

CHEMICAL MODELS OF SOLUTE ACQUISITION IN GLACIAL MELT WATERS

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ABSTRACT. Chemical models for the evolution of bulk melt waters can be constructed by assuming that rock mineral weathering and solute acquisition are controlled by carbonate equilibria. Different open- and closed-system models are defined by variations in the rates of weathering relative to the rate of hydrogen-ion supply by the dissolution and dissociation of CO₂, and can be recognized by characteristic pH and Σ^+ relationships. The observed and inferred compositions of englacial and subglacial melt suggest that mixing is unlikely to be conservative and that closed-system conditions result where post-mixing weathering reactions occur. The final composition of bulk melt waters is determined by the mixing ratio between englacial and subglacial melt, the extent of post-mixing evolution, and opportunity for mixing with ground waters or re-equilibration with the atmosphere.

RÉSUMÉ. Modèles chimiques des processus de dissolution dans les eaux de fusions glaciaires. On peut construire des modèles chimiques reproduisant l'évolution des eaux de fusion résurgentes en partant de l'hypothèse que l'attaque des minéraux des roches et l'acquisition de matière dissoute sont contrôlés par l'équilibre des carbonates. Différents systèmes modèles ouverts ou fermés sont définis par des variations dans les vitesses d'attaque selon le taux de dissolution du gaz carbonique issu de l'atmosphère, et peuvent être distingués par des pH caractéristiques et des relations Σ^+ . Les compositions observées et déduites des eaux intraglaciales et sous-glaciaires font penser que les mélanges ne sont probablement pas durables et que les conditions

INTRODUCTION

There have been many chemical studies of melt waters following their emergence from the glacier portal (e.g. Rainwater and Guy, 1961; Reynolds and Johnson, 1972; Lorrain and Souchez, 1972; Slatt, 1972; Church, 1974; Collins, [1978]; Lemmens and Roger, 1978; Souchez and others, 1973; Collins, 1979[a],[b]; Collins and Young, 1981), but relatively little attention has been directed towards identifying the nature and controls of solute acquisition by water-rock interactions in the glacial system. Lorrain and Souchez (1972) suggest that cations are acquired by desorption from suspended sediment, whilst Lemmens and Roger (1978) show that the relative abundance of different cations is determined by their rates of leaching from silicate minerals and replacement by hydrogen ions. Reynolds and Johnson (1972) have also shown that hydrogen-ion concentrations exert a significant influence on water-rock interactions in melt waters, as they do in general on most weathering reactions.

In surface waters, hydrogen-ion concentrations are principally controlled by carbonate equilibria, which can only be quantified by analysis for cations, dissolved carbonate species and pH. It is the purpose of this paper to present chemical models which define the controls of solute acquisition by glacial melt waters in terms of carbonate equilibria.

CHEMICAL WEATHERING PROCESSES

The nature of water-rock interactions in the glacial system has a strong parallel in the dissolution and weathering reactions in the soil system, with the

d'un système clos se produisent lorsque les réactions d'attaque après le mélange surviennent. La composition finale des eaux de fonte à la sortie du glacier est déterminée par le taux de mélange des eaux de fusion intra et sous-glaciaires, l'importance de l'évolution après mélange, et les possibilités de mélange avec des eaux souterraines ou de rééquilibrage avec l'atmosphère.

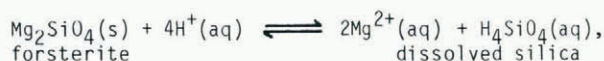
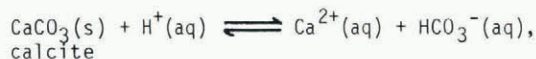
ZUSAMMENFASSUNG. Chemische Modelle für die Lösungsanreicherung in glazialen Schmelzwässern. Chemische Modelle für die Entwicklung von Massen-Schmelzwässern können aus der Annahme hergeleitet werden, dass die Verwitterung von Felsmineralen und die Anreicherung mit Lösungen durch Carbonat-Gleichgewichte kontrolliert wird. Verschiedene Modelle für offene und geschlossene Systeme sind durch Veränderungen in der Verwitterungsrate relativ zur Aufnahme von Kohlendioxid aus der Atmosphäre gekennzeichnet und können durch charakteristische pH- und Σ^+ -Beziehungen erkannt werden. Die beobachteten und angenommenen Zusammensetzungen von inner- und subglazialen Schmelzwässern lassen vermuten, dass der Mischvorgang nicht konservative ist und dass sich Bedingungen eines geschlossenen Systems einstellen, wenn Verwitterungsreaktionen nach der Mischung auftreten. Die endgültige Zusammensetzung von Massen-Schmelzwässern ist durch das Mischungsverhältnis zwischen inner- und subglazialen Schmelzwasser, durch das Ausmass der Entwicklung nach der Mischung und die Möglichkeit der Einmischung von Grundwasser oder des Austausches mit der Atmosphäre bestimmt.

important difference that dissolved organic material may be a significant source of acidity in soils (Graustein and others, 1977) but is present at very low concentrations in melt waters (personal communication from T.C. Loder). Furthermore, material within the glacial drainage system is freshly ground, whereas grains in other surface-weathering environments are often coated with adsorbed organic compounds which modify their surface properties and reactivity (Hunter and Liss, 1982; Tipping, 1981). The absence of such organic materials in the glacial drainage system (excluding the pro-glacial environment) allows the consideration of purely inorganic reactions and is an important simplifying factor.

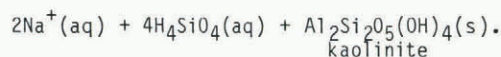
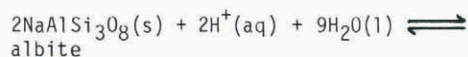
Studies of soil weathering do however suggest that the influence of three chemical factors (water composition, water flow rate, and rock mineralogy) is paramount, although these factors are themselves dependent on many other variables, e.g. relief, drainage, biogenic activity, and climate. These three chemical factors are briefly evaluated below, with reference to the glacial system. More detailed discussions of chemical weathering can be found in Berner (1971), Curtis ([C1976]), Bolt and Bruggenwert (1978), Raiswell and others (1980), and Stumm and Morgan (1981).

Water composition

The single most important mechanism by which rock minerals are weathered is acid hydrolysis, the general principles of which can be demonstrated by reference to just three types of minerals; carbonates, silicates, and aluminosilicates.



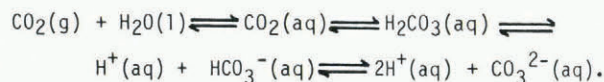
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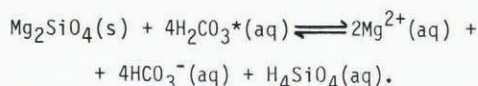
In each of these reactions a metal cation is released to solution by a fixed amount of hydrogen ions and the anionic component of the mineral is completely solubilized (calcite, forsterite) or partially solubilized (albite) to give dissolved carbonate or silica species. Because of the partial solubilization of aluminosilicates (incongruent dissolution), a number of different chemical reactions can be written to produce different residual solid phases (gibbsite, kaolinite, montmorillonite) depending on the degree of solubilization. However, the same relationship between hydrogen ions consumed and cations released still applies.

It follows from this that the chemical weathering of rock minerals is controlled to a great extent by the supply of hydrogen ions by acids (Curtis, [1976]). The main sources of acids in natural systems arise from CO_2 (dissolved from the atmosphere and from biogenic respiratory sources), sulphide oxidation and pollutant acid gases such as SO_2 . The present paper is restricted to modelling weathering reactions in melt waters prior to their emergence at the glacier portal (where biogenic contributions should be negligible) in glacial systems unperturbed by anthropogenic inputs. Hence the main sources of acids are considered to be from the equilibration of melt waters with atmospheric CO_2 and from the weathering of sulphide minerals in bedrock.

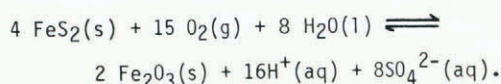
An aqueous solution of carbon dioxide contains simple dissolved CO_2 molecules ($\text{CO}_2(\text{aq})$) as well as the hydrated species H_2CO_3 , although the former is greatly predominant. Since the hydration equilibrium is established rapidly (less than a few minutes) the species $\text{CO}_2(\text{aq})$ and H_2CO_3 may be considered together and are so designated as H_2CO_3^* , following the approach of Stumm and Morgan (1981). The H_2CO_3 may be dissociated in two steps to produce the hydrogen ions required for acid hydrolysis.



The final dissociation to CO_3^{2-} occurs only at high pH and does not make a significant contribution to hydrogen ions in most melt waters (see later). Thus, the weathering of forsterite can be re-written as;



An important general principle is indicated; the anionic components of melt waters demonstrate the acid source used in the dissolution and weathering of rock minerals. Similarly where acids are supplied by the oxidation of sulphides (commonly pyrite), sulphate is the dominant anion.



This brief summary of the role of hydrogen ions in weathering emphasizes that attention must be directed towards the anionic composition of melt waters, as indicators of the hydrogen-ion sources which determined the nature and extent of chemical weathering.

Water flow rate

The influence of water flow rate can be assessed by considering the example of albite weathering (see above). The equilibrium constant for this reaction

can be written as below and its value derived from thermodynamic data.

$$K_{\text{eq}} = \frac{[\text{Na}^+]^2 [\text{H}_4\text{SiO}_4]^4}{[\text{H}^+]^2} = 10^{-15.9}.$$

Many silicate and aluminosilicate weathering reactions have equilibrium constants of a similar magnitude, indicating that only small increases in the concentrations of the aqueous products (and decreases in $[\text{H}^+]$) are needed to approach equilibrium and stabilize the solid phases. In these circumstances water flow rate can exert a critical control on the rate and extent of dissolution, since high flow rates have the effect of supplying a fresh source of H^+ and flushing away the dissolved products of weathering. A close approach to equilibrium is therefore prevented and hence it is generally assumed that increased flushing rates cause an increased rate of mineral dissolution. Strictly this is only true when the waters are sufficiently close to saturation for the reactivity of the minerals to be neglected (Berner, 1978).

Rock mineralogy

Minerals weather at different rates and may additionally weather in a variety of ways to produce different solid-phase products (see earlier). Glacial bedrock mostly contains silicates, aluminosilicates, and carbonates with accessory sulphide minerals. Sulphides break down exceedingly rapidly in oxygenated surface environments and carbonate minerals generally weather more rapidly than silicates and aluminosilicates, although considerable variations result from grain-size and crystallinity effects. Despite these variations in the rate and directions of weathering, chemical evolution of the water phase always proceeds in the same direction and produces fixed quantitative relationships between the gain in cations and bicarbonate and the consumption of hydrogen ions.

CHEMICAL CONTROLS OF MELT-WATER COMPOSITION

Compositional variations in melt waters

Existing chemical data permit some useful limits to be placed on the range of compositional variation in glacial melt waters. Although these data have been obtained by many different sampling, storage and analytical methods, they are used uncritically with the limited objective of defining realistic constraints for chemical models. Nine studies of melt-water composition (Rainwater and Guy, 1961; Keller and Reesman, 1963; Reynolds and Johnson, 1972; Slatt, 1972; Church, 1974; Zeman and Slaymaker, 1975; Hallet and others, 1978; Lemmens and Roger, 1978, Thomas, unpublished) have been used, covering nearly 40 melt-water systems. Some systems are represented by only one analysis, others have been analysed several or more times by different workers. Any data set with two or more analyses is represented by two points which give the compositional extremes for pH, Σ^+ (the sum of the cation equivalents), cation composition, and anion composition.

Hydrogen-ion concentration. Variations in pH (Fig. 1) range from 4-9.5, with most values between 6.5 and 8. Most samples were measured under field conditions and only four samples are specified as laboratory measurements under ambient conditions.

Cation equivalents. Most data sets record only cation concentrations and the best measure of solute load is Σ^+ . Glacial melt waters (Fig. 2) are dilute ($\Sigma^+ \leq 3 \times 10^{-3}$ eq.l⁻¹).

Cation composition. Calcium is the dominant cation in approximately 88% of the melt waters (Fig. 3) and often comprises more than 70% of the total cation equivalents.

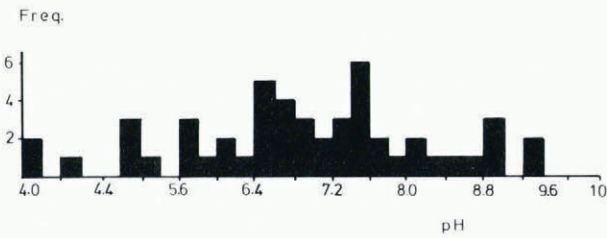


Fig.1. Range of pH variations in glacial melt waters.

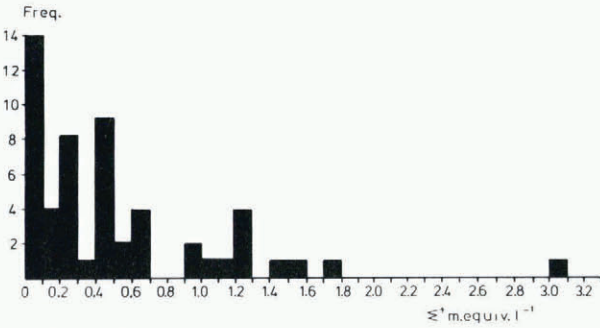


Fig.2. Range of solute load variations (expressed as ΣT) in glacial melt waters.

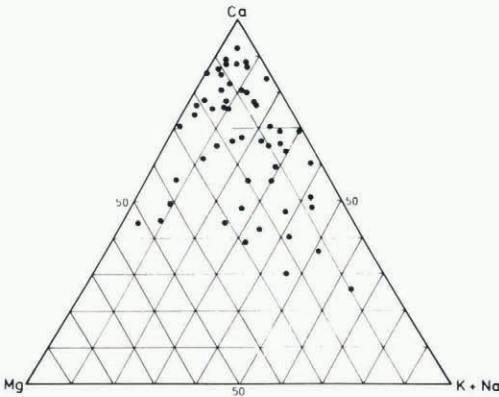


Fig.3. Variations in the cation composition of glacial melt waters.

Anion composition. Data are sparse. Only 23 data sets give HCO₃⁻ (strictly alkalinity), SO₄²⁻, and Cl⁻ and in eight of these sets Cl⁻ is below detection limit (<10⁻⁶ mol l⁻¹). In the remaining melt waters HCO₃⁻ and SO₄²⁻ are each dominant in approximately half the analyses and Cl⁻ is almost invariably low.

The anion observations suggest that a simple and reasonably valid model of melt-water chemistry may be constructed by reference to systems where the hydrogen ions used in weathering are supplied through carbonate equilibria. Such models may have their usefulness extended by correcting for a limited supply of H⁺ from pyrite oxidation, but melt waters with high sulphate concentrations require a more complex treatment.

The above data suggest a maximum of pH of c. 9.5 and, since

$$K_2 \text{ at } 0^\circ\text{C} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = 10^{-10.62},$$

then

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{10^{-10.62}}{[\text{H}^+]}$$

For any pH 9.62 the [CO₃²⁻] is less than 10% of the [HCO₃⁻] and treatment of the carbonate equilibria is simplified by ignoring the presence of [CO₃²⁻]. For many melt waters the errors so introduced will be negligible.

A further useful simplification is to assume that activity and concentration are equal. In an ideal solution it is assumed that there are no interactions between dissolved ions, in fact in real solutions electrostatic interactions may give rise to both non-specific and specific (i.e. ion-pair) interactions. It can be shown that both of these effects can be safely neglected in most melt waters, which are sufficiently dilute to approximate to ideal solutions. Dealing first with non-specific interactions for a Ca²⁺ and HCO₃⁻ melt water, with ΣT = 10⁻³ eq.l⁻¹; the ionic strength I is given by I = Σc_iz_i²/2 where c_i is the concentration of ion i and z_i its charge. This results in the numerical value

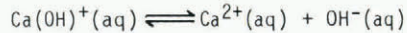
$$I = 1.5 \times 10^{-3}.$$

The non-specific interactions between dissolved species cause them to exhibit an activity which is less than their total concentration, thus the activity is γ times the concentration where γ is the activity coefficient. Values of γ depend on ionic strength and can be estimated by Debye-Hückel theory (Garrels and Christ, 1965)

$$-\log \gamma = \frac{Az_i^2 \sqrt{I}}{1 + Ba_0 \sqrt{I}}$$

The parameters A B depend only on temperature and solvent and a₀ is constant for a specified ion. For Ca²⁺ in water at 0°C their values are respectively 0.4883, 0.3241 x 10⁻⁸ and 6 x 10⁻⁸. The Debye-Hückel expression then gives γ(Ca²⁺) = 0.85. Thus, for Ca²⁺, assuming an equality between activity and concentration will introduce a comparatively small error. Univalent ions exhibit smaller electrostatic interactions and γ(HCO₃⁻) = 0.96 for the same solution.

In addition to these non-specific interactions, various dissolved species may form complexes or ion pairs in solution. Again using the simple Ca²⁺ and HCO₃⁻ melt water as a model, ion pairs of the form Ca(OH)⁺, Ca(HCO₃)⁺ and CaCO₃⁰ may be expected. The dissociation constant for the reaction



has the value (Garrels and Christ, 1965)

$$K_{\text{diss}} = \frac{[\text{Ca}^{2+}][\text{OH}^-]}{[\text{Ca(OH)}^+]} = 10^{-1.3}$$

In the pH range of melt waters the highest [OH⁻] is approximately 10^{-4.5}. Thus

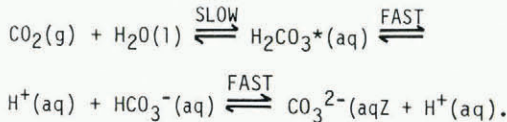
$$\frac{[\text{Ca(OH)}^+]}{[\text{Ca}^{2+}]} \leq \frac{10^{-4.5}}{10^{-1.3}} \leq 10^{-3.2}.$$

Clearly, the ion pair Ca(OH)⁺ is less than 0.1% of the free Ca²⁺ ion and ion pair formation can be neglected for these species. A similar conclusion can be reached for Ca(HCO₃)⁺ and CaCO₃⁰ (Garrels and Christ, 1965). It is concluded that both specific and non-specific interactions are negligible in dilute melt waters (ΣT < 10⁻³ eq.l⁻¹).

Finally, the following carbonate equilibria models are constructed using thermodynamic data for one atmosphere pressure and 0°C. Reduced pressures at high altitudes cause a small effect (equivalent to a reduction in p(CO₂) ≈ 10% at 2000 m a.s.l.). Changes in temperature produce a similarly small effect, as the dissociation constants for H₂CO₃ change by only 15% between 0 and 5°C. Most melt waters are in the range 0 - 2°C on emergence.

Chemical models: rationale

It has been demonstrated that chemical weathering in melt waters results in quantitative relationships between gains in cations and HCO_3^- and losses of H^+ for any carbonate, silicate, or aluminosilicate bed-rock. Weathering thus always progresses in a similar direction although the extent of progression is determined by time-dependent (i.e. kinetic) factors, e.g. rates of H^+ supply, rates of mineral reaction, and melt-water-rock contact times. Although the reaction stoichiometry of mineral dissolution suggests that simple numerical relationships exist between gains in cations and HCO_3^- and losses of H^+ , the situation is complicated because H^+ and HCO_3^- are linked through the carbonate equilibria.



As hydrogen ions are consumed by weathering, so these equilibria are perturbed to the right, with H_2CO_3^* being progressively dissociated to H^+ and HCO_3^- . Where waters are in contact with the atmosphere ($p(\text{CO}_2) = 10^{-3.5}$ bar) the continued dissolution of CO_2 gas will occur to replace the H_2CO_3^* used in weathering. Continued weathering causes the solution to accumulate HCO_3^- , in the absence of removal mechanisms, hence pH is constrained by the increasing $[\text{HCO}_3^-]$ and constant $[\text{H}_2\text{CO}_3^*]$ values (see Equations (1) and (2)). Clearly, the continued availability of H^+ depends on the dissolution of $\text{CO}_2(\text{g})$ to form H_2CO_3^* . However, the rate of CO_2 solution and transfer across the gas-liquid interface is slow, often slower than reactions (such as weathering and dissolution) which consume H_2CO_3^* (Stumm and Morgan, 1981).

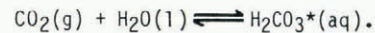
The simplest example to consider is that in which it is assumed that no depletion of H_2CO_3^* occurs, indicating continued equilibrium or near-equilibrium with atmospheric CO_2 . This constrains the variations in HCO_3^- and H^+ , through the first dissociation constant of H_2CO_3^* , such that their product must remain constant. However with continued weathering the increases in HCO_3^- greatly exceed the depletions in H^+ and thus the rate of H^+ supply by CO_2 dissolution must approach the rate of H^+ consumption (and HCO_3^- formation) by weathering. This case occurs with poorly reactive minerals where the rate of weathering is slow and the system behaves as though there were free and rapid CO_2 dissolution to maintain H_2CO_3^* concentrations. This system can be designated as open (i.e. to CO_2 dissolution) and may therefore show large increases in total dissolved carbonate species during weathering. However the H^+ used in weathering may also be derived from a flow of fresh, unreacted solution and in general H_2CO_3^* concentrations remain constant if the rates of H^+ supply by flow and re-equilibration are sufficient to approach the rates of H^+ consumption by weathering.

A closed system model can now be defined conversely by the requirement that there is no dissolution of $\text{CO}_2(\text{g})$ to replace the H_2CO_3^* used in weathering, hence the total concentrations of dissolved carbonate species remains constant. In this case the supply of H^+ by the dissociation of H_2CO_3^* reduces the concentration of undissociated H_2CO_3^* in the water. Since $p(\text{CO}_2)$ is directly proportional to H_2CO_3^* , the consequence of rapid H^+ removal is to reduce the calculated equilibrium carbon dioxide content of the gas phase in contact with the water. Waters with these characteristics are so recognized and defined as closed system. This need not imply a physical constraint on access to atmospheric CO_2 but can be simply a kinetic effect which is maintained as long as rates of CO_2 removal exceed rates of supply. Clearly, closed-system weathering is limited in extent because the initial concentration of H_2CO_3^* can

only supply an equivalent concentration of H^+ . Once this H^+ has been consumed further weathering by acid hydrolysis is impossible. The closed-system model is recognized by H_2CO_3^* concentrations which correspond to $p(\text{CO}_2)$ below atmospheric ($<10^{-3.5}$ bar) and the extent of weathering is constrained by the original concentrations of H_2CO_3^* , which determine H^+ availability. Re-equilibration with the atmosphere does not occur instantaneously because of the small concentration gradient between gas and aqueous phases, hence waters with closed-system characteristics can retain a significant memory of their closed-system history for a period of 20-30 min after contact with atmospheric CO_2 (Thomas, unpublished).

Basic equations

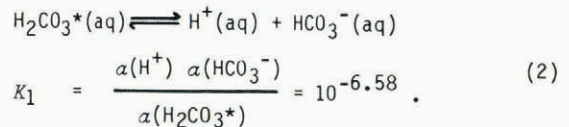
The approach which follows has been modified from the more thorough treatments by Garrels and Christ (1965), Stumm and Morgan (1981), and Butler (1982). When $\text{CO}_2(\text{g})$ dissolves in water the following equilibrium is established:



Concentrations of $\text{CO}_2(\text{g})$ are usually expressed as atmospheric partial pressures, so that Henry's Law for the solution of CO_2 in water is written as below. Activities are denoted by a followed by the chemical formula in parentheses and all equilibrium constants are for 0°C and dilute solutions with zero ionic strength, as in Garrels and Christ (1965).

$$K(\text{CO}_2) = \frac{a(\text{H}_2\text{CO}_3^*)}{p(\text{CO}_2)} = 10^{-1.12} \quad (1)$$

The dissociation of H_2CO_3^* proceeds by



A mass-balance equation can also be written for the total dissolved carbonate C_T , where

$$C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] \quad (3)$$

This mass-balance equation must be written in concentrations (as denoted by square brackets). Solutions must also preserve electroneutrality, so that;

$$z^+ + [\text{H}^+] = [\text{HCO}_3^-] + [\text{OH}^-] \quad (4)$$

For most melt waters this expression simplifies to

$$z^+ = [\text{HCO}_3^-]$$

because both $[\text{H}^+]$ and $[\text{OH}^-]$ become insignificant provided $[\text{HCO}_3^-] \geq 10^{-4} \text{ mol l}^{-1}$ and the pH lies between 5 and 9.

Equations (1) - (4) are sufficient for a complete description of the carbonate equilibria in melt waters, together with the following relationship between $a(\text{H}^+)$ and $a(\text{OH}^-)$:

$$a(\text{H}^+) a(\text{OH}^-) = K_W = 10^{-14.9} \text{ at } 0^\circ\text{C}. \quad (5)$$

Equations (1), (2), and (5) are written in terms of activities, whereas Equations (3) and (4) are expressed in concentrations. Since it is assumed that activity and concentration are equal all the terms in the following equations are expressed as concentrations, except for H^+ .

OPEN SYSTEM MODEL

Since open-system melt waters retain equilibrium with atmospheric CO₂ at 10^{-3.5} bar, Equation (1) gives

$$[H_2CO_3^*] = p(CO_2) K(CO_2) = 10^{-4.62}.$$

Substituting in Equation (2),

$$\alpha(H^+) = \frac{K_1 [H_2CO_3^*]}{[HCO_3^-]} = \frac{10^{-11.2}}{[HCO_3^-]}$$

$$\log [HCO_3^-] = pH - 11.2. \tag{6}$$

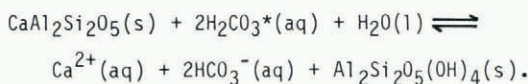
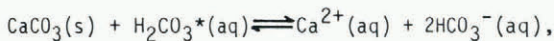
Using Equation (4) and subject to the provisos specified,

$$\log [\Sigma^+] = pH - 11.2. \tag{7}$$

Equations (6) and (7) demonstrate the chemical evolution of melt waters which undergo open-system weathering. Although variations in bedrock mineralogy will influence the nature of the cations contributing to Σ⁺, the numerical value of the latter is independent of mineralogy. Thus these equations are of general application to carbonate, silicate, and aluminosilicate weathering, with the provisos specified.

CLOSED-SYSTEM MODELS

It is assumed that waters undergoing closed-system evolution were originally in equilibrium with atmospheric p(CO₂). Thus, the extent and direction of weathering is determined by the undissociated H₂CO₃* present initially in the water and which is not significantly renewed. However, waters in a closed system may have undergone different degrees of open-system weathering prior to their closed-system evolution. Furthermore, the pathways of closed-system silicate and carbonate weathering differ because dissolution of the latter increases total dissolved carbonate, which remains constant during silicate dissolution. Comparing dissolution equations shows that solution composition is identical, but only one mole of H₂CO₃* is required to liberate each mole of Ca²⁺ in carbonate dissolution, compared to the two required by the silicate:



Thus, for any fixed concentration of H₂CO₃*, the solution of CaCO₃ can supply a larger dissolved load than silicate or aluminosilicate dissolution. These two cases must therefore be considered separately.

Relationships between pH and p(CO₂) for silicate weathering

Melt waters with a previous open-system weathering history must satisfy Equations (6) and (7) on their removal to a closed system, and must also be in equilibrium with atmospheric p(CO₂). Hence [H₂CO₃*] is fixed but [HCO₃⁻] may vary. On initiation of closed-system conditions there can be no further addition of dissolved carbonate species (C_T constant) and weathering only proceeds to the extent that H₂CO₃* can dissociate to form H⁺.

$$C_T = [H_2CO_3^*] + [HCO_3^-] = \text{constant}.$$

From Equations (1) and (2),

$$[HCO_3^-] = \frac{p(CO_2) 10^{-7.7}}{[H^+]},$$

$$C_T = p(CO_2) 10^{-1.12} + \frac{p(CO_2) 10^{-7.7}}{\alpha(H^+)}.$$

$$\text{Hence, } pH = \log (C_T - p(CO_2) 10^{-1.12}) - \log p(CO_2) + 7.7. \tag{8}$$

This equation defines the relationship between pH and p(CO₂) for any fixed amount of prior open-system weathering (as defined by C_T) of silicate or aluminosilicate minerals. The minimum value of C_T is fixed by the total dissolved carbonate in pure water in equilibrium with atmospheric p(CO₂), which is mainly H₂CO₃* and therefore only fractionally larger than the term p(CO₂)10^{-1.12}. In actual melt-water systems, minimum values of C_T seem to be approximately 10⁻⁴, sufficiently large that the term (C_T - p(CO₂)10^{-1.12}) remains essentially constant and graphs of pH and -log p(CO₂) plot as straight lines for different chosen C_T values (Fig. 4).

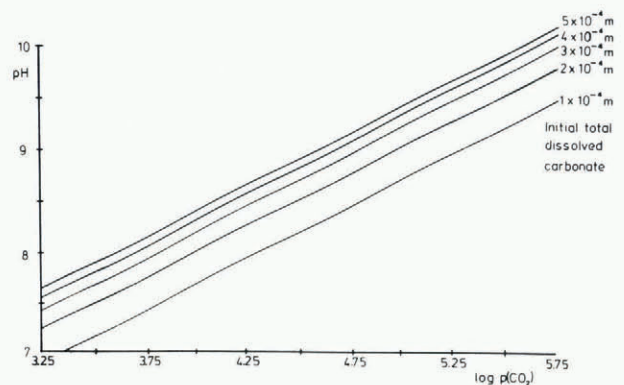


Fig.4. Theoretical relationships between pH and p(CO₂), for different degrees of initial open-system weathering.

Relationships between pH and p(CO₂) for carbonate weathering

This example is more complex because variations in C_T occur which may become significant when the extent of open-system weathering is small. The initial [H₂CO₃*] is fixed by equilibrium with the atmosphere, so the maximum amount of weathering that can occur corresponds to complete dissociation of H₂CO₃* to HCO₃⁻ (giving a maximum of 2.4 x 10⁻⁵ equivalents of H⁺). Since silicate weathering may generate this amount of HCO₃⁻ eq., carbonate dissolution may generate up to 4.8 x 10⁻⁵ eq. of HCO₃⁻ and C_T may increase during carbonate dissolution by 2.4 x 10⁻⁵. However this increase may often be disregarded, either because it is small compared to C_T, or because carbonate dissolution may not be occurring to any significant extent. Raiswell and Thomas (1984) found C_T to be 2-3 x 10⁻⁴ mol l⁻¹ at Fjallsjökull, rendering the p(CO₂) 10^{-7.7} term negligible in comparison to C_T for all p(CO₂) ≤ 10^{-3.5} bar. With this proviso,

$$pH = \log C_T - \log p(CO_2) + 7.7$$

and Figure 4 is also valid for carbonate weathering.

Relationship between Σ⁺ and pH, for silicate weathering

The expressions used in the previous section can be also rearranged to define the relationship between solute load (i.e. Σ⁺) and pH. From Equations (1), (2), and (3),

$$C_T = [H_2CO_3^*] + [HCO_3^-] = \frac{\alpha(H^+) [HCO_3^-]}{10^{-6.58}} + [HCO_3^-],$$

$$[HCO_3^-] = \frac{C_T}{\alpha(H^+)10^{6.58} + 1}$$

Using Equation (4) and expressing each term in terms of H^+

$$\Sigma^+ = \frac{C_T}{\alpha(H^+)10^{-6.58} + 1} + \frac{10^{-14.9}}{\alpha(H^+)} - \alpha(H^+).$$

Inspection of this expression suggests that the first term dominates in the pH range of most melt waters, for any $C_T > 10^{-5} \text{ mol l}^{-1}$. This approximation is valid for any pH from 6.6 - 9.6, the upper limit being fixed by the requirement that $[HCO_3^-] \gg [CO_3^{2-}]$. Hence

$$\Sigma^+ = \frac{C_T}{\alpha(H^+)10^{6.58} + 1} \tag{9}$$

and plots of this expression (Fig. 5) show an asymptotic tendency, due to the existence of a maximum solute load which is fixed by complete dissociation of $H_2CO_3^*$.

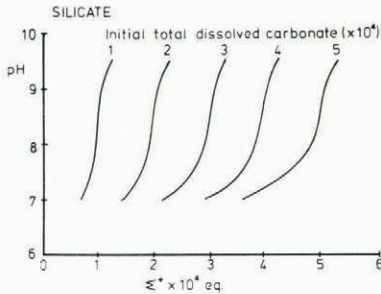


Fig. 5. Theoretical relationships between Σ^+ and pH during the closed-system weathering of silicate minerals, for different degrees of prior open-system weathering which produce concentrations of total dissolved carbonate of $1-5 \times 10^{-4} \text{ mol l}^{-1}$.

Relationship between Σ^+ and pH for carbonate weathering

This example is relevant to the acquisition of solutes by groundwaters in karstic terrain and has been treated theoretically by Langmuir (1971), who derived the following expression.

$$C_i = [HCO_3^-] (2\alpha(H^+) + \kappa_1)$$

$$= 2[HCO_3^-] \alpha(H^+) + [HCO_3^-] 10^{-6.58} \tag{10}$$

where C_i is a constant for any particular water and is determined by the extent of its prior open-system weathering history, as shown below.

But in an open system in equilibrium with the atmosphere:

$$\alpha(H^+)[HCO_3^-] = 10^{-6.58} [H_2CO_3^*] = 10^{-11.2}.$$

Substituting in Equation (10),

$$10^{-10.9} + [HCO_3^-] 10^{-6.58} = C_i.$$

Figure 6 shows the numerical variation of C_i with $[HCO_3^-]$. For any $[HCO_3^-] < 10^{-5} \text{ mol l}^{-1}$ values of C_i asymptotically approach a minimum of 1.3×10^{-11} . Using the electroneutrality relationship

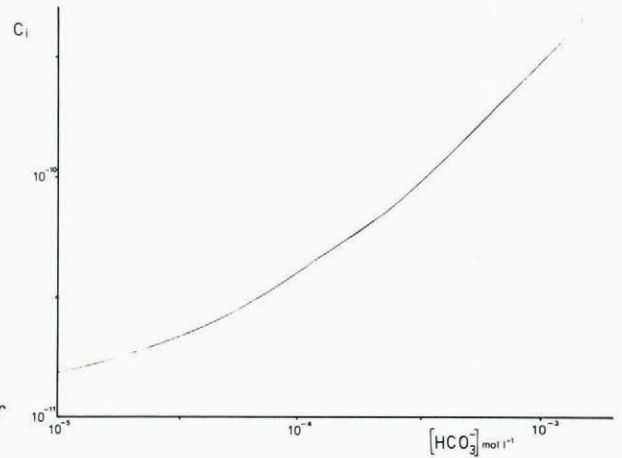


Fig. 6. Variations in C_i with HCO_3^- concentration during open-system weathering, $p(CO_2) \approx 10^{-3.5} \text{ bar}$.

$$\Sigma^+ = [HCO_3^-] + [OH^-] - \alpha(H^+)$$

$$\Sigma^+ = \frac{C_i}{2\alpha(H^+) + 10^{-6.58}} + \frac{10^{-14.9}}{\alpha(H^+)} + \alpha(H^+).$$

Inspection of this expression reveals that the first term is smallest when C_i is a minimum, yet even then this term still dominates for any pH in the approximate range 6 to 9.6. Hence the above expression can be simplified for most melt waters to

$$\Sigma^+ = \frac{C_i}{2\alpha[H^+] + 10^{-6.58}} \tag{11}$$

Note that Equations (9) and (11) (Figs. 5 and 7) indicate that Σ^+ values are asymptotic for increasing pH, since additional cations (over and above those acquired in the prior open-system weathering) can only be derived to the extent represented by complete dissociation of $H_2CO_3^*$ to HCO_3^- .

DISCUSSION AND CONCLUSIONS

The proposed chemical models of solute acquisition in glacial melt waters provide a simple theoretical framework capable of identifying the nature and extent of solute acquisition as melt waters chemically evolve during their transit through the glacier. The models can be tested, and their uses described, in the context of the hydrological models proposed by Collins ([1978], 1979[b]). These studies suggest

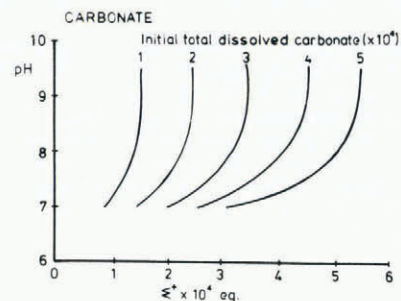


Fig. 7. Theoretical relationships between Σ^+ and pH during the closed-system weathering of carbonate minerals, following different degrees of open-system weathering which produce concentrations of total dissolved carbonate of $1-5 \times 10^{-4} \text{ mol l}^{-1}$.

that two main components of glacial discharge can be recognized; a dilute, surface melt water which flows rapidly with little alteration through englacial channels (the englacial component) and solute-rich waters flowing more slowly through the subglacial system (the subglacial component). A simple two-component mixing model can be used to explain the temporal variations of the bulk melt water (that emerging at the portal) in terms of varying quantities of water routed through the englacial and subglacial system. However, mixing ratios vary on both a diurnal and a seasonal basis, such that a given discharge may be associated with a range of dissolved loads (Collins, 1979[a]). It may be possible to discern the reasons for such temporal variations by focusing attention on the mechanisms of solute acquisition in different glaciological environments.

The supraglacial environment

The dissolved and suspended loads of supraglacial melt waters are low (Collins, 1978; 1979[a], [b]) and the extent of mineral-water reactions must generally be limited by:

- (i) Time. The model residence time of water on the glacier surface is relatively small, probably of less than 24 h duration (Elliston, 1973; Collins 1979[b]).
- (ii) Surface Area. The low suspended-sediment loads suggest that fine-grained, readily reactive material is not abundant in the supraglacial environment.
- (iii) Reactivity. Rock debris may have a long residence time on the glacier surface with little opportunity for surface abrasion. High flushing rates ensure that surfaces will experience some weathering and hence may become partially protected by residual, low-reactivity weathering products.

Under these circumstances the rates of H⁺ consumption by weathering will be low, or even negligible, and supraglacial melt should maintain open-system weathering characteristics. Samples of precipitation may be compared to supraglacial melt to ascertain the extent of solute acquisition in the latter, as revealed by higher pH and Σ⁺ (Equation (7)). Raiswell and Thomas (1984) show that supraglacial melt at Fjallsjökull exhibits open-system characteristics and that little weathering occurs in the supraglacial environment.

The englacial environment

The time, surface area, and reactivity constraints of the supraglacial environment are likely to be similar, or more limiting, in the englacial environment. Thus, although the englacial system may be isolated from physical contact with atmospheric CO₂, the limited capacity for mineral-water reactions should ensure that H₂CO₃* concentrations are undepleted and that these waters display open-system behaviour. No observations of englacial melt are, at present, available.

The subglacial environment

The subglacial environment is in many respects the antithesis of the supraglacial and englacial systems. The residence time of subglacial melt is likely to be at least several days, since subglacial recession flows can be maintained in the absence of ablation and after the drainage of englacial reservoirs (Elliston, 1973; Collins, 1978, 1979[b]). Furthermore, the suspended sediment load of the bulk melt water is almost exclusively contributed by the subglacial component (Collins, 1979[a]) and may contain a significant fraction of fine-grained material. The <2µm fraction of suspended sediment typically ranged from 10-20% (by weight) in the Argentière and Fjallsjökull melt waters (Thomas, unpublished). The suspended load also contains abundant sub-micrometre sized particles of enhanced solubility (paper on microparticle production, preservation, and adhesion in laboratory and glacial systems in preparation by R. Raiswell and M. Tranter). The reactivity of mineral grains is also maintained at an optimal level by abrasion, crushing,

and fracture processes which continuously generate fresh surfaces.

These factors indicate that rapid weathering and dissolution are likely to be initiated in the subglacial environment, with the consequence that this component should exhibit closed-system characteristics. The depletion of H₂CO₃* and resulting p(CO₂) values less than 10^{-3.5} bar reflect the superiority of mineral dissolution kinetics over rates of CO₂ dissolution and hydration, and/or physical constraints on the access of atmospheric CO₂ to the subglacial environment. Observations of subglacial melt at Argentière (Thomas and Raiswell, 1984) confirm that subglacial melt displays closed-system characteristics.

Post-mixing behaviour

The englacial and subglacial components probably mix over a region of several kilometres near the glacier portal. Previous studies have assumed that mixing is conservative, i.e. that there is no change in the mass of solutes although concentration changes occur by dilution. However, the proposed and observed characteristics of the englacial and subglacial components suggest otherwise. A subglacial

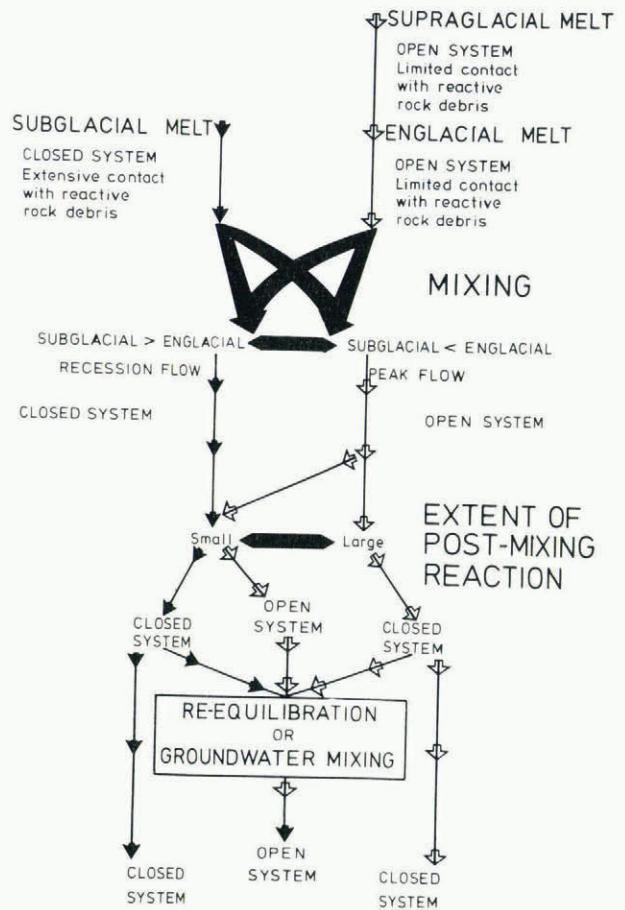


Fig.8. Schematic representation of the possibilities for the chemical evolution of glacial melt waters. Melt waters dominated by englacial (originally supraglacial) melt are identified by open arrows, subglacially dominated melts by filled arrows. Open- and closed-system characteristics are controlled initially by the extent of contact with reactive rock debris, then modified successively by the mixing ratio between englacial and subglacial melt, the extent of renewed reaction with rock debris, and lastly by the possibility of re-equilibration with the atmosphere or mixing with open-system ground waters.

water with closed-system characteristics has a limited capacity for mineral dissolution determined initially by its undissociated H_2CO_3^* concentrations. There is no *a priori* reason to believe that this must be more than sufficient to react with all the available, freshly abraded solid phases. Solute acquisition in the subglacial component may instead be limited by the availability of hydrogen ions. Thus, subglacial melt at Argentière (Thomas and Raiswell, 1984) has a high pH (9.4 to 9.7), is close to equilibrium with carbonate phases, and has little further capacity for dissolution. However, the accompanying suspended sediment may still contain reactive material. Under these circumstances an englacial water with open-system characteristics (i.e. with undissociated H_2CO_3^* available for dissolution reactions) may initiate further solute acquisition after mixing.

The various complex possibilities for post-mixing behaviour can be evaluated by reference to Fig. 8. The initial factor which determines the characteristics of the bulk melt water is the mixing ratio between the englacial and subglacial components. During recession flows the subglacial component predominates and the bulk melt water may be expected to retain subglacial characteristics. However, during sustained ablation and typical diurnal discharge variations the bulk melt water may be 60–80% englacial (Collins, 1979[b]) and mixing will initially result in a bulk melt water which has essentially open-system characteristics, provided no H_2CO_3^* is consumed by sediment-melt-water weathering reactions. The behaviour of the carbonate equilibria during mixing depends on many factors and does not exhibit a simple linear variation with the mixing ratio (Wigley and Plummer, 1976). However depending on the magnitude of the mixing ratio, the bulk melt water may range through various degrees of closed-system behaviour to essentially open-system behaviour. However, there is also the possibility for further solute acquisition if reactive solid phases are available (either from suspended sediment originally supplied by the subglacial component or by contact with moraine debris). The time scale for further dissolution is short (possibly only hours), but the presence of abundant reactive solid phases may still cause the bulk melt waters to exhibit more closed-system behaviour. Thus, the bulk melt will lie on the appropriate $\text{pH}/\text{p}(\text{CO}_2)$ and pH/Σ^+ contour as fixed by the dissolved carbonate content of the supraglacial component (Figs 4 and 5 or 7), and the proposed chemical models may be tested by matching supraglacial melt composition with bulk meltwater composition. Data obtained at Fjallsjökull (Raiswell and Thomas, 1984) are consistent with the proposed models. The pH/Σ^+ relationships (Equation (11)) also suggest that solute sources (carbonates or silicates) can be recognized, but the distinctions are not large and it is likely that only predominantly carbonate or silicate systems will be recognized with any confidence. Accurate analytical data will be required even for this purpose.

Lastly, closed-system bulk melt waters may evolve towards open-system conditions either by re-equilibration with atmospheric CO_2 or by mixing with another open-system water (either ground water or surface water).

The proposed models depend on the assumption that the hydrogen ions consumed in weathering are generated through carbonate equilibria. The presence of high sulphate concentrations suggests that hydrogen ions are supplied by pyrite oxidation. Assuming these H^+ ions are completely utilized in dissolution, the models may still be used if values of Σ^+ are reduced by their equivalent sulphate concentrations.

This correction is valid where:

1. Carbonate equilibria are the dominant H^+ source, as demonstrated by $[\text{HCO}_3^-] \gg [\text{SO}_4^{2-}]$.
2. Atmospheric inputs of sulphate are negligible, as shown by the chemistry of precipitation samples.
3. We have open systems, where the $\Sigma^+/\text{p}(\text{CO}_2)$ and

Σ^+/pH relationships are essentially independent of mineralogy.

In closed systems the correction to be applied must be either equal to the equivalent sulphate concentrations (for silicate weathering) as above, or must be twice the equivalent sulphate concentrations (for carbonate weathering). Independent evidence of the relative contributions of carbonate and silicate phases will generally be absent and the best procedure is to apply the minimum correction initially and interpret the data accordingly (see Raiswell and Thomas, 1984). Melt waters with low sulphate contents will show little ambiguity.

Finally, it should be emphasized that the different pathways of open- and closed-system evolution could also be distinguished by other variables than pH and Σ^+ . The use of these variables in the models considered here was determined by the literature survey of melt-water analysis, which indicated that these are probably the variables most readily measured. Combinations of other variables, for example Σ^+ and $[\text{HCO}_3^-]$ could be derived from the equations presented here.

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