The composition of the englacial and subglacial component in bulk meltwaters draining the Gornergletscher, Switzerland

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ABSTRACT. A new method of hydrograph separation for bulk meltwaters draining Alpine glaciers is proposed. It is based on the two-component (subglacial and englacial) mixing model of Collins (1978), but allows the composition of the subglacial component to vary between ascending and descending lines of the hydrograph. The mean englacial component can be derived from linear relationships between sulphate concentrations and other ions in bulk meltwaters. On certain occasions during the ablation season, the maximum concentration of ions in the subglacial component can be determined from the linear relationship between bulk meltwater sulphate concentrations and discharge. The bulk discharge is then a direct measure of the mass fraction of the englacial component. At maximum discharge, the contribution of the subglacial component approaches zero, which has implications for the storage and mixing of waters in subglacial reservoirs. Further, the subglacial component is not of constant composition, and may itself be a mixture of dilute supraglacial and concentrated subglacial water.

INTRODUCTION

Alpine glacial meltwaters exhibit diurnal, inverse relationships between discharge and total dissolved solids (or conductivity) during the ablation season (Collins, 1978). Each day, maximum concentrations of solute are found in meltwaters at low discharge, and, conversely, minimum concentrations are found at maximum discharge (see Fig. 1). The simplest model of melt-water hydrochemistry considers that the meltwaters issuing from the portal, *the bulk meltwaters*, consist of two components (Collins, 1978), although more complex models exist (e.g. Oerter and others, 1980). Here, we consider hydrograph separation based on the two-component mixing model, and begin by describing the components. The first, *the englacial component*, has a significant contribution of waters generated near the snout, which have a rapid transit through the hydroglacial system, largely in ice-walled channels. A proportion of englacial meltwaters is generated farther from the snout, and can be considered to be present in, or passing through, a longer-term, ice-walled reservoir. However, englacial waters are relatively dilute, because the suspended load is
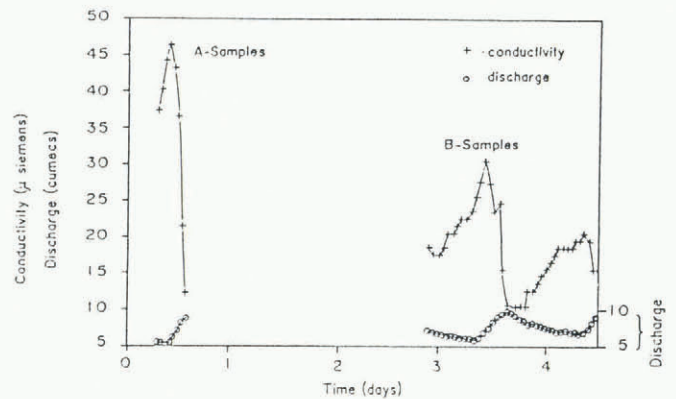

Fig. 1. Discharge and conductivity variations for the Gornera, the main stream draining Gornergletscher. (a) 16 September 1980; (b) 18–20 September 1980.

small and rock–water contact times are relatively short. Hence, the potential for solute acquisition is limited to rapid reactions such as surface exchange (Lerman, 1979). By contrast, the second, or *subglacial component*, is composed of waters, which have had a relatively slow transit through the hydrological system, are subglacially routed and have had at least some contact with till and/or the glacier bed or with debris-rich basal ice (Collins, 1978). Subglacial waters are relatively concentrated because rock–water contact times are long, allowing solute acquisition both by

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surface exchange and slower dissolution of glacial flour. Bulk meltwaters are believed to form by the mixing of these two components in conduits in the near-snout region.

Hydrograph separation has been performed by assigning conductivity values to each of the components (Collins, 1978, 1979a). The conductivity of the englacial component is set at the minimum recorded conductivity of the bulk meltwaters or that of supraglacial streams, while that of the subglacial component is set at the maximum recorded conductivity. This pragmatic method has two main weaknesses. It is assumed that neither component exhibits any temporal variation in chemical composition and that no post-mixing chemical evolution of meltwaters occurs. However, it is likely that each component will demonstrate some temporal variation during the course of the ablation season (e.g. due to the development of different hydrological routings) and that post-mixing chemical evolution will occur when relatively reactive sediment is transported into and through the mixing environment (Raiswell and Thomas, 1984; Tranter and others, 1989).

Here, we examine the characteristics of bulk meltwater chemistry with the aim of achieving a unique hydrograph separation over a short time-scale. Information is presented from the late ablation season, where the seasonal maximum and minimum conductivity values may not be representative of the true composition of the components.

METHODOLOGY

Study area

The catchment of the Gornergletscher is located in canton Wallis, Switzerland. It has been the subject of several studies of the composition of glacial meltwater (Collins, 1978, 1979a, b, c). Approximately 80% of the 82 km^2 catchment is glacierized. The lithology of the catchment is diverse, and consists of gneiss, mica-schist, gabbro and serpentine. Calcareous mica-schist and dolomite comprise 5% of the bedrock (Collins, 1979b).

Discharge

Discharge was obtained directly from the Grande Dixence gauging station, located approximately 1 km downstream from the snout. The accuracy of the discharge measurements is $\pm 10\%$ (personal communication from D.N. Collins).

Conductivity measurement

All bulk meltwater samples of approximately 1 litre were collected near to the gauging station from a mid-channel location. Conductivity was determined on a 50 ml aliquot of unfiltered sample by use of a portable Hach Model 17250 mini-conductivity meter with a probe-type sensor. The instrument was calibrated with 0.005 M KCl (conductivity 780 μS cm^{-1} at 25°C). Automatic temperature compensation was employed.

Alkalinity

The alkalinity of a rapidly filtered 50 ml aliquot was performed by titration with 4.0 mM HCl to an end point of pH 4.5, as determined by a mixed BDH indicator. The titration precision was ± 0.03 cm^3 over a range of titres from 1.50 to 3.00 cm^3.

Cations and other anions

A 100 ml aliquot of filtered solution was stored in pre-cleaned plastic bottles and acidified with 1.0 cm^3 of
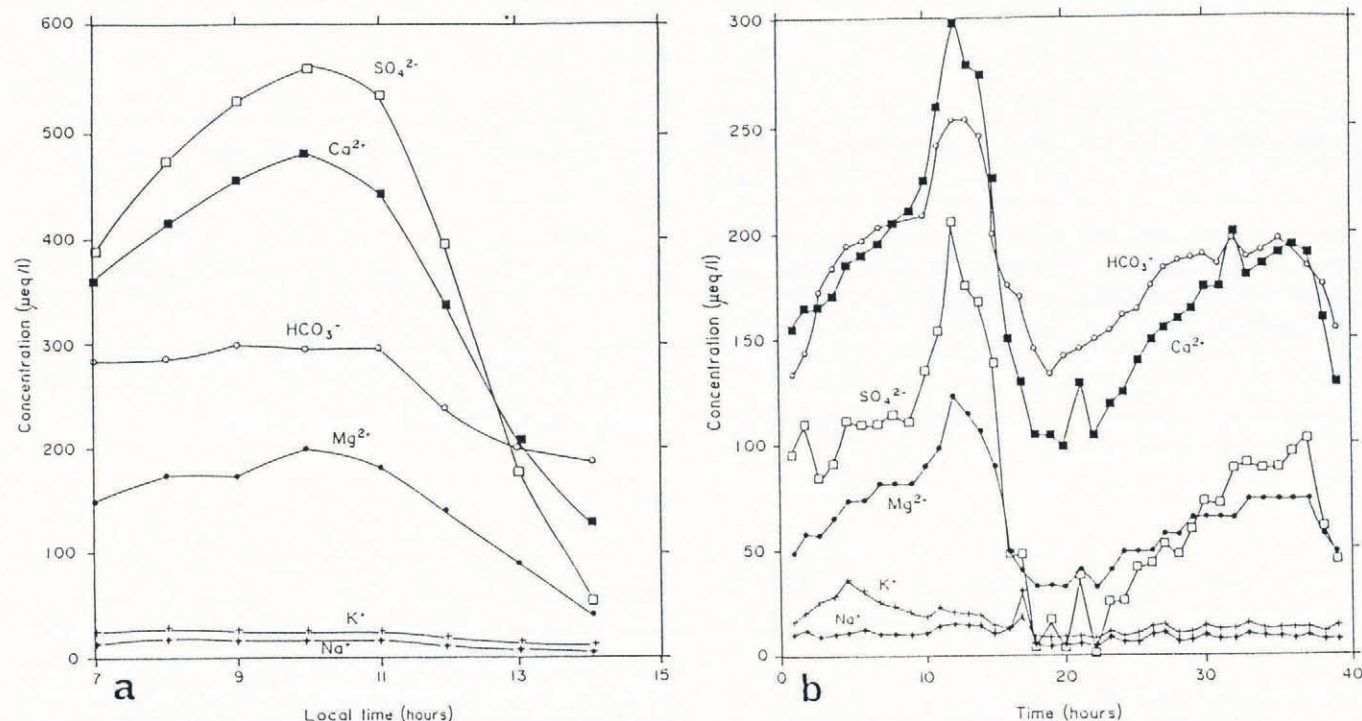

Fig. 2. Variation in meltwater chemistry. (a) 16 September (A samples); (b) 18–20 September (B samples). Note that sulphate concentrations for the B samples are estimated from the charge-balance deficit (see Appendix).

conc. HCl. A similar volume of acidified solution was stored and used for anion analysis.

Base cations were determined by atomic adsorption spectrophotometry on a Pye-Unicam SP9. Detection limits were: Ca^{2+}, $1\,\mu eq.\,l^{-1}$; Mg^{2+}, $0.3\,\mu eq.\,l^{-1}$; K^{+}, $0.3\,\mu eq.\,l^{-1}$; and Na^{+}, $0.4\,\mu eq.\,l^{-1}$. Precision was $\pm 4\%$ ($\pm 10\%$ for Na^{+}). Sulphate and chloride were determined by ion chromatography on a Dionex Model 12 Ion Chromatograph, or were estimated from charge-balance errors (see Appendix). Detection limits were $2\,\mu eq.\,l^{-1}$ for SO_4^{2-} and NO_3^{-}, and $0.3\,\mu eq.\,l^{-1}$ for Cl^{-}. Precision was $\pm 5\%$.

RESULTS

Two suites of samples, hereafter referred to as the A and B samples, were collected on 16 September and 18–20 September 1980, respectively. Sulphate analyses are only available for the A samples. Discharge and conductivity curves from the two sampling periods are shown in Figure 1. Discharge varies from 5.4 to $9.2\,m^3\,s^{-1}$, and conductivity from 10 to $48\,\mu S\,cm^{-1}$.

The temporal variation of the chemical compositon of the meltwaters is shown in Figure 2. The cations are dominated by calcium and magnesium. The anions are dominated by bicarbonate and sulphate. The molar ratio

Table 1

Correlation matrix for the A samples (n = 8)

	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}
Ca^{2+}	1.000	0.991	0.970	0.975	0.966	0.997
Mg^{2+}		1.000	0.962	0.954	0.948	0.991
Na^+			1.000	0.980	0.976	0.960
K^+				1.000	0.985	0.946
HCO_3^-					1.000	0.950
SO_4^{2-}						1.000

Critical value of R is 0.905 (0.1%).

Correlation matrix for the B samples (n = 39)

	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}
Ca^{2+}	1.000	0.985	0.395	0.505	0.939	0.965
Mg^{2+}		1.000	0.361	0.521	0.942	0.953
Na^+			1.000	0.485	0.420	0.455
K^+				1.000	0.474	0.632
HCO_3^-					1.000	0.530
SO_4^{2-}						1.000

Critical value of R is 0.480 (0.1%).

N.B. Sulphate concentrations were determined from charge-balance errors (see Appendix).

of SO_4^{2-} : HCO_3^- in the more dilute meltwaters is 1 : 3.3, while the ratio in more concentrated meltwaters approaches 1.9 : 1. Nitrate and chloride were detected, but only in small concentrations ($< 2\,\mu eq.\,l^{-1}$).

All major ion concentrations (Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-}) are well correlated (Table 1).

THE COMPOSITION OF THE ENGLACIAL AND SUB-GLACIAL COMPONENTS AND HYDROGRAPH SEPARATION OF THE BULK MELTWATERS

Bulk meltwaters can be considered to be derived from the mixing of at least two components (Collins and Young, 1981). Here, we assume that there are only two components, the englacial and subglacial components, whose conservative mixing requires that

$$Q_b C_b^{\,i} = Q_e C_e^{\,i} + Q_s C_s^{\,i} \qquad (1)$$

where Q represents the water discharge and C is the concentration of species i. Subscripts b, e and s denote the bulk, englacial and subglacial components, respectively.

Continuity of flow requires that

$$Q_b = Q_e + Q_s. \qquad (2)$$

Combining Equations (1) and (2) gives the following expression:

$$Q_e = Q_b (C_s^{\,i} - C_b^{\,i})/(C_s^{\,i} - C_e^{\,i}). \qquad (3)$$

Equation (3) illustrates that four parameters must be determined to perform a hydrograph separation. Of these, only two, Q_b and $C_b^{\,i}$ are routinely measured. Hence, the other two parameters, $C_e^{\,i}$ and $C_s^{\,i}$, need to be evaluated by independent means. The usual method is to equate $C_e^{\,i}$ and $C_s^{\,i}$ with the minimum and maximum conductivity values recorded during the sampling season (Collins, 1978, 1979b). As noted earlier, this pragmatic approach has a major weakness because the composition of either or both components may vary throughout the season.

The chemistry of the Gornergletscher bulk meltwaters allows the determination of $C_e^{\,i}$ by a more rigorous method, which depends on the sulphate concentration of englacial waters being essentially zero during the late ablation season. There are two lines of evidence to support this view.

First, the sulphate concentration of supraglacial meltwaters collected during the sampling period is zero (see Table 3). This is consistent with sulphate being largely removed from snow and ice early in the ablation season. Data on sulphate concentrations in Alpine snow and ice are only sparsely available in the literature, but values are typically $< 20\,\mu eq./1$ (Psenner and Nickus, 1987; Delmas, 1989). Successive diurnal melting of snow and ice rapidly leaches most of the sulphate from the snow and ice crystals (Davies and others, 1987). Hence, later on in the season, the leached snow and ice gives rise to sulphate-depleted supraglacial meltwaters. Since supraglacial meltwaters evolve to form waters of the englacial component, the sulphate concentration of the englacial

component is likely to be negligible during all except the early melt season.

Secondly, Figure 2a shows that the sulphate concentration of the A samples approaches zero at maximum discharge (note that maximum discharge is not shown). This is also the case for the estimated sulphate concentrations of the B samples (see Fig. 2b). The data clearly indicate that the bulk sulphate concentration is close to zero at maximum discharge. Since the englacial component dominates at maximum discharge, it follows that the sulphate concentration of the englacial component must also be negligible. We will assume that the sulphate concentration of the englacial component is zero. Hence, sulphate is only found in the subglacial component, where it is formed by the oxidation of pyrite (Lerman, 1979). Pyrite is a ubiquitous mineral, being found in many sedimentary, metamorphic and igneous rocks. We therefore assume that sulphate is formed from the oxidation of pyrite throughout the subglacial hydrological system where freshly comminuted rock flour comes into contact with oxygenated meltwaters.

The regression equations of Table 2 now enable us to determine the composition of the englacial component. The concentration of any ion in the englacial component (C_e^i) is given by the regression constant, i.e. the value when sulphate concentrations are zero. It can be seen that the composition of the englacial component (Table 2) is that of a dilute bicarbonate solution, as would from the weathering of aluminosilicate, silicate and carbonate minerals by relatively pure water. The estimated cation concentration of the englacial component is somewhat larger than that measured in supraglacial meltwaters (see Table 3), probably because of post-mixing chemical evolution of bulk meltwaters (Raiswell and Thomas, 1984; Tranter and others, 1989).

Since sulphate is not found in significant concentrations in the englacial component at this stage of the ablation season, it acts as a marker for the subglacial component. Figure 3 shows a plot of bulk sulphate (A samples) and estimated sulphate concentrations (B samples, see Appendix) against discharge. It is apparent that the bulk sulphate concentration is linearly related to discharge, both for ascending and descending limbs of the hydrograph. The precise relationship may change between successive ascending and descending limbs of the hydrograph, since a number of straight-line relationships may be defined (see Fig. 3a and b). We note that for the A samples, there is some scatter of points around the minimum discharge. This phenomenon has been attributed to the flushing of subglacial waters by englacial waters at the onset of rising discharge (Collins, 1979a; Gurnell and Fenn, 1984).

Similar linear relationships between bulk sulphate and discharge have been observed in other Alpine glaciers, Les Bossons (see Fig. 4; from Tranter, 1982) and Upper Arolla (Brown and Tranter, 1990). Hence, on occasion, the linear relationship between sulphate and discharge may also be common to other Alpine glaciers.

Two component-mixing relationships are normally plotted with the independent variable representing the *mass fraction* of one of the components. The composition of each component or end member is defined when the mass fraction is 0 and 1, respectively. The interpretation of

Table 2. Regression equations for the relationship between bulk meltwater sulphate concentrations and other ions (units: $\mu eq.\ l^{-1}$)

Regression equations for the A samples (n = 8)

$$(Ca^{2+}) = 0.68\ (SO_4^{2-}) + 86$$
$$(Mg^{2+}) = 0.28\ (SO_4^{2-}) + 32$$
$$(K^+) = 0.032\ (SO_4^{2-}) + 5.6$$
$$(Na^+) = 0.027\ (SO_4^{2-}) + 2.3$$
$$(HCO_3^- = 0.24\ (SO_4^{2-}) + 170$$

Regression equations for the B samples (n = 39)

$$(Ca^{2+}) = 0.96\ (SO_4^{2-}) + 96$$
$$(Mg^{2+}) = 0.44\ (SO_4^{2-}) + 29$$
$$(HCO_3^-) = 0.27\ (SO_4^{2-}) + 160$$

The englacial component is defined by the regression constants (see text for details).

Table 3. The range in composition of supraglacial meltwaters (units: $\mu eq.\ l^{-1}$)

Ca^{2+}	14–44
Mg^{2+}	0–17
K^+	0–4
Na^+	0–3
HCO_3^-	36–72
SO_4^{2-}	<0.01

The number of samples is eight, but only the most concentrated sample was analysed for sulphate. Charge-balance calculations imply that sulphate concentrations in the other samples should be near zero.

Figure 3 is obscured because the independent variable, Q_b, is not obviously related to the mass fraction of the englacial component, defined as Q_e/Q_b. It will be demonstrated that this is the case if there is a linear relationship between bulk sulphate and discharge.

For sulphate, assuming $C_e^s = 0$; Equation (3) can be rewritten as follows:

$$Q_e/Q_b = (C_s^s - C_b^s)/C_s^s \tag{4}$$

where the superscript s denotes sulphate. There is a linear relationship between bulk sulphate and discharge. Hence,

$$C_b^s = mQ_b + c \tag{5}$$

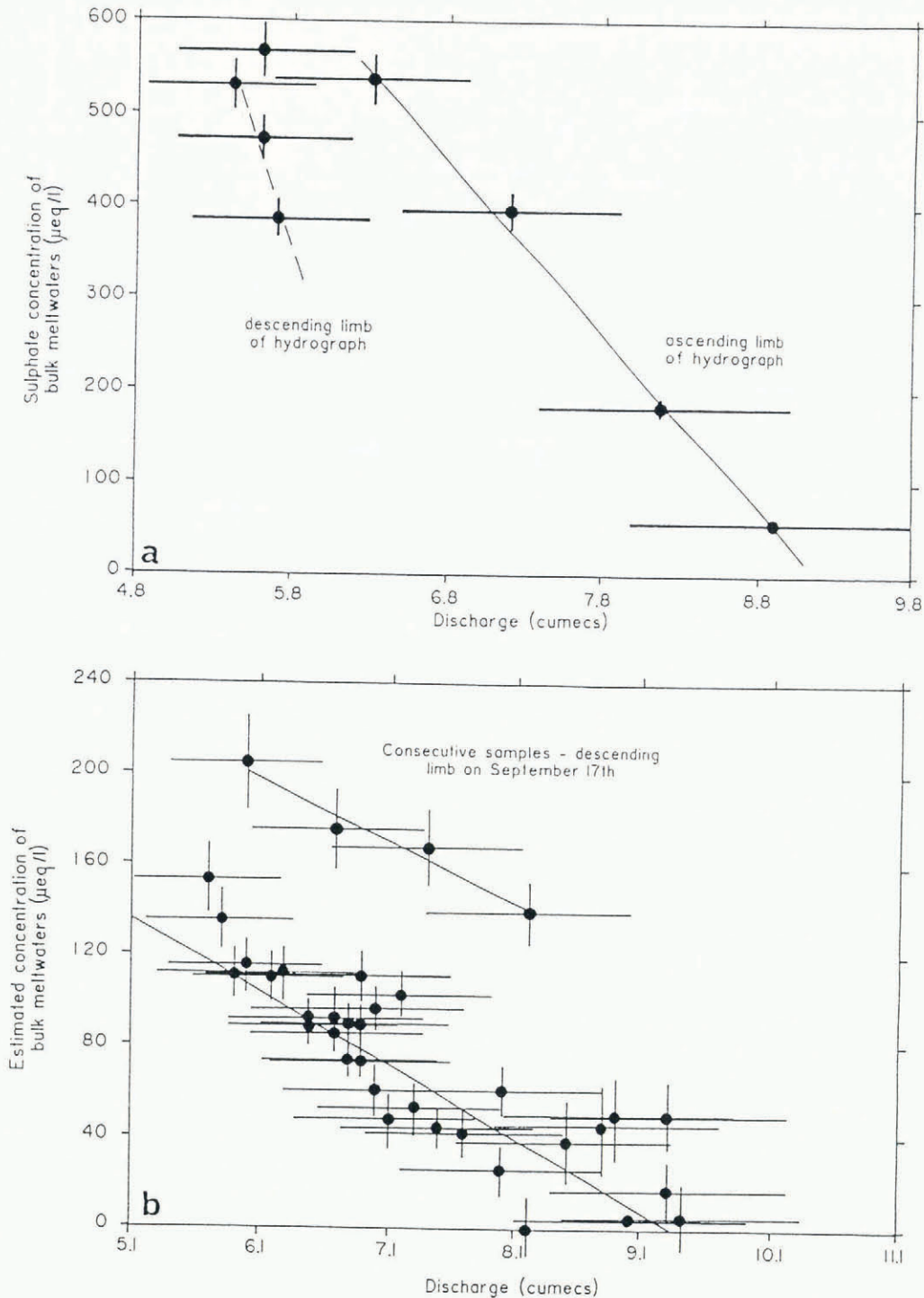where m and c are constants.

Fig. 3. (a) A samples. Measured sulphate concentration versus discharge. The ascending limb of the hydrograph follows the linear relationship: $SO_4^{2-} = -190Q_b + 1700$ $(R = -0.998; n = 4)$. We are not confident of the trend defined by the four points on the descending limb of the hydrograph. (b) B samples. Sulphate concentrations, estimated from the charge-balance deficit (see Appendix), versus discharge.
Two distinct linear trends are evident. The first is defined by four consecutive points on the ascending limb of the hydrograph on the morning of 17 September: $SO_4^{2-} = -28Q_b + 370$ $(R = -0.982; n = 4)$. The remainder of the data defines the following relationship: $SO_4^{2-} = -32Q_b + 300$ $(R = -0.872; n = 34)$. Both correlation coefficients are significant at 0.1%.

Hence, combining Equations (4) and (5) gives

$$Q_c/Q_b = 1 - (c/C_s^s) - (m/C_s^s)Q_b. \qquad (6)$$

On the righthand side of Equation (6), only Q_b is a variable. Hence, *the bulk discharge, Q_b, is a simple measure of the mass fraction of the englacial component in the bulk discharge.*

The subglacial component is defined when the mass fraction of the englacial component is zero, that is, when the lefthand side of Equation (6) is zero. Examination of Equation (6) reveals that the *maximum* concentration of sulphate in the subglacial component is c, the regression constant from the linear bulk sulphate versus bulk discharge relationship, since by setting the mass fraction
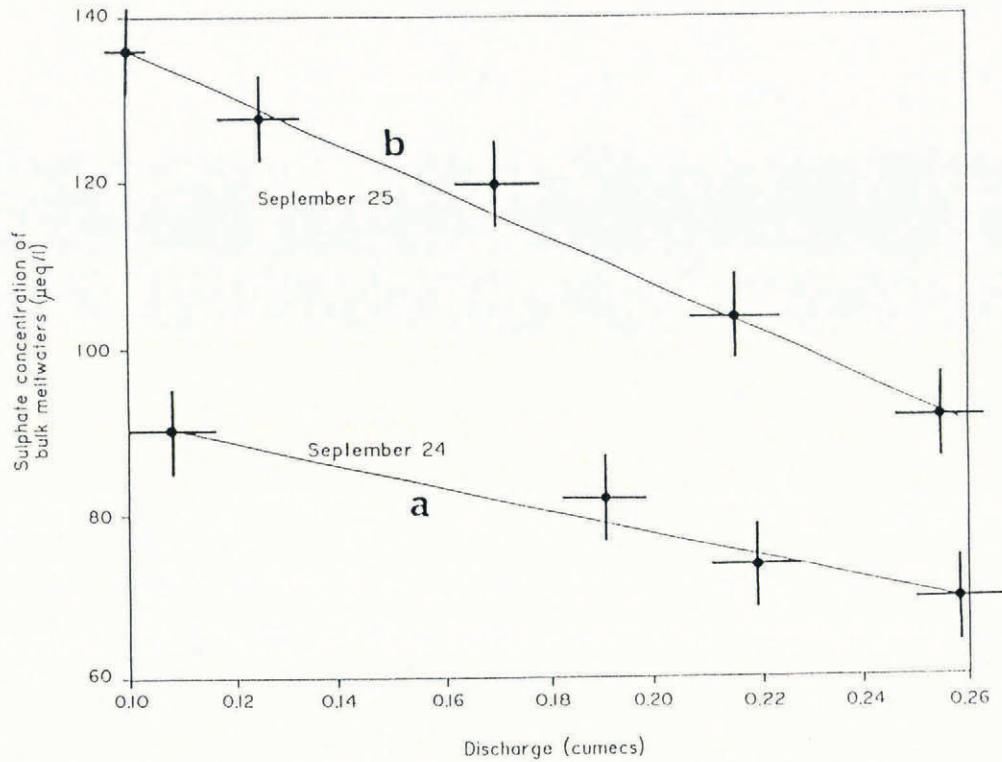
Fig. 4. *The relationship between sulphate and discharge (ascending limb of the hydrograph) in the main stream draining Les Bossons. (a) 24 September 1981. The four points on the ascending limb of the hydrograph define the following expression: $SO_4^{2-} = -140Q_b + 110$ (R = -0.986; n = 4). (b) 25 September 1981. The five points on the ascending limb of the hydrograph define the following expression: $SO_4^{2-} = -290Q_b + 170$ (R = -0.995; n = 5). Both correlation coefficients are significant at 0.1%.*

of the englacial component to zero, C_s^s is a maximum when Q_b is zero (Q_b cannot be a negative number).

The following calculations and discussion are based on the assumption that the composition of the subglacial component is set at the maximum permissible value, c. Calculated discharge of the subglacial component will therefore be a minimum estimate.

Table 4 gives the composition of the subglacial component. The sulphate concentrations were derived

Table 4. *Composition of the subglacial component (units: μeq. l^{-1})*

	A samples		B samples
		Morning, 17 September	All other times
Ca^{2+}	1200	450	400
Mg^{2+}	510	190	170
K^+	60	*	*
Na^+	48	*	*
HCO_3^-	850	260	250
SO_4^{2-}	1700	370	320

*Correlation coefficients are such that these concentrations cannot be determined with certitude.

from the linear bulk discharge–sulphate relationships defined in Figure 3. Given these sulphate concentrations, the regression equations in Table 2 were used to determine the cation and bicarbonate concentrations. Because the major ions are well correlated, apportionment of the other ions between the two components based on sulphate concentrations in the subglacial component leads to observed and calculated masses of ions in the bulk meltwaters being nearly identical. Figure 5 shows the hydrograph separation derived from Equations (3) and (4), based on the sulphate concentrations in Table 4.

DISCUSSION

The above method of hydrograph separation produces results which are similar to the conductivity-based separation of Collins (1979b). The proportion of the subglacial component decreases from 30 to 50% at minimum discharge to near zero at maximum discharge. A refinement of the present method is that the assumption of constant composition throughout the ablation season can be partially tested. On different days, a new mixing line may be defined (see Fig. 3b). If the same method is applied to Les Bossons bulk meltwaters, the subglacial sulphate concentration changes from 110 to 170 μeq./l on consecutive days (see Fig. 4). Apart from the poorly defined mixing line for the ascending limb, shown in Figure 3a, the other mixing lines do not intercept at low bulk discharge. Hence, even though we calculate maximum compositions, the composition of the subglacial component must have changed.
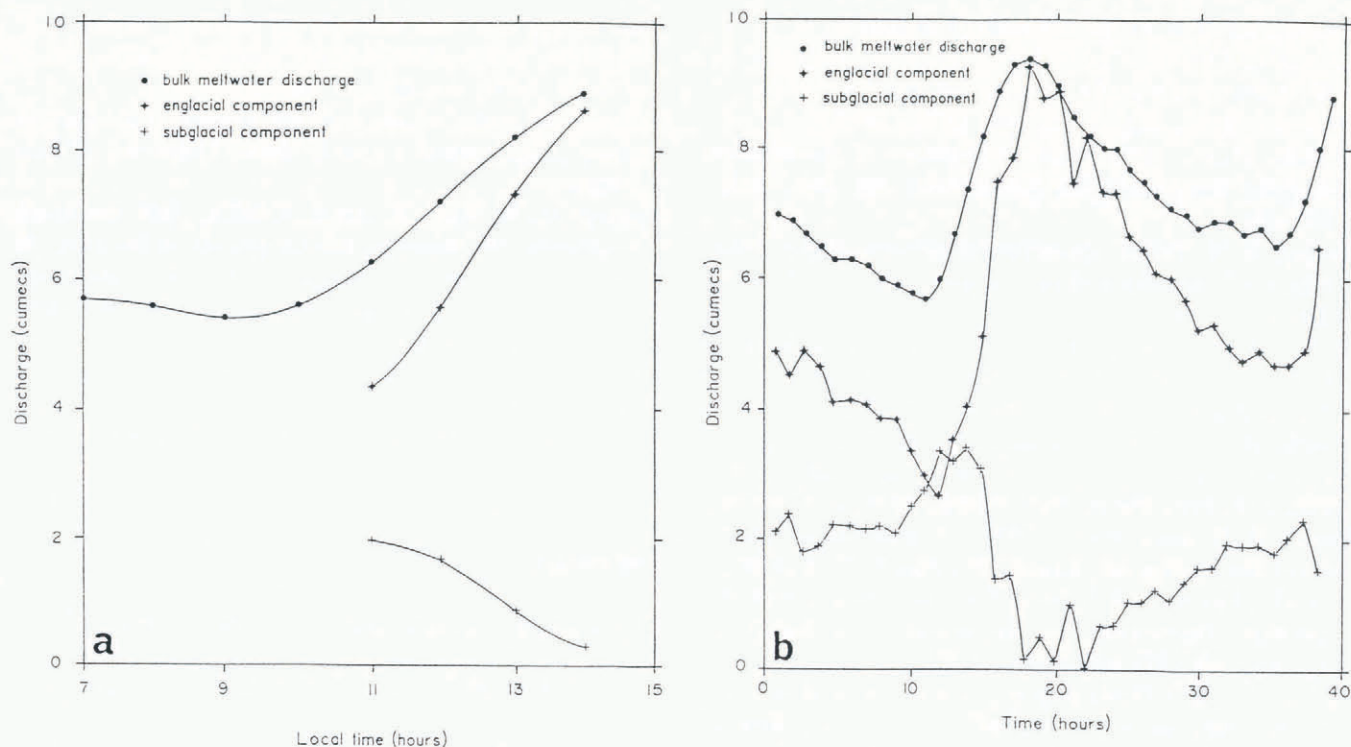
Fig. 5. Hydrograph separation of bulk meltwaters draining Gornergletscher. (a) 16 September 1980 (A samples);
(b) 18–20 September 1980 (B samples).

For the Gornergletscher, the composition of the subglacial component may remain constant during successive descending and ascending limbs of the hydrograph (see the main mixing line defined in Figure 3b). However, Figures 3b and 4 show that significant changes in the concentration of the subglacial component may occur between consecutive ascending and descending limbs of the hydrograph, and between consecutive ascending limbs.

This rather stepwise variability in the composition of the subglacial component, alternating between periods of relatively constant composition and times of relatively large change, has important implications. Methods of hydrograph separation which rely on the composition of the subglacial component remaining constant throughout the melt season will clearly be in error on occasions. The stepwise variability suggests that the composition of subglacial waters is controlled by physical, rather than chemical, processes, since the latter impart chemical inertia to the system as concentration increases. Rather like the composition of bulk meltwaters is determined by the mixing of concentrated and dilute components, the composition of the subglacial component may be controlled by similar mixing processes. This hypothesis requires the transfer of concentrated and dilute meltwaters between subglacial reservoirs at specific times during the diurnal discharge cycle. However, it seems premature to speculate further on the dynamic controls on the composition of the subglacial component given the limited data set presented here.

CONCLUSIONS

A new method of separating the hydrograph of the

Gornergletscher into englacial and subglacial components has been presented. The englacial component is found to be dilute, but more concentrated than supraglacial meltwaters. This suggests that post-mixing chemical weathering reactions lead to the acquisition of cations and bicarbonate. The subglacial component is concentrated and may remain essentially constant over much of the ascending and descending limb of the diurnal hydrograph. The proportion of the subglacial component approaches zero at maximum discharge, and approximately 50% at minimum discharge. However, the composition of the subglacial component may vary between consecutive ascending limbs, and between consecutive ascending and descending limbs. This stepwise change in composition suggests that the subglacial component could itself be a mixture of concentrated and dilute waters, and that extension of the simple two-component mixing model is necessary (e.g. Oerter and others, 1980).

ACKNOWLEDGEMENTS

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The accuracy of references in the text and in this list is the responsibility of the authors, to whom queries should be addressed.

APPENDIX

The following expression was used to define $(SO_4^{2-})^*$:

$$(SO_4^{2-})^* = (H^+) + (Ca^{2+}) + (Mg^{2+}) + (Na^+)$$
$$+ (K^+) - (HCO_3^-) - (OH^-) \qquad (A1)$$

Concentration is expressed in units of equivalents. The calculation of $(SO_4^{2-})^*$ can be checked by comparing estimated against real values for the A samples. The best-fit regression equation is $(SO_4^{2-})^* = 0.79(SO_4^{2-}) - 41$; $R = 0.997$; $n = 7$. This implies that the method of estimation is accurate, but that cation concentrations are underestimated. The underestimation of cations in glacial meltwater samples is likely to be a common problem because matrices of samples and standards are often not matched, and is addressed in detail by Brown and Tranter (paper in preparation). The fact that the cations are underestimated does not detract from the conclusions reached in this paper, although the precise concentration of cations in each component is likely to be underestimated by up to 20%.