

## THE USE OF SULFATE AS A TRACER FOR THE DELAYED FLOW COMPONENT OF ALPINE GLACIAL RUNOFF

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**ABSTRACT** A method for separating alpine glacial runoff into two components, quickflow and delayed flow, is presented and is based on the dilution characteristics of sulfate relative to other major ions. These components followed different flowpaths before they mixed in basal arterial channels. Quickflow was relatively dilute. The quickflow composition was controlled by post mixing reactions, whose magnitude varied diurnally. A principal control of the quickflow composition was suspended-sediment concentration. In contrast, the composition of delayed flow remained relatively constant throughout the ablation season. The proportion of quickflow early in the ablation season ranged from 0-40%, and increased to 60-70% during periods of maximum runoff.

### INTRODUCTION

The chemistry of alpine glacial meltwaters has been used to determine water routing through Alpine glaciers. Water routing, in turn, controls glacier shape, velocity and erosive capacity (Collins, 1978, 1979; Drewry, 1986). These early studies paid little attention to the chemical processes which furnish the meltwaters with solute or to their rates of reaction, because field logistics demanded that continuous measurements of conductivity be used as a surrogate measurement of solute load. Consequently, a mechanistic determination of water quality genesis has not been achieved until recently for alpine glacial runoff. Also, misinterpretation of seasonal and diurnal variations in meltwater chemistry has arisen because of ignorance about the chemical processes which operate along different hydrologic flowpaths.

Earlier studies of meltwater quality genesis identified carbonation and sulfide oxidation as important mechanisms for solute acquisition (Church, 1972), and Raiswell (1984) explained how carbonation establishes an association between dissolved carbon dioxide species, principally  $\text{HCO}_3^-$ , and total dissolved base cations, which depends on the type of rock being weathered and whether the water-rock system is open or closed to the atmosphere. It is only recently that a conceptual model of solute acquisition by glacial meltwaters has been proposed. The model demonstrates how different coupled reactions are likely to dominate the different drainage pathways through the glacier (Tranter *et al.*, in press). In particular,  $\text{SO}_4^{2-}$  is believed to be generated largely from sulfide oxidation in the slowly draining, so-called "distributed system". Hence, naturally derived  $\text{SO}_4^{2-}$  can be used to trace water flowing through the distributed system.

In this paper, we investigate the use of  $\text{SO}_4^{2-}$  to separate glacial meltwaters into two components, relatively concentrated "delayed flow" and relatively dilute "quickflow". In so doing, we hope to establish that the concentration of species in quickflow is seasonally variable, and dependent on factors such as the water-rock ratio in the turbid runoff.

## THE TWO COMPONENTS OF GLACIAL RUNOFF

Dye tracing reveals that a two-component mixing model adequately describes the sub-glacial transport of meltwaters at the Haut Glacier d'Arolla (P. Nienow, pers. comm.). We assumed that the total runoff consists of two components. The first component, quickflow, is derived largely from icemelt, which flows rapidly through the glacier in ice-walled conduits and has limited access to rock flour. The second component, delayed flow, is derived largely from snowmelt, which drains more slowly through the distributed system at the ice-bedrock interface. In the distributed system, rock-water ratios are high as a result of contact with reactive, finely comminuted glacial flour or moraine. The two components mix in arterial channels at the glacier bed, before draining from the portal.

It is unlikely that the composition of the bulk meltwaters reflects two-component conservative mixing for many of the major ions. The composition of quickflow is more concentrated than icemelt, and it follows that quickflow must acquire solute during transit through the glacier, most likely in the basal arterial channels following mixing with delayed flow (Brown, 1991; Tranter & Raiswell, 1991). This leads us to believe that the composition of quickflow is largely determined by "post-mixing reactions", which are dominated by carbonation (Tranter *et al.*, in press). Carbonation is dependent on factors such as the suspended sediment load, the duration of water-rock contact, and access of atmospheric CO<sub>2</sub> to the basal arterial channels. The impact and magnitude of these factors evolves during the ablation season, and hence, the composition of quickflow should likewise evolve.

## AREA OF STUDY

Sampling was undertaken at the Haut Glacier d'Arolla, the most southerly glacier in the Arolla valley, Val d'Hérens, Switzerland. Geochemically reactive minerals, such as pyrite and calcite, have been identified both in the field and by microscopic study of thin sections, and are present in trace quantities in the bedrock and moraine.

## SAMPLING, METHODS AND TECHNIQUES

Nine diurnal cycles were intensively sampled during the 1989 and 1990 ablation seasons. Three cycles were sampled hourly during 1989 on 22-23 June, 17-18 July, and 16-17 August. The remaining six were sampled hourly between 10:00 and 17:00 h and every 3 h between 17:00 h and the following 10:00 h during 1990 on 14-15 and 25-26 June, 11-12 and 23-24 July, and 9-10 and 16-17 August. A description of the discharge and suspended sediment monitoring can be found in Gurnell *et al.* (in press), and that of the water sample collection and treatment may be found in Brown (1991). In summary, alkalinity (largely HCO<sub>3</sub><sup>-</sup>) was determined in the field on filtered samples, and pH was measured in the field laboratory. The major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>) and the other major anion, SO<sub>4</sub><sup>2-</sup>, were determined in the laboratory by atomic adsorption spectrophotometry and ion chromatography, respectively (Brown, 1991).

## RESULTS

The seasonal discharge records for 1989 and 1990, and the sampling period of each diurnal cycle are shown in Fig. 1. The low diurnal discharge (<2 m<sup>3</sup> s<sup>-1</sup>) and amplitude (0.6 m<sup>3</sup> s<sup>-1</sup>) during early June increased as the season progressed, which gave rise to higher, increasingly peaked hydrographs of high diurnal amplitude (>3.0 m<sup>3</sup> s<sup>-1</sup>) during July and August. Also, the asymmetry in the diurnal hydrograph heightened, as the time to peak between the

onset of daily ablation and maximum bulk discharge was reduced.

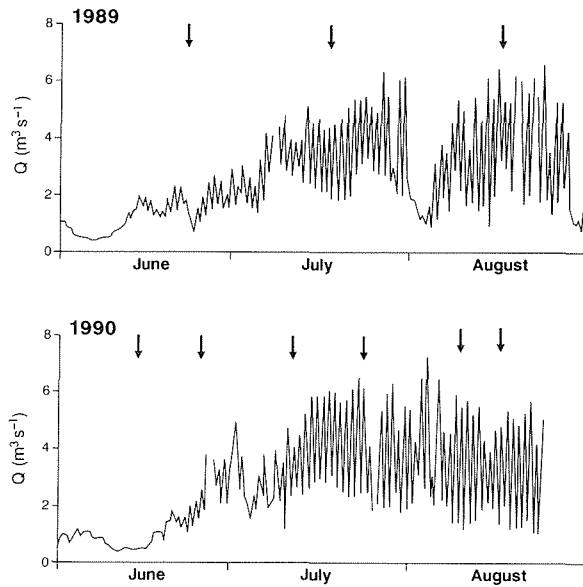


FIG. 1 The variability in runoff during the 1989 and 1990 ablation seasons. Arrows indicate when diurnal cycles were sampled.

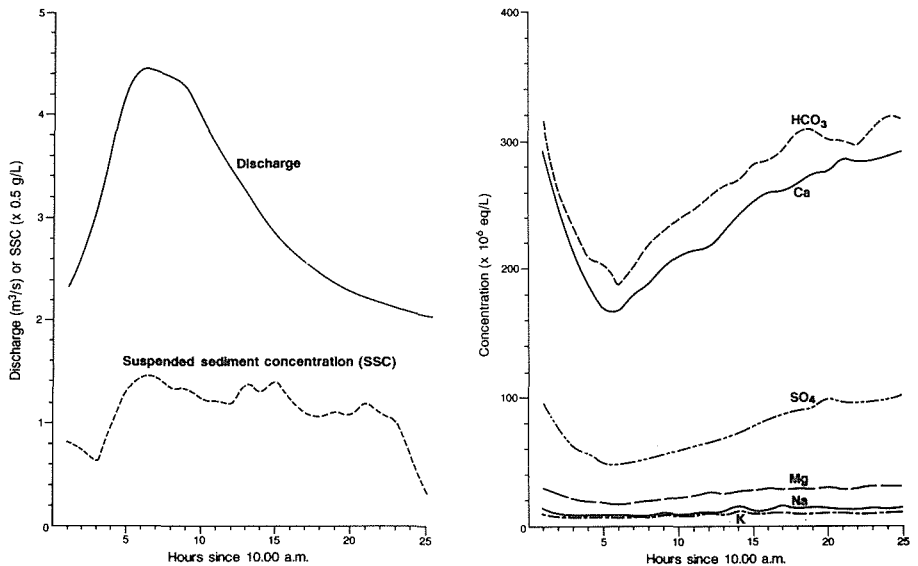


FIG. 2 Diurnal variations in discharge and the concentrations of suspended sediment and major ions for 17-18 July 1989. This diurnal cycle is representative of the nine cycles that were sampled.

TABLE 1 Summary characteristics of the nine diurnal cycles.

Parameter	June 1989		July 1989		August 1989	
	Min	Max	Min	Max	Min	Max
Q	1.4	2.0	2.0	4.5	3.4	6.9
EC	17	20	15	24	14	18
Ca <sup>2+</sup>	200	240	170	290	180	240
Mg <sup>2+</sup>	26	43	16	31	15	31
Na <sup>+</sup>	9.2	17	7.2	17	7.7	14
K <sup>+</sup>	6.2	14	5.6	12	7.5	13
HCO <sub>3</sub> <sup>-</sup>	210	260	190	320	240	280
SO <sub>4</sub> <sup>2-</sup>	64	83	47	100	26	57
pH	7.3	7.8	8.2	9.0	8.5	9.2
SSC	0.014	0.29	0.16	0.73	1.4	4.0
	June A 1990		July A 1990		August A 1990	
Q	0.45	0.59	2.3	4.3	1.3	5.5
EC	26	31	14	22	11	25
Ca <sup>2+</sup>	280	480	190	310	190	350
Mg <sup>2+</sup>	32	40	20	33	20	42
Na <sup>+</sup>	7.1	18	1.1	7.5	3.8	7.5
K <sup>+</sup>	8	12	2.5	4.7	5.0	8.1
HCO <sub>3</sub> <sup>-</sup>	300	380	210	340	240	320
SO <sub>4</sub> <sup>2-</sup>	140	170	46	92	35	110
pH	6.7	7.2	6.5	7.1	7.1	9.0
SSC	0.041	0.57	0.66	2.2	0.19	4.5
	June B 1990		July B 1990		August B 1990	
Q	1.6	3.6	1.5	6.0	1.5	4.7
EC	14	20	/	/	15	26
Ca <sup>2+</sup>	220	280	150	300	210	360
Mg <sup>2+</sup>	14	38	16	33	26	43
Na <sup>+</sup>	2.9	7.9	2.9	8.5	3.6	11
K <sup>+</sup>	4.1	12	2.0	7.5	4.0	11
HCO <sub>3</sub> <sup>-</sup>	210	300	190	320	250	340
SO <sub>4</sub> <sup>2-</sup>	53	90	32	92	41	110
pH	6.6	7.1	6.5	7.1	7.0	9.1
SSC	0.23	5.7	0.56	3.2	1.2	5.6

Units are  $\mu\text{eq l}^{-1}$ , except: discharge (Q), in  $\text{m}^3 \text{s}^{-1}$ ; suspended-sediment concentration (SSC), in  $\text{g l}^{-1}$ ; electrical conductivity (EC), in  $\mu\text{S cm}^{-1}$ ; and pH. Missing data is denoted by “/”.

The variations in discharge, and concentrations of suspended sediment, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> for the diurnal cycle in July 1989 are shown in Fig. 2, and were representative of the entire sampling period. Characteristics of each diurnal cycle are summarized in Table 1. The dissolved ion concentrations and electrical conductivity were inversely related to discharge (Fig. 2). The diurnal variation in solute concentrations in-

creased as the ablation season progressed (Table 1). A notable exception was the cycle in June 1990. The variation of pH broadly followed those of other major ions during June and July, and was inversely related to discharge. However, this pattern reversed during August.

TABLE 2 Linear regression relations of concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  on  $\text{SO}_4^{2-}$  for each diurnal cycle. Points falling outside the 95% confidence limit of the central tendency were excluded, and the number of rejected values are indicated in the column labelled Missing. The number of points from which the best fit linear regression was obtained is denoted "n."

Date	Ion	Slope	Intercept	n	Missing	r
June 1989	$\text{Ca}^{2+}$	2.2	58	22	1	0.98
	$\text{HCO}_3^-$	2.3	67	23	0	0.91
June A 1990	$\text{Ca}^{2+}$	2.7	15	11	0	0.98
	$\text{HCO}_3^-$	2.1	4.3	10	3	0.98
June B 1990	$\text{Ca}^{2+}$	1.3	150	14	0	0.75
	$\text{HCO}_3^-$	1.3	160	14	0	0.55
July 1989	$\text{Ca}^{2+}$	2.2	75	24	0	0.99
	$\text{HCO}_3^-$	2.1	110	24	0	0.97
July A 1990	$\text{Ca}^{2+}$	2.4	92	14	0	0.78
	$\text{HCO}_3^-$	2.6	100	14	0	0.88
July B 1990	$\text{Ca}^{2+}$	1.5	130	9	5	0.83
	$\text{HCO}_3^-$	1.7	150	18	1	0.97
August 1989	$\text{Ca}^{2+}$	1.4	150	14	1	0.91
	$\text{HCO}_3^-$	1.1	210	13	1	0.92
August A 1990	$\text{Ca}^{2+}$	1.6	150	11	1	0.96
	$\text{HCO}_3^-$	0.71	240	13	0	0.72
August B 1990	$\text{Ca}^{2+}$	1.6	140	15	0	0.84
	$\text{HCO}_3^-$	0.58	250	15	0	0.63

Tranter & Raiswell (1991) devised a method for determining the composition of quickflow. The method assumed that  $\text{SO}_4^{2-}$  was absent from quickflow. This assumption was based on field observations (Tranter & Raiswell, 1991; Brown, 1991) and consideration of the likely weathering reactions which occurred along different flowpaths (Tranter *et al.*, in press). Further evidence for quickflow containing "zero sulfate" was provided by laboratory dissolution experiments. Most major ion concentrations exhibited a strong linear association with  $\text{SO}_4^{2-}$  concentration. The intercept of the linear regression of an ion concentration on  $\text{SO}_4^{2-}$  defined the concentration of that ion in quickflow.

The intercept and slope of the linear regression of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations on  $\text{SO}_4^{2-}$  concentrations are listed in Table 2. Some data points (outliers) were rejected and excluded from the analysis based on the 95% confidence limits for the best fit relation. These outliers resulted from methodological artifacts or processes other than simple, two-component conservative mixing that was assumed to be operating at the time of sampling. The intercept defined the average composition of quickflow during each diurnal cycle, and results indicate that seasonal variation in the composition of quickflow occurred for both

ions. In general, the quickflow concentrations were highest in August, intermediate in July, and lowest in June. A similar analysis could have been presented for the other base cations ( $Mg^{2+}$ ,  $Na^+$ , and  $K^+$ ), but because their concentrations were low relative to  $Ca^{2+}$  (their sum was ~15% of the  $Ca^{2+}$ ), their intercepts were too uncertain.

As anticipated, the quickflow  $Ca^{2+}$  and  $HCO_3^-$  concentrations were highly correlated, which was expected because they were the dominant ions in quickflow. The linear regression on  $Ca^{2+}$  concentration on  $HCO_3^-$  was:

$$Ca^{2+} = 0.55 HCO_3^- + 27 \quad (r=0.92; n=9) \quad (1)$$

The regression relation indicates that  $Ca^{2+}$  was probably overestimated in the dilute quickflow and underestimated in the more-concentrated quickflow. An ideal relation would have had a slope of ~0.85, assuming that sum of the other base cations was 15% of  $Ca^{2+}$ , and an intercept of 0.0, assuming that  $Ca^{2+}$  concentrations decrease to zero as  $HCO_3^-$  concentrations decrease to zero. Hence, the quickflow values are more indicative of the seasonal trend than the actual concentrations.

A method was devised for determining the composition of delayed flow and was based on the dilution characteristics of two ions over several hydrographs. The method assumed that the composition of delayed flow was relatively constant, whereas the composition of quickflow varied between different hydrological events. For each event, however, the composition of the two components was assumed to remain constant during the event. A linear relation between the concentration of the two ions was computed for each event. For example, the linear relation for the concentrations of  $Ca^{2+}$  and  $SO_4^{2-}$  was of the form:

$$Ca^{2+} = M_i SO_4^{2-} + I_i \quad (2)$$

where  $M_i$  and  $I_i$  are the best fit linear regression slope and intercept for event  $i$ , respectively.

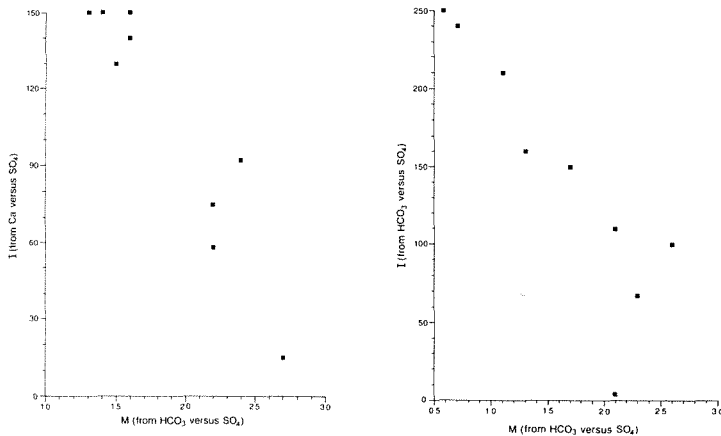


FIG. 3 Determination of the delayed flow  $Ca^{2+}$ ,  $HCO_3^-$ , and  $SO_4^{2-}$  concentrations. Best fit equations are: -a)  $Ca^{2+}: I = -92 * M + 279$  ( $r = -0.94$ ;  $n = 9$ ) and b)  $HCO_3^-: I = -100 * M + 304$  ( $r = -0.88$ ;  $n = 9$ )

A linear regression relation, therefore, could be obtained for each of several events and the equations would be common with respect to the delayed flow component as follows:

$$\text{Ca}^{2+} (\text{delayed flow}) = M_n \text{SO}_4^{2-} (\text{delayed flow}) + I_n \quad (3)$$

where  $\text{Ca}^{2+}$  (delayed flow) and  $\text{SO}_4^{2-}$  (delayed flow) are the  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations of the delayed flow, and  $n$  denotes the number of the event. Provided a linear relation exists between  $I$  and  $M$  for all events, the intercept of this relation would be the delayed flow  $\text{Ca}^{2+}$  concentration and the negative slope the delayed flow  $\text{SO}_4^{2-}$  concentration.

The linear regression relation of each individual diurnal cycle can be used to determine the composition of delayed flow in the glacial runoff. The intercept of the linear relations for  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations were graphed against the corresponding slopes (see Table 2) in Figs. 3a and 3b, respectively, and a linear relation was clearly evident. The intercept of the best fit line provided an estimate of the concentration of  $\text{Ca}^{2+}$  or  $\text{HCO}_3^-$  in the delayed flow, and the slope provided an estimate of  $\text{SO}_4^{2-}$  in the delayed flow. The  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations of delayed flow were  $279 (\pm 25)$  and  $304 (\pm 36) \mu\text{eq l}^{-1}$ , respectively. The estimated  $\text{SO}_4^{2-}$  concentration of delayed flow from the two relations agreed quite well; the  $\text{SO}_4^{2-}$  concentration of delayed flow was  $92 (\pm 13) \mu\text{eq l}^{-1}$  for the  $\text{Ca}^{2+}$  relation (Fig. 3a) and  $100 (\pm 20) \mu\text{eq l}^{-1}$  for the  $\text{HCO}_3^-$  relation (Fig. 3b).

For the first time, this method enabled the glacial hydrograph to be separated with some confidence, based on the following assumptions: a) the  $\text{SO}_4^{2-}$  content of quickflow was zero; b)  $\text{SO}_4^{2-}$  was not liberated from post-mixing reactions; c) the delayed flow concentrations of  $\text{SO}_4^{2-}$  and other major ions remained relatively constant throughout the ablation season; and d) the composition of quickflow remained constant during diurnal cycles. Hence, the proportion of delayed flow in runoff, after Collins (1978), was:

$$Q_d / Q_t = (\text{SO}_4^{2-})_t / (\text{SO}_4^{2-})_d \quad (4)$$

where  $Q$  is discharge,  $t$  is total or bulk runoff, and  $d$  is delayed flow.

These assumptions should be scrutinized closely in future studies, because hydrograph separation which resulted from this method may conflict with those of dye return studies at the same site. The proportion of delayed flow in runoff draining the Haut Glacier d'Arolla during the 1989 ablation season, based on  $\text{SO}_4^{2-}$  data from Brown (1991) and the mean of

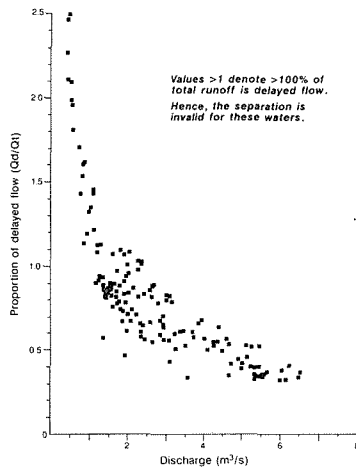


FIG. 4 The relation between the proportion of delayed flow in total runoff and the magnitude of runoff.

the delayed flow  $\text{SO}_4^{2-}$  values presented above, are shown in Fig. 4. The method did not produce a meaningful hydrograph separation early in the ablation season ( $Q < 1.6 \text{ m}^3 \text{ s}^{-1}$ ), when only a distributed drainage system was in operation. Later in the ablation season, when runoff peaked, much of the subglacial drainage was expected to consist of quickflow, but the hydrograph separation method estimated a high proportion (~30-40%) of delayed flow (Fig. 5). Hence, effort needs to be directed toward resolving this apparent discrepancy.

## DISCUSSION

Our interest in determining the composition of the two major components of alpine glacial meltwaters stems from a desire to perform a meaningful two component hydrograph separation. We believe that post-mixing chemical reactions modify the composition of bulk meltwaters, so that if water chemistry is to be used to separate the hydrograph, the additional solute must be apportioned to either or both components. The simplest solution is to apportion the solute to only one of the components. Tranter *et al.* (in press) constructed a conceptual model of solute acquisition by meltwaters that distinguished the dominant reactions to be carbonate dissolution and sulfide oxidation in the distributed system and carbonation in basal arterial channels. We built on this model, by assuming that  $\text{SO}_4^{2-}$  was liberated from the distributed system only, and that all post-mixing solute acquisition in basal arterial channels was apportioned to the quickflow component (which is a tacit assumption of the Tranter & Raiswell (1991) method of determining the composition of quickflow).

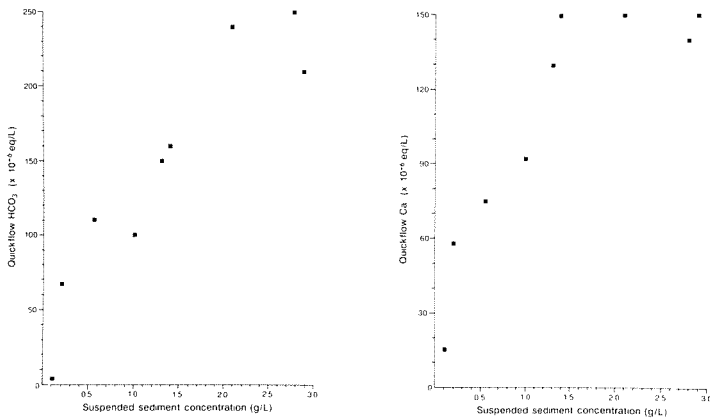
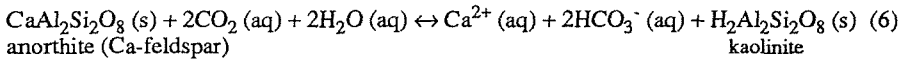
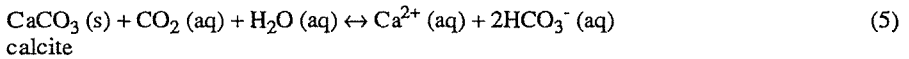


FIG. 5 The relation between the concentration of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  in quickflow and the average suspended sediment concentration during the diurnal cycle.

Quickflow was derived largely from icemelt, which is routed rapidly through ice-walled englacial conduits, and had only limited contact with sediment. Hence, quickflow in englacial channels maintained the composition of icemelt, and was extremely dilute. High sediment concentrations were encountered only after the quickflow mixed with the delayed flow at the bed of the glacier. The composition of quickflow was then fixed by carbonation reactions in the large arterial channels at the glacier bed (Tranter *et al.*, in press). The carbonation reactions were broadly as follows:





The common feature of these reactions is that dissolved  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (i.e. carbonic acid) dissolve rock minerals to give rise to base cations and bicarbonate ions in solution. The base cation most commonly liberated during chemical weathering reactions is  $\text{Ca}^{2+}$ , since carbonates, such as calcite, have rapid dissolution kinetics, and because silicates and aluminosilicates which contain several different base cations, such as feldspars, usually release  $\text{Ca}^{2+}$  most rapidly (Lerman, 1979). This preferential release makes  $\text{Ca}^{2+}$  the dominant cation in alpine glacial meltwaters (Raiswell, 1984), and in most freshwaters (Holland, 1978).

Tranter & Raiswell (1991) showed that the composition of quickflow was dominated by  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , supporting the hypothesis that carbonation reactions cause a preferential release of  $\text{Ca}^{2+}$  and control the composition of quickflow. A full derivation of quickflow composition from these data would present a similar result, and the chemical characteristics of quickflow also were reproduced in simple laboratory dissolution experiments using rock flour derived from runoff from the Haut Glacier d'Arolla. The  $\text{HCO}_3^-$  concentrations estimated for quickflow during August (210-250  $\mu\text{eq l}^{-1}$ ) were similar to that of delayed flow (304  $\mu\text{eq l}^{-1}$ ), whereas quickflow concentrations of  $\text{HCO}_3^-$  were lower in the early ablation season (4.3-160  $\mu\text{eq l}^{-1}$ ). A similar argument could be constructed for the major base cations. Hence, although concentrations of certain ions in quickflow and delayed flow may have deviated at the beginning of the ablation season, their concentrations converged as the season progressed.

Although the composition of quickflow was controlled by factors such as the type and concentration of suspended sediment, the duration of rock-water contact, and the relatively rapid transfer of atmospheric  $\text{CO}_2$  (Tranter *et al.*, in press), suspended sediment concentrations may have been a major control of the quickflow composition at the Haut Glacier d'Arolla, particularly with the present transit times within the basal arterial channel (<3 h). Alpine glacial meltwaters may transport high suspended sediment concentrations during periods of sustained ablation, as a consequence of increased discharge and hydroglacial reorganization (Gurnell, 1987; Collins, 1989). As runoff increased from June through August, suspended sediment concentrations also generally increased (Table 1) and the mean suspended-sediment concentration varied diurnally (Fig. 2). The  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations of quickflow were highly correlated with the mean suspended sediment concentration (Fig. 5, Table 2). The simplest explanation of this linear association is that more suspended sediment increased the potential for carbonation, which produced a more concentrated quickflow. These results imply that the residence times of bulk meltwaters in the basal arterial channels were not so long that the major ions achieved equilibrium with any common mineral phase, such as calcite.

There are two subglacial drainage components for much of the ablation season, corresponding to  $Q > 2 \text{ m}^3 \text{ s}^{-1}$  on Fig. 4 (note that this value is not a critical or threshold value). The proportion of delayed flow in the runoff appears to be linearly related to the magnitude of the runoff during this period. The contribution of delayed flow to total flow decreased from 60-90% at runoff of  $\sim 2 \text{ m}^3 \text{ s}^{-1}$  to 30-40% at runoff of  $\sim 6 \text{ m}^3 \text{ s}^{-1}$ . Higher ablation rates, therefore, might be linked to higher recharge rates of both the distributed and the conduit systems, because the discharge of delayed flow may have increased from 1.2-1.8  $\text{m}^3 \text{ s}^{-1}$  at low flow to 1.8-2.4  $\text{m}^3 \text{ s}^{-1}$  at high flow. The distributed system progressively shrank during

the ablation season, hence the increased discharge of delayed flow must have been accompanied by higher velocities through the system and/or an increase in cross-sectional area of the residual, distributed system.

## CONCLUSIONS

Naturally occurring sulfate was used to trace waters draining the distributed system of an alpine glacier. A method of hydrograph separation of runoff into two components, quickflow and delayed flow, using solute concentrations was presented. Whereas quickflow is believed to vary in composition throughout the ablation season, delayed flow is assumed to be relatively constant. Glacial flour was more geochemically reactive than hitherto appreciated by water routing studies. Post-mixing reactions occurred when quickflow diluted delayed flow in basal arterial conduits. We assumed that the additional solute was apportioned to quickflow. The composition of quickflow, which approximated the composition of icemelt during transit through ice-walled conduits, was fixed in basal arterial channels by carbonation reactions. The magnitude of individual solute concentrations depended on factors such as the rock:water ratio, the duration of rock:water contact, and the availability of atmospheric CO<sub>2</sub>. Quickflow became increasingly concentrated during the ablation season, and the concentration increase was associated with increased suspended sediment concentrations in the total runoff. The proportion of quickflow was calculated to be 10-40% of runoff at low discharge early in the ablation season, and 60-70% of runoff at high discharge later in the ablation season.

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## REFERENCES

- Brown, G. H. (1991) Solute provenance and transport pathways in alpine glaciers. Unpublished Ph.D. thesis, University of Southampton.
- Collins, D. N. (1978) Hydrology of an alpine glacier as indicated by the chemical composition of meltwater. *Zeitschrift für Gletscherkunde und Glazialgeologie* **13**:219-238.
- Collins, D. N. (1979) Quantitative determination of the subglacial hydrology of two alpine glaciers. *J. Glaciol.* **23**:347-361.
- Collins, D. N. (1989) Seasonal development of subglacial drainage and suspended sediment delivery to melt waters beneath an alpine glacier. *Annals of Glaciol.* **13**:45-50.
- Drewry, D. (1986) Glacial geological processes. Edward Arnold.
- Gurnell, A. M. (1987) Suspended sediment. In: *Glacio-Fluvial Sediment Transfer: An Alpine Perspective*, A. M. Gurnell & M. J. Clark (eds.), John Wiley & Sons, Chichester, 305-354.
- Gurnell A. M., Brown, G. H. & Tranter, M. (in press) A sampling strategy to describe the temporal hydrochemical characteristics of an alpine proglacial stream. *Hydrol. Proc.*
- Holland, H. D. (1978) The chemistry of atmospheres and oceans. Wiley-Interscience.
- Lerman, A. (1979) Geochemical Processes Water and Sediment Environments. John Wiley & Sons, Chichester.
- Raiswell, R. (1984) Chemical models of solute acquisition in glacial meltwaters. *J. Glaciol.* **30**:49-57.
- Tranter, M. & Raiswell, R. (1991) The composition of the englacial and subglacial components in bulk meltwaters draining the Gornergletscher. *J. Glaciol.* **125**:59-66.
- Tranter, M., Brown, G. H., Raiswell, R., Sharp, M. J. & Gurnell, A. M. (in press) On solute acquisition by alpine glacial meltwaters. *J. Glaciol.*