $p(CO_2)$ solutions to be leached from soils into the main river system.

Earlier work in Svalbard has found chemical weathering environments in glacierised basins that are similar to temperate glacier basins (e.g. Wadham et al., 1998). We have found that this is clearly not the case in the Bayelva basin because the glaciers present have a sub-freezing temperature structure that effectively precludes contact between meltwaters and freshly comminuted sulphide, carbonate and silicate mineral surfaces at the glacier bed. Future studies of the composition of runoff in polar settings should therefore give emphasis to solute acquisition in proglacial and ice marginal environments, rather than sub-glacial environments alone.

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