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Dissolution Kinetics, Transit Times Through Subglacial Hydrological Pathways and Diurnal Variations of Solute Content of Meltwaters Draining From an Alpine Glacier

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ABSTRACT

Experimental results are reported for dissolved solids concentration increase when clear meltwaters from the surface of an Alpine glacier were reacted with suspended sediment derived from the subsole. The experiments, at Findelengletscher, Switzerland, were conducted at temperatures of about 1° C. Rates of reaction, which decrease through time as solute content rises, were slower in meltwaters which had not been allowed to equilibrate with the atmosphere before sediment was added. Diurnal variations in transit times of meltwater from the surface to the glacier portal were derived from injections of rhodamine dye into large moulin-conduit systems. Experimentally-determined rates of increase of electrical conductivity were used together with observed transit times in a Lagrangian formulation. This model was used to assess the contributions of rate of reaction and flow-through velocity to production of observed variations of solute concentration with portal meltwater discharge. The observed diurnal concentrations varied inversely but in phase with portal discharge. Diurnal variations in discharge through such moulin-conduit systems lead to substantial changes in flow-through velocity, altering the periods of time available for parcels of meltwater to react with basally-entrained suspended sediment en route to the portal. Hence, there is considerable variability in the amount of solute acquired by meltwaters in transit. A diurnal pattern of solute concentration variation with discharge is generated by the model, although absolute levels of solute concentration are underestimated. Parcels of meltwaters flowing more slowly, having entered the glacier down small cracks, crevasses and tiny moulins, acquire larger concentrations of solute during longer transit times. These waters, which cumulatively account for a significant proportion of total discharge, mix with those traversing moulin-conduit systems and presumably raise the overall solute content of the total discharge from Findelengletscher to the measured levels.

Key words: Glacier hydrology, meltwater, solute concentration, dissolution kinetics.

INTRODUCTION

During the ablation season, rhythmic diurnal variations of meltwater discharge from portals of alpine glaciers, arising from daily ablation of snow and ice on the glacier surface, are accompanied by roughly phased but inverse fluctuations in meltwater solute concentration (e.g. Collins 1979a). Serrated daily peaks of discharge are superimposed on a more gently undulating background flow suggesting that whilst a sizable fraction of the meltwater may spend more than 12h in transit from the area of production on the surface, through the internal hydrological system of the glacier to the portal, other meltwaters run off rapidly within a few hours of production. The subglacial pathways provide unequal opportunity for solute acquisition by parcels of meltwater. Evidently, in July and August, most of the meltwater arising from the melting of bare ice exposed to ablation descends rapidly to the glacier

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subsole through moulins. Considerable quantities of suspended sediment are entrained from channel margins throughout the length of flow pathways, and transported to the terminus. Plausible models of meltwater flow and solute acquisition within subglacial pathways are needed to explain the diurnal variation of solute concentration of portal meltwaters. These concentrations are considerably higher than those of surface melt (e.g. Collins 1979b). Implicitly, such models are essentially based on reaction kinetics, in that the longer the period of time a parcel of meltwater is in contact with suspended sediment (either in transit in the basal drainage system or during percolation through basal sediment), the greater the potential for chemical weathering reactions to raise the solute content (Collins 1979a, Tranter *et al.* 1993).

Substantial diurnal variations in transit (or residence) time for meltwaters descending from moulins and presumably flowing through basal arterial conduits have been demonstrated by dye-tracer tests in alpine glaciers, with 3-fold increases in flow-through velocity resulting from doubling of discharges (e.g. Collins 1982, 1995a). Parcels of meltwater following the same pathway to the portal at different times will presumably differentially acquire solute according to the inverse variation of transit time with discharge. Diurnal variation of solute concentration in portal meltwaters with discharge might be expected to reflect the mixing of parcels of meltwater arriving at the same time but having followed all possible flowpaths, each parcel with a solute content appropriate to the length of time in transit from base of moulin to terminus. Hence diurnal variations of solute content will respond to changes through time in average flow-through velocity within the glacier of all the meltwaters originating from all moulins, and other inlets such as cracks and crevasses. The extent to which an aliquot of water evolves chemically en route to the terminus will depend therefore on the interaction of the rate of reaction with the length of time in contact with sediment through the basal hydrological pathway.

The aim of this paper is to describe diurnal variations of solute content of meltwaters with discharge at the portal of an Alpine glacier during the ice-melt dominated part of the ablation season (in late July, August and September). Diurnal variations in velocities of flow of meltwaters through moulin-conduit systems obtained from dye tracer tests are also described. Rates of chemical weathering of basally-derived sediment in meltwaters had to be determined experimentally. Transit times and weathering rates are combined in an attempt to model the interaction between dissolution kinetics and flow-through velocities. The objective is to ascertain whether the interaction is sufficient to account for the observed overall level and diurnal variation of solute content of portal meltwaters.

SOLUTE ACQUISITION BY MELTWATERS BENEATH GLACIERS

Chemical characteristics of meltwaters are altered by dissolution of and chemical reactions with gases and minerals along the flow path between the ice surface and the glacier portal. The solute content of surface meltwaters derived from ice is low, comparable with, or purer than, precipitation (Collins 1978). Ice-melt water contains little dissolved material since ions have been rejected from the solid during progressive recrystallisation of ice. Because gases in snow are compressed into bubbles during firnification to ice, and are subsequently largely lost to the atmosphere when bubbles in ice burst at the glacier surface during ablation, meltwater derived from glacier ice usually has dissolved gas contents lower than those which would arise from equilibration with the atmosphere (Berner *et al.* 1977). Some re-aeration of such meltwater will occur during flow over the surface, before descent into the glacier, and will continue during transit through basal passageways, except at times when levels of discharge are sufficient to fill the cross-sectional areas of passageways completely.

Subglacially, water composition is probably largely controlled by dissolution of carbonates and gypsum, and by the weathering of aluminosilicates, as in natural waters in general (e.g. Stumm & Morgan 1970, Morel & Hering 1993). According to Raiswell (1984), oxidation of pyrite could release protons, which might in turn react with other minerals. Each of these processes will have an individual rate of reaction. Freshly abraded, finely divided products of glacial erosion will react readily with meltwaters. Small quantities of meltwater will acquire solutes by percolating slowly through stored subglacial sediment. Considerable, if temporally-variable, concentrations of comminuted reactants are derived from channel margins along the entire

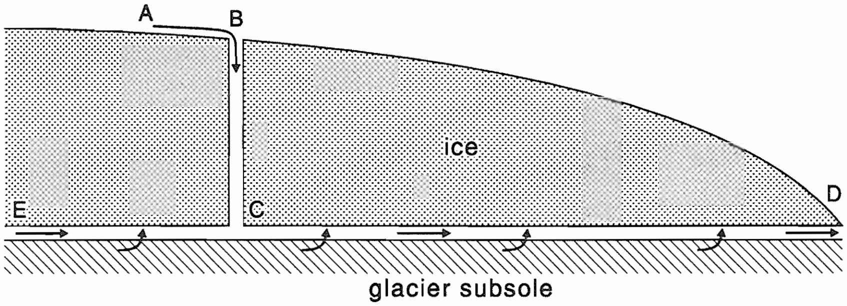

Figure 1. Schematic diagram of the basic unit of plumbing of the internal hydrological system of an alpine glacier.

length of basal hydrological pathways. These become suspended in meltwaters flowing through the network of interlinked subglacial cavities and conduits.

In the mid to late ablation season, much of the meltwater originating in the ablation zone flows a short distance across the ice surface in a supraglacial stream (AB in Fig. 1) before quickly descending a moulin (BC) to the glacier sole at C and reaching the portal (D) through a basal passageway. The glacier hydrological system consists of many such pathways ABCD, the basic unit of the plumbing. Between A and B gases are exchanged between atmosphere and meltwater. Sediment is entrained by parcels of water in transit from C to the portal and reactions between minerals and meltwater commence at C. Also, at C or between C and D, water from B may mix with meltwaters flowing from upglacier moulins (E) which already contain sediment and which will exhibit solute levels commensurate with the length of time in contact with minerals upstream. Some of this water will be from the snow-covered area and will have been delayed in the snow before reaching B. For snow melt, the distance CD will also be relatively large. For an entire glacier, discharge and solute content of meltwaters at the portal, at a particular point in time, are the sums of the volume and solute concentrations of the aliquots of water arriving at that time from all possible pathways ABCD, which will be of varying lengths. Not only will there be a range of transit times for the various distances CD making up the basal drainage net but that range will also vary with the overall level of discharge through the system. Both the absolute levels and daily ranges of measured portal solute concentration depend upon the reaction rate and the lengths of the transit times, and their variability with diurnal discharge fluctuations.

STUDY AREA

Field measurements and weathering experiments were undertaken in the basin of Findelengletscher, Kanton Wallis, Switzerland (Fig. 2). Meltwaters from Findelengletscher drain to one proglacial meltwater stream, Findelenbach, which is gauged at a structure 200m from the terminus of the glacier. The basin extends from the gauge at 2500m a.s.l. to a maximum elevation of 4199m, covering an area of 24.9 km^2 of which about 76% is glacierised. Part of the basin is underlain by granite, gneiss and other metamorphic rocks of the Monte Rosa group, but a larger area is based on metamorphosed Mesozoic sediments and ophiolite, amphibolite and ultrabasic metamorphic rocks (Bearth 1953). Gypsum and dolomite are present in Triassic sediments which are widely exposed just to the north of the terminus of Findelengletscher, and on the Gornergrat, a ridge to the south of the basin which rises towards the Stockhorn (Fig. 2). It is not improbable that these rocks also form part of the substrate beneath morainic deposits on the lower slopes of the basin and under Findelengletscher itself.

FIELD MEASUREMENTS

Discharge of portal meltwater

The discharge of meltwater from the portal of Findelengletscher was recorded continuously at the stream gauge, which operated from early May through to mid-October in 1990. These data, reduced to hourly averages of flow, are shown in Fig. 3. In the spring, discharge remained low, with limited diurnal range as thickness and extent of winter snow cover reduced. Both general levels of flow and amplitude of diurnal range of discharge increased from mid-June to early

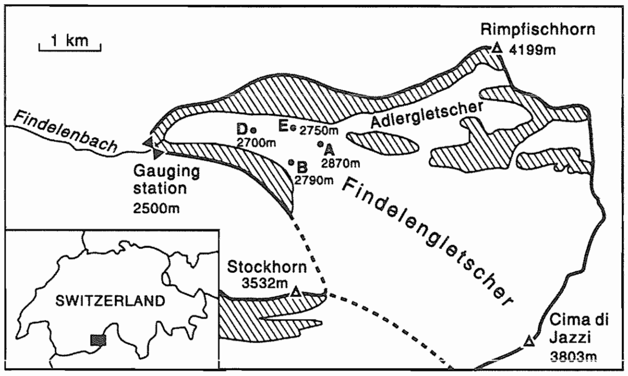

Figure 2. Map showing the location of the gauging station on the Findelenbach and the positions of moulins A, B, D and E in the ablation area of Findelengletscher, Kanton Wallis, Switzerland.

August, as the area of bare ice exposed to melting became enlarged through depletion of the snow cover. Diurnal range and general level of discharge (Q) declined with falling energy inputs from early August.

Solute concentration and solute flux in portal meltwater

Electrical conductivity (EC), a measure of total ionic strength, of meltwater in the Findelenbach was measured continuously at the gauge between 12 July and 14 October. A pHOX Systems 1006 rack system conductivity module and a dip cell consisting of carbon electrodes in resin was used. Hourly average values of EC, uncorrected for temperature (the temperature of measurement being between 0.1 and 1.0° C), were obtained from records logged by a Technolog Tinylog. Hourly average solute flux (Q.EC) was calculated as the product of hourly means of EC and Q in arbitrary rate units, analogous to kg s^{-1}.

The underlying level of EC increased with widening diurnal range as discharge declined from mid-August through September (Fig. 3). Solute flux followed the broad pattern of discharge, but rose slightly in late August and early September before declining towards the end of September. Strong diurnal fluctuations of discharge from the portal were accompanied by inverse phase variations of EC, and direct phase variations of solute flux, as described by Collins (1995b). Diurnal increases in solute flux with discharge indicate that chemical reactions are occurring rather than a simple dilution of subglacial water by relatively pure surface meltwaters.

Suspended sediment content of portal meltwater

A Manning S-4050 automatic pumping sampler was programmed to collect samples of about 250ml of meltwater and suspended sediment from the Findelenbach every hour. Samples were collected during several periods including times when dye-tracing tests were conducted. Samples were filtered through Whatman No. 1 papers and the quantity of sediment was determined gravimetrically to give suspended sediment concentration. Considerable variation in sediment concentration in portal meltwater occurred from hour to hour (Fig. 3).

Dye-tracer tests of rates of meltwater throughflow

Velocity of flow of meltwater in contact with sediment (i.e. through a pathway CD) can be obtained from the time taken for an injection of tracer into a supraglacial stream entering a moulin to reappear at the portal, assuming near instantaneous fall from B to C. Diurnal variations in transit times were investigated by a programme of injections of about 50g of Rhodamine BSA, at intervals of several hours, into meltwaters immediately upstream of moulins ‘A’, ‘B’, ‘D’ and ‘E’. These moulins are between 1 and 3km from the portal of Findelengletscher (Fig. 2). The tracer tests were undertaken on days having a wide range of discharge levels in late August 1990 (Collins 1995a). Dye presence in portal meltwater was detected by a calibrated Turner Model 10 field fluorometer at the terminus of the glacier.

As an example of data generated by the tracing programme, detailed results of tests from moulin ‘A’ during the daily discharge cycle of 23 August 1990 are presented in Fig. 4. Moulin ‘A’ was located at an elevation 370m higher than that of the gauge, at a horizontal distance of 2850m measured along the thalweg. Surface melt is schematically represented by the curve of air temperature variation in Fig. 4. An injection at 06.45h took 288 min to appear at the portal with a maximum velocity of 0.165 m s^{-1}. Peak dye concentration occurred after 293 min, before being overhauled by the 09.30h injection. The latter needed only 141 min to peak at a velocity of 0.328 m s^{-1}. During the passage of these two parcels of dye, flow of meltwater from the portal increased from 3.6 to 5.9 m^3 s^{-1}. Delay of the 06.45h injection probably resulted from detention

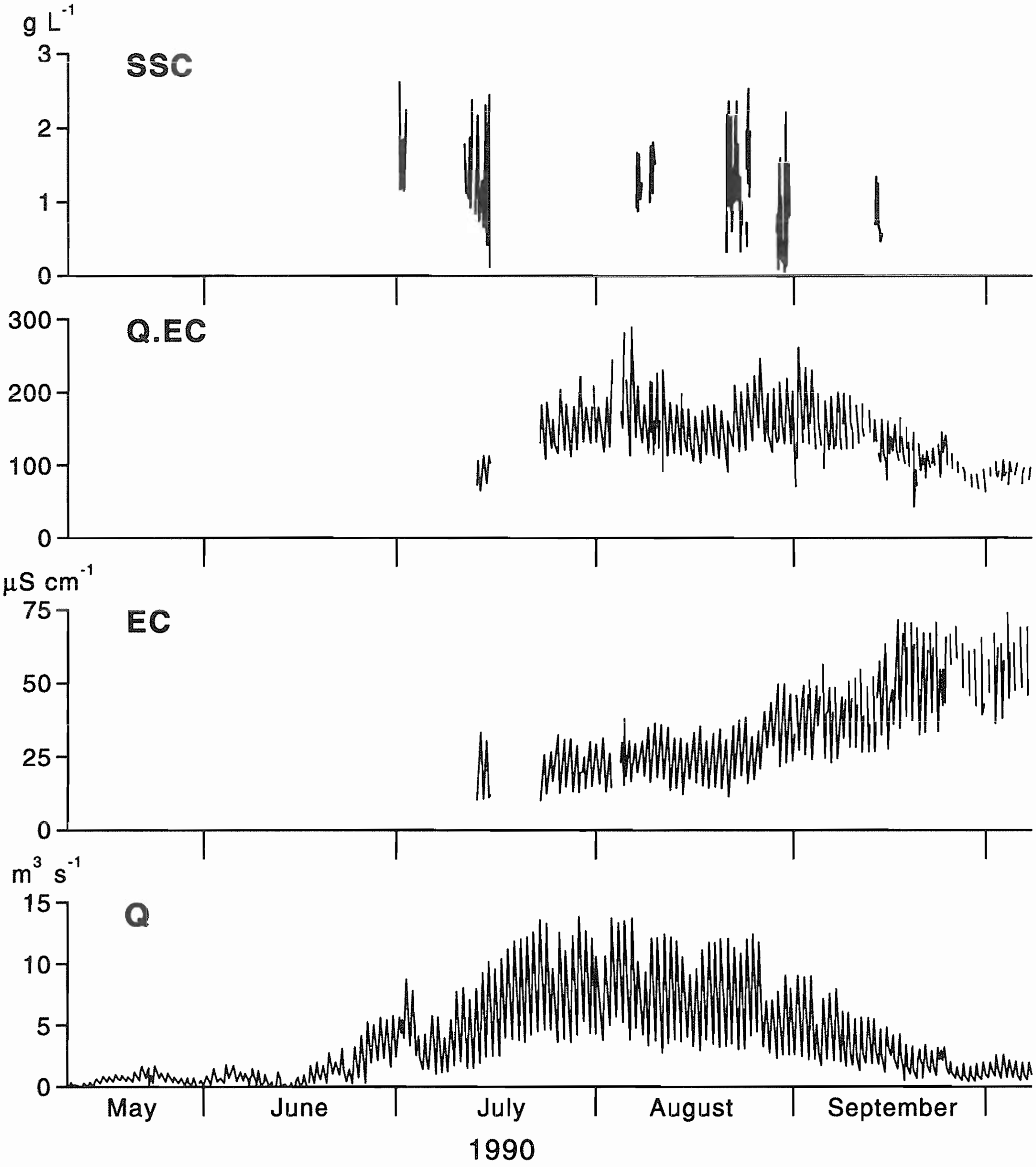

Figure 3. Hourly suspended sediment concentration (SSC) and hourly mean values of solute flux (Q.EC), electrical conductivity (EC) and discharge (Q) of meltwaters in the Findelenbach from May through October 1990.

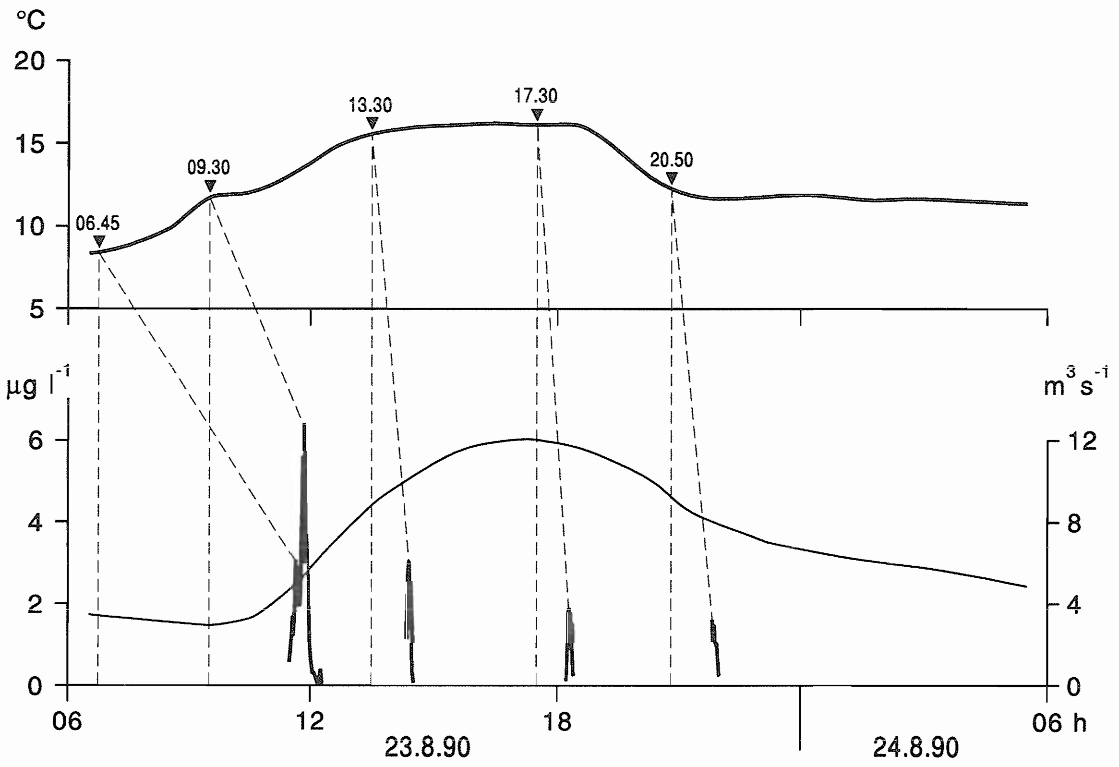

Figure 4. Dye concentrations at the gauge resulting from five rhodamine injections into moulin 'A' on 23 - 24 August 1990 in relation to air temperature and discharge.

of the dye in plunge pools within the moulin shaft; water passes slowly through these storage pools when surface meltwater input is very low. Dye-tracer tests provide a poor estimate of contact time between sediment and meltwater under low flow conditions (Collins 1995a). The highest velocity (0.990 m s^{-1}) was associated with the 17.30h injection, during which discharge at the portal declined from 12.0 to 11.6 m^3 s^{-1}. The transit time for 50 per cent of the dye to appear was 48 min. Dye was detected for 5 minutes only, suggesting little dispersion of the dye parcel. With falling discharge in the evening, average flow-through velocity from the 20.50h injection was reduced to 0.699 m s^{-1}, giving a transit time of 68 min. During this time discharge at the portal fell from 9.4 to 8.0 m^3 s^{-1}.

Results of all but the early morning tracer tests undertaken between 20 and 29 August from the four moulins are shown in Fig. 5. This plot shows the envelope within which transit times of parcels of meltwater entering the glacier at various points on the surface vary with portal discharge. The length of the vertical bar representing each test represents the time taken for the dye cloud to pass the portal. Average transit time from major moulins, 1-3 km from the portal, (shown as a pecked line in Fig. 5) decreases with increasing discharge from over 3h at 2.5 m^3s^{-1} to under 1h at 12.5 m^3s^{-1}. At higher discharge levels, transit times are reduced at a lesser rate and the dispersion of dye, from all moulins, is also diminished. This may explain the relative insensitivity of minimum daily values of EC to changing levels of maximum daily portal discharge between mid-July and mid-August. These transit times are for waters routed through major moulin-conduit pathways and therefore represent minimum transit times from the zone.

The zone of the glacier surface in which the tested moulins are located is relatively close to the portal and so the average transit times represented by these traces will be lower than those that might be expected for the moulin-conduit systems of the entire glacier. Flow contributed from melt occurring up glacier will increase velocity and reduce transit times for meltwaters to pass through the lower part of the glacier at a given overall level of discharge (Collins 1995a).

EXPERIMENTAL DETERMINATION OF RATES OF REACTION

In order to relate solute concentration in meltwater to length of time of meltwater contact with sediment or transit time, it is necessary to know the overall rate of dissolution of suspended sediment. This was determined experimentally. Samples of meltwater derived from ice were collected from small surficial streams on Findelengletscher at about 2600m a.s.l. in carefully prewashed polyethylene bottles, which were sealed when full. The bottles were then immersed in a bucket of meltwater, which was carried down to the gauging station. The duration of transportation and storage before the start of an experiment was less than 30 min. 250ml samples of ice-melt water were used in the experiments, which were undertaken at 2500m, at temperatures of less than 1.3° C in insulated polyethylene containers, with continuous gentle stirring. A Russell gel-filled glass pH electrode and Sproule electrical conductivity dip cell were inserted and left in place with readings noted every few minutes. The pH electrode had been allowed to stand in a sample of meltwater of the same initial composition as that to be used in an experiment, or in the aliquot to be used, for several minutes to ensure a stable first reading.

A typical result from a series of experiments in which icemelt-derived waters were allowed to equilibrate with the atmosphere at 2500m is shown in Fig. 6 (a). pH initially fell rapidly and then at a decreasing rate as dissolution of CO$_{2\,(g)}$ raised H^{+} concentration, giving an equilibrium pH of 5.9 after about 8 min.

In a further series of experiments, about 0.5g of suspended sediment, (collected wet after being deposited at the proglacial channel margin during high flow events and hence having had the shortest possible contact time with meltwater), was added to meltwaters which had been allowed to equilibrate with and which were left open to the atmosphere. Although rate of dissolution will depend on the concentration of sediment in the water, as indicated by Brown *et al.* (1994), a fixed concentration of about 2 kg m^{-3} was used in the experiments described here. A plot of the increase in EC and pH through time is presented for one of those experiments in Fig. 6 (b). pH rose quickly to about 8.0 in the first 6 - 7 min, the rate slowing towards pH 8.85 after 30 min. EC (a measure of total ionic strength and hence indicating the overall effect of dissolution and reaction between meltwater and sediment) increased from the initial level of ice melt, 4 μS cm^{-1}, to 8 μS cm^{-1} in 10 min, and, with the rate of increase easing off, to 10 μS cm^{-1} after 25 min. With the growth rate continuing to decline, EC steadily increased to 17 μS cm^{-1} after 180 min and so on to about 30 μS cm^{-1} after 5 h. In three experiments conducted over longer periods of time, EC continued to rise, to 37 μS cm^{-1} after 10h, and to 74.0 μS cm^{-1} after 24 h. The temperature of the suspension in these experiments also increased and reached a maximum of 7.6°C. The EC values are reported at the measurement temperature. Increases in the temperature of the suspension led to a maximum enhancement of the measured EC to a level about 15% above the value at 1° C. After 5 days, EC reached 145 μS cm^{-1}. Similar quantities of sediment were also

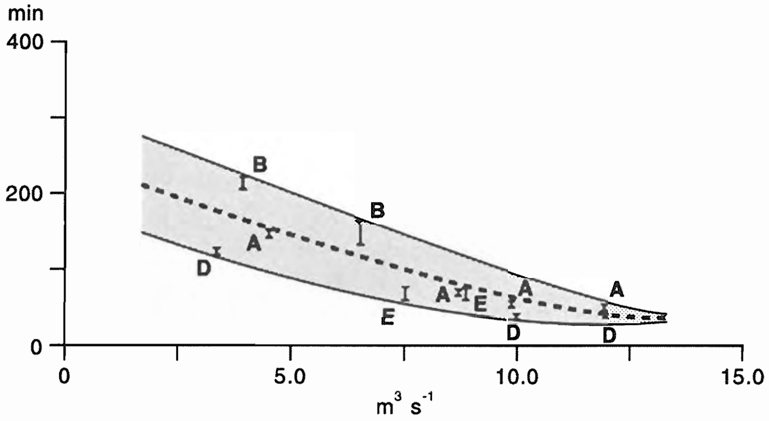

Figure 5. Variation with portal discharge of meltwater transit times through Findelengletscher from individual moulins (shaded area) together with the average transit time (pecked line).

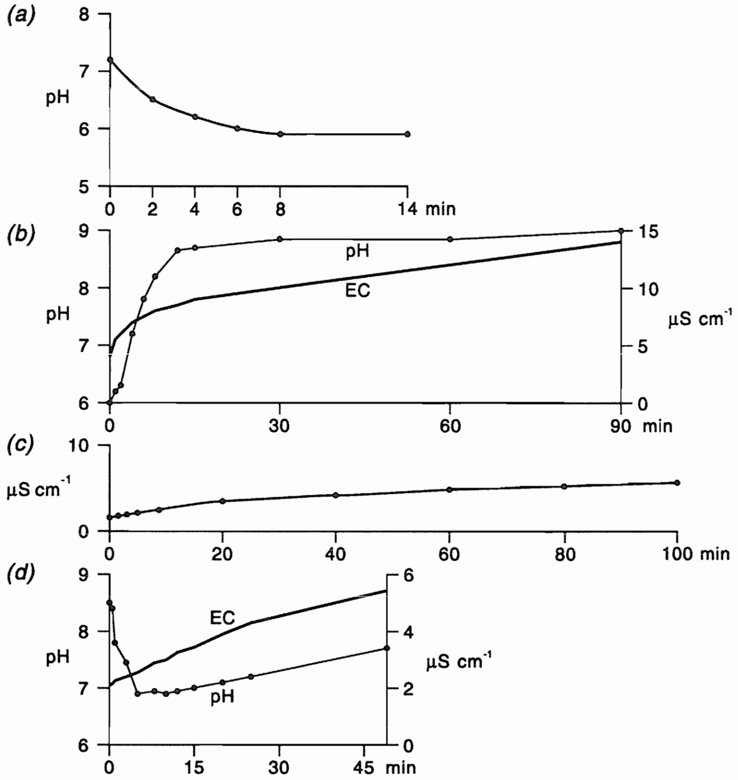

Figure 6. Changes of pH and EC during experiments in which (a) meltwater equilibrated with the atmosphere, and sediment was added to, (b) equilibrated meltwater open, (c) non-equilibrated meltwater open and (d) non-equilibrated meltwater closed to the atmosphere.

added to samples of surface meltwater which had not been allowed to equilibrate fully with the atmosphere. These experiments were left open to the atmosphere from the time of addition of the sediment. EC increased at a slower rate, which also declined through time (Fig. 6 (c)). Experiments were also conducted in which sediment was added to meltwaters which had not fully equilibrated and which were maintained closed to the atmosphere. pH increased immediately to about 8.5 before falling after 5 min to about 6.9 and then rising slowly (Fig 6 (d)). EC increased more rapidly in the first 30 min than later in the experiment. The rate of increase of EC in non-equilibrated meltwaters was slower than in those which had first equilibrated with the atmosphere.

Another possible analogue of sediment-meltwater interaction was investigated. After 3h of an experiment in which sediment had been added to atmospherically-equilibrated meltwater, an additional equal volume (250 ml) of equilibrated meltwater was added. This procedure was intended to represent the mixing of surface meltwater at the base of a moulin (point C in Fig. 1) with meltwater which had already reacted with sediment upstream (in transit from point E). EC was reduced on mixing but commenced recovery immediately. pH declined more gently, before starting to increase after 30 min (Fig. 7). Sediment concentration was reduced by the addition of the second aliquot of meltwater.

First order reaction kinetics can be used to describe the change in concentration C of a dissolved species as a function of time t:

$$dC/dt = k\,(C_s - C) \qquad [1]$$

where k is the reaction or dissolution rate constant and C_s is the equilibrium or steady-state concentration to which the solution tends with time. The rate of reaction or dissolution dC/dt is a function of the distance of C from C_s (Lerman 1979). Rate constants of order 10^{-3} s^{-1} for the release of H^+ from dissolution of CO_2 gas from the atmosphere were indicated by the experiments.

Although first order reaction kinetics have been applied to sediment dissolution in meltwaters (e.g. Fountain 1992), the pure surface-controlled dissolution model appears to be more appropriate (Stumm 1992, Morel & Hering 1993). After an initial rapid increase in EC on addition of sediment (Fig 6(b)), the rate of weathering slowed down to give a steady continuing rise in EC. After about 45 min, rates of increase of EC of about 0.065 μS cm^{-1} min^{-1} for meltwaters fully-aerated and of about 0.035 for meltwaters partially-aerated at the start, both open to the atmosphere during the experiments, were obtained. Size of suspended sediment particles will additionally influence the rate of increase of EC with time, as may agitation of the suspension in water.

COUPLING TRANSIT TIMES AND RATES OF SOLUTE ACQUISITION

Transit times of meltwater from moulins to portal can be coupled in several ways with the rate of solute acquisition by meltwaters from dissolution of suspended sediment. Position in the moulin-conduit-portal pathway through time as a parcel of meltwater moves downstream and the degree of chemical evolution achieved by that parcel can be calculated for a given level of portal discharge. Undertaking these calculations for varying stages of flow allows the contribution of the solute content of specific parcels of meltwater to be separated from the diurnal variation of solute concentration of all meltwaters emerging from the glacier portal. From the average transit time for meltwaters to pass from a group of several moulins dispersed over the lower ablation area, the solute concentration that would be expected for meltwaters from that area on arrival at the portal can be estimated. Inversely, the experimentally-determined rate of solute acquisition can be coupled with observed diurnal variation of solute concentration in the portal meltwaters to enable estimation of the average transit time (from initial contact with sediment) for all meltwater arriving at the portal at a particular time.

In estimating natural rates of chemical weathering, extrapolation of dissolution rates obtained experimentally to field conditions is questionable. In general, rates obtained from laboratory experiments tend to be higher than those estimated in the field (Schnoor 1990), and some caution is necessary in extrapolating experimental data to the field. Extrapolation will only be valid if the same weathering mechanisms operate under both field and laboratory conditions.

A LAGRANGIAN MODEL OF SOLUTE ACQUISITION BY MELTWATER DURING TRANSIT THROUGH THE BASAL DRAINAGE SYSTEM

The use of dye to determine transit times of meltwater from moulins to portal and the use of these transit times to characterise diurnal variation in the length of period of contact between suspended sediment and meltwater beneath the glacier allow a simple Lagrangian coupling with experimentally-determined rates of increase of EC through time. This model provides an indication of the level and diurnal variation of solute concentration that parcels of meltwater draining from the moulins in the lower ablation zone would exhibit on reaching the portal of Findelengletscher.

Flow from C to D can be considered as a series of discrete parcels of meltwater moving as

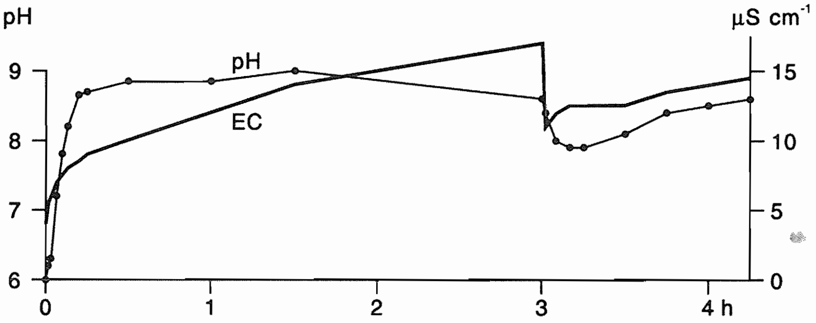

Figure 7. Changes of pH and EC in an experiment in which sediment was mixed with equilibrated meltwater, to which, after 3 h, additional meltwater was added.

a consecutive sequence of blocks downstream. Chemical reaction rates and solute concentration within each block will change through time as the blocks pass along the pathway. The rate of movement of a block is taken as the uniform flow-through velocity from a particular moulin for the appropriate part of the day, so that the position of a block can be tracked through time within the glacier. The rate of reaction can be obtained for appropriate points along the trajectory. In a first-order model, concentration of solute, C, as a function of time is given by integration of [1]:

$$C = C_s + (C_0 - C_s)\, e^{-kt} \qquad [2]$$

where C_0 is the initial concentration at $t = 0$. However, for the steady increase of electrical conductivity, the value of EC reached after a particular time was taken directly from the experimental data.

Assuming uniform velocity of flow, initial EC of 4 µS cm^{-1} at point C, and meltwater equilibrated with the atmosphere on arrival at C, both electrical conductivity and the positioning of a parcel of meltwater in the pathway through time can be calculated. As an example, EC and positions in the pathway for water entering moulin 'A' and travelling through the system at 09.30h and 17.30h on 23 August 1990 are illustrated. Plots of calculated EC against distance show the impact of flow-though velocity on solute concentration of the parcels of water en route to the portal (Fig. 8). At high discharge, with high velocities (0.93 -1.03 m s^{-1} for the tail and front of the cloud of dye respectively, which indicate some elongation or dispersion of the block), the EC of the meltwater would have risen to 11.1 µS cm^{-1} in 46 min by the time the portal was reached, and 11.5 µS cm^{-1} in 51 min as the tail of the block leaves the glacier. During low flow conditions, transit times ranged from 141 to 152 min for the front and tail of the block, and EC would have risen to more than 18 µS cm^{-1}. Experimentally-determined average transit times (50% dye-return) from the tracer tests from moulin 'A' on 23 August 1990 yield portal EC values between 11.3 and 18.2 µS cm^{-1}. The calculated diurnal variation is in phase with the measured variation of EC of portal meltwater on that day (14 - 29 µS cm^{-1} for the equivalent range of flows), but with lower absolute levels and reduced amplitude. For meltwater equilibrated with the atmosphere before descent into moulin 'B', 2.33 km from the portal, portal EC would range between 17.3 and 22.0 µS cm^{-1}, meltwater from injections at 17.30h and 09.30h having taken 143 and 211 min in transit respectively . These values reflect the smaller volumes of water travelling at lower velocities for at least part of the pathway length (see Collins 1995a). Using the reaction rate for sediment with meltwaters not fully-equilibrated with the atmosphere, portal EC of parcels of meltwater passing 2.85 km from moulin 'A' in passageways open to the atmosphere would range from 7.25 to 10.0 µS cm^{-1}, substantially less than for initially fully-aerated meltwaters.

The solute concentration at the portal to which meltwaters arising in the area making up the lower 3km of the ablation zone would evolve can be estimated from the average transit time

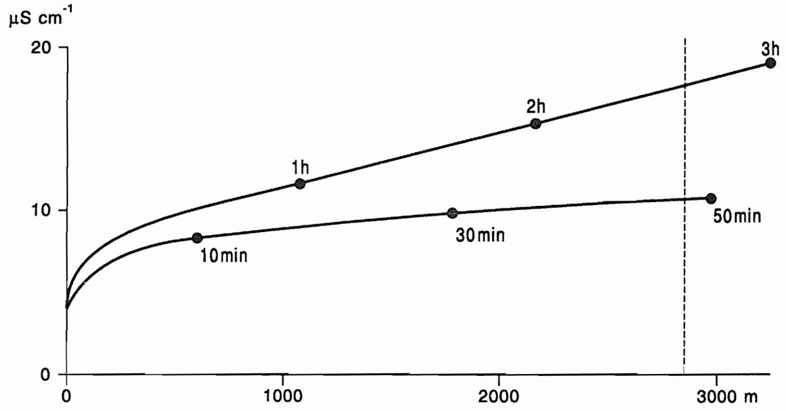

Figure 8. Calculated positions and EC of meltwater parcels after entering moulin 'A' at 17.30h (lower) and 09.30h (upper) en route to the portal 2850 m downstream.

shown in Fig. 5. As an example, with the same assumptions as used in the calculation for the individual moulin, meltwater being taken as having equilibrated with the atmosphere on the glacier surface, the reaction rate was coupled with average transit times for the range of discharges that occurred on 23-24 August. The model estimates that hourly average EC for meltwaters derived from the lower ablation area would have been in the range 10 - 25 µS cm^{-1} on arrival at the portal. This considerable diurnal variation is parallel with that of the observed EC of portal meltwaters, but underestimates absolute values by up to 40% (Fig. 9).

Average transit time for the total discharge to pass through Findelengletscher can also be inferred from the experimental kinetic data. Again, taking observed values on 23-24 August, a measured EC of portal meltwaters of 38.62 µS cm^{-1} would imply an average transit time of 470 min (almost 8h) at a portal discharge of 3.3 m^{3}s^{-1}. Minimum measured EC of 16.05 µS cm^{-1} indicates an average transit time of 122 min, at a discharge of 11.5 m^{3}s^{-1}. These values compare with average transit times obtained from the tracer experiments for parcels of meltwaters to reach the portal from the lower ablation area of 260 and 40 min respectively. A large proportion of the total meltwater flow in August will be routed quickly through larger moulin-conduit systems. Parcels of meltwater travelling through other pathways must therefore pass to the portal with transit times considerably greater than the average indicated for the total discharge. Greater opportunity for solute acquisition in such slow flowing meltwater in smaller channels would then account for the remainder of the solute content needed to produce observed concentrations at the portal. The implication would be that this flow is in thin filaments, each with a small discharge and hence low through-flow velocity, for some distance before acceleration on confluence with larger faster-flowing streams.

DISCUSSION

The weathering experiments and flow-through measurements described in this paper suggest that rates of reaction combined with transit times in main conduits leading from major moulins are sufficient to produce inverse diurnal variations in solute content with fluctuations of discharge of portal meltwaters, but are insufficient to account for the absolute levels observed. The moulins from which flow-through measurements are available lie within 3 km of the portal, but moulins are distributed at considerably greater distances up glacier. The water from some of these distant moulins will have longer transit times because discharge in upstream reaches will be less and meltwaters flow at slower rates in smaller conduits Collins (1995a). These longer transit times increase the opportunity for solute acquisition. Not all surface water enters relatively fast-flowing moulin-conduit pathways. An unknown proportion of the total meltwater drains into cracks and crevasses, in small volume flows, which, on reaching the subsole, will flow very slowly in small filaments with considerable opportunity for dissolution en route to major conduits.

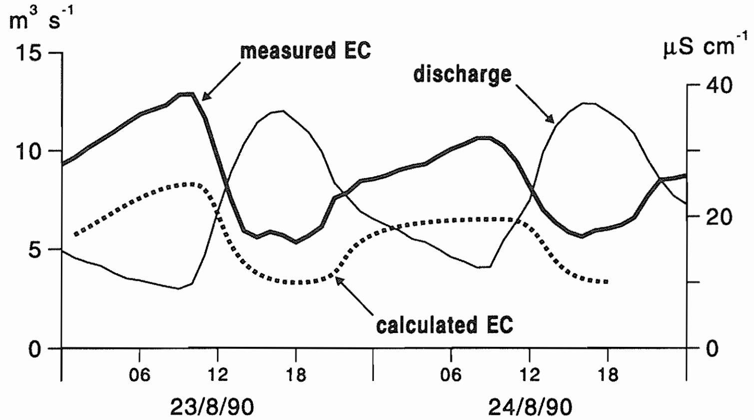

Figure 9. Calculated portal EC of meltwater from the lower ablation area, measured EC of portal meltwaters and diurnal variations of discharge from Findelengletscher on 23 - 24 August 1990.

Meltwater arriving from upglacier (from E in Fig. 1) may already have a relatively high solute concentration at point C. Addition of surface meltwaters at points like C in the glacier will be greatest during melt in the daytime, and may cease at night. The experimental data shown in Fig. 7 indicate how solute concentration might be reduced by mixing in the daytime. Solute concentration in meltwaters draining slowly from upglacier and arriving at a point C in the night will not be diluted by mixing, and the solute content of meltwater reaching the portal at night should be higher than that during the day. EC at the portal will reflect the mixing of water having different transit times and different concentrations of solute. Diurnal variations of EC will reflect changes in the proportions of meltwater contributing to total flow that have taken various times in transit through basal pathways. The absolute volume of the proportion of total melt routed through large moulin-conduit pathways probably determines the changing underlying level of EC during the ablation season. EC at the portal will also reflect initial aeration status of meltwater, various transit times in contact with sediment through differing basal pathways in which meltwater may not always be in contact with air, and various sediment concentrations, all of which influence the rate of dissolution of sediment.

In Nature, the rate of processes which increase EC may be faster than that indicated by experiments involving gentle stirring and instantaneous sediment addition. Turbulent flow will enhance mixing of reactants, and sediment added from channel margins throughout the length of basal pathways may increase mineral concentration in the water and counter declining rates of reaction downstream. The concentration of suspended sediment used in the experiments (2 kg m^{-3}) was in the range observed at the portal of Findelengletscher during the dye-tracing experiments on 23 August 1990 (0.430 - 2.535 kg m^{-3}), but higher than the mean of 1.251 kg m^{-3}. It is unlikely, however, that sediment content of meltwater is uniform throughout the basal drainage system at any time. Measurements at the portal are also unlikely to reflect accurately concentration of sediment elsewhere in the system. The concentration of sediment in meltwaters will, however, influence the rate of solute acquisition. The diurnal increase of suspended sediment concentration with discharge might increase the rate of solute acquisition at times when high flow-through velocities are reducing the length of time sediment is in contact with meltwater.

Transit times in contact with basal sediment may be longer in smaller, more tortuous pathways, such as linked cavities. Appearance at the portal of those meltwaters will be delayed and the solute concentration will be increased. These solute-rich waters appear at the portal later than surface meltwater produced at the same time that has flowed through efficient moulin - conduit systems. Both discharge and EC variations at the portal will be influenced by the spatial arrangement of moulins, structure and topology of the basal drainage network (and hence how velocity and discharge are related), areal distribution of surface meltwater into zones with various travel-times to the portal, and partitioning of flow both on the surface and within the basal drainage net into faster and slower moving pathways.

The weathering experiments appear to simulate the natural processes fairly closely, in that the magnitude of the experimentally-determined weathering rates seems plausible in the context of the overall interaction of the hydrological and hydrochemical systems of Findelengletscher. Active mineral surface area per unit weight of suspended sediment in a small sample presumably reflects that area for the total mass of suspended sediment in the glacier basal hydrological system in general. Contact between meltwater and basally-derived suspended sediment dominates solute acquisition by meltwaters and so the experimental analogue well reflects the processes occurring in Nature.

An open question concerns groundwater flow. In winter and in spring, before the onset of melt, clear sediment-free water is discharged from Findelengletscher. Measurements of the EC of Findelenbach at the gauge have been made sporadically under winter conditions, and are listed in Table 1. EC was in the range 240 - 301 μS cm^{-1}. Discharge was not recorded in winter but was estimated to be in the range 25 - 50 l s^{-1}, a specific yield of 1-2 l s^{-1} km^{-2}. Huber *et al.* (1950) suggested that winter discharge consisted of groundwater which had percolated through moraine. Huber *et al.* (1950) measured 4.6 l s^{-1} km^{-2} for the Findelenbach at Winkelmatten, 5km downstream from the terminus of Findelengletscher, where the basin of Findelenbach and is both larger and less-glacierised than at the portal of the glacier. Subaerial springs in and around the Findelengletscher basin continue to flow

Table 1. Electrical conductivity of winter discharge in the Findelenbach at the gauging station.

Date	*Time*	*Measured electrical conductivity ($\mu S\ cm^{-1}$)*	*Water temperture (°C)*
3 May 1982	15.15	240.0	0.4
30 April 1983	16.30	253.0	-
29 March 1987	16.20	301.0	-

throughout summer. Assuming that subglacial groundwater continues to flow at a constant discharge throughout summer, a small contribution will be made to the solute flux from the basin. As a proportion of the total flux, groundwater solute flux will be higher at times when discharge of water derived from glacier surface melt is reduced. However, there remains the possibility that during snowmelt in early summer groundwater recharge may increase discharge from springs, and thereby raise the solute flux from that source. This would raise the level of EC in portal meltwaters in the early part of the ablation season, particularly when direct meltwater runoff is reduced at night.

CONCLUSION

Experimentally-derived rates of chemical reaction between suspended sediment and meltwater coupled with transit times of meltwater flow from major moulins through pathways beneath Findelengletscher suggest that, in mid to late summer, parcels of meltwaters passing from the lower ablation area would be expected to have acquired a considerable solute concentration on arrival at the portal. Diurnal variations in discharge through such systems produce substantial changes in flow-through velocity which are sufficient to produce a diurnal pattern of variation of solute concentration at the portal. However, the level of solute concentration predicted by the Lagrangian model is lower than observed. Slower-flowing meltwaters, entering the glacier in many small filaments of flow down cracks and through crevasses but cumulatively accounting for a significant proportion of total discharge acquire larger concentrations of solute during long transit times. Slower-flowing meltwaters will raise solute concentration in portal discharge at all times, but will probably contribute an increasing proportion of the solute-rich discharge from the portal through the night and into the morning. Groundwater continuously provides a small contribution of solute to the total flux.

Variations in initial aeration of meltwater appear to influence the rate of chemical reaction. Meltwaters having less initial opportunity for equilibration with the atmosphere will have reduced levels of solute concentration on reaching the portal. The net rate at which various reactions proceed to increase electrical conductivity of meltwaters is initially rapid but decreases in the first 30-40 minutes. It then remains steady as solute concentration rises. Further experiments, at temperatures of 0° C and lasting for periods of several days, are required to determine the level to which EC will continue to rise. Quantification of the kinetics of individual reactions such as carbonate dissolution and weathering of alumino-silicates at about 0° C may help to explain variations of individual ionic species with discharge. The influences of suspended sediment concentration and particle size on rates of reaction also require investigation.

Actual measurement of transit times associated with small flows of water entering crevasses or cracks by dye-tracer tests remains an outstanding task. More difficult still will be an assessment of the relative proportion of the total surface melt which descends into the glacier in large streams through moulins from that which enters through small surface flows and minor orifices.

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