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Review

Glacier meltwater hydrochemistry

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Abstract

Glacierised areas present an ideal environment in which to study water-rock interaction, since chemical weathering rates are high and anthropogenic impacts are often minimal. Detailed investigations of meltwater quality variations have suggested the importance of these environments in estimates of terrestrial chemical erosion and global biogeochemical cycles. Most notably, the role of meltwaters in CO_2 sequestration during episodes of deglaciation has attracted considerable attention, since this may impact on climate at glacial-interglacial timescales. However, there is still considerable uncertainty surrounding estimates of CO_2 drawdown by meltwaters which remains to be resolved. Water flow through glaciers exerts an important control on ice mass dynamics, and influences the quantity and quality of water delivered to environments downstream of glacierised basins. Thus, the study of the configuration and dynamics of subglacial drainage systems is important not only to enhance scientific understanding, but also to allow effective water resource utilisation in glacierised headwater catchments. Bulk meltwater quality characteristics draining terrestrial ice masses also offer the potential to provide unique information on hydrological and hydrochemical processes operating in the inaccessible subglacial environment. Here, significant advances have been made in understanding the controls on chemical weathering reactions, based on the identification of key dissolved indicator species. This has allowed water quality variations to be exploited as a tool for both subglacial hydrochemical and hydrological investigations. As a result, this area of glaciology has received considerable attention in recent years, utilising an increasing range of dissolved ions, and integrating field and laboratory studies. However, uncertainty still surrounds certain areas of meltwater quality science, including the role of microorganisms in a system which to date has largely been viewed as abiotic. A better understanding of the processes and rates of chemical weathering in glacierised environments has the potential to enhance our understanding of the environment, and to facilitate the exploitation of water quality variations for both scientific and applied objectives. In this paper the development and current state of meltwater quality science as a tool for investigating subglacial hydrology and geochemistry is detailed, and problems and future directions identified. This will hopefully stimulate wider interest in an important area of aquatic chemistry with significant applied implications.

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1. Introduction

The generation of snow- and icemelt in glacierised catchments produces an annual hydrograph which is generally inverse to that exhibited in temperate fluvial environments, with maximum flow occurring during the summer months when precipitation is at a minimum (Röthlisberger and Lang, 1987; Brown and Fuge, 1998a) (Fig. 1). This meltwater is a valuable resource, which has long been utilised for irrigation (e.g. Butz, 1989; Bratt, 1995), and for hydroelectric power (HEP) generation, particularly in the European Alps and Scandinavia (e.g. Bezinge et al., 1973; Bezinge, 1987; Bogen, 1989). The success of these schemes requires a clear understanding of the principles of subglacial water flow and sediment transport (Benn and Evans, 1998).

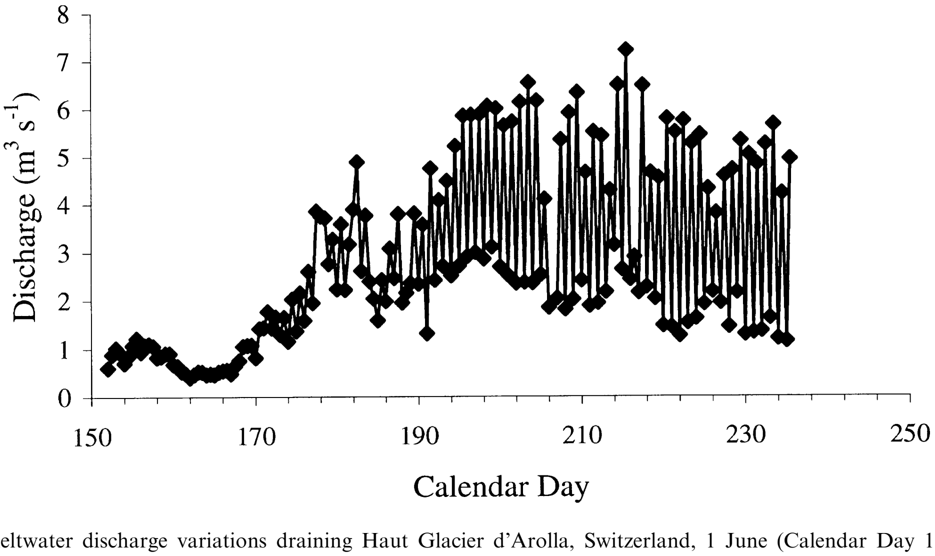

Fig. 1. Bulk meltwater discharge variations draining Haut Glacier d'Arolla, Switzerland, 1 June (Calendar Day 152)–31 August (Calendar Day 243) 1990.

This includes the ability to predict not only the timing and magnitude of meltwater delivery, but also the location of major subglacial drainage pathways, since some HEP schemes involve trapping water in subglacial locations [e.g. Glacier d'Argentière (Hantz and Lliboutry, 1983), Bondhusbreen (Wold and Østrem, 1979; Hooke et al., 1988), Engabreen (Jansson et al., 1996)]. Conversely, glacier outburst floods represent a hazard in mountainous regions, often originating from water stored subglacially (e.g. Björnsson, 1992; Lawler et al., 1996; Tómasson, 1996; Walder and Costa, 1996; Reynolds, 1998).

Meltwater quality variations have been proposed as a tool for investigating the configuration and dynamic nature of the subglacial hydrological system. This is based on the premise that the ionic composition of these waters reflects different types and durations of chemical weathering reactions furnishing solute to meltwaters during transit through the hydroglacial system (e.g. Collins, 1978; Tranter and Raiswell, 1991; Tranter et al., 1993, 1996; Brown et al., 1994a; Hubbard and Nienow, 1997). These chemical weathering reactions are controlled by the characteristics of the hydrological flowpaths, and the dynamic nature of the hydroglacial system as meltwater sources change and transport pathways evolve through the ablation season. The configuration and seasonal evolution of the subglacial hydrological system influences the primary factors governing the magnitude and processes of solute acquisition e.g. proton availability, the grain-size, shape and surface morphology of subglacial sediments, the water:rock ratio and suspended sediment mobilisation (Sharp, 1991). Thus, variations in the chemical composition of meltwaters draining glaciers have been used, with varying degrees of success, as a remote-sensing tool for investigating hydrological and geochemical processes operating in the inaccessible subglacial environment.

More recently, interest in the rate of chemical denudation in glacierised catchments has been revived, driven by advances in our understanding of geochemical processes and their rapidity in these environments, and the need to quantify rates of chemical erosion during the Quaternary (e.g. Sharp et al., 1995a; Tranter, 1996; Gibbs and Kump, 1994, 1996). These studies suggest that the negative effects of low temperatures, sparse vegetation and poorly developed soils on chemical weathering rates are offset by factors such as high meltwaters fluxes and access to freshly comminuted sediment (Velbel, 1993a; Brown et al., 1996a; Gibbs and Kump, 1996). This has stimulated interest in the role of glaciers and glaciation in global biogeochemical cycles.

Many of the problems associated with the study of glacier hydrochemistry, especially the inaccessibility of the environment under consideration, are akin to those experienced by groundwater hydrologists. For example, both disciplines need to consider the hydrological, geological and hydraulic properties of flowpaths using a variety of environmental monitoring techniques to determine remotely the properties of the subsurface system (Freeze and Cherry, 1979; Hubbard and Nienow, 1997; Fountain and Walder, 1998). They both have to contend with water movement at a range of velocities within the same hydrological system (Price, 1996). One common investigative technique is the use of water quality parameters to understand and model inaccessible hydrological environments. Further, both hydrogeologists and glaciologists have utilised laboratory experiments to explore water-rock interaction (e.g. Freeze and Cherry, 1979; Brown et al., 1996a, in press).

Studies of groundwater have received considerable attention in the geochemical literature, using a variety of chemical indicators to address problems such as aquifer recharge (e.g. Fritz, 1985), travel times of component waters (e.g. Edmunds and Smedley, 1998), waste disposal (e.g. Cherry et al., 1973; US Environmental Protection Agency, 1977) and groundwater pollution (e.g. Fried, 1975; Bouwer et al., 1985; Macpherson, 1998). It is, therefore, common for groundwater textbooks to have a chapter on the chemical principles and processes operating in groundwater systems. However, the study of subglacial hydrology by environmental and applied geochemists has received relatively little attention, and has been largely restricted to the glaciological, hydrological and geomorphological literature. The purpose of this review is to detail the development and current state of meltwater quality science as a tool for investigating subglacial hydrology and geochemistry, and to stimulate wider interest in an important area of aquatic chemistry with significant applied implications.

Research conducted at Haut Glacier d'Arolla, Valais, Switzerland is used to highlight the application of meltwater quality to hydrological and geochemical problems in glacierised environments. The discussion is limited to solute variations in glacial meltwater systems. The solid component of streamwater quality (suspended sediment) is discussed in relation to its influence on solution chemistry. However, systematic reviews of suspended sediment dynamics in glacial environments are available elsewhere (e.g. Gurnell, 1987; Hallet et al., 1996; Hodson et al., 1998; Hodson and Ferguson, 1999).

2. Subglacial drainage system structure

The temperature of ice exerts an important control on a wide variety of glacial processes (Benn and Evans, 1998), including those which influence chemical weathering and the composition of meltwaters in glacierised environments (e.g. meltwater flow, sediment production, gas availability). Thus, glaciers are classified according to their temperature regime (Benn and Evans, 1998). *Temperate* (*warm-based*) glaciers are composed of warm ice at the pressure melting point, and meltwater is present at the ice-bed interface (Bennett and Glasser, 1996). These glaciers contrast with *polar* (*cold-based*) glaciers, which are composed of cold ice below the melting point, and are frozen to their beds. Here, no meltwater is present at the ice-bedrock interface. Intermediate between these two are *subpolar* (*polythermal*) *glaciers*, where an inner temperate region is surrounded by a cold-based margin (Tranter et al., 1996; Benn and Evans, 1998). However, this broad classification masks spatial and temporal variations within geographical areas and beneath individual glaciers.

Meltwater drainage beneath an alpine glacier is usually distributed between two major flow components (Fig. 2); (i) a widespread distributed drainage system comprised of elements such as film-flow (e.g. Weertman, 1972), porous flow through permeable subglacial sediments (e.g. Boulton and Hindmarsh, 1987; Clarke, 1987), linked cavities (e.g. Hooke, 1989) and broad, low canals (Walder and Fowler, 1994), all of which transport meltwaters relatively slowly (e.g. <0.05 m s^{-1} beneath Haut Glacier d'Arolla) in an environment with high water:rock ratios, and (ii) a more discrete channelised system incised either upwards into the basal ice layer (e.g. Röthlisberger, 1972; Hooke, 1989) or engraved into the underlying bedrock (e.g. Nye, 1973) which transports meltwaters rapidly (>0.5–1.0 m s^{-1} beneath Haut Glacier d'Arolla) through the glacier. In these major

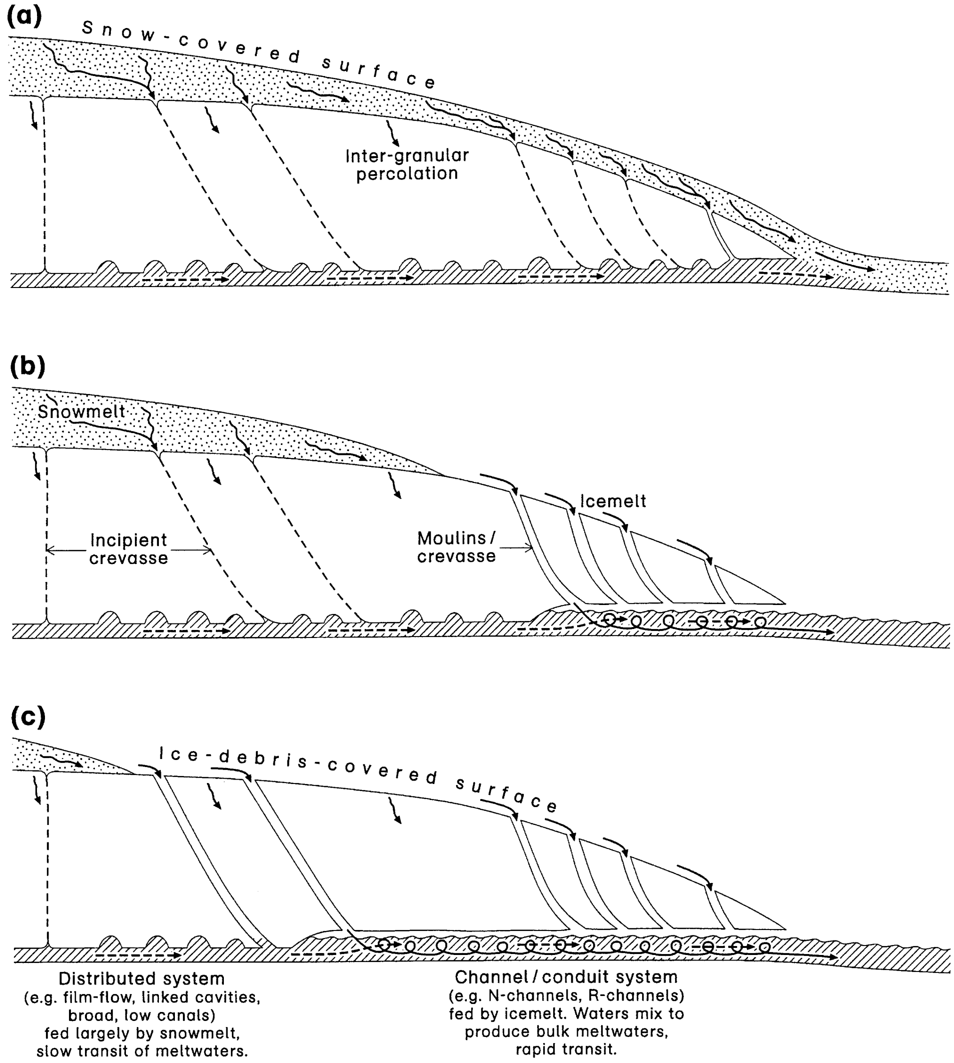

Fig. 2. Schematic representation of the seasonal development of the subglacial drainage system beneath an alpine glacier (after Tranter et al., 1994). As the meltseason progresses through June (a), July (b) and August (c) the seasonal snowcover retreats up-glacier. The position of the transient snowline is closely associated with the up-glacier development of the subglacial channelised drainage system (Nienow et al., 1996).

arterial conduits, turbulent meltwaters access, mobilise, transport and evacuate significant quantities of suspended sediment from the subglacial environment (Gurnell, 1987; Willis et al., 1996; Hubbard and Nienow, 1997). As the ablation season progresses, this channelised system expands headwards, following the retreat of the seasonal snowcover (Fig. 2; Brown et al., 1994a; Nienow et al., 1996). For example, dye tracing experiments at Haut Glacier d'Arolla indicate that during 1990 the average rate of channel head extension was 59 m day^{-1} between 9 June and 19 July, and 19 m day^{-1} between 19 July and 18 August (Nienow et al., 1996).

It is important to understand how different drainage configurations control the processes and rates of solute acquisition in the subglacial environment (Raiswell, 1984; Sharp et al., 1998). This may allow water quality responses to specific hydrological conditions to be predicted, and bulk meltwater quality variations to be more effectively exploited in studies of subglacial hydrology and hydrochemistry (Sharp, 1991; Tranter et al., 1993).

3. Chemical weathering in glacial environments

The initial focus on water quality variations in glacial environments was to characterise water quality in relation to other Earth surface environments, establish removal rates of major cations, and define geochemical denudation rates (e.g. Rainwater and Guy, 1961; Keller and Reesman, 1963; Reynolds and Johnson, 1972; Slatt, 1972; Church, 1974; Sasseville et al., 1977; Eyles et al., 1982; Collins, 1983; Dixon et al., 1984; Brown et al., 1994a, 1996b; Sharp et al., 1995a; Anderson et al., 1997; Hodgkins et al., 1997; Hasnain and Thayyen, 1999).

Glacial runoff at the present day is $\sim 0.45\times10^3$ km^3 a^{-1} (Huybrechts and T'siobel, 1995; Jones et al., in press), which accounts for approximately 1% of the total runoff ($\sim$45–47$\times10^3$ km^3 a^{-1}) from the land, exposed shelves and glaciers (Gibb and Kump, 1996; Korzun, 1978). Most glacier meltwater hydrochemistry data currently available is from valley glaciers. Table 1 indicates that the dominant cation in bulk glacial outflow is generally Ca^{2+}, with lesser quantities of Mg^{2+}, Na^+ and K^+ (Raiswell, 1984; Tranter et al., 1993, 1994, 1996; Brown et al., 1996a,b). The dominant anions are HCO_3^- and SO_4^{2-} in varying proportions (Table 1). This is consistent with the general chemistry of surface waters which tend to be dominated by these ions and in particular by calcium bicarbonate (e.g. Holland, 1978; Chester, 1990; Berner and Berner, 1996; Langmuir, 1997; Faure, 1998). However, glacial meltwaters demonstrate significant chemical enrichment over relatively short distances (e.g. a few km), between their origin as dilute snow- and icemelt (ionic strength of $\sim$ 10 μeq l^{-1}) and their emergence at the glacier portal, where ionic strengths may exceed 1000 μeq l^{-1} during recession flow conditions (Tranter et al., 1993; Brown et al., 1994a, 1996b; Brown and Fuge, 1998a). Many minor and trace elements also show significant increases in concentration during transit through the subglacial hydrological system (Table 2).

Further, anthropogenic influences are often low in glacial environments, allowing the investigation of natural controls on streamwater quality (Brown and Fuge, 1998a,b). This contrasts with many other world river systems, which have been significantly contaminated by anthropogenic activity. For example, a recent re-evaluation of streamwater quality data by Berner and Berner (1987) suggests contamination has increased concentrations of Ca^{2+} in average river water by 9%, Na^+ by 28%, Cl^- by 30% and SO_4^{2-} by 43% (Faure, 1998).

Studies of water quality in glacial environments have also documented high rates of chemical weathering (Table 3). Estimates of cationic denudation rates in glacial catchments (excluding Scott Turnerbreen, see below) range between 454 and 4160 meq m^{-2} a^{-1}, and contrast markedly with the Fraser River (380 meq m^{-2} a^{-1}), the North American continental average (380 meq m^{-2} a^{-1}) and the estimated global continental average (390 meq m^{-2} a^{-1}) (Livingstone, 1963). These studies have overturned the traditional argument that chemical weathering is least intense in glacial environments, founded on the premise that low temperatures, thin soils and a lack of vegetation with little seasonal change in biomass, inhibit chemical processes (Peltier, 1950; Drever and Zobrist, 1982; Drever, 1998). However, some caution is required when comparing the results from glaciersied catchments with other studies (Sharp et al., 1995a), and uncertainties surrounding these estimates of chemical denudation need to be considered. Several factors, in addition to inputs from mineral weathering, may potentially influence dissolved solute concentrations and hence chemical denudation rates (Sharp et al., 1995a; Horton et al., 1999). These include; (i) discharge conditions at the time of sampling, (ii) the contribution of dissolved and particulate matter from the atmosphere during wet and dry deposition, (iii) inputs and outputs from the soil exchange pool, (iv) uptake of organic nutrients by biomass and local variations in non-living organic material (humus), and (v) changes in topography and soil development. Of these, (i) and (ii) are likely to impact most significantly on estimates of lithogenically-derived fluxes in glaciersied basins. In non-glacierised catchments it is often assumed that precipitation events are of minor significance when compared to the effect of seasonal changes in stream discharge between peak and baseflow conditions (Horton et al., 1999). However, in glacierised catchments large ablation-driven diurnal discharge variations are superimposed on the seasonal hydrograph (Fig. 1). Thus, the time of sample collection and the number of samples analysed needs careful consideration and more frequent sampling may be necessary in

Table 1
Major dissolved ion concentrations measured in meltwaters draining selected glaciers[a]

		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-
Anderson et al. (2000)	Bench Glacier (Alaska)	550	36	25	61	427	2	262	–
Brown et al. (1996b)	Haut Glacier d'Arolla (Switzerland)	160–470	15–49	5.1–36	5.4–18	180–360	0.85–92	30–240	0.0–30
Brown (unpublished)	Nigardsbreen (Norway)	8.8–38	1.6–7.8	8.3–25	0.98–4.4	1.4–8.5	9.8–25	7.0–41	1.9–11
Collins (1979)	Gornergletscher (Switzerland)	130–334	16–190	8.7–43	2.6–33	–	–	–	–
De Mora et al. (1994)	Walcott Glacier (Antarctica)	226–1292	16–188	17–97	2.3–33	206–1030	9.5–87	42–678	–
De Mora et al. (1994)	Koettlitz Glacier (Antarctica)	72–92	5.8–6.6	11–34	0.77–6.9	91–132	0.55–1.2	3.4–7.6	–
De Mora et al. (1994)	Howchin Glacier (Antarctica)	1072–1342	122–194	364–610	44–68	1360–1560	119–257	342–1165	–
De Mora et al. (1994)	Ward Galcier (Antarctica)	722–828	288–336	879–1436	90–109	1080–1450	667–1020	218–230	–
Eyles et al. (1982)	Berendon (Canada)	90–763	1.6–19	0.87–7.8	0.38–5.1	230–785	25–27		
Fairchild et al. (1994a)	Tsanfleuron (Switzerland)	638	92	4.9	6.3	627	5.5	118	11
Hasnain et al. (1989)	Chhota-Shigri	75–260	6.6–41	25–65	22–51	–	–	–	–
Hodgkins et al. (1998)	Scott Turnerbreen (Svalbard)	120–300	99–290	110–740	5.1–19	110–260		96–200	–
Raiswell and Thomas (1984)	Fjallsjökull (Iceland)	208–274	32–60	30–120	2.8–7.2	190–300		26–66	–
Rainwater and Guy (1961)	Chamberlain (USA)	75–304	8.2–123	4.3–8.7	0.0–5.1	150–200	5.6–20	29–310	–
Ruffles (1999)	Engabreen (Norway)	82–623	4–65	11–212	0–27	51–675	10–191	0–142	0–15
Steinpórsson and Óskarsson (1983)	Grimsvotn (Iceland)	359	115	482	12	573	87	132	–
Theakstone and Knudsen (1996)	Austre Okstindbreen (Norway)	411–281	8.2–41	15–137	4.3–29	–	–	–	–
Thomas and Raiswell (1984)	Argentière (France)	20–480	6–66	10–89	6.0–5.2	110–400	–	10–60	–
Livingstone (1963)[b]	North America	1048	211	391	36	1114	226	416	16
Livingstone (1963)[b]	Europe	1552	461	235	43	1557	195	500	60
Livingstone (1963)[b]	Asia	918	461	404	–	1294	245	175	11
Livingstone (1963)[b]	World	749	337	274	59	957	220	233	16

[a] Units are in μeq l^{-1}. Where a single figure is presented this represents the mean concentration. Where two figures are presented separated by a rule this represents the range of concentrations measured.

[b] Mean composition of river waters cited in Holland (1978).

Table 2
Minor and trace elements in supraglacial waters and bulk meltwaters, Haut Glacier d'Arolla, Switzerland, August 1996 (Brown and Fuge, 1998a,b), and in terrestrial waters (after Langmuir, 1997)

Metal	Supraglacial waters ($n = 5$) ($\mu g\ l^{-1}$)			Bulk meltwaters ($n = 24$) ($\mu g\ l^{-1}$)			Terrestrial waters ($\mu g\ l^{-1}$)
	Maximum	Minimum	Median	Maximum	Minimum	Median	Median
Al	5.7	3.5	4.5	175	93	140	10
Ti	0.7	0.4	0.5	9.0	3.1	6.5	3
Fe	120	60	85	650	334	480	100
Mn	2.2	1.8	1.9	7.0	3.7	5.5	15
Sr	1.3	0.1	0.7	21	8.9	15	400
Ba	0.0	0.0	<0.1	2.3	0.2	1.2	20
Rb	0.1	0.0	0.07	0.9	0.1	0.5	1
Co	0.1	0.0	0.02	0.4	0.1	0.2	0.1
Cu	0.5	0.3	0.5	2.3	0.2	0.6	3
Ni	0.4	0.2	0.4	1.6	0.6	0.8	1.5
Pb	0.1	0.0	0.1	0.9	0.0	0.3	3
Zn	0.9	0.3	0.8	3.5	0.2	0.8	20
U	0.0	0.0	0.01	1.1	0.3	0.7	0.5

Table 3
Estimated cationic denudation rates from a variety of glaciated catchments. The two values from Haut Glacier d'Arolla, Switzerland, represent the 1989 and 1990 ablation seasons respectively[a]

Glacier	Denudation Rate (meq m^{-2} yr^{-1})	Author(s)
South Cascade (USA)	930	Reynolds and Johnson (1972)
Berendon (USA)	970	Sasseville et al. (1977)
Berendon (USA)	947	Eyles et al. (1982)
Gornergletscher (Switzerland)	454	Collins (1983)
Gornergletscher (Switzerland)	1010±505	Metcalf (1986)
Tsijiore Nouve (Switzerland)	508	Souchez and Lemmens (1987)
Haut Glacier d'Arolla (Switzerland)	640/685	Sharp et al. (1995a)
Scott Turnerbreen (Svalbard)	160	Hodgkins et al. (1997)
Dokriani Glacier (Himalaya)	4160	Hasnain and Thayyen (1999)
Frazer River (USA)	*380*	Livingstone (1963)
North American Continent	*380*	Livingstone (1963)
Estimated Global Average	*390*	Livingstone (1963)

[a] Figures in italics provide estimates from other locations for comparison.

order to effectively constrain denudation rates. Further, estimates of denudation rates frequently incorporate atmospherically-derived components, limiting the reliability of many estimates (Hodson et al., 2000). Disaggregation of glacial solute fluxes into atmospherically, snowpack, and crustally-derived components is now generally performed using a standardised suite of assumptions, based on conceptual models of solute acquisition developed by Raiswell (1984) and Tranter et al. (1993). However, uncertainty still surrounds the amount of HCO_3^- that can be attributed to the oxidation of organic C in subglacial environments and to the extent of carbonate hydrolysis (Skidmore et al., 2000; Hodson et al., 2000). A further problem with dissolved flux estimates in glacial environments is that there are often no measurements of water quality or discharge outside the meltseason (Fairchild et al., 1999b). Another factor missing in most studies is the exchangeable ion load, which may be significant (Mitchell et al., in press). The role of soil and vegetation development on chemical weathering (and hence solute fluxes) will become increasingly important with distance from the glacier margin, though there is little information on the comparative effectiveness of chemical weathering in unvegetated proglacial and glacier-covered parts of glacierised catchments, and their relative importance is not clear (see Anderson et al., 2000).

The switch to glacial processes above the snowline in alpine environments generates important differences between low- and high-altitude chemical weathering processes (Anderson et al., 1997). The effectiveness of chemical weathering in glacial environments during the meltseason has been attributed to (i) high meltwater flushing rates; (ii) an abundance of finely-ground, geochemically-reactive suspended sediment resulting from physical abrasion and crushing; (iii) turbulent meltwaters capable of mobilising these sediments and providing a rough water surface for air-meltwater gas exchange; and (iv) the generally low buffering capacity of meltwaters (Sharp et al., 1995b). This contrasts with many other Earth surface environments, where biological activity in the soil may significantly impact on chemical weathering processes. For example, a well aerated soil may contain ~20% O_2, whereas in isolated environments near plant roots this value may drop to ~2% (Borggaard, 1997). Similarly, soil air may contain between 0.33 and 3% CO_2, but at the bottom of the root zone CO_2 levels may approach 10% in the vicinity of the roots (Borggaard, 1997). Additionally, dissolved organic matter in the soil system may be a significant source of acidity (Graustein et al., 1977). The controls on gas diffusion may also be different under a glacier, with ice forming an effective barrier to the supply and exchange of O_2 and CO_2. Further, glacial material is freshly ground, whereas grains in other surface-weathering environments are often coated with adsorbed organic compounds which modify their surface properties and reactivity (Tipping, 1981; Hunter and Liss, 1982; Raiswell, 1984). Differences in chemical weathering processes may also influence the composition of suspended material transported by glacial and non-glacial rivers. For example, in tropical environments where rates of mechanical erosion are low, particulate material transported by rivers originates largely from highly developed soil material that has undergone significant chemical weathering (Chester, 1990). Therefore, suspended sediments may be enriched in relatively insoluble elements (e.g. Al, Ti, Fe), and depleted in more soluble elements (e.g. Na, Ca). Conversely, glacierised drainage basins may experience rates of mechanical erosion which greatly exceed rates of chemical weathering (e.g. Sharp et al., 1995a). As a result, suspended solids are likely to exhibit a composition which is closer to that of the parent rock.

Glacierised basins may also exhibit different temporal variations in water quality relative to catchments experiencing other hydroclimatological conditions, since the bulk of the streamflow is decoupled from precipitation events (Röthlisberger and Lang, 1987). For example, in temperate fluvial basins, maximum precipitation generally occurs during the winter months, with relatively rapid delivery of a significant proportion of this storm water to the river channel. Conversely, while the bulk of the precipitation in an alpine glacial catchment falls during the winter months, this precipitation is predominantly in the form of snow. Cumulative snowfalls store winter precipitation on the land surface until spring, when the seasonal snowpack is eradicated and snowmelt is replaced by glacier icemelt. The annual hydrograph is, therefore, concentrated into a relatively short (3–5 month) period (Fig. 1).

Recently, estimates of chemical denudation rates in glaciersied catchments have been critically evaluated (Anderson et al., 1997). Their study suggests that, while cationic denudation rates in glaciated basins are higher than the global mean, they do not appear to exceed non-glacierised basins with a similar discharge. Further, silica denudation rates are not enhanced in glacierised catchments, despite the abundance of freshly ground, geochemically-reactive sediment. This may suggest that high rates of chemical erosion in these environments primarily result from increased runoff production, rather than enhanced physical erosion (Anderson et al., 1997). Interestingly, low weathering rates at Scott Turnerbreen relative to other glaciated catchments (Table 3) have been attributed to the short meltseason and low specific water flux in this Svalbard catchment (Hodgkins et al., 1997).

4. Glacier hydrology—mixing models

The second focus of meltwater quality investigations has been to attempt to utilise variations in water quality to differentiate runoff components and hydrological pathways through glacierised basins (e.g. Zeman and Slaymaker, 1975; Collins, 1978, 1979; Gurnell and Fenn, 1984; Brown and Tranter, 1990; Tranter and Raiswell, 1991; Lecce, 1993; Vatne et al., 1996). These studies initially focused upon the modelling of subglacial hydrological systems using bulk meltwater quality variations, based on the application of simple two-component conservative chemical mixing models imported from the temperate fluvial literature (e.g. Pinder and Jones, 1969; Hall, 1970, 1971). Total (bulk) discharge is usually separated into two hydrological components (Collins, 1978, 1979) [Eq. (1)].

$$Q_\mathrm{b} = Q_\mathrm{q} + Q_\mathrm{d} \tag{1}$$

where Q = discharge,
b = bulk,
q = quickflow,
d = delayed flow

In this model, the *quickflow* component is perceived to flow rapidly through the hydroglacial system, predominantly in ice-walled conduits at the glacier bed (Collins, 1978, 1979). Water–rock contact times are short, and Water:rock ratios low, limiting the potential for solute acquisition to rapid surface exchange reactions (Tranter et al., 1993). Conversely, the *delayed flow* component transports meltwaters relatively slowly through a distributed hydrological system at the ice–bedrock interface. Here water:rock ratios are high and meltwaters intimately interact with the products of subglacial physical abrasion and crushing, including finely comminuted glacial flour, debris-rich basal ice, and subglacial moraine. Hence the potential for solute acquisition by delayed flow waters is high, as weathering may include slower dissolution as well as surface exchange reactions (Tranter et al., 1993). Thus, assuming conservative mixing, continuity of mass requires that [Eq. (2)]:

$$Q_b C_b^i = Q_q C_q^i + Q_d C_d^i \tag{2}$$

where C = concentration,
i = electrical conductivity or an individual dissolved ion

Q_b and C_b^i are routinely measured. However, effective hydrograph separations rely on distinct chemical signatures being identified for each reservoir, allowing Eq. (2) to be re-written to derive the magnitude of the two discharge components (Q_q and Q_d) [Eqs. (3) and (4)]:

$$Q_d = Q_b \frac{(C_b^i - C_q^i)}{(C_d^i - C_q^i)} \tag{3}$$

$$Q_q = Q_b \frac{(C_d^i - C_b^i)}{(C_d^i - C_q^i)} \tag{4}$$

Unfortunately, subglacial hydrological interpretations based on such simple two-component mixing models are fraught with uncertainty, since the approach is limited by simplistic geochemical assumptions (Brown and Tranter, 1990; Sharp, 1991; Tranter and Raiswell, 1991; Sharp et al., 1995a). For example, the model assumes the existence of only two hydrological components, which are characterised by a single, invariant value of electrical conductivity throughout the summer meltseason. Thus, the quickflow component is assumed to retain a dilute supraglacial signature during transit through the hydroglacial system, and the delayed flow component is characterised by a near-equilibrium value, assuming residence times are sufficiently long and conditions sufficiently favourable for dissolution reactions to be slowed as chemical equilibrium is approached (the model also cannot account for chemical precipitation). Further, recharge is not considered. Variations in bulk meltwater chemistry are therefore assumed to result solely from mixing (i.e. dilution) processes. Further, the model assumes conservative mixing of the two flow components, with no post-mixing solute acquisition [e.g. Eqs. (2)–(4) assume that the mass of solute remains unchanged after the flow components mix].

These assumptions fail to account for temporal variations in the chemical composition of the two components resulting from factors such as variable residence times, lateral and headwards channel migration (Nienow et al., 1998), variable suspended sediment concentrations (Brown et al., 1994a), and chemical fractionation of atmospherically-derived ions from the seasonal snowcover (Johannessen and Henriksen, 1978; Tranter, 1991; Fountain, 1996; Tranter and Jones, 2001). Inaccuracies in end member definitions are translated into errors in both the proportion of bulk outflow attributed to the quick- and delayed flow component, and the shape of the individual constituent hydrographs (e.g. Brown and Tranter, 1990; Sharp et al., 1995a) (Fig. 3). This is further compounded where electrical conductivity is used in water quality-based hydrograph separations, since the accuracy of the separation depends on the degree of chemical conservatism of the chosen indicator species. Electrical conductivity has clearly been illustrated to be a non-conservative parameter in meltwaters systems using the multivariate mixing model SOLMINEQ88 (Sharp et al., 1995b; Kharaka and Barnes, 1973). In addition, experimental investigations of solute acquisition from suspended sediment (see below) clearly indicate that significant

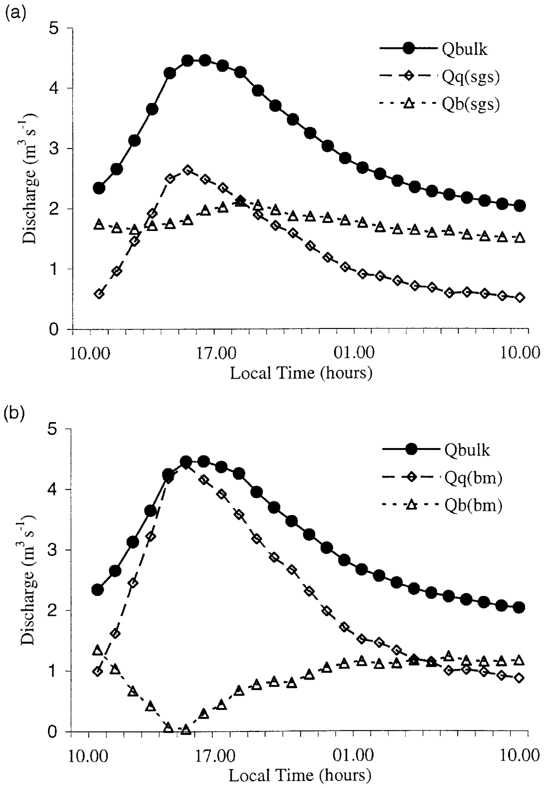

Fig. 3. Hydrograph separations of bulk meltwaters over a diurnal discharge cycle (17–18 July 1989), Haut Glacier d'Arolla (after Brown and Tranter, 1990). The hydrographs are separated assuming that the Ca^{2+} composition of the englacial component (C_q) is (a) that of a concentrated supraglacial (sgs) water (16 μeq l^{-1}), and (b) that of the season's minimum recorded bulk meltwater (bm) value (165 μeq l^{-1}). C_d for both plots is defined by the intercept derived from regressing bulk Ca^{2+} versus bulk discharge (390 μeq l^{-1}, after Tranter and Raiswell, 1991).

chemical enrichment results from post-mixing chemical Water–rock interaction (Tranter et al., 1989; Brown et al., 1994a, 1996a). However, the manner in which these solutions depart from simple mixtures provides valuable information about geochemical processes operating in subglacial environments. This is discussed in more detail in the next section.

More recently, hydrograph separations founded on a more realistic geochemical basis have been proposed, based on quasi-conservative dissolved species (e.g. SO_4^{2-}) (Tranter and Raiswell, 1991). These allow definitions of C_q and C_d to vary over shorter (e.g. 24 h) timescales in order to account for the dynamic nature of the subglacial hydrological system. The use of SO_4^{2-} is founded on the premise that in meltwaters draining alpine glaciers SO_4^{2-} appears to be exclusive to delayed flow waters, based on observations of supraglacial meltwater chemistry following elution of the seasonal snowpack, and virtually zero SO_4^{2-} in bulk meltwaters at maximum diurnal discharge (when quickflow waters dominate the hydrograph) draining Gornergletscher, Switzerland (Tranter and Raiswell, 1991; Tranter et al., 1993). These observations are supported by controlled laboratory dissolution experiments (Brown et al., 1996a). Given that SO_4^{2-} is largely absent from quickflow waters, Eq. (2) may be re-written [Eq. (5)], and the strong linear association between bulk discharge and $C_b^{SO_4}$ exploited to define $C_d^{SO_4}$ at a diurnal timescale throughout the meltseason (Tranter and Raiswell, 1991).

$$Q_b C_b^{SO_4} = Q_d C_d^{SO_4} \tag{5}$$

However, the use of SO_4^{2-} to parameterise the model is also equivocal. In addition to having an atmospheric and lithogenic provenance (see below), studies of meltwater quality draining Scott Turnerbreen, Svalbard (Hodgkins et al., 1997, 1998) suggest that rather than being subglacially-derived, SO_4^{2-} in early-season meltwaters draining the glacier is acquired from a proglacial icing. This not only highlights further deficiencies in the application of chemical mixing models to glacier hydrology, but also problems in transferring hydrochemical and hydrological assumptions from alpine to Arctic locales (Hodgkins, 1997). Thus, considerable uncertainty still surrounds the results of this improved method of chemically-based hydrograph separation, and restraint in its application to glacier drainage systems has been advocated (Sharp et al., 1995b).

5. Dissolved indicators of subglacial hydrology and geochemistry

The uncertainties described above surrounding the application of chemically-based mixing models in the investigation of glacier hydrology have resulted in a shift in meltwater quality science towards the use of individual dissolved species in subglacial hydrological and hydrochemical investigations. This is based on the premise that the composition of meltwaters in the various subglacial transport paths reflect differing types and durations of chemical weathering reactions furnishing solute to meltwaters during transit (Tranter et al., 1993). Therefore, variations in bulk meltwater chemistry reflect a composite signature of dynamic individual hydrological flowpaths (Collins, 1981; Sharp, 1991 (Fig. 4)). However, the chemical weathering reactions controlling solute acquisition in meltwater solutions need to be understood if water quality data are to be fully exploited in glacier hydrological and geochemical studies. Hence, recent investigations have focused on identifying likely sources of solute (Tranter et al., 1993; Sharp et al., 1995a; Brown et al., 1996b; Brown and Fuge, 1998a,b), defining key weathering reactions and the likely links between them (Raiswell, 1984; Tranter et al., 1993, 1996, in press; Brown et al., 1994b; Fairchild et al., 1994a,b, 1999a,b), and quantifying the rates of these reactions (Brown et al., 1994a, 1996a,b, in press; Fairchild and Killawee, 1995). This information may then be integrated in order to identify chemical fingerprints which may be applied to studies of subglacial environments, which obviate the need to invoke simplistic mixing models (e.g. Brown et al., 1994a; Fairchild et al., 1994a; Lamb et al., 1995; Hodgkins et al., 1997, 1998; Tranter et al., 1997).

5.1. Key dissolved indicator species

It is now recognised that in order to deconvolute the chemical signature of bulk glacial meltwaters, dissolved species in the solid, liquid and gas phases need to be considered, since these control mineral breakdown, water composition and proton supply, respectively (Raiswell, 1984; Tranter et al., 1993; Brown et al., 1994b). In addition, studies of glacier hydrology and hydrochemistry have been constrained because the processes and rates of solute acquisition in alpine glacial environments were poorly known, limiting the insights offered by meltwater quality studies into the character and behaviour of subglacial systems (Sharp, 1991; Sharp et al., 1995a,b). This was partly due to the methodologies of previous hydrochemical investigations in glacierised regions (Sharp, 1991), which:

(a) were designed without due regard to the insights provided by theoretical analyses of subglacial water flow and processes of solute acquisition;
(b) were technology led, based largely on electrical conductivity measurements;
(c) failed to monitor the necessary parameters (e.g. anions, O_2, pH [see below]);
(d) implemented simplistic mixing, rating and time-series models; and

(e) failed to make independent measurements (e.g. dye tracing, water balance, borehole water pressure studies) to verify the modelling assumptions on water flow paths.

Recent studies have utilised both detailed investigations of meltwater chemistry and controlled laboratory investigations to address many of these issues.

The single most important mechanism by which rock minerals are weathered is acid hydrolysis (Raiswell, 1984). While pH describes H^+ activity in solution, it cannot reveal the source of the protons, their rate of supply, and the weathering processes involved in subglacial chemical erosion. In surface waters, H^+ concentrations are principally controlled by carbonate equilibria, which can only be quantified by detailed meltwater quality analyses, including cations, dissolved carbonate species and pH (Raiswell, 1984). Further, Raiswell (1984) proposed that the dissolved anionic signature of the meltwaters indicates the source of the protons driving acid hydrolysis reactions, of which the dissolution and dissociation of atmospheric CO_2 [Eq. (6)] and sulphide oxidation [Eq. (7)] predominate (Tranter et al., 1993; Brown et al., 1996b).

$$CaCO_3(s) + H_2CO_3(aq) \longleftrightarrow Ca^{2+}(aq) + 2HCO_3^-(aq) \quad (6)$$

$$4FeS_2(s) + 14H_2O(l) + 15O_2(aq) \longleftrightarrow 16H^+(aq) + 8SO_4^{2-}(aq) + 4Fe(OH)_3(s) \quad (7)$$

Therefore, the relative proportions of HCO_3^- and SO_4^{2-} in the bulk outflow reflect the dominance of the two major sources of aqueous protons driving subglacial weathering reactions (Raiswell, 1984). Protons associated with anthropogenically-derived acid sulphate and nitrate aerosols, either scavenged by snow in the atmosphere or dry-deposited on to the glacier surface, have been shown to be limited to the early meltseason (Brown et al., 1996b). Pyrite oxidation is often assumed to be coupled to carbonate dissolution (e.g. Raiswell and Thomas, 1984; Thomas and Raiswell, 1984; Sharp, 1991; Tranter et al., 1993; Fairchild et al., 1994a) [Eq. (8)].

$$4FeS_2(s) + 16CaCO_3(s) + 14H_2O(l) + 15O_2(aq) \longleftrightarrow 4Fe(OH)_3(s) + 8SO_4^{2-}(aq) + 8Ca^{2+}(aq) + 16HCO_3^-(aq) \quad (8)$$

Brown et al. (1996b) evaluate changes in the proportion of these two major anions using the C-ratio $[HCO_3^-/(HCO_3^- + SO_4^{2-})]$. A ratio of 1 signifies weathering by carbonation reactions (Reynolds and Johnson, 1972), where protons are derived exclusively from the dissolution and dissociation of atmospheric CO_2 [Eq. (6)]. Conversely, a ratio of 0.5 signifies coupled sulphide oxidation and carbonate dissolution (SO/CD) reactions, with protons derived from the oxidation of pyrite [Eq. (8)]. Others authors (e.g. Tranter et al., 1997, in press) have adopted the S-ratio $[SO_4^{2-}/(SO_4^{2-} + HCO_3^-)]$, which gives a ratio of 0.5 for coupled SO/CD [Eq. (8)] and zero for carbonation.

At Haut Glacier d'Arolla seasonal variations in the C-ratio clearly illustrate a change in the dominant proton source as the ablation season progresses (Brown et al., 1996b) (Fig. 4h). As the ablation season progresses the ratio increases to between ~ 0.75 and ~ 0.9, indicative of a chemical weathering regime driven predominantly by atmospherically-derived H^+ associated with the dissolution and dissociation of CO_2. Dye-tracing experiments suggest that, despite significant variability between and at individual injection sites, water flows largely under open channel conditions during its passage through the main arterial conduits beneath Haut Glacier d'Arolla (Nienow et al., 1996). This is the case over a range of flow conditions, and spans periods when diurnal discharges were high. Thus, atmospheric CO_2 may be a significant source of protons to channelised waters, which increasingly dominate the bulk meltwater hydrograph as the ablation season progresses.

Proton consumption is largely controlled by carbonate equilibria (Raiswell, 1984). Thus, continued weathering depends on H^+ supply through the dissolution of $CO_2(g)$ to form $H_2CO_3^*$ [where $H_2CO_3^* = CO_2(aq) + H_2CO_3(aq)$]. However, the reaction $CO_2(g) \leftrightarrow CO_2(aq)$ is often slower than the reactions which consume $H_2CO_3^*$. Therefore, the amount of CO_2 in solution [$CO_2(aq)$] relative to the partial pressure of CO_2 in the overlying gas phase [$p(CO_2)$] offers a linkage between reactions that supply protons and those that consume them [Eq. (9)], providing a natural basis for the classification of subglacial weathering regimes (Raiswell, 1984; Tranter et al., 1993) (Table 4).

$$\log p(CO_2) = \log(HCO_3^-) - pH + pKCO_2 + pK_1 \quad (9)$$

where $pKCO_2 = 1.12$, and $pK_1 = 6.58$, assuming a water temperature of 0 °C (Ford and Williams, 1989).

Where proton supply equals consumption, the $p(CO_2)$ of the solution remains in equilibrium with the atmosphere, and the system is said to be *open*. Conversely, where the two sets of reactions proceed at different rates, the system is said to be *closed* (e.g. $p(CO_2)(aq) \neq p(CO_2)(g)$). Closed-system low $p(CO_2)$ conditions occur when protons are consumed more rapidly than they are supplied. This may arise when large quantities of reactive rock material are brought into contact with relatively pure water (Tranter et al., 1993; Brown et al., 1994a, 1996a,b). This decreases the $p(CO_2)$ of the meltwaters so the solution is in *apparent* equilibrium with an atmosphere which is depleted in CO_2, promoting CO_2 influx across the air-meltwater interface. Conversely, closed-system

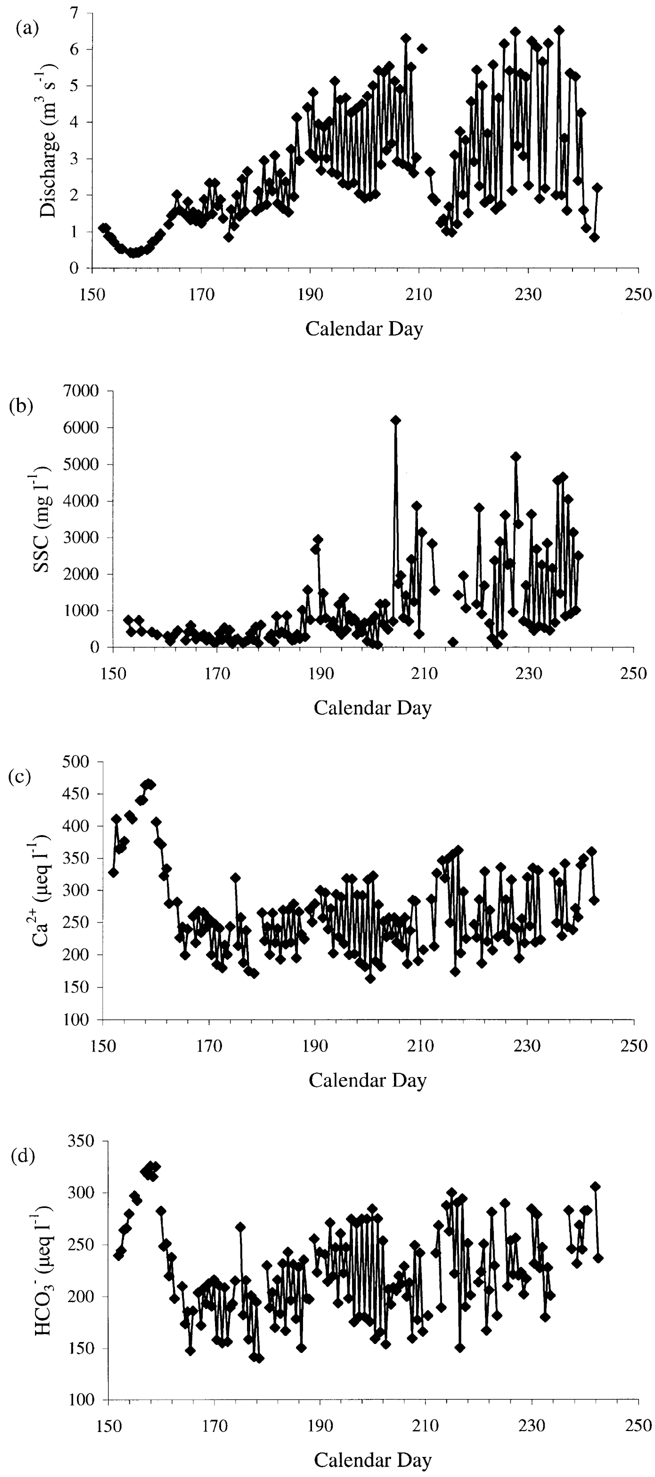

Fig. 4. Variability in (a) meltwater discharge, (b) suspended sediment concentration (SSC), (c) Ca^{2+}, (d) HCO_3^-, (e) SO_4^{2-}, (f) pH, (g) $p(CO_2)$ and (h) C-ratio in bulk runoff draining Haut Glacier d'Arolla, June-August 1989. All units are in $\mu eq\ l^{-1}$ except discharge ($m^3\ s^{-1}$), suspended sediment ($mg\ l^{-1}$), pH and $p(CO_2)$. The horizontal line in figure (g) denotes open-system $p(CO_2)$ conditions at 2560 m a.s.l. (−3.61) (*continued on next page*).

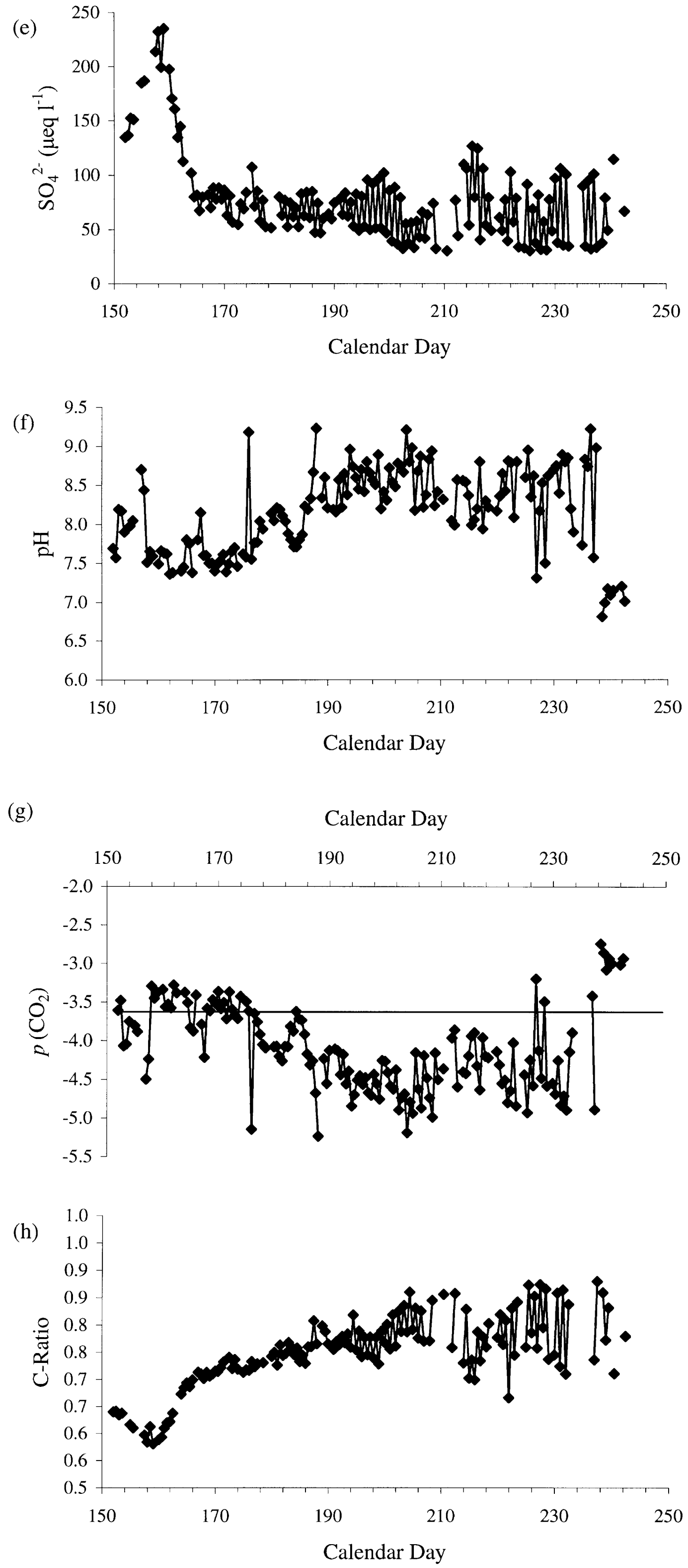

Fig. 4 (*continued*).

Table 4
End-members in the relationship between CO_2(aq) and $p(CO_2)$ in glacial meltwaters

Model	$p(CO_2)$ Diffusion State	CO$_2$ Relations	Possible Hydroglacial Setting
Open-system	CO_2 (aq) in equilibrium with $p(CO_2)$	$p(CO_2)(aq) = p(CO_2)(g)$	Low rock:water ratio or relatively unreactive minerals, free access to an air-meltwater interface, sustained supply of $H_2CO_3^*$ by the flow of freash, unreacted solution
Closed-system low $p(CO_2)$	CO_2 (aq) depleted faster than CO_2 (g) can diffuse into solution	$p(CO_2)(aq) < p(CO_2)(g)$	Large supply of comminuted rock material plus pure water
Closed-system high $p(CO_2)$	CO_2 added to solution	$p(CO_2)(aq) > p(CO_2)(g)$	(a) H^+ added to solution (e.g. by sulphide oxidation); (b) neutralisation of acidity by carbonates; (c) gas expulsion during freezing of water body

high $p(CO_2)$ conditions arise when protons are supplied to solution more rapidly than they are consumed (Tranter et al., 1993). In the glacial system this may arise from an input of aqueous protons (e.g. from snowmelt or sulphide oxidation), freezing of meltwaters (which excludes CO_2 from the growing ice lattice), and/or the neutralisation of acidity by carbonates [Eq. (10)].

$$CaCO_3(s) + 2H^+(aq) \longleftrightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g) \tag{10}$$

Note that closed-system $p(CO_2)$ conditions may result from either physical conditions (e.g. closed-channel flow, where there is no air–meltwater interface for CO_2 influx or efflux) or kinetic factors (e.g. when the rate of CO_2 transfer across the gas–water interface is slower than H^+ consumption during acid hydrolysis reactions).

5.2. Other dissolved ions

Previously, meltwater quality studies generally provided an insufficient range of dissolved ion determinations to ascertain spatial and temporal changes in the relative importance of the channelised and distributed subglacial weathering environments, and to permit evaluation of their hydrological significance. However, detailed data now exist from a limited number of alpine and sub-Polar glaciers (e.g. Haut Glacier d'Arolla, Glacier de Tsanfleuron [Switzerland, e.g. Brown et al., 1994a,b, 1996b; Tranter et al., 1994], Engabreen [Norway, e.g. Ruffles, 1999], Austre Brøggerbreen, Scott Turnerbreen [Svalbard, e.g. Tranter et al.,1994; Hodgkins et al., 1997; Wadham et al., 1998, 2000; Hodson et al., 2000;], Small River Glacier [Canada, e.g. Brown, unpublished]) to evaluate seasonal changes in the $p(CO_2)$ signature, and hence provide stronger geochemical evidence for the evolution of the subglacial hydrological system. For example, as the meltseason progresses at Haut Glacier d'Arolla, Tranter et al. (1993) showed that $p(CO_2)$ decreases from closed-system high $p(CO_2)$ conditions to closed-system low $p(CO_2)$ conditions, as discharge and suspended sediment concentrations increase (Fig. 4g). This reflects the increasing dominance of a channelised subglacial hydrological network as the system expands headwards during the ablation season, within which the weathering of suspended sediment is fuelled by carbonation reactions (Table 4).

Other dissolved ion variations have also been employed in hydrological investigations, both at individual sites and in comparisons of alpine and Arctic glacier hydrological systems. For example, a range of dissolved ions (e.g. Cl^-, Na^+, Ca^{2+}, HCO_3^- and Si) have been exploited by Hodgkins et al. (1997, 1998) to identify 4 main features of the observed solute time-series at Scott Turnerbreen, Svalbard; (i) a brief, early-season high-magnitude flux from a proglacial icing, characterised by rapidly decreasing concentrations of Na^+, HCO_3^- and to a lesser extent SO_4^{2-}; (ii) a brief, early-season high-magnitude flux associated with elution of the seasonal snowcover, characterised by increasing, then exponentially-decreasing Cl^- concentrations (waters draining Svalbard glaciers exhibit a greater atmospheric ion signature due to their maritime location, transporting a proportionally greater seasalt-derived flux [Hodgkins et al., 1997]; (iii) a subsequent progressive dilution of bulk meltwaters, accompanied by; (iv) an increasing contribution of dissolved solute associated with the weathering of suspended sediment.

Despite recent advances in our understanding of solute provenance and chemical weathering processes in glacial environments, different ions may give conflicting results regarding the configuration of subglacial hydrological systems. For example, Tranter et al. (1994, 1996) use NO_3^-, HCO_3^- and SO_4^{2-} variations to explore hydrological differences between an alpine (Haut Glacier d'Arolla, Switzerland) and sub-Polar (Austre Braøggerbreen, Svalbard) glacier. Assuming NO_3^- is derived exclusively from the atmosphere, associated with the dissolution of sea-salt aerosol and acidic NO_3^- aerosol (Tranter et al., 1993), bulk meltwaters draining the alpine Haut Glacier d'Arolla demonstrate a gradual decline in NO_3^- concentration as the meltseason progresses, reflecting the temporary storage of NO_3^--rich snowmelt in the distributed component of the subglacial hydrological system. Conversely, the sub-Polar Austre Brøggerbreen experiences a rapid, exponential decline in bulk runoff NO_3^- concentrations, which has been interpreted as a reflection of the progressive leaching of the seasonal snowcover, and subsequent routing of meltwaters largely via sub-aerial-or englacial hydrological pathways to the proglacial stream. This may allow significant solute to be acquired extra-glacially from ice marginal sediments and proglacial icings. Thus, hydrochemical parameters have indicated their potential to elucidate differences in hydroglacial configurations between predominantly warm-based alpine and polythermal/cold-based Arctic glaciers. However, comparison of the concentrations of lithogenic HCO_3^- and SO_4^{2-} in runoff draining Haut Glacier d'Arolla and Austre Brøggerbreen suggest that a limited distributed system exists beneath both glaciers, albeit much more limited beneath Austre Brøggerbreen (Tranter et al., 1996). More work is needed to resolve discrepancies between dissolved species and to identify ions capable of providing unequivocal information on subglacial hydrology and hydrochemistry.

In addition to exploiting variations in individual dissolved ions to differentiate meltwater provenance and routing through the hydroglacial system, there have also been a limited number of studies based on the stable isotope composition of snow, ice and river water in glacial environments (e.g. Behrens et al., 1971; Ambach et al., 1976; Oerter et al., 1980; Theakstone, 1988; Theakstone and Knudsen, 1996). Winter snow, rain and glacier ice differ in their stable isotopic composition. Additionally, the isotopic composition of winter snow exhibits considerable variability, influenced by patterns of atmospheric circulation and air temperature during precipitation events (Theakstone and Knudsen, 1996). Therefore, variations in the stable isotope composition of waters draining a glacier reflect the proportion of the meltwater derived from snow- and icemelt (which depends on the amount of winter snowfall and the summer temperature), the age of the snowpack (since the isotopic composition of the snowpack changes with the onset of melting), the composition of each source (the snowpack component of which varies between years), and the composition and amount of summer precipitation. Consistent with this,extended time-series of stable isotope variations in glacial meltwaters from a few glaciers (e.g. Austre Okstindbreen, Norway) have largely succeeded in identifying variations in water source, rather than subglacial water routing.

Variations in meltwater quality also offer the potential to forecast geothermally-driven flood events (Lawler et al., 1996), and offer insights into the controls on water chemistry in environments subject to subglacial volcanic and geothermal activity (e.g. Sigvaldason, 1963; Gíslason and Eugster, 1987a,b; Lawler et al., 1996). Enhanced concentrations of geothermally-derived ions (e.g. H_2S, SO_4^{2-}, pH and total dissolved carbonate [C_T]) in meltwaters draining Jökulsá á Sólheimasandi glacial river, southern Iceland, clearly illustrate a geothermal event during the 1989 meltseason, manifested through an increase in H_2S, SO_4^{2-} and C_T, a pH depression from 6.7 to 5.75, and small increases in Ca^{2+} and Mg^{2+}. There is also a reversal of the SO_4^{2-}-discharge relationship from a pre-/post-event negative correlation to clockwise hysteresis effects during the geothermal event. These hydrochemical perturbations were prefaced by subglacial seismic activity, and followed by a sudden and significant increase in river discharge. This indicates the potential to use meltwater quality variations to forecast volcanically and geothermally-driven outburst events (jökulhlaups), and indicates the 'open' nature of subglacial systems in areas where CO_2 may be supplied from below the glacier by volcanic/geothermal activity (Lawler et al., 1996).

5.3. Borehole investigations

A better understanding of the chemical weathering processes and solute sources controlling meltwater quality has increased the utility of hydrochemistry as a hydrological and geochemical tool. However, the discussion above details indirect methods of evaluating subglacial chemical weathering processes, based on variations in the composition of bulk meltwaters emerging from the glacier snout. Boreholes drilled to the ice bedrock interface using pressurised hot water (e.g. Hodge, 1976; Englehardt et al., 1978; Iken and Bindschadler, 1986; Stone et al., 1993; Hubbard et al., 1995) have allowed in-situ sampling of meltwaters flowing in the subglacial hydrological system. Continuous records of EC from instrumented boreholes (e.g. Hubbard et al., 1995; Stone and Clark, 1996; Gordon et al., 1998) have been augmented by grab samples for detailed chemical analyses (e.g. Sharp et al., 1995a; Lamb et al., 1995; Tranter et al., 1997, in press). Borehole chemistry samples from Haut Glacier d'Arolla have revealed at least 3 subglacial runoff components, characterised by distinct chemistries, and relating to unconnected (Mode 1), channel marginal (Mode 2) and distributed (Mode 3) flow components respectively (Tranter et al., 1997). The chemical compositions of these subglacial waters are broadly in line with predictions based on bulk meltwaters (Tranter et al., 1993). For example, high NO_3^- concentrations in Mode 3 (concentrated distributed system) waters suggest a snowmelt provenance, accompanied by long residence times in the hydroglacial system. S-ratios in Mode 3 waters are ~ 0.3, suggesting that coupled SO/CD cannot provide all the HCO_3^- to solution, indicating either rapid carbonate hydroloysis preceding sulphide oxidation (Fairchild et al., 1994a) or a subglacial source of CO_2 [either from bubbles in glacier ice, englacial voids, oxidation of inorganic C or microbial activity (see below)]. However, borehole water samples have also indicated significant deviations from both simple mixtures of end-member solutions and models of the chemical evolution of subglacial meltwaters.

Early-season bulk meltwaters exhibit a C-ratio of ~0.65, suggesting chemical weathering reactions are driven primarily (though not exclusively) by the oxidation of sulphide minerals (Fig. 4g). However, coupled SO/CD cannot account for all the solute acquisition by distributed system waters, since the regression equations of $Ca^{2+}+Mg^{2+}$ and HCO_3^- versus SO_4^{2-} have large positive intercepts (Tranter et al., in press). This suggests that waters have acquired $Ca^{2+}+Mg^{2+}$ and HCO_3^- concentrations of ~180–230 μeq l^{-1} prior to the acquisition of SO_4^{2-} (Fairchild et al., 1994a; Tranter et al., in press). It is likely that these environments are water filled, and therefore out of contact with atmospheric CO_2, and the solute is, therefore, predominantly lithogenically derived. This suggests that the positive intercept is a result of initial carbonate hydrolysis, which is rapid and does not require a proton source (Plummer and Wigley, 1976). These waters subsequently drain into partly filled channels and out into the proglacial environment, allowing atmospheric CO_2-driven weathering to take over. Further, $(Ca^{2+}+Mg^{2+}):HCO_3^-$ ratios are < 1:1 in the more dilute subglacial meltwaters, where pure carbonate hydrolysis should produce waters with a ratio of ~ 1:1 [Eq. (6) above; Tranter et al., in press]. The excess HCO_3^- is balanced by Na^+ and K^+, which are unlikely to come from carbonates in any significant quantities. This suggests cation exchange may also impact on subglacial meltwater composition, and that some of the Ca^{2+} and Mg^{2+} liberated by carbonate hydrolysis is exchanged for Na^+ and K^+ held on surface exchange sites on the subglacial debris at low ionic strengths (Stumm and Morgan, 1996; Tranter et al., in press). However, it is unlikely that all the Na^+ and K^+ initially released to solution can be derived from cation exchange, and that some is released by silicate hydrolysis. This increases the pH of the solution, thereby decreasing the amount of carbonate that can be initially dissolved in a closed system (Garrels and Christ, 1965; Tranter et al., in press). After hydrolysis and cation exchange, the next most likely reactions are coupled SO/CD, SO/silicate dissolution, and carbonate-silicate dissolution, since subglacial gas sources, and hence carbonation, are likely to be limited. Regression analysis suggests that ~ 84% of the protons liberated by sulphide oxidation are used to dissolve carbonates (Tranter et al., in press). The remainder are assumed to dissolve Ca^{2+}–Mg^{2+} silicates (7%) and Na^+–K^+ silicates (~10%). Tranter et al. (in press) estimate a crude ratio of carbonate and silicate dissolution associated with sulphide oxidation of ~ 5:1. This compares with the global terrestrial average of ~ 1.3:1 (Holland, 1978), suggesting that meltwater at Haut Glacier d'Arolla preferentially dissolves carbonates, despite the bedrock being dominated by silicates. Recent studies have indicated excess Ca^{2+} in many surface and groundwaters in excess of that predicted from simple stiochiometric considerations (e.g. White et al., 1999; Horton et al., 1999). These are discussed in more detail below.

In catchments predominantly underlain by carbonates, dissolution of pure calcite cannot completely couple the acid produced by pyrite oxidation because the solution becomes saturated before the coupled reaction is complete (Fairchild et al., 1994a). However, for most SO_4^{2-}-rich solutions calcite is significantly undersaturated, which implies that carbonate dissolution continues to lag pyrite oxidation. Modelling suggests that the acquisition of cations in carbonate catchments is staged, with the pure dissolution of carbonate preceding the oxidation of pyrite coupled with carbonate dissolution, or the introduction of CO_2 partly balanced by carbonate dissolution. Many of the observed solutions remain undersaturated with respect to calcite, the reasons for which remain to be investigated (Fairchild et al., 1994a).

In a closed system the maximum amount of SO_4^{2-} liberated in a closed-system by waters initially saturated with O_2 is ~520 μeq l^{-1}, assuming no other subglacial sources or sinks of O_2 (Tranter et al., in press). At altitude (lower saturated O_2 contents) and where surface water are predominantly derived from snow- and ice-melt [which are undersaturated with respect to atmospheric pO_2 values (Brown et al., 1994b)] this value will be reduced. However, many subglacial waters have SO_4^{2-} concentrations in excess of 520 μeq l^{-1}, with values of up to ~1200 μeq l^{-1} recorded in boreholes at Haut Glacier d'Arolla (Tranter et al., in press). This may result from refreezing of subglacial waters, a subglacial source of O_2, and alterative sources of SO_4^{2-} such as gypsum or an additional sulphide oxidation mechanism. Of these possibilities, extensive refreezing and gypsum sources (either as a primary mineral in the bedrock or resulting from the weathering of secondary gypsum precipitates) are unlikely (Tranter et al., in press). Subglacial sources of O_2 may be present, though sampling difficulties preclude their unequivocal identification. Further, it is likely that anoxic conditions exist in certain regions of the subglacial hydrological system, resulting from very slow meltwater flow rates, high water:rock ratios and the relatively high concentrations of sulphide minerals and/or organic C (Tranter et al., in press). In these environments, biogeochemical mechanisms could drive subglacial sulphide oxidation, whereby microbial activity (Sharp et al., 1999, Skidmore et al.,

2000) may catalyse sulphide oxidation (Singer and Stumm, 1970) and oxidise organic C. These reactions lower the pO_2 in solution, and the continued oxidation of sulphide minerals requires alternative oxidising agents such as NO_3^- (Tranter et al., 1993, 1994; Brown et al., 1994b), and Fe(III) (Drever, 1988; Tranter et al., in press). The role of subglacial microbial activity and the provenance and impact of Fe(III) in the oxidation of sulphides now need further investigation if the major controls on subglacial chemical weathering are to be identified (Tranter et al., in press).

Borehole studies have both corroborated and extended our understanding of geochemical processes at the ice-bedrock interface, providing insights beyond those available from proglacial investigations. However, considerable uncertainty surrounds such borehole samples, resulting from limitations in the spatial extent of borehole arrays or number of available boreholes, and uncertainty surrounding the nature of the hydrological system which has been sampled (e.g. linked cavity, permeable sediment) and the hydrological conditions at the time of sampling (e.g. whether the basal waters sampled are derived from subglacial, englacial or supraglacial sources). This demonstrates that water quality studies based on borehole sampling must be undertaken in conjunction with complementary independent measurements of borehole hydrology (Smart, 1996; Gordon et al., 1998).

5.4. *Laboratory experiments and modelling*

Laboratory experiments have been widely used to investigate the kinetics and mechanism of mineral dissolution (e.g. Wollast, 1967; Busenberg and Clemency, 1975; Plummer et al., 1978; Holdren and Berner, 1979; Chou et al., 1989; Nagy and Lasaga, 1992). However, the rates of reactions controlling meltwater composition are often known only qualitatively, and there has been little detailed study of the sources of solutes transported by meltwaters or the way in which these are determined by the nature of the hydrological environment at the glacier bed. Therefore, in order to strengthen chemoglacial interpretations, links need to be made between in vivo and in vitro studies (e.g. Brown et al., 1994a, 1996a, in press a, b; Fairchild et al., 1994a; Sharp et al., 1995a; Tranter et al., 1989, 1993). Controlled laboratory investigations of water-rock interaction, constrained by field data from the glacier in question, have allowed the effects of different geochemical parameters (e.g. water:rock ratio, sediment particle size, crushing, repeated wetting and proton availability) on solute acquisition in subglacial channels to be isolated and quantified (Table 5) (e.g. Fig. 5). These experiments indicate that glacial flour is extremely geochemically reactive, with 4 g l^{-1} of mixed size-fraction suspended sediment derived from the proglacial zone of Haut Glacier d'Arolla liberating > 150 μeq l^{-1} of Ca^{2+} in

Table 5
Laboratory investigations of the controls on solute acquisition in glacial environments, linking geochemical controls to glacial processes (summarised from Brown et al., 1996a)

Experiment	Geochemical control	Glacial process
Effect of particle size distribution	Surface area exposed to solution increases, relative to volume, as particle size decreases	Mechanical comminution processes (abrasion, crushing) are especially effective in the subglacial environment
Effect of water: rock ratio	Solute acquisition is a function of the *concentration* of SSC and the *duration* of SSC-meltwater contact	Bulk meltwater suspended sediment concentrations exhibit a broadly positive association with bulk discharge, hysteresis is common, random changes in suspended sediment concentration occur
Effect of crushing	Controls surface area exposed to solution, and reactivity of mineral surfaces (micro-particles, brittle fracture, plastic deformation, fresh mineral surfaces)	Combination of basal sliding and incorporation of tractive particles leads to *abrasion* and *crushing*
Effect of repeated wetting	Destruction of microparticles, amorphous zones, removal of fresh reactive surface sites (e.g. dislocations, blades), removal of rapidly weathered minerals (e.g. calcite)	Seasonal/diurnal variations in discharge magnitude result in cycles of sediment mobilisation and deposition within channels
Effect of initial solution chemistry	Effect of water composition on dissolution rate operates mainly through H^+ ion	Seasonal variations in proton provenance
Closed/open system effects	Chemical weathering reactions involve species in solid, liquid and gas phases (especially O_2 and CO_2)	Closed/open channel flow

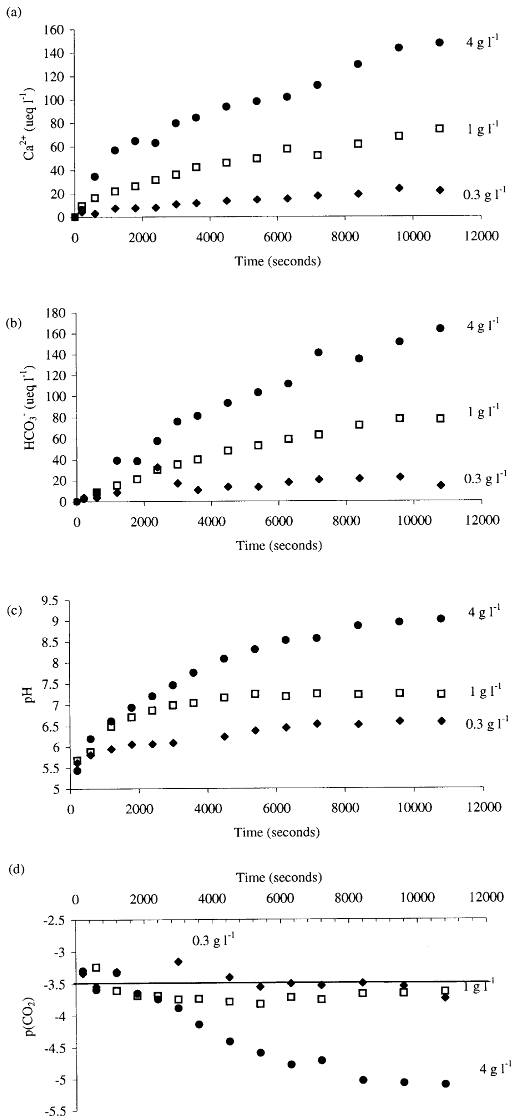

Fig. 5. Temporal variations in (a) Ca^{2+} (μeq l^{-1}), (b) HCO_3^- (μeq l^{-1}), (c) pH and (d) $p(CO_2)$ during 'free drift' laboratory experiments using different water–rock ratios (0.3, 1 and 4 g l^{-1}). Sediment used in the experiments was collected from the proglacial plain (after Brown et al., 1996a). The horzontal line in the lowest figure denotes open-system $p(CO_2)$ conditions at sea level (−3.5).

180 min with free contact with the laboratory atmosphere (so-called 'free-drift' conditions).

Limited attention has been focused on modelling water-rock interactions in glacial meltwater systems, linking advances in the theoretical understanding of mineral-water interactions to natural systems (e.g. Lasaga and Kirkpatrick, 1981; Hochella and White, 1990; Stumm, 1990, 1992). Work undertaken by Fairchild et al. (1994a, 1999a) and Sharp (1996) has advanced beyond simple *identification* of major lithogenic sources and dominant chemical weathering processes to investigate the dynamic evolution of chemical weathering systems. Values of $p(CO_2)$ during dissolution experiments are shown in Fig. 5d, and are clearly a function of the water-rock ratio and the duration of water-rock contact. At 0.3 g l^{-1} the $p(CO_2)$ of the solution remains in equilibrium with the atmosphere ($10^{-3.5}$). However, at a sediment concentration of 1 g l^{-1} there is a slight lowering to sub-atmospheric [closed system low $p(CO_2)$] conditions, and at 4 g l^{-1} $p(CO_2)$ values reach $\sim 10^{-5}$ after 3 h of water-rock interaction. As the solution has free access to the atmosphere this suggests that the consumption of protons supplied by the dissolution and dissociation of atmospheric CO_2 exceeds the supply of atmospheric CO_2 across the air-solution interface (Brown et al., 1996a). However, while these time-series illustrate the pCO_2 status of the meltwater, they provide little information on the dynamic evolution of the water as CO_2 is added or removed from solution. Fairchild et al. (1994a) present a model of water quality evolution for carbonate-meltwater interaction which considers 'opening' and 'closing' systems, which has subsequently been extended by Sharp (1996) to encompass meltwater-silicate dissolution pathways. These models suggest that the character of the weathering pathway experienced by meltwaters is controlled by kinetic rather than physical processes, with the water–rock ratio, sediment lithology and duration of water–rock interaction controlling the chemical evolution of waters (Sharp, 1996). Where $p(CO_2)$ values are high (i.e. above equilibrium with the atmosphere), addition of acid to the solution by sulphide oxidation is required to explain high CO_2 partial pressures (Fairchild et al., 1994a). However, these weathering studies focus on solute acquisition in proglacial streams, where air-meltwater CO_2 transfer is unconstrained. Such models urgently need to be extended to simulate weathering conditions in the subglacial environment, where the availability of atmospheric gases may be limited and/or dynamic at seasonal and diurnal timescales. For example, current models of post-mixing solute acquisition (e.g. Brown et al., 1994a) assume free access to an atmospheric source of CO_2. However, hydraulic conditions in the channelised component of the subglacial hydrological system may alternate between closed- and open-channel flow conditions during a diurnal discharge cycle (Nienow et al., 1996).

The relationship between mineral weathering rates derived under laboratory conditions and rates of geochemical reactions in natural systems requires careful consideration (cf. Casey et al., 1993; Velbel, 1993b), and has received relatively little attention in the glaciological literature. Chemical weathering rates calculated from mass-balance studies in natural watersheds may be more than 3 orders of magnitude slower than in the laboratory (e.g. Schnoor, 1990; Drever, 1994; Hoch et al., 1999), suggesting that either rate constants may be lower in nature or that environmental factors alter some other term in the rate equation (Velbel, 1993b). Velbel (1993b) suggests that, rather than compositionally- or chemically-driven differences between weathering rates in nature and in the laboratory, physical processes (e.g. hydrological) factors are responsible. This may reduce the reactive surface area available for weathering as a result of processes such as heterogeneous flow in pore/fracture networks and soils. In glaciological investigations the latter may be a problem when laboratory studies are extended to the distributed component of the subglacial hydrological system. However, to date studies have concentrated on suspended sediment-meltwater interaction in the channelised component, where mixing is vigorous and water-rock contact times are short. Here, laboratory-derived rates may more realistically reflect natural rates, since both systems combine freshly-crushed, geochemically-reactive, fine-grained material containing micro-particles with low-ionic strength weathering solutions (Brown et al., 1996a). Further, water-rock contact times and other experimental conditions (e.g. water:rock ratios) may be effectively constrained by field measurements (Brown et al., 1994a; in press a,b). However, this assumption has not been tested.

5.5. Solute provenance

Achieving a better understanding of the factors controlling the denudation rates of rocks at the surface of the Earth is a major concern in the Earth Sciences (Sverdrup and Warfinge, 1995; Gaillardet et al., 1999a). Solute provenance studies are especially important, as the balance between carbonate and silicate weathering driven by atmospherically-derived CO_2 influences the long-term global CO_2 balance (e.g. Raymo and Ruddiman, 1992; Gibbs and Kump, 1994, 1996; Tranter, 1996; Gaillardet et al., 1999b; White et al., 1999). These weathering rates have been addressed through examination of river dissolved loads using experimental approaches, small scale studies and global estimates based on large rivers (Gaillardet et al., 1999b).

Deconvoluting water quality signatures has been predominantly achieved by utilising river water quality data and allocating each solute to the dissolution of a rock type following a series of steps (e.g. Garrels and Mackenzie, 1971). In glacierised catchments, studies of solute provenance in glacial environments have had two aims: first to disaggregate the solute load into crustal, atmospheric and snowpack sources (Sharp et al., 1995b; Brown et al., 1996b; Hodgkins et al., 1997; Hodson et al., 2000), and secondly to identify variations in solute sources and weathering mechanisms at both seasonal (Tranter et al., 1993; Brown et al., 1996b; Hodgkins et al., 1997) and diurnal timescales (Brown et al., 1994a).

These studies, based on major dissolved ions (e.g. Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, NO_3^-, Cl^-) have indicated that the bulk of the solute is crustally-derived in alpine locales, with geochemically-reactive trace minerals (e.g. carbonate and sulphide minerals) contributing the majority of the solute found in bulk runoff. Coupled sulphide oxidation and carbonate weathering and the carbonation of carbonate minerals generate approximately equal amounts of solute, and show distinct seasonal variations, reflecting the dynamic nature of the subglacial hydrological system (Fig. 6a) (Sharp et al., 1995b; Brown et al., 1996b). Conversely, the weathering of silicate minerals by carbonation reactions supplies a relatively constant proportion of bulk meltwaters solutes (Fig. 6b).

These studies are consistent with other studies of water-rock interaction in alpine (e.g. Raiswell, 1984; Drever and Hurcomb, 1986) and other (e.g. Anderson et

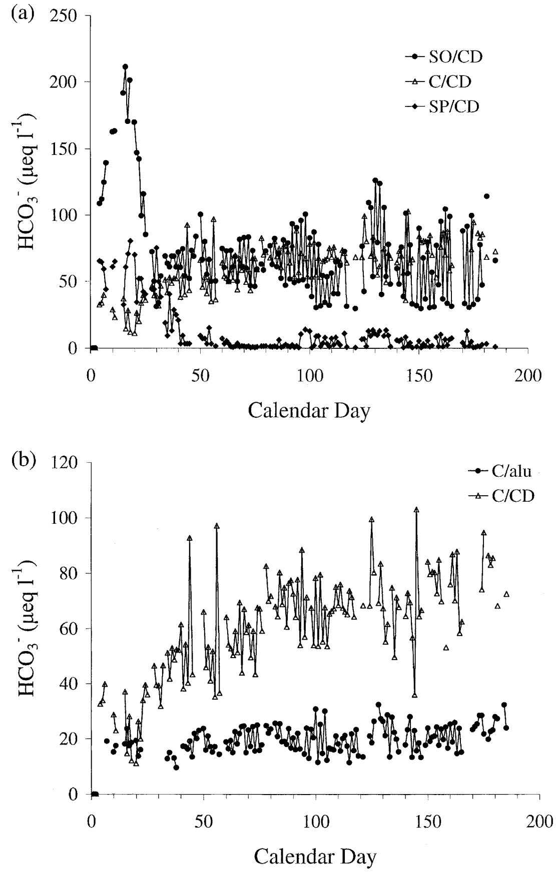

Fig. 6. Crustal HCO_3^- provenance in bulk runoff during the 1989 ablation season at Haut Glacier d'Arolla. (a) SO/CD = coupled sulphide oxidation and carbonate dissolution (Equation 8), C/CD = carbonation of carbonate minerals (Equation 6), SP/CD = dissolution of carbonates by snowpack-derived acidity. (b) C/alu = carbonation of silicate minerals, C/CD = carbonation of carbonate minerals.

al., 1997; Gaillardet et al., 1999b; White et al., 1999; Horton et al., 1999) Earth surface environments, which indicate that carbonate-derived Ca^{2+} may be the dominant cation in catchments underlain predominantly by igneous and metamorphic bedrock. Leaching of trace amounts of disseminated calcite has also been recognised as an important contributor to Ca^{2+} fluxes in watersheds underlain by granitoid rocks (e.g. Horton et al., 1999; White et al., 1999). The impact of calcite on Ca^{2+} concentrations in weathering solutions depends not only on the amount of calcite present, but also on the intensity of the weathering environment (White et al., 1999; Anderson et al., 2000). This suggests that the concept of chemically- and physically-limited weathering regimes (e.g. Drever and Zobrist, 1982; Stallard and Edmond, 1983) may be useful in reappraising the voracity of chemical weathering processes in glacial systems relative to other environments. Chemically-limited systems are those where mechanical erosion exceeds chemical weathering. The latter is highly selective, and dependent on mineral-specific reaction rates. Thus, the most reactive minerals (e.g. calcite) contribute to solute fluxes disproportionately to their abundance, and are selectively leached. Conversely, in physically-limited systems mechanical erosion is less intense, and the most reactive mineral phases have been depleted from accessible rock and sediment surfaces. Here, chemical weathering is no longer dependent on mineral reaction kinetics but on fluid transport (White et al., 1999). Thus, calcite can contribute a significant proportion of the total dissolved Ca^{2+} (and HCO_3^-) during and following periods of glaciation, since this exposes fresh mineral surfaces. This suggest that calcite dissolution may be *watershed* and not *climatically* driven (White et al., 1999), which has important implications for the timing and location of long-term CO_2 drawdown associated with terrestrial ice mass dynamics (see below). However, solute provenance and routing based on major dissolved ions is often equivocal, since dissolved species may be derived from more than one source (Brown and Fuge, 1998a).

More detailed investigations of solute provenance have been undertaken for specific lithologies, which extend our understanding of solute sources in glacial environments. For example, Fairchild et al. (1994a; 1999b) demonstrate that glacial meltwaters flowing over a carbonate lithology may acquire Na^+ from both carbonates (e.g. aragonite) and silicates. This is in contrast to studies of subglacial solute provenance beneath glaciers underlain predominantly by igneous/metamorphic lithologies (e.g. Haut Glacier d'Arolla), which have assumed that lithogenic Na^+ is derived solely from aluminiosilicate weathering (Sharp et al., 1995b; Brown et al., 1996b). However, more accurate definitions of solute provenance are necessary if meltwater composition is to be used effectively in disaggregating solute fluxes into silicate and carbonate sources. Minor and trace elements may be of value in this respect, and have recently attracted attention in provenance studies (e.g. Brown and Fuge, 1998a,b; Mitchell et al., in press).

6. Chemical weathering and climate change in glacierised basins

It has long been recognised that rates of terrestrial chemical erosion may influence the atmospheric concentration of CO_2, a radiatively-important gas contributing to mean global temperature regulation (e.g. Chamberlain, 1899; Walker et al., 1981; Berner et al., 1983; Raymo, 1991; Raymo and Ruddiman, 1992). Carbonation reactions involving the dissolution and dissociation of atmospheric CO_2 constitute a significant component of chemical weathering processes operating in alpine glacierised basins (e.g. Metcalf, 1984; Sharp et al., 1995b; Brown et al., 1996b; Hodgkins et al., 1997; Hodson et al., 2000). Sharp et al. (1995b) demonstrated a strong positive relationship between CO_2 drawdown (from the atmosphere into the meltwater solution) and discharge at Haut Glacier d'Arolla, Switzerland. The greatest rates of CO_2 drawdown were associated with high suspended sediment fluxes and with waters which have low $p(CO_2)$ characteristics. This emphasises the importance of carbonation reactions and suspended sediment transport in major channels at the glacier bed in controlling the rate and magnitude of CO_2 drawdown in glacial meltwaters. At high sediment concentrations, these reactions consume protons more rapidly than they can be re-supplied by CO_2 diffusion across the gas-meltwater interface (Figs. 4 and 5). The apparent $p(CO_2)$ of the water decreases, and CO_2 drawdown occurs by steepening the atmosphere-meltwater CO_2 concentration gradient (which increases the rate of diffusion of CO_2 into solution).

The link between discharge and CO_2 drawdown suggests a potentially important role for glacially-driven chemical weathering in C cycling over glacial-interglacial time scales. Meltwater runoff from ice sheets peaks during episodes of deglaciation (Oerlemens, 1993). Considerable amounts of CO_2 could be removed from the atmosphere if contemporary rates of chemical weathering in alpine catchments are applicable to glaciers and ice sheets during glacial-interglacial cycles, and CO_2 drawdown is proportional to meltwater discharge during deglacial discharge pulses. Such changes in the global cycling of CO_2 may influence climate change (Sharp et al., 1995b; Anderson et al., 1996; Tranter, 1996). However, much uncertainty still surrounds these estimates, since there is no modern analogue for the mid- to high-latitude Quaternary ice sheets (Gibbs and Kump, 1996; Jones et al., 1999, in press). Furthermore, the nature of the hydrological conditions beneath Quaternary ice sheets, which may exert an important control on the magnitude of CO_2 supply (and hence CO_2 sequestration through carbonation reactions), is unclear.

The magnitude of both meltwater discharge and suspended sediment fluxes associated with the growth and decay of the major terrestrial ice sheets means that the potential for glacial runoff to act as a sink for atmospheric CO_2 warrants further attention. To date, CO_2 drawdown figures have been largely presented as *total* drawdown (e.g. Sharp et al., 1995b; Tranter, 1996), combining both short- and long-term rates. Short-term CO_2 drawdown is associated with the carbonation of carbonates, with CO_2 returned to the atmosphere via re-precipitation of carbonate in the oceans. Conversely, the carbonation of silicates and aluminosilicates in glacial meltwaters may influence CO_2 drawdown over longer time-scales, since CO_2 consumed during weathering is not re-introduced to the atmosphere from the oceans via carbonate precipitation. Additionally, much uncertainty still surrounds the role of chemical erosion in CO_2 consumption. Gaillardet et al. (1999b) suggest that the positive correlation between chemical weathering and physical weathering rates for the major world rivers acts in favour of a coupling between physical and chemical erosion of silicates. Thus, where physical erosion is most active, these are the regions where aluminosilicates dissolve at the highest rate, and where CO_2 consumption by silicate weathering is most important. However, while high physical weathering rates continuously produce new mineral surfaces which enhances chemical weathering fluxes, other studies (e.g. White et al, 1999; Anderson et al., 2000) have suggested that carbonate weathering is more important than silicate weathering in chemically-limited systems (see above). This suggests more work is needed in order to resolve these uncertainties, and a better understanding of the rates of carbonate and silicate weathering under terrestrial ice masses is needed to evaluate the importance of glaciers and ice sheets in the global cycling of CO_2 during cycles of ice sheet growth and decay.

While weathering is driven mainly by atmospheric CO_2 or biologically-derived CO_2 in soils (Raiswell et al., 1980; Berner and Berner, 1996; Drever, 1998), chemical weathering in the distributed component of the subglacial hydrological system appears to depend on sulphide oxidation and Fe(III) reduction, with high pH values (usually between 7 and 9) limiting aluminosilicate dissolution (Lerman, 1979; Tranter et al., in press). These subglacial reactions appear to progress in the following order; (i) carbonate and silicate hydrolysis (ii) sulphide oxidation (fuelled first by O_2 and then by Fe(III)), which drives further carbonate and silicate weathering. Thus, Tranter et al. (in press) infer that a significant proportion of the subglacial chemical weathering may not be associated with the sequestration of atmospheric CO_2. Additionally, recent estimates of terrestrial chemical erosion during the last deglaciation have suggested that glacial meltwaters may have less of an impact (~5.5 ppm at most) on atmospheric CO_2 concentrations than was previously thought (Jones et al., in press). This may dramatically alter estimates of CO_2 drawdown associated with glacial conditions, and the role of glacially-driven carbonation reactions over glacial-interglacial timescales.

7. Subglacial biological activity

In addition to uncertainties surrounding inorganic processes operating in the glacial environments, a recent study by Sharp et al. (1999) has cast doubt on the validity of predicting rates of subglacial chemical weathering from thermodynamic or kinetic considerations alone, and challenges the view that meltwater chemistry maybe explained solely by examination of purely inorganic reactions. Samples of basal ice and subglacial meltwaters from Glacier de Tsanfleuron and Haut Glacier d'Arolla, Switzerland have yielded active bacterial populations comparable to those in the active layer of permafrost, and orders of magnitude larger than those found in ice cores from ice sheets (Sharp et al., 1999). Microbially-mediated oxidation of sulphide minerals and organic C at glacier beds could potentially provide acidity to the subglacial environment. This reduces dependence on the supply of atmospheric gases to drive acid hydrolysis reactions at temperate glacier beds (e.g. CO_2 and O_2). This has important implications for estimates of chemical erosion and CO_2 drawdown over glacial-interglacial time-scales, since subglacial weathering may not be limited by the lack of an atmospheric CO_2 source (Gibbs and Kump, 1994; Hallet et al., 1996; Kump and Alley, 1994; Sharp et al., 1999).

Subglacial bacterial populations may be sustained by the presence of liquid water at warm-based glaciers which acts as a cryoprotector (Gilichinsky et al., 1995) and supplies nutrients either from the surface (e.g. NO_3^- and NH_4^+) or from subglacial sediments (e.g. Fe and SiO_2). Further, organic C, which provides a substrate for heterotrophic respiration, may be derived from bedrock, soils and plant material over-ridden during glacial advance (Röthlisberger and Schneeberli, 1979; Sharp et al., 1999). This raises the possibility that microbial mediation of redox reactions may be a significant proton source beneath glaciers and ice sheets where meltwaters are isolated from a source of atmospheric CO_2. The presence of organic C may have important implications for estimates of terrestrial chemical erosion at glacial-interglacial timescales, as previous models have assumed that weathering beneath ice sheets may be limited by the lack of an atmospheric CO_2 source (e.g. Gibbs and Kump, 1994; Kump and Alley, 1994). Further, these findings suggest that it may not be possible to predict the processes and rates of subglacial chemical weathering from thermodynamic or kinetic considerations alone (Sharp et al., 1999). Similar findings have been made in basal ice from John Evans Glacier, Arctic Canada, which suggest that the subglacial environment beneath a polythermal glacier provides a viable habitat for microbial life, as long as temperate basal thermal conditions, water and organic C from glacially overridden soils are present (Skidmore et al., 2000). This has important implications for C cycling during glacial periods.

8. The future

A decade ago, Sharp (1991) highlighted the unfulfilled potential of meltwater quality studies in furthering our understanding of subglacial hydrochemistry and hydrology. Much progress has been made in response to the call for the better characterisation of temporal variations of source waters, the monitoring of individual dissolved ions (especially SO_4^{2-} and HCO_3^-, pH and dissolved O_2), coupled measurement of suspended sediment and subglacial hydrological conditions, and caution in applying two-component mixing models. However, much remains to be done, and hydrochemical research in glacierised catchments still needs to:

8.1. Evaluate the role of glacial meltwaters in estimates of contemporary and palaeo chemical erosion rates and global biogeochemical cycles

Recent research has suggested that chemical weathering in glacierised catchments may influence global C cycling over glacial-interglacial timecales (e.g. Gibbs and Kump, 1994; Sharp et al., 1995b; Tranter, 1996; Hodson and Tranter, 1999). However, much uncertainty surrounds both estimates of CO_2 drawdown in glacierised regions today, and the importance of chemical weathering beneath the Pleistocene ice sheets. For example, it is often assumed that all areas covered by ice have an effective chemical erosion flux of zero (Gibbs and Kump, 1994; Kump and Alley, 1994), which focused studies of palaeoerosion predominantly on ice-free areas. This is based on the assumption that a large fraction of the Pleistocene ice sheets were likely to be frozen to their beds, and, therefore, were effectively closed systems with a limited supply of CO_2 (Gibbs and Kump, 1994). If this is the case then alpine analogues may only apply during early- or late-stages of a glacial cycle (Anderson et al., 1997) or at the ice sheet margins (Gibbs and Kump, 1994, 1996; Tranter, 1996). In order to resolve these issues, research needs to focus on broadening the geographical distribution of meltwater hydrochemical studies to encompass different lithologies (especially those which underlay the Laurentide and Fennoscandian Ice Sheets), basal thermal regimes and the large ice sheets (currently observations are derived predominantly from small valley glaciers which are warm or polythermal at the base). This may be complicated by the fact that no modern analogues exist for the massive mid- to high-latitude ice sheets (Gibbs and Kump, 1996). Extrapolation is problematic e.g. what proportion of the ice sheet was warm and dry-based? How pervasive were the atmospheric connections to the bed? How high were transient rates of chemical erosion during deglaciation events? How variable were subglacial hydrological and hydrochemical regimes throughout glacial cycles? (the Laurentide Ice Sheet may have been completely warm-based during periods of stagnation and decay (Clark and Walder, 1994), which suggests alpine conditions may be an effective analogue at certain times). Addressing these issues will remove a key uncertainty surrounding current estimates of palaeo-chemical erosion, namely the extreme extrapolation between contemporary studies in alpine catchments and large Quaternary ice sheets (Gibbs and Kump, 1996). However, differences in basal conditions between past and present ice sheets must be carefully considered (e.g. Boulton et al., 1995; Siegert, 2000), since these will influence factors such as access to atmospheric gases (Gibbs and Kump, 1994) and the presence of organic C from overridden soils and peat deposits (Skidmore et al., 2000).

A focus of meltwater quality research in glacial environments has been to elucidate processes operating in the inaccessible subglacial environment. This has resulted in the proglacial zone being largely ignored. However, interest in ice-marginal environments is increasing (e.g. Axtmann and Stallard, 1995; Anderson et al., 2000) driven by global cycling issues and the need to quantify rates of terrestrial chemical erosion over glacial-interglacial time-scales. For example, Anderson et al. (2000) showed that the effects of glaciers on chemical weathering rates extends beyond the margins of glaciers, demonstrating that solute fluxes, $^{87}Sr/^{86}Sr$ ratios, and chemical denudation rates vary systematically with distance from the ice margin. Their study also suggests that silicate weathering reactions only become important after a vegetation cover is established, suggesting that the subglacial and ice-marginal environment may not be a long-term sink for atmospheric CO_2. However, the impact of fine-grained glacio-fluvial sediments on downstream weathering fluxes remains unknown (Anderson et al., 2000). There is, therefore, a need to quantify the relative rates of silicate versus carbonate erosion between glacierised, proglacial and non-glacierised environments. Further, Anderson et al. (1997) have also questioned the overall rate of chemical erosion (and hence CO_2 consumption) in glacial catchments, which they suggest may be no higher than temperate catchments with an equivalent water flux. However, despite similar *rates* of denudation, the chemistry of the waters draining glacierised and non-glacierised areas may be distinct (e.g. Drever and Hurcomb, 1986; Mast and Drever, 1990; Axtmann and Stallard, 1995; Anderson et al., 1997, 2000; Hoch et al., 1999). For example, biotite weathering proceeds rapidly in subglacial environment, enhanced by the voracity of physical weathering processes. This increases the K^+/Na^+ ratio relative to other surface waters. Conversely, Si concentrations in waters draining glacier-covered catchments are low relative to their discharge. This is important for our understanding of the processes and rates of CO_2 drawdown in mountain environments/associated with tectonic uplift (cf. Raymo and Ruddiman, 1992). Alpine environments with high rates of mechanical weathering may provide a natural context for the pre-steady-state dissolution kinetics observed in the laboratory (Holdren and Berner, 1979; Hoch et al., 1999). Further, the role of glaciers bordering the Arctic seas in supplying meltwaters enriched in nutrients such as N, P, Si and C, and their relationship to biological productivity needs to be examined (cf. Watson et al., 2000).

8.2. Expand models of suspended sediment-meltwater interaction to improve the links between hydrology and suspended sediment dynamics

Estimates of post-mixing chemical erosion and solute acquisition are currently based on proglacial measurements of sediment and solute concentrations. However, these proglacial loads are a bulk measure of water parcels which have *pre-weathered* suspended sediment prior to emergence at the glacier portal. The concentration and geochemical reactivity of suspended sediments are likely to vary along subglacial flowpaths as a result of changes in sediment availability, hydraulic conditions and the duration of water-rock contact. There is, therefore, a need to couple models of solute acquisition to models that are capable of quantifying sediment transport in both time and also in space, as meltwaters progress through the subglacial hydrological network and the hydrological system evolves during the meltseason (e.g. Clarke, 1996; Seagren, 1999; Brown et al., in press a,b). In order to avoid a purely empirical framework, and hence allow model results to be generalised and transferred to other glaciers, kinetic order and rate parameters need to be derived from laboratory experiments. To date, laboratory investigations of water-rock interaction in glacial environments have been conducted predominantly under 'free-drift' conditions in order to quantify solute acquisition within the subglacial channels. This has limited their ability to accommodate flow in pressurised conduits at peak diurnal discharges, and to predict solute acquisition in other components of the subglacial hydrological system [e.g. the distributed system and channel marginal zone (Hubbard et al., 1995)]. Therefore, the range of laboratory experiments must be extended to investigate solute acquisition under closed-system conditions, and to establish the role of biological activity in subglacial chemical weathering.

8.3. Improve the separation of dissolved constituents into atmospheric and lithogenic components and establishing proton sources

While the potential of trace elements in provenance studies has been indicted by preliminary investigations (e.g. Brown and Fuge, 1998a,b), more detailed studies from a range of catchments over longer (seasonal) timescales, coupled to laboratory experiments, are needed for their full potential to be realised. This is particularly important in relation to estimating the proportion of silicate versus carbonate weathering, and the role of dissolved gases in subglacial chemical erosion.

8.4. The chemical composition of individual runoff components needs to be more effectively characterised if more realistic bulk meltwater separations are to be achieved

This will be dependent on establishing better links between laboratory, borehole and field investigations, coupled with the identification of more exclusive dissolved indicator species in solute provenance studies.

8.5. Establishing the geochemistry of Antarctic sub-ice lakes

The chemical evolution, sedimentology and biological potential of Antarctic sub ice lakes (e.g. Lake Vostok) has recently attracted considerable attention (e.g. Siegert, 1999, 2000; Siegert et al., 2000). Geothermal fluids, bottom sediments and ice-melt at the lake surface may all supply impurities to Lake Vostok, including sediment, gas hydrates and dissolved ionic species (Dowdeswell and Siegert, 1999). In addition, this influx of impurities may also provide sustenance for life, which may have evolved in isolation since Lake Vostok was formed between several thousand years and several million years (Siegert, 1999). However, until the technology exists to sample the lake waters directly, our understanding of the chemical dynamics of the lake will be restricted to modelling results.

9. Conclusions

Water quality variations supported by isotopic data may provide valuable and unique insights into the behaviour of hydrological and geochemical systems (Nash and McCall, 1995; Price 1996; Sharp, 1991; Tranter et al., 1993) and at a minimum can provide a qualitative framework within which appropriate questions can be posed (Freeze and Cherry, 1979). Sharp et al. (1998) made the case that glacier hydrology has remained somewhat isolated as a result of being published in glaciological and geophysical journals, rather than in the mainstream hydrological literature. The aim of this review is to avoid a similar fate happening to studies of meltwater quality, and to stimulate interest in the wider geochemical community. The recent interest in water quality issues in glacierised areas was largely initiated by an applied stimulus, namely to elucidate hydrological processes in the inaccessible subglacial environment. As the gaps in our chemoglacial knowledge are addressed, studies of the quality characteristics of meltwaters draining from glaciers and ice sheets have the potential to provide important information about the character of subglacial drainage systems and their evolution over time, and the role of terrestrial ice masses in chemical denudation and climate change. However, to realise the full potential of this branch of geochemistry, participation needs to be broadened. This will enable the full potential of water quality variations to be exploited and the impact of chemical weathering on global biogeochemical cycles to be established in the 21st Century.

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