SOLUTE ACQUISITION IN GLACIAL MELT WATERS. I. FJALLSJÖKULL (SOUTH-EAST ICELAND):
BULK MELT WATERS WITH CLOSED-SYSTEM CHARACTERISTICS

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Abstract. Variations in dissolved cations, total alkalinity, sulphate, and field pH are recorded for samples of precipitation, supraglacial melt, and bulk melt waters (those emerging at the portal) from Fjallsjökull (south-east Iceland). The composition of supraglacial melt indicates derivation from precipitation by the acquisition of solutes from the weathering and dissolution of rock debris, in a system open to atmospheric carbon dioxide. Bulk melt waters have variable compositions, approaching saturation with calcite, which can be derived from supraglacial melt water by continued solute acquisition in a system closed to atmospheric carbon dioxide. Solute – discharge relationships suggest that chemical evolution of the bulk melt waters occurs when aggressive englacial waters are mixed with the solute and sediment-rich subglacial component. Simple mixing behaviour occurs over intermediate discharges as long as variations in the extent of post-mixing evolution are small compared to changes in the mixing ratio.

Résumé. Dissolutions par les eaux de fusion glaciaires. I. Fjallsjökull sud-est de l'Islande: Eaux de fusion résurgentes avec des caractéristiques de systeme clos. On a enregistré les variations des teneurs en cations dissous, alcalinité totale, sulfate et pH courant pour des échantillons de précipitations, d'eau de fonte glaciaire de surface et d'eaux de fusion résurgentes, (celles qui sortent du portail sous-glaciaire) prélevés au Fjallsjökull (sud-est de l'Islande). La composition de l'eau de fusion de surface montre des modifications par rapport aux précipitations par l'acquisition de substances dissoutes provenant de l'altération et de la dissolution de débris rocheux, dans un système ouvert au gaz carbonique atmosphérique. Les eaux résurgentes ont des compositions variables proches de la saturation pour les calcites, qui peuvent provenir de l'eau de fonte de surface par l'acquisition continue de matière dissoute dans un système lié au gaz carbonique atmosphérique. La

liaison entre le débit et la charge en matière dissoute peut être expliquée par l'évolution chimique des eaux de fusion résurgentes lorsque les eaux intra-glaciaires aggressives se trouvent mélangées avec les eaux sous-glaciaires riches en éléments dissous et en suspension. Il se produit un simple mélange pour les débits intermédiaires tant que les variations dans l'importance de l'évolution après mélange sont faibles au regard des changements dans les proportions du mélange.

Zusammenfassung. Lösungsanreicherung in Gletscherschmelzwasser. I. Fjallsjökull (Süd-Ost Island): Massen-Schmelzwasser aus einem geschlossenen System. Für Proben des Niederschlages, der oberflächlichen Schmelze und des Massen-Schmelzwassers (austretend am Gletschertor) am Fjallsjökull (Süd-Ost Island) wurden die Änderungen in gelösten Kationen, der Gesamt-alkalinität, des Schwefelgehaltes und des Feld-pH-Wertes festgestellt. Die Zusamensetzung der oberflächlichen Schmelze lässt auf deren Herkunft aus dem Niederschlag unter Anreicherung mit Lösungen aus dem verwitternden und zerstörten Felsschutt in einem System, das dem Kohlendioxyd der Luft zugänglich ist, schliessen. Massen-Schmelzwässer haben unterschiedliche Zusammensetzungen; sie weisen angenäherte Sättigung mit Kalzit auf, das aus oberflächlichem Schmelzwasser unter ständiger Lösungsanreicherung, diesmal unter Abschlus gegenüber dem atmosphärischen Kohlendioxyd, stammen kann. Die Beziehungen zwischen Lösung und Abfluss lassen darauf schliessen, dass die chemische Entwicklung der Massen-Schmelzwässer eintritt, wenn aggressives intraglaziales Wasser mit de lösungs- und sedimentreichen subglazialen Komponente vermischt wird. Einfaches Mischverhalten tritt bei Zwischen-abflüssen auf, solange die Schwankungen im Ausmass der Entwicklung nach der Vermischung im Vergleich zu den Änderungen des Mischverhältnisses klein sind.

INTRODUCTION

Chemical models for the evolution of bulk melt waters (Raiswell, 1984) have been constructed on the assumption that the hydrogen ions used in weathering rock minerals are mainly derived from the dissolution and dissociation of CO_2. Different open and closed system models can then be defined by kinetic factors, principally rates of weathering relative to rates of CO_2 dissolution. Closed-system conditions result where rates of weathering are relatively rapid. Under these conditions the models indicate that bulk melt water composition is constrained by the composition of supraglacial melt. Analytical data for melt waters at Fjallsjökull (south-east Iceland) are presented and discussed in terms of the closed-system model.

SAMPLING LOCALITY

The glacier at Fjallsjökull is one of a series draining the ice cap Vatnajökull through deep valleys cut in the flanking mountains. Two kilometres from its eastern margin the glacier is only 1.5 km wide but it broadens into a lobe 4 km wide at the snout. The sampling locality lay to the north of the glacier where the steep ice front is paralleled by the main melt-water stream, which is fed by a series of tributaries emerging with considerable force from the portals. To the south the glacier terminates in the proglacial lake of Fjallsarlon (Fig. 1).

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Extrusive volcanic rocks, mainly basaltic lavas with some rhyolite, predominate in the area and are likely to form the glacial bedrock. Normative mineral computations from wet chemical data (personal communication from M.S. Brotherton) with X-ray diffraction and optical studies indicate the major mineral phases in the basalts to be feldspars (45-55%), pyroxene (15-30%), and quartz (7-8%) with opaque minerals and some calcite. The rhyolites are more abundant in feldspar (60-70%) and quartz (c. 25%) and also contain some calcite.
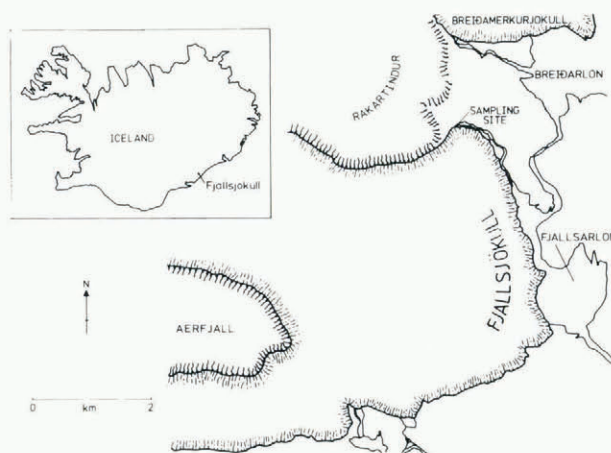

Fig.1. Sampling locality at Fjallsjökull (south-east Iceland).

35

SAMPLING AND ANALYTICAL TECHNIQUES

Water samples were collected at approximately hourly intervals in rinsed, one-litre polythene bottles and deep-frozen for transport to the laboratory. Field measurements of air temperature, water temperature, conductivity, pH, and discharge were made at the time of collection. The technique for pH measurement followed that described in Skoog and West ([1969]) whilst discharge was estimated from determinations of stream velocity and cross-sectional area, as detailed by Østrem (1964).

Prior to chemical analysis the suspended sediments (>0.1 μm) were removed by centrifugation. The cations Na^+, K^+, Ca^{2+}, Mg^{2+} were determined by atomic absorption spectrometry and sulphate by a Technicon Autoanalyser method (Persson, 1966). Dissolved carbonate species were measured by titration to pH 8.2 (phenolpthalein alkalinity) and pH 4.2-5.4 (total alkalinity) as described in Golterman and Clymo (1969).

RESULTS

All the chemical (Na^+, K^+, Ca^{2+}, Mg^{2+}, total alkalinity, SO_4^{2-}, and pH) and physical (air temperature and discharge) measurements at the Fjallsjökull outlet are recorded in Table I, for a single 24 h period. Throughout the following results and discussion, the terms "englacial" and "subglacial" are applied to melt waters in the sense of Collins (1979[b]) and are distinguished essentially on the magnitude of temporal and areal contact with solute sources. Thus englacial waters, which are fast-flowing, dilute, and almost sediment-free, include those being transmitted through the main arterial channel at the ice-rock interface, as well as waters in ice-walled conduits. By contrast subglacial waters have low flow rates and higher sediment and solute loads due to increased contact with bedrock, percolation through morainic debris and interaction with sediment-laden basal ice.

Discharge variations

Temporal variations in discharge are plotted in Figure 2. The characteristic diurnal variation in discharge recognized elsewhere (e.g. Rainwater and
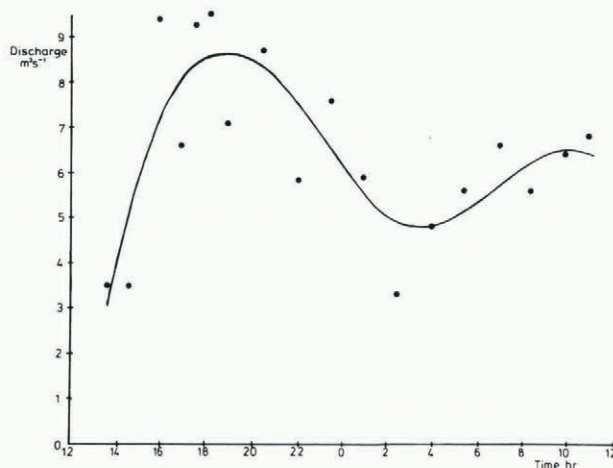

Fig.2. Temporal variations in discharge at Fjallsjökull, showing best fit curve ($r = 0.52$) of form $y = a + b \sin x + c \cos x$.

Guy, 1961; Collins, [1978]) is also apparent at Fjallsjökull, despite scatter in the data. Such diurnal variations generally reflect changes in the amounts of supraglacial melt water produced in response to daily variations in radiation input.

Water may be derived from a number of sources in predominantly glacierized catchments namely subglacial melting, precipitation, ground-water, surface melting, and internal melting (Collins, [1978]). Subglacial and internal melting produce only trivial quantities of water (Shreve, 1972) and both chemical (Collins, 1979[b]) and isotopic (Behrens and others, 1971) measurements indicate that surface melt waters are the major source of water from Alpine glaciers during the summer ablation period. A further significant source of water from Alpine glaciers may arise from subglacial ground-water systems (Ambach and others, 1972) but this situation may not be common. At Fjallsjökull precipitation was absent both during, and for 10 d preceding, the measurements. Assuming that the ground-water contribution is negligible, the major

TABLE I. PHYSICAL AND CHEMICAL DATA

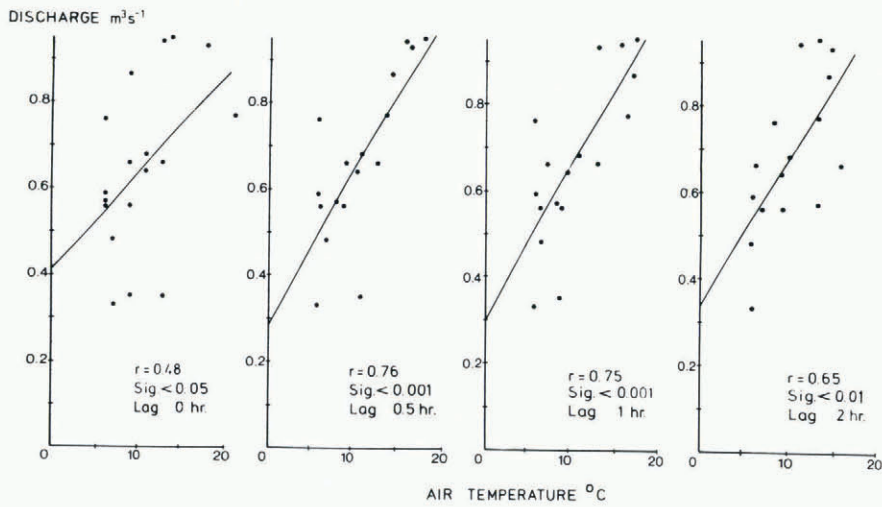|	Sample	Ca^{2+}	Mg^{2+}	K^+	Na^+	HCO_3^-	SO_4^{2-}	pH	Discharge	Air temperature	Σ^+
Type	Time	mmol ℓ^{-1}	mmol ℓ^{-1}	mmol ℓ^{-1}	mmol ℓ^{-1}	mmol ℓ^{-1}	mmol ℓ^{-1}		$m^3 s^{-1}$	°C	meq. ℓ^{-1}
	12.30	0.104	0.0156	0.0028	0.0309	0.22	0.0128	8.85	0.35	9	0.273
	13.30	0.122	0.0263	0.0054	0.0770	0.28	0.0234	9.1	0.35	15	0.380
	15.00	0.115	0.0247	0.0049	0.0757	0.25	0.0124	8.95	0.94	13	0.360
	16.00	0.126	0.0259	0.0051	0.0683	0.255	0.0212	9.15	0.66	14	0.377
Bulk melt waters	16.40	0.120	0.0255	0.0051	0.0726	0.29	0.0239	9.2	0.93	17	0.368
	17.20	0.137	0.0284	0.0056	0.0705	0.30	0.0291	9.4	0.95	15.5	0.407
	18.00	0.121	0.0218	0.0072	0.0774	0.27	0.0218	9.45	0.71	21	0.369
	19.30	0.111	0.0160	0.0033	0.0896	0.19	0.0202	9.5	0.87	9	0.346
	21.00	0.129	0.0276	0.0066	0.0870	0.29	0.0135	9.3	0.57	6	0.408
	22.30	0.123	0.0177	0.0033	0.0313	0.26	0.0187	9.5	0.76	6	0.348
	00.00	0.120	0.0280	0.0056	0.0957	0.24	0.0176	9.6	0.59	5.5	0.397
	01.30	0.129	0.0284	0.0063	0.1031	0.25	0.0239	9.65	0.33	7	0.423
	03.00	0.135	0.0292	0.0061	0.1044	0.32	0.0332	9.65	0.48	6.5	0.439
	04.30	0.133	0.0292	0.0060	0.1135	0.30	0.0260	9.55	0.56	8.5	0.443
	06.00	0.105	0.0300	0.0069	0.1209	0.26	0.0280	9.4	0.66	9	0.398
	07.30	0.137	0.0280	0.0061	0.0761	0.255	0.0249	9.35	0.56	9	0.412
	09.00	0.118	0.0304	0.0069	0.1109	0.21	0.0270	9.3	0.64	11.5	0.414
	10.00	0.106	0.0280	0.0064	0.1018	0.23	0.0265	9.4	0.68	11	0.375
Supraglacial	-	0.061	0.0045	0.0018	0.0022	0.18	0.0067	7.7	-	-	0.136
	-	0.101	0.0037	0.0018	0.0065	0.29	0.0101	7.5	-	-	0.218
Precipitation	-	0.017	n.d.	0.0014	0.0207	0.01	0.018	7.37	-	-	0.056
	-	0.012	n.d.	0.0012	0.0087	0.01	0.017	6.4	-	-	0.034

n.d. = not detected

Fig.3. *Scatter diagrams of instantaneous discharge and air temperature readings, with discharge values lagging air temperature by 0, 0.5, 1 and 2 h respectively. Best correlation of discharge and air temperature is achieved if values of the former are taken at 0.5 to 1 h later than the corresponding air temperature reading.*

source of water at Fjallsjökull is likely to arise from surface melt.

Various heat sources can contribute to surface ablation, but only radiation, convection, and heat of condensation can vary diurnally and hence initiate the observed discharge variations. There are no data on the relative magnitudes of these different heat fluxes at Fjallsjökull, but Paterson (1969) has estimated that the dominant heat input is convection, with a minor contribution from radiation, at the Hoffelsjökull (another outlet glacier from Vatnajökull, 50 km north of Fjallsjökull).

Using air temperature as a crude measure of convectional energy input, the links between discharge and convectional energy input can be explored in a series of scatter diagrams (Fig. 3). A direct plot of air temperature against discharge gives a correlation coefficient $r = 0.48$ (significant at the 5% level). However it seems unlikely that there could be an instantaneous relationship between the two variables, because of the finite time taken to induce melting and transmit water from the glacier surface to the snout, through the internal hydrological system. An estimate of the delay time can be made by interpolating from the air temperature/time graph the values for air temperature at times 0.5, 1.0, and 2.0 h before the corresponding discharge value. Thus scatter diagrams can be plotted for discharge against air temperature for each of these lag times. The best correlations between discharge and temperature are achieved at lag times of 0.5–1.0 h ($r = 0.7$, significant at <0.1% level). This period of time can be envisaged as the most common or modal time taken for the melting and transit of supraglacial waters. The mean time is likely to be considerably longer as some supraglacial melt may be delayed by up to 24 h (Elliston, 1973; Collins, 1979[b]). Similar modal transit times have been identified by Meier and Tangborn (1961) for South Cascade Glacier (4 h) and by Lang (1968) for Grosser Aletschergletscher (1 h). These times are broadly consistent with the picture of glacial hydrology developed by Collins ([1978], 1979[b]) in which the bulk of the melt water (supraglacial in origin) is envisaged to flow rapidly through the glacier from the surface to the snout.

Variations in total dissolved load

Hydrological investigations of non-glacierized catchments suggest that there is often an inverse relationship between conductivity (as a measure of dissolved load) and discharge. Solute-rich base flows are produced from water percolating slowly through sediments and are diluted during precipitation events by rapid surface and sub-surface run-off, giving the following relationship between discharge and dissolved load (Hem, 1970):

$$C = aQ^{-k}$$

where C is the conductivity, Q the discharge, and a and k are constants. This relationship is usually plotted as the straight line

$$\log C = \log a - k \log Q.$$

Dilution relationships of this type have been identified in glacial melt waters by Rainwater and Guy (1961) and Lemmens and Roger (1978). However Collins (1979[a]) has argued that simple mixing models of this type are inappropriate for melt waters draining from the Gornergletscher, because a range of
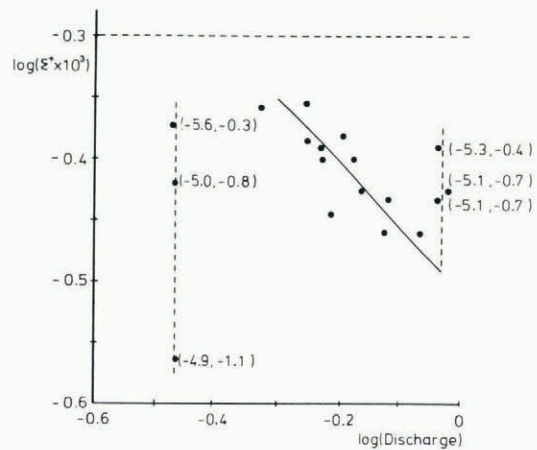

Fig.4. *Relationship between logarithm of discharge and Σ^+. Twelve points define the plotted regression line ($r = 0.88$) and represent simple mixing behaviour. The three highest and lowest discharge samples lying on the vertical dashed lines represent deviations from simple mixing behaviour and are shown with their $p(CO_2)$ and $(SI)_{calcite}$ values respectively. Horizontal dashed line represents the approximate position of melt waters with $(SI)_{calcite} = 0$.*

37

TABLE II.   CORRELATION MATRIX FOR THE DIURNAL SAMPLES

	Calcium	Sodium	Potassium	Magnesium	Bicarbonate	Sulphate
Sulphate	0.30	0.53***	0.48***	0.52***	0.50***	-
Bicarbonate	0.67**	0.20	0.49***	0.54***	-	
Magnesium	0.41	0.73*	0.82*	-		
Potassium	0.29	0.71*	-			
Sodium	0.04	-				
Calcium	-					

*	Significant at less than 0.1% level
**	Significant at less than 1% level
***	Significant at less than 2-5% level

dissolved loads may be associated with a given dis-
charge. Whilst this is demonstrably true on time
scales which encompass more than one diurnal cycle,
the mixing model may still prove to be useful over a
single cycle, where it can assist in the recognition
of chemical evolution in the melt waters on rela-
tively short time scales.

Figure 4 shows the relationships between the loga-
rithm of discharge and that of dissolved load, the
latter expressed as Σ^+(meq. l^{-1}), the sum of the
cation equivalents. Twelve points define a good
straight line (r = 0.88, significant at the <0.1%
level) but pronounced deviations exist at both high
discharge (where solute contents are high) and low
discharge (where solute contents are low). A combina-
tion of the errors involved in discharge measurement
and analysis (10-15%) is insufficient to explain
these deviations.

Variations in ionic composition

Relationships between the different dissolved
species in the bulk melt waters are expressed in a
correlation matrix (Table II), which provides an in-
dication of the sources of each element. Calcium,
potassium and magnesium are at least fairly well
correlated with bicarbonate (significant at the 4%
level or better) as a result of weathering reactions
which involve the concomitant production of bicarb-
onate ions from dissolved carbon dioxide and release
of cations from rock minerals (see later). Calcium
is however poorly correlated with magnesium (signifi-
cant at the 10% level) and not at all related to
potassium and sodium. These relationships are con-
sistent with a dominant carbonate source (for most
Ca^{2+} and some Mg^{2+}) together with various silicate
minerals as the main sources of Na^+, K^+, and the
remaining Mg^{2+}. The contributions of dissolved salts
originally in precipitation cannot be reliably esti-
mated in view of contamination effects (see later).

The different melt waters show relatively little
variation in cation composition. The main variations
are in Ca^{2+} (53-77% of the total cation equiva-
lents) and K^+ + Na^+ (12-32%), with Mg^{2+} relatively
constant (9-15%). Variations in cation composition
show no consistent relationship with discharge.

Carbonate equilibria

In general the hydrogen ions required for
weathering and dissolution reactions in melt waters
are derived from the solution of atmospheric carbon
dioxide and the oxidative breakdown of sulphide
minerals (Raiswell, 1984). The relative impact of
both contributions can be evaluated if melt waters
are fully analysed for anionic species. The analyses
of total alkalinity and pH reported here allow a full
description of the dissolved carbonate speciation,

by solution of the carbonate equilibria using the
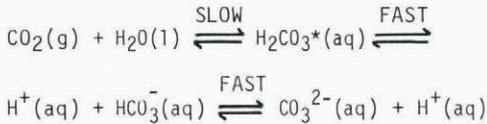computer programme WATSPEC (Wigley, 1977).

WATSPEC uses input data of temperature, density,
pH, and alkalinity together with the measured concen-
trations of the individual cationic and anionic
species. Its output relevant to the present dis-
cussion is the partial pressure of carbon dioxide
$p(CO_2)$ in equilibrium with the water and the extent
of the saturation of the water by various minerals,
as estimated by the logarithm of the ratio of ion
activity product to solubility product, known as the
saturation index (SI). Waters with (SI)<0 indicate
their thermodynamic potential for dissolution (under-
saturation) and (SI)>0 indicates potential for pre-
cipitation (oversaturation). Table III summarizes the
measured and computed variables relevant to carbon-
ate equilibria in the bulk melt water, supraglacial
run-off, and precipitation at Fjallsjökull. The bulk
melt waters generally have lower $p(CO_2)$ values and

TABLE III.   CARBONATE EQUILIBRIA DATA

Sample			
Type	Time	$- log_{10}p(CO_2)$	$(SI)_{calcite}$
	12.30	4.85	- 1.14
	13.30	5.02	- 0.75
	15.00	4.46	- 1.31
	16.00	5.1	- 0.71
	16.40	5.11	- 0.65
	17.20	5.31	- 0.39
	18.00	5.41	- 0.45
	19.30	5.63	- 0.60
	21.00	5.21	- 0.52
Bulk melt waters	22.30	5.49	- 0.42
	00.00	5.64	- 0.38
	01.30	5.63	- 0.34
	03.00	5.54	- 0.14
	04.30	5.49	- 0.29
	06.00	5.37	- 0.56
	07.30	5.33	- 0.50
	09.00	5.26	- 0.60
	10.00	5.43	- 0.61
Precipi- Supra-tation glacial	-	3.4	- 3.5
	-	3.7	- 2.6
	-	2.83	- 4.86

higher $(SI)_{calcite}$ (the saturation index of calcite) values than precipitation or supraglacial melt.

(i) $p(CO_2)$ values. Surface waters in equilibrium with the atmosphere should have $p(CO_2) \approx 10^{-3 \cdot 5}$ bar. Such waters apparently undergo chemical weathering in an open system where there is unrestricted transport of CO_2 between gas and water phases. However the rate of CO_2 transfer across the gas-liquid interface is frequently slower than reactions (such as weathering and dissolution) which consume CO_2 in the aqueous phase (Stumm and Morgan, 1981). In these circumstances the supply of hydrogen ions by the dissociation of $H_2CO_3^*$ reduces the concentration of undissociated $H_2CO_3^*$ detected in the water,

$$CO_2(g) + H_2O(l) \overset{SLOW}{\rightleftharpoons} H_2CO_3^*(aq) \overset{FAST}{\rightleftharpoons}$$

$$H^+(aq) + HCO_3^-(aq) \overset{FAST}{\rightleftharpoons} CO_3^{2-}(aq) + H^+(aq)$$

where (g), (l), (aq), and (s) denote gaseous, liquid, aqueous and solid phases respectively. The apparent CO_2 content of the gas phase in contact with the water (as calculated from water analyses) is thus reduced, and waters with these characteristics are held to have evolved in a closed system. This need not imply a physical constraint on access to atmospheric CO_2 but can simply be a kinetic effect which is maintained only as long as rates of CO_2 removal exceed rates of supply. Clearly waters in contact with the atmosphere may exhibit different characteristics depending on the rates at which hydrogen ions are consumed by weathering. Slow rates of weathering, comparable with rates of CO_2 transfer, allow waters to maintain equilibrium with atmospheric CO_2 ($p(CO_2) = 10^{-3 \cdot 5}$ bar). Conversely with typical, rapid weathering waters become depleted in $H_2CO_3^*$ and are no longer in equilibrium with the atmosphere ($p(CO_2) < 10^{-3 \cdot 5}$ bar). Re-equilibration with the atmosphere takes place relatively slowly, since the low levels of $p(CO_2)$ in the atmosphere result at best in only a small concentration gradient between gas and aqueous phases. Hence waters with closed-system characteristics will retain a memory of their closed-system history for a subsequent period of approximately 20-30 min.

The samples of precipitation and supraglacial melt have $p(CO_2)$ values close to those expected for open-system conditions, where equilibration with atmospheric CO_2 occurs. However the $p(CO_2)$ values of the bulk melt waters have values considerably below $10^{-3 \cdot 5}$ bar and are characteristic of closed-system evolution. The open-system $p(CO_2)$ values for supraglacial melt and precipitation are to be expected in view of their continued access to the atmosphere and the limited extent of their solute acquisition by weathering, but the detection of closed-system conditions for the evolution of the bulk melt waters is of considerable significance. Where $p(CO_2)$ values are low, the depletion of hydrogen ions is likely to control the extent and nature of solute acquisition by mineral-water reactions.

(ii) $(SI)_{calcite}$ values. The $(SI)_{calcite}$ value for precipitation (-5.7, -4.9) and supraglacial melt (-3.5, -2.6) indicate that these samples are several orders of magnitude undersaturated with respect to calcite. These values of $(SI)_{calcite}$ are very much lower than for the bulk melt waters (-1.3 to -0.14), where lower $(SI)_{calcite}$ values are clearly correlated with lower dissolved loads (as indicated by Σ^+ values). The maximum value recorded (-0.14) in the sample taken at 3.00 h indicates near saturation with calcite and the higher $(SI)_{calcite}$ values are linked to high pH and total alkalinity and low $p(CO)_2$. Some of the bulk melt waters have $(SI)_{calcite}$ values which are sufficiently high to indicate that the subglacial waters may be saturated with calcite, prior to mixing and dilution with englacial water. Although subglacial

precipitates have not been recorded at Fjallsjökull, the concentration of solutes by freezing subglacial water would certainly create the necessary oversaturation with respect to calcite.

DISCUSSION

Chemical evolution in the supraglacial environment

Precipitation must clearly be the source material for supraglacial melt and, although the number of samples is too small to account for temporal and spatial variations, some useful comparisons between precipitation and supraglacial melt can be made. Thus both precipitation and supraglacial melt clearly have lower solute contents, pH, and total alkalinity than the bulk melt waters (Table I). The values of $p(CO_2)$ and $(SI)_{calcite}$ should be regarded as no more than indicative in the case of precipitation because there are considerable difficulties in the determination of pH in poorly buffered samples and also because the total alkalinity values are close to the detection limit. Despite these errors, both groups of samples have $p(CO_2)$ values which are generally much closer to equilibrium with atmospheric levels (Table III), suggesting that solutes have been acquired in open-system weathering conditions. The $(SI)_{calcite}$ values steadily increase in passing from precipitation to supraglacial melt and thence to the bulk melt waters. The precipitation samples have rather low solute levels (cf. $\Sigma^+ = 0.121$ meq. 1^{-1} in average rainwater; Garrels and Mackenzie, 1971) but show considerable variability, possibly due to the dissolution of wind-blown dust found in all the samples There are however significantly higher solute levels in the supraglacial samples than in the precipitation and it is clear that some chemical reaction has occurred in the supraglacial environment. Under open-system weathering conditions it can be shown that solutes are acquired according to the relationship (Raiswell, 1984)

$$\log [\Sigma^+] = pH - 11.2$$

where $[\Sigma^+]$ the concentration of cation equivalents. Figure 5 shows both the precipitation and supraglacial samples plotted on a graph of $\log [\Sigma^+]$ against pH. Considering the errors in the determination of pH in dilute solutions (Bates, 1973), both sample groups
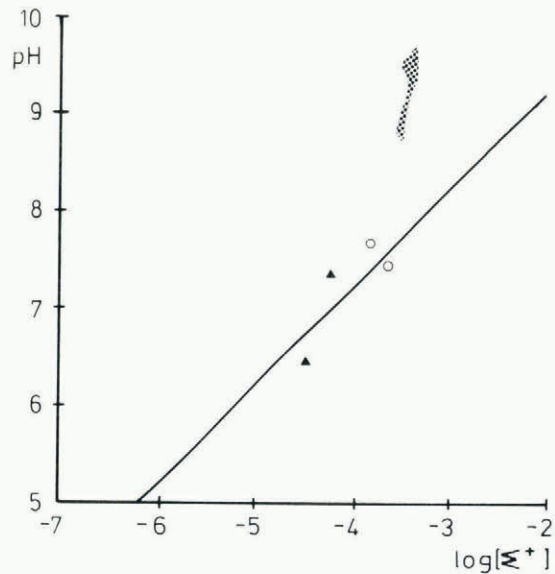
Fig.5. *Relationship between* $\log (\Sigma^+)$ *and pH. Theoretical open-system relationship shown by straight line, positions of precipitation (▲) and supraglacial melt (○) as shown.*

lie close to the straight line representing open-system weathering. The separation of precipitation samples from supraglacial melt occurs along the straight line in the direction expected, in view of the more extensive weathering history of the latter. These solute/pH relationships indicate the occurrence of chemical weathering in the supraglacial environment, since concentration or modification by firnification or regelation (Collins, 1979[b]) could not produce measurable changes in pH. Note that the points for the bulk melt waters plot in the shaded area lying above the open-system weathering line. Clearly, supraglacial melt can chemically evolve from precipitation by open-system weathering, but different reaction conditions or source materials are required to produce the bulk melt waters.

Chemical evolution in the englacial and subglacial environments

All the bulk melt waters are characterized by $p(CO_2) < 10^{-3.5}$ bar (Table III), indicating that hydrogen-ion removal by weathering exceeded supply by CO_2 transfer. Hence continued weathering depended on hydrogen ions supplied by the dissociation of $H_2CO_3^*$ inherited from the preceding phases of open-system evolution. The only other glacial melt waters for which reliable analytical data are available are from the Chamberlain, South Cascade, Argentière, Mer de Glace, and des Bosson glaciers, all of which exhibit open-system characteristics (Thomas and Raiswell, 1984). In the case of Argentière, the mixing of closed-system, subglacial waters with open-system, englacial waters still gives bulk melt waters with open-system characteristics, which suggests that the nature of the bulk melt waters is mainly determined by the relatively large englacial component. Since the modal transit time of the englacial component is approximately 0.5-1.0 h, rapid solute acquisition must occur to give closed-system characteristics. The development of closed-system characteristics thus reflects:

(i) Availability of easily weathered minerals (such as $CaCO_3$) to the englacial component. Solute acquisition by the englacial component prior to mixing seems unlikely, but post-mixing reactions may occur with the sediment supplied by the subglacial component. The comparatively long transit times and high sediment loads of the subglacial component suggest a near-equilibrium between solids and solution (see later), allowing the possible survival of reactive minerals. Mixing with the englacial component could then initi-
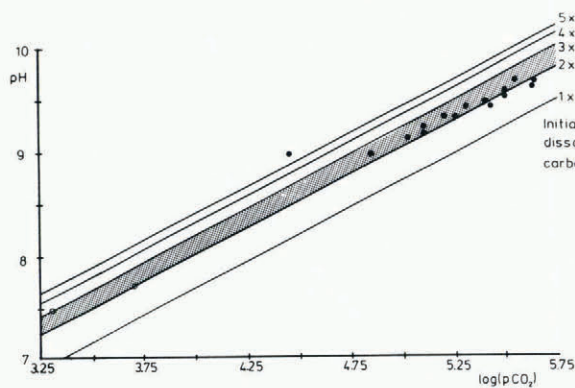
ate the continuation of further weathering and solute acquisition.

(ii) Hydrological variables which constrain rates of CO_2 transfer to the melt waters, either directly by limiting access to atmospheric CO_2 or indirectly by affecting rates of CO_2 transfer from gas to liquid (e.g. by reduced turbulence).

The relative influence of these factors cannot yet be distinguished. Figure 6 shows the changes in pH and $p(CO_2)$ (Raiswell, 1984) expected for closed-system evolution of supraglacial melt waters with different initial dissolved carbonate contents. With one exception all the bulk melt waters plot within the pH and $p(CO_2)$ values expected for the closed-system weathering of supraglacial melts with $2-3 \times 10^{-4}$ mol l^{-1} dissolved carbonate (close to the observed range of $1.8-2.9 \times 10^{-4}$ mol l^{-1}). Thus the compositional trends from supraglacial melt to the bulk melt waters are entirely those expected where solutes are acquired under closed-system conditions. The pH/$p(CO_2)$ relationships represent trends in the mean chemical weathering history of the bulk melt-waters, as determined by variations in the mixing ratio of englacial and subglacial components (the latter with a more extensive weathering history) and post-mixing evolution.

The relationships between pH and Σ^+ are plotted in Figure 7 for the closed-system evolution of waters with different initial dissolved carbonate contents, but with cations derived by either silicate weathering or carbonate dissolution. Under closed system conditions the dissolution of $CaCO_3$ requires only one mole of $H_2CO_3^*$ to produce a mole of Ca^{2+}. By contrast one mole of $H_2CO_3^*$ is required for each mole of a univalent ion derived from silicate weathering (Raiswell, 1984). This important distinction indicates that solution of $CaCO_3$ can supply a larger dissolved load (expressed as Σ^+) than can result from the

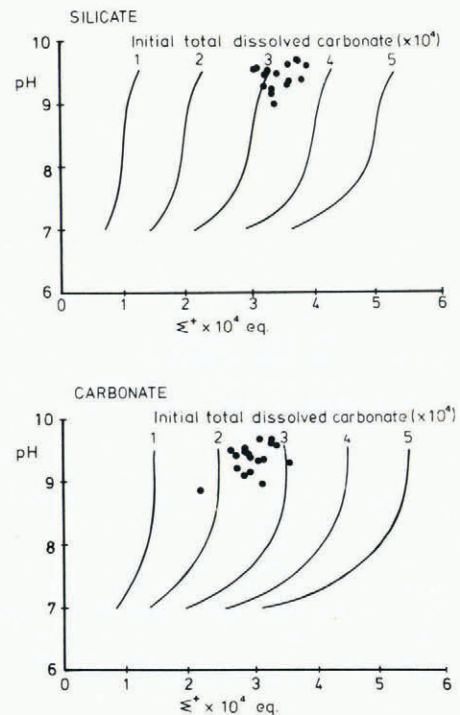Fig.6. Relationships between pH and p(CO_2) for the closed-system evolution of supraglacial melt waters with different initial dissolved carbonate contents. The shaded area shows the observed range of dissolved carbonate contents in supraglacial melt at Fjallsjökull (o). Bulk melt waters (•) emerging from the glacier portal fall within the shaded area, as expected for closed-system evolution from the observed composition of supraglacial melt.

Fig.7. Relationship between pH and Σ^+ for the closed-system evolution of bulk melt waters with different initial dissolved carbonate contents (obtained in the supraglacial environment). Upper diagram refers to subsequent closed-system evolution by reaction with silicates, lower diagram to reaction with carbonates. Bulk melt waters are corrected for the influence of solute acquisition by sulphide oxidation.

40

dissolution of silicates, for any fixed H^+ concentration. In closed-system weathering, where the availability of H^+ is limited by the initial dissolved CO_2, this distinction produces different curves for the pH/Σ^+ relationships.

Curves of pH against cation load (Fig.7) are shown for solute acquisition by carbonate dissolution and silicate weathering, at each of the two initial dissolved carbonate contents (2 and 3 x 10^{-4} mol l^{-1}) corresponding to the range observed in the supraglacial melts. Both sets of curves show that supraglacial melt composition exerts an important influence on the extent of subsequent closed-system evolution. In the present data, supraglacial melt composition is characterized by only two samples and errors may arise if these are unrepresentative. Agreement between observed and predicted $pH/p(CO_2)$ relationships suggests that this error is relatively small in comparison with that arising from the assumption that hydrogen ions are only supplied by dissociation of dissolved CO_2. Sulphate concentrations in the bulk melt waters are too large to originate solely from atmospheric precipitation, since Cl^-/SO_4^{2-} < 0.08 in melt waters compared with c. 5.4 in average rain-water (Garrels and Mackenzie, 1971). Oxidative weathering of sulphides (commonly pyrite) is the main alternative source of sulphate, augmented by acidic sulphur gases in areas of atmospheric pollution.

$$2FeS_2(s) + \frac{15}{2}O_2(g) + 4H_2O(l) \rightarrow$$

$$Fe_2O_3(s) + 4SO_4^{2-}(aq) + 8H^+(aq).$$
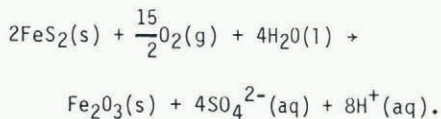
Oxidative weathering produces a 2:1 molar ratio of hydrogen ions to sulphate and so, assuming these hydrogen ions generate an equivalent amount of cations, the sulphate analyses can be used to correct for the extra cations resulting from sulphide breakdown. The melt waters with corrected cation contents (Fig.7) plot close to the curves showing pH/cation values for closed system $CaCO_3$ dissolution (starting from supraglacial melts with 2-3 x 10^{-4} mol l^{-1} dissolved carbonate), but lie outside the curves for closed-system silicate dissolution. Using the larger Σ^+ corrections appropriate for closed-system carbonate dissolution (Raiswell, 1984), either with or without further corrections for the sulphate content of supraglacial melt or precipitation, does not significantly modify the distribution of the data. These plots suggest that the major source of solutes was from $CaCO_3$ dissolution, and that oxidative weathering of sulphides accounted for perhaps 15% of the cation load. The conclusion that $CaCO_3$ dissolution was the major source of solutes agrees with the inter-element correlations (see earlier). Calcite, however, only constitutes 1-3% of the bedrock and its disproportionately large solute contribution arises because the modal residence time of water in the glacial hydrological system is short and because calcite is dissolved more readily than silicates. These features are common to many other glacial systems and, provided $CaCO_3$ is available even in small quantities, its dissolution may often be the major source of solutes.

Solute/discharge relationships

A linear, inverse relationship between solute levels and discharge implies that bulk melt-water composition is determined by a variable mixing ratio between englacial and subglacial components of constant composition. However preceding sections indicate that post-mixing evolution exerted an important influence on bulk melt-water chemistry. Thus the solute/discharge relationships (Fig.4) show that a simple mixing model is only valid over intermediate discharge and that large deviations occur at high and low discharge. However, the clearly defined mixing behaviour ($r = 0.88$) provides a useful starting point to consider solute/discharge behaviour. The mixing line spans a range of dissolved load from $\Sigma^+ = 0.34-0.45$ meq. l^{-1} approximately, representing the range where variations in the composition of either the englacial or subglacial components are relatively small and bulk melt water composition is mainly controlled by changes in the ratio of englacial to subglacial water. Collins (1979[b]) assumes that the englacial component undergoes little or no chemical evolution and hence is similar in composition to supraglacial melts (observed range in Σ^+ of 0.14-0.22 meq. l^{-1}). In the case of the subglacial component, Collins (1979[b]) assumes that the composition is that of the repeatedly observed value for maximum dissolved load, as measured during periods of recession flows induced by snow-fall. In the absence of such data at Fjallsjökull a theoretical, rather than an observational, approach must be adopted. Consider the samples taken at 3.00 and 4.30 h which contain the highest dissolved loads on the mixing line and which are close to saturation with calcite ($(SI)_{calcite}$ = -0.14 and -0.29 respectively). It is unlikely that these two low-discharge samples consist entirely of subglacial water. During stable diurnal cycles, Collins (1979[b]) estimated that minimum observed flows consisted of 30-70% subglacial water. Thus these two low-discharge samples at the solute-rich end of the mixing line have almost certainly experienced some dilution by englacial waters and must have lower dissolved loads than subglacial water. In the case of Fjallsjökull, where calcite dissolution is the main source of solutes (see above), there must also be a maximum possible dissolved load which corresponds to saturation or near-saturation with calcite (marked by the horizontal dashed line in Fig.4). Thus the composition of subglacial waters must lie close to, or within, the limits of dissolved load represented by calcite saturation levels ($\Sigma^+ = 0.5$ meq. l^{-1}), and the samples taken at 3.00 and 4.30 h ($\Sigma^+ = 0.44$ meq. l^{-1}). Assuming that the minimum composition of the englacial waters is $\Sigma^+ = 0.14-0.22$ meq. l^{-1} and that the subglacial waters are saturated with calcite, then samples 3.00 and 4.30 h would have a maximum subglacial contribution of approximately 80%. The existence of repeatedly observed maximum dissolved loads is entirely to be expected if the composition of subglacial waters is limited by saturation with respect to a solid phase such as calcite, as was the case in subglacial streams from Argentière (Thomas and Raiswell, 1984).

The deviations from mixing behaviour are represented by two groups of samples occurring at the highest and lowest discharges. Each group of samples shows a significant range in dissolved load ($\Sigma^+ = 0.37-0.41$ and 0.27-0.41 meq. l^{-1} respectively) with little variation in discharge. It is considered that these samples are particularly influenced by hydrological events which affect the degree of post-mixing evolution and which are masked at intermediate discharges by larger variations in the mixing ratio. Rates of mineral dissolution (Berner, 1978) decline markedly close to saturation, thus closed-system, solute-rich subglacial melt at Fjallsjökull (inferred to be close to saturation with calcite) and at Argentière (close to saturation with calcite and aluminosilicates; Thomas and Raiswell, 1984) are capable of only slow rates of solute acquisition. By contrast the englacial waters are dilute and are capable of undergoing rapid weathering and dissolution on contact with reactive rock minerals. However the negligible sediment loads of supraglacial melt (Collins, [1978]) which constitutes most of the englacial component, implies that the opportunity for further reaction in the englacial system is minimal. The chemical situation changes dramatically on mixing with sediment-rich subglacial water and further solute acquisition by the englacial component (more strictly the bulk melt waters) is possible.

Clearly mixing-line behaviour will occur as long

as the extent of post-mixing evolution remains constant. However short-term hydrological events which significantly modify the transit time of a portion of the melt waters (before or after mixing) will cause deviations from mixing behaviour. Collins (1979[b]) also recognized the importance of time-dependent chemical evolution in suggesting that stored and chemically enriched water can be returned to the main flow system at high discharge, following the ablation peak. An explanation of this type may apply to the high-discharge deviations from mixing behaviour at Fjallsjökull. In general terms, the hydrological environment beneath glaciers is complex and dissolved loads in bulk melt waters will be sensitive to a variety of factors which influence the kinetics of solute acquisition, principally water composition (extent of saturation with respect to rock minerals and aluminosilicate weathering products), reactivity of rock debris (grain-size, abundance, and composition), and duration of access to rock debris (mean flow rates and storage times).

CONCLUSIONS

1. Melt-water discharge from Fjallsjökull follows a characteristic diurnal pattern which lags observed variations in air temperature by approximately 0.5-1.0 h. This time interval represents the modal time required for the production of supraglacial melt and its subsequent transmission through the internal drainage system of the glacier.

2. The composition of precipitation samples and supraglacial melt lie on an open-system chemical weathering continuum. Supraglacial melt has a higher solute content and total alkalinity than precipitation, but similar $p(CO_2)$ values, indicating equilibration with the atmosphere. These chemical properties are as expected if waters with the composition of precipitation undergo chemical weathering in an open system, where the rate and extent of CO_2 (aq) consumption by weathering reactions does not exceed renewal by dissolution of $CO_2(g)$. The low availability of fine-grained and easily weathered minerals principally limits the extent of weathering and determines that open-system conditions exist.

3. The bulk melt waters have higher solute contents, pH, and total alkalinity than supraglacial melt, but have lower $p(CO_2)$ values indicating chemical evolution in a closed system, where rates of CO_2 (aqueous) consumption by weathering exceed renewal by dissolution. The existence of closed-system conditions is determined by the presence of abundant reactive minerals in the bulk melt waters and constrained rates of CO_2 transfer from gas to liquid phases.

4. The bulk melt waters show consistent and predictable chemical relationships (in terms of pH/CO_2 and pH/cation load) for chemical evolution from waters with the composition of supraglacial melt in a system closed to atmospheric CO_2.

5. The closed-system weathering models suggest that the major source of hydrogen ions for solute acquisition by chemical weathering arises from the dissolution and dissociation of atmospheric CO_2. An additional 15% approximately of the solute load arises from hydrogen ions supplied by the oxidative weathering of sulphides. The major source of solutes was from calcite dissolution.

6. Solute/discharge relationships at Fjallsjökull are complex. A simple mixing model between dilute englacial water (derived from, and compositionally similar to, supraglacial melt) and more concentrated subglacial water only applies over intermediate discharges (0.5-0.9 m^3 s^{-1}), where variations in the composition of either component are small compared to

variations in their mixing ratio. Time-dependent chemical reactions occur after mixing and exert significant effects on composition at either discharge extreme.

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