

INSTRUMENTS & METHODS

FIELD pH DETERMINATIONS IN GLACIAL MELT WATERS

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ABSTRACT. Laboratory pH analyses of glacial melt waters are unrepresentative of *in situ* values, due primarily to CO₂ gas exchange between the sample and the atmosphere, and solute enrichment from chemical reaction with sediment and colloidal particles. A method is presented which enables field pH measurements that are reproducible within ± 0.04 pH units to be made in glacial melt waters, using commonly available digital pH meters with combination electrodes.

During initial spring snow melt in May 1981 at Gornergletscher, Switzerland, melt waters in the proglacial stream leaving the glacier terminus were oversaturated with respect to atmospheric $p(\text{CO}_2)$, and rapidly increased pH during CO₂ outgassing at *in situ* temperature and pressure. Summer ice melt from glaciers which are temperate in the ablation zone are usually undersaturated by about ten times with respect to atmospheric $p(\text{CO}_2)$, and rapidly lower their pH values to achieve equilibrium upon encountering the atmosphere, as observed at Gornergletscher during July and August 1981. Gornergletscher summer proglacial stream waters, sometimes show pH increases from rock weathering, with the rate limited by the transfer rate of CO₂ across the air-water interface to drive the weathering reactions. Throughout the year, any water parcel at equilibrium with atmospheric CO₂ is generally at an equilibrium pH value, if filtration prohibits solute enrichment. For these reasons, laboratory pH measurements are unacceptable for quantitative studies of melt-water chemistry and should be discontinued.

RÉSUMÉ. Déterminations sur le terrain des pH des eaux de fusion glaciaires. Les analyses de pH en laboratoire des eaux de fusion glaciaires ne sont pas représentatives des valeurs *in situ*, en raison d'abord des échanges gazeux de CO₂ entre l'échantillon et l'atmosphère et de l'enrichissement en matière dissoute à partir de réactions chimiques avec les particules sédimentaires et colloïdales. On présente une méthode permettant des mesures sur le terrain pH fiables dans une fourchette de $\pm 0,04$ unités pH dans les eaux de fusion glaciaires, en utilisant un pH mètre digital facile à se procurer avec des électrodes incorporées.

Pendant la fusion printanière initiale en mai 1981 au Gornergletscher en Suisse, les eaux de fusion dans l'émissaire proglaciaire à la sortie du front du glacier était sursaturé par rapport à la pression partielle en CO₂ de l'atmosphère, et il y avait une croissance rapide du pH pendant le dégazage en CO₂ à la température et à la pression ambiantes. Les eaux de fusion d'été à partir de glaciers qui sont tempérés dans la zone d'ablation, sont d'habitude sous-saturées de 10 fois par rapport à la pression partielle de

CO₂ dans l'atmosphère et abaissent rapidement leur valeur du pH pour s'équilibrer avec l'atmosphère rencontré, comme cela a été observé au Gornergletscher en juillet et août 1981. L'émissaire du Gornergletscher montre parfois en été des augmentations de pH à la suite de désagrégation de roche, à une vitesse limitée par la vitesse de transfert du CO₂ à travers l'interface eau-air qui règle les réactions de désagrégation. Sur l'ensemble de l'année, un volume d'eau en équilibre avec le CO₂ de l'atmosphère, est en général à un pH stable si la filtration empêche l'enrichissement en matière dissoute. C'est pourquoi les mesures de pH en laboratoire sont inacceptables pour des études quantitatives de la chimie des eaux de fusion et devraient être abandonnées.

ZUSAMMENFASSUNG. Bestimmung de pH-Wertes von Gletscher-Schmelzwasser im Feld. Vor allem wegen des CO₂-Gasaustausches zwischen einer Probe und der Atmosphäre und der Lösungsanreicherung aus chemischen Reaktionen mit Ablagerungs- und Colloid-Partikeln sind pH-Analysen von Gletscherschmelzwasser im Labor nicht repräsentativ für *in situ*-Werte. Es wird ein Verfahren beschrieben, das mit allgemein verfügbaren digitalen pH-Metern mit Kombinationselektroden pH-Messungen in Gletscherschmelzwasser im Feld ermöglicht, die innerhalb von ± 0.04 pH-Einheiten reproduzierbar sind.

Während der anfänglichen Frühlingsschneeschmelze im Mai 1981 waren Schmelzwasser im Gletscherbach des Gornergletschers (Schweiz), die aus dem Gletscherende kamen, übersättigt im Hinblick auf atmosphärisches $p(\text{CO}_2)$; ihr pH-Wert nahm schnell zu, als CO₂ unter *in situ*-Temperatur und -Druck entwich. Sommerschmelzwasser von Gletschern, die in der Ablationszone temperiert sind, sind gewöhnlich um den Faktor 10 im Vergleich zu atmosphärischem $p(\text{CO}_2)$ untersättigt und verringern ihre pH-Werte schnell bis zum Gleichgewicht, wenn sie mit der Atmosphäre in Berührung kommen, wie im Juli und August 1981 am Gornergletscher beobachtet wurde. Sommerliche Schmelzwasser im Vorfeld des Gornergletschers zeigen manchmal pH-Zuwächse infolge Felsverwitterung, wobei die Rate durch die Übergangsrate von CO₂ durch die Grenzfläche zwischen Luft und Wasser begrenzt ist. Während des ganzen Jahres besitzt jedes Wasserpaket, das mit atmosphärischem CO₂ im Gleichgewicht steht, einen pH-Gleichgewichtswert, wenn Filtration eine Anreicherung mit Lösungen verhindert. Deshalb sind Labor-pH-Messungen für quantitative Studien der Schmelzwasserchemie unannehmbar; sie sollten nicht mehr ausgeführt werden.

INTRODUCTION

The correct assessment of hydrogen-ion activity is critical to understanding the detailed chemistry of glacial melt water. Evaluations of weathering reaction paths and clay-mineral assemblages using thermodynamic stability diagrams, such as Drever (1982, p.175) has presented, are incorrect if input pH values are unrepresentative. Representative values of $p(\text{CO}_2)$ and pH are crucial inputs to modern (Hallet, 1976, p.1007; Hallet and others, 1978, p.318) models of subglacial precipitation and ice formation during regelation sliding at the glacier bed. pH values "contaminated" by CO₂ in Arctic ice melt are a significant error in studies of acid snow (Koerner and Fisher, 1982, p.138); measurements of samples subjected to differing times and temperatures of ice melt will show pH variations induced by varying amounts of CO₂ transfer.

Early glacial melt-water pH work was conducted in laboratories months after samples had been collected (Rainwater and Guy, 1961; Keller and Reesman, 1963). Slatt (1972) showed that major solute changes can occur during such storage. Ek (1964, 1966) and Metcalf

(unpublished, 1979) suggested that summer melt waters can be greatly undersaturated with respect to atmospheric CO₂, and that laboratory pH values can change significantly from *in situ* measurements for the same water sample. The present study was undertaken to discover the cause of the cited discrepancies between laboratory and field measurements, and to develop a reliable field method for routine determination of pH in glacial melt waters, using commonly available equipment.

METHOD

Three buffer solutions of pH 4, 7, and 10 are cooled to the sampling temperature in an ice-water bath, or the glacial stream, in order to perform the "span" calibration (testing the slope in millivolts per pH unit between three points of known pH).

After the buffer solutions are sufficiently cool, the temperature compensation dial of the pH meter is adjusted to the measured sample temperature. This adjustment compensates for the lowered voltage output per pH unit with decreasing temperature (decreasing "slope") described by Westcott (1978, p.25). Tempera-

ture is measured with a digital thermometer (precision = 0.1 deg), calibrated in the ice-water bath, before buffer rinsing, at 0.0°C.

A minimum period of ten minutes should be allowed for a nearly complete electrode response before any instrumental adjustment to a buffer solution is attempted. If the "span" calibration shows a deviation of more than about 0.05 pH units between actual and measured pH for the pH 4 and 10 buffers, there is a fault with the electrode or instrument.

CO₂ gas transfer between the sample and the atmosphere may begin immediately upon collection, so that collecting and transporting time should be minimized to one or two minutes. Immediately upon collection, water samples are filtered with two, stacked, cellulose filters held in a "Perspex" (polymethyl methacrylate) cylinder, driven by a bicycle tyre pump, as described by Collins (1981, p.222-23). Glass fibre filters were avoided because Jackson and Inch (1980, p.30) have shown that some types contribute significant sodium and titration alkalinity to a filtered sample.

Samples are filtered into 0.25 dm³ polyethylene beakers and placed in the ice-water bath at 0°C. During summer pH measurements, the sample is shaded from solar heating and insulated by closed-cell foam. Direct sunlight can quickly heat summer samples in the bath to the unacceptable range of 4-10°C. As the sample heats, CO₂ solubility decreases, and outgassing of CO₂ from a previously undersaturated (at 0°C) sample can occur. Figure 1 documents this effect during a d(pH)/dt experiment on Gornergletscher melt water from 29 July 1981. It shows a pH reversal from CO₂ outgassing, correlated with an increase of sample temperature and visual confirmation of gas bubbles leaving the sample. Such reversals were observed only when samples were heated above 3 or 4°C, which is the upper limit of acceptable sample temperature in the ice-water bath.

Both the thermometer and pH probes are placed in the bottom of the beaker simultaneously, in a position where they cannot move. Measurements take place in the beaker bottom water, in the least susceptible location to gas and heat exchange with the atmosphere. A probe located in this position yields the closest approximation to *in situ* pH values if CO₂ gas transfer takes place in a sample. These measurements can, however, be subject to substantial delay in reaching equilibrium pH values with the atmosphere due to the time necessary for CO₂ to diffuse from the water surface to the electrode, and

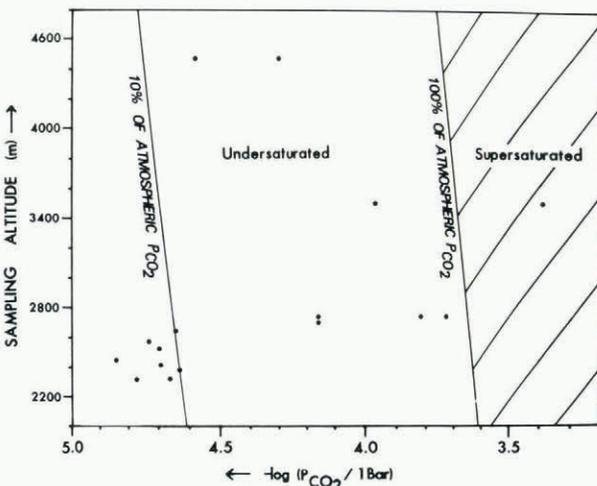


Fig.1. Field d(pH)/dt experiment of 29 July 1981 showing a pH reversal at 20 min due to CO₂ outgassing from solution after the base of the sample had heated above 4°C without an ice-water bath. Gas bubbles coming out of solution were visible on the beaker walls after 32 min.

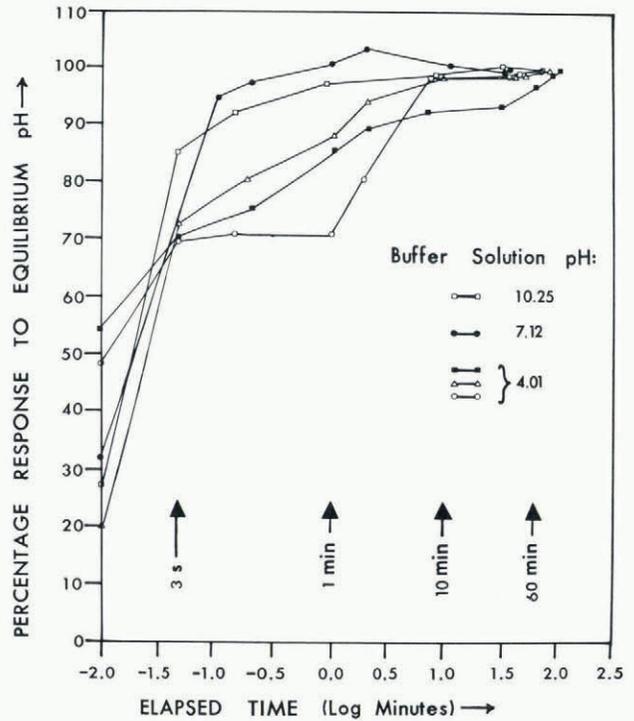


Fig.2. Field d(pH)/dt experiment of 14 May 1981 showing an increase of pH with time for initial spring melt waters leaving the Gornergletscher terminus. Noise at 25 min was caused by convection during thermometer insertion and at 54 min by vibration from a nearby avalanche.

resulting from the density circulation induced by surface-water heating from near 0 to 4°C. Proper probe placement also avoids two sources of pH signal noise in dilute water samples (Westcott, 1978, p.102, 129); (1) changes in the liquid-junction potential from stirring, and (2) the great increase in electrode resistance with decrease of sample temperature (nearly doubling the resistance for every 7 deg lowered). Such noise, caused by convection currents initiated during insertion and removal of the temperature probe, is unacceptable (see Fig. 2). During May 1981 field experiments at the terminus of Gornergletscher, noise caused by slight electrode movements from the air blast and ground vibration of nearby avalanches was often noted as a small, superposed anomaly on the variation of pH signal with time. Figure 2 shows this effect to have been more significant than noise from thermometer insertion during the d(pH)/dt experiment of 14 May 1981.

A standard combination electrode, with saturated KCl solution (about 4 mol/dm³), was connected by shielded cable to a high-input-impedance digital pH meter. KCl leakage had negligible effect on pH during field experiments lasting 4 h. Laboratory experiments showed KCl leakage of 0.3-1.2 mg d⁻¹ in de-ionized, double-distilled water purged of CO₂ with Ar. Precipitation of silver chloride complexes on the internal reference electrode and near the liquid junction, from low-temperature operation, did not noticeably affect performance in standard buffers. The saturated KCl filling solution freezes at -11°C; the electrode must be protected from freezing in most winter conditions while not in use. Volume expansion of the filling solution upon freezing threatens the integrity of the glass electrode-liquid junction, which is critical to proper electrode response. At first during field operations, body heat was used to keep the electrode as warm as possible, thinking this would accelerate electrode response once it was placed in the sample. Experiments showed this logic to be wrong. For optimum response time, the sample and

electrode must be in thermal equilibrium (Westcott, 1978, p.101).

pH measurements and water temperature are observed continuously until the electrode reaches equilibrium. Although not strictly correct, a convenient operational definition for pH equilibrium is when no pH changes (less than 0.01 pH unit) are observed in 20 min. Replicate samples showed this procedure produced a mean error of less than -0.04 pH units.

The electrode response to 99% of the equilibrium pH normally takes from 6 to 30 min in the field at 0°C, but appears strongly affected by variations in sample buffer capacity and the degree of saturation with respect to atmospheric $p(\text{CO}_2)$. Definitive experiments to understand this effect have not been made, but some work is currently in progress. Preliminary results suggest that samples with low buffer capacity which are greatly undersaturated, or oversaturated, with respect to atmospheric $p(\text{CO}_2)$ approach equilibrium pH values faster than samples in equilibrium with atmospheric $p(\text{CO}_2)$.

Typical laboratory response curves for one pH electrode tested in standard buffer solutions at 0°C are shown in Figure 3. The exponential approach to an

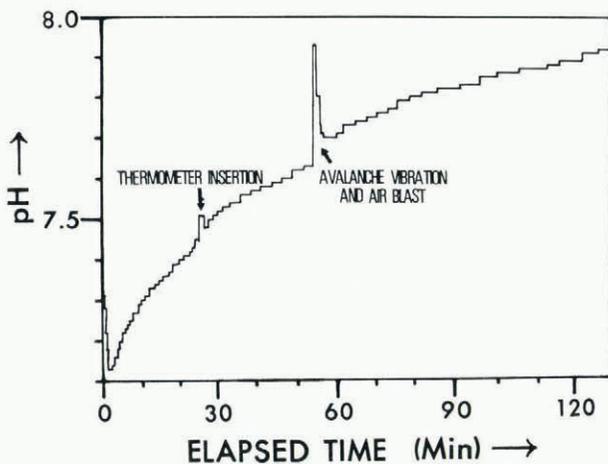


Fig.3. Logarithmic response time of a combination pH electrode in various buffers at 0°C in laboratory tests.

equilibrium pH value is readily apparent, especially the increasing time delay for additional pH changes after 90% of the equilibrium response has been reached in less than 10 min.

For high precision $d(\text{pH})/dt$ analysis of CO_2 gas transfer in samples, field chart recorders lacked sufficient sensitivity over the wide pH and time scales needed. Instead, hand recording of pH to 0.01 pH unit and elapsed time to ± 1 s in 4 h with a digital stopwatch was employed.

COMPLICATIONS FROM FIELD CONDITIONS

CO₂ gas transfer

If an adequately filtered water sample is measured at the *in situ* temperature and atmospheric pressure, the major source of pH drift, or error, comes from CO_2 gas entering or leaving the sample while approaching equilibrium with atmospheric CO_2 . Ek (1964, p.140) and Metcalf (unpublished; 1979, p.235) used pH and titration alkalinity, and pH and carbonate saturometer measurements, respectively, to show that summer melt waters were often severely undersaturated (by one to two orders of magnitude) with respect to atmospheric $p(\text{CO}_2)$. Weiss and others (1972), Stauffer and Berner (1978), and Berner (1979) have shown with highly sensitive gas chromatography that Swiss glacier ice is progressively depleted in total CO_2 content towards the glacier terminus. As Hallet (1976, p.1005) noted,

melt water from such ice will be significantly undersaturated with respect to atmospheric CO_2 . If all of the CO_2 contained in "temperate" ice remains in the melt water (rather than some escaping to the atmosphere as bubbles are opened) upon melting, it is usually about ten times less than the concentration of aqueous CO_2 needed to be in equilibrium with atmospheric CO_2 partial pressures, based on the gas chromatographic measurements mentioned above (Fig. 4). Additionally, Harrison and Raymond (1976) have demonstrated that the electrical conductivity of Blue Glacier ice melt is significantly less than the conductivity to be expected if the melt was in equilibrium with atmospheric $p(\text{CO}_2)$ at 0°C.

Figure 5 shows an example of the pH changes associated with CO_2 gas uptake by a supraglacial ice-melt stream sample at *in situ* pressure and temperature. Change of pH with time, temperature, and titration alkalinity were measured in the field at Gornergletscher, Switzerland, during 7 August 1981. An iterative computer calculation available from the author, assuming constant alkalinity during CO_2 uptake, was employed to back-calculate CO_2 partial pressures from the carbonate equilibria equations. This approximation was verified by comparison with atmospheric $p(\text{CO}_2)$ at equilibrium pH, and with a replicate analysis after the solution had reached equilibrium (Fig. 5). A second crucial assumption that CO_2 -species control the pH of the tested sample has been verified by W.E. Gordon (personal communication in 1982). Gordon (1979; 1982) has described the computational procedure used to evaluate pK_a values, and species concentrations participating in acid-base titrations in solutions of unknown composition. His analysis of the field titration alkalinity data confirmed that the alkalinity is in the form of HCO_3^- ($61 \pm 2, 59 \pm 3 \mu\text{mol dm}^{-3}$), the free acid is CO_2 , and the measured pK_a value for the $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ conjugate pair is about 6.3. Details of the $p(\text{CO}_2)$ calculation procedure are lengthy, and are presented elsewhere (Metcalf, in press).

The general trend of decreasing pH with time observed in Figure 5 can only be explained by an acid addition or base removal from the solution. Base removal is discounted as no precipitation was observed. Three serpentinite grains 3-5 μm across were found in the beaker after the experiment, but these contain no minerals commonly forming acids so quickly in such water. The only plausible explanation is acid addition from CO_2 transfer from the air. A measurement with an

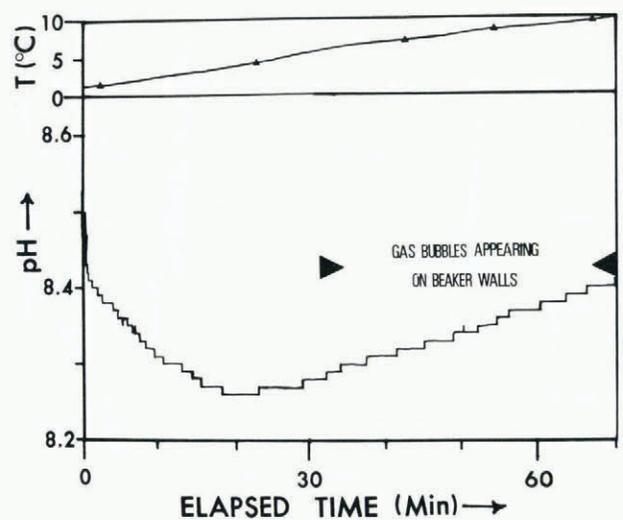


Fig.4. Calculated $p(\text{CO}_2)$ values in equilibrium with Swiss glacier ice melt at 0°C, derived using gas chromatographic measurements and Henry's Law, compared to atmospheric $p(\text{CO}_2)$ for dry air at the sampling altitude.

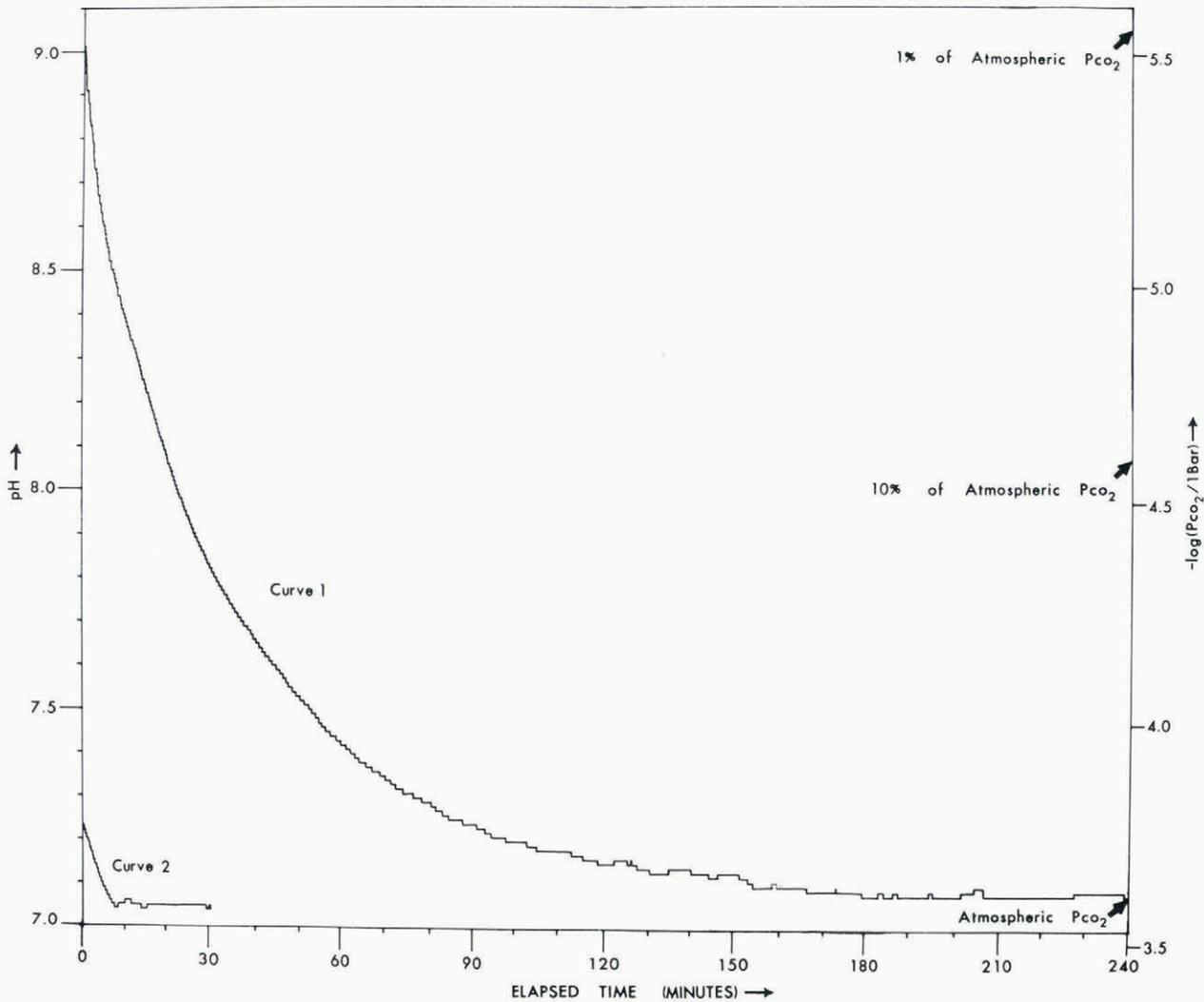


Fig. 5. Field $d(\text{pH})/dt$ measurements of 7 August 1981 showing: CO_2 gas uptake in melt water beginning 1 min after sample collection from a supraglacial/englacial stream (Curve 1), and CO_2 equilibrium in a replicate sample measured 242 min after collection (Curve 2).

electrode sensitive to CO_2 qualitatively confirmed this argument.

A further proof that the pH change observed is caused by CO_2 transfer across the air-water interface is that an approximate first-order reaction rate may be calculated by using least-squares fits of the exponential $d(\text{pH})/dt$ curves, such as given in Figure 5 or 2. The nature of the process assures that the transfer rate must be the same during CO_2 gas uptake or outgassing, so that Figures 2 and 5 should yield rate constants of identical magnitude, within experimental errors. Figure 2 yields a rate constant of $1.85 \times 10^{-4} \text{ s}^{-1}$ ($n = 57$, $r = 0.963$) and Figure 5 yields a rate constant of $-2.95 \times 10^{-4} \text{ s}^{-1}$ ($n = 199$, $r = 0.822$). Temperatures varied from $0.8 - 1.9^\circ\text{C}$ during these experiments, and water purity is shown by titration alkalinities of 300 and $60 \mu\text{mol dm}^{-3}$, respectively. The laboratory value for the CO_2 gas transfer constant from distilled water at 0°C has been given by Bohr (1899, p.512) as $2.60 \times 10^{-4} \text{ s}^{-1}$ after 120 min. The accuracy of Bohr's (1899) experiments may be appreciated when one realizes that present CO_2 solubility constants are derived from his measurements (Stümm and Morgan, 1981, p. 204). Also, the ratio of surface area to volume for the solution is about equal to that for the present study (0.14 cm^{-1}), and Bohr's (1899) work (0.21 cm^{-1}), so transfer rates are directly comparable.

Concurrent with the $d(\text{pH})/dt$ data taken in Figure 2, hundreds of gas bubbles, 10 to 16 mm across, appeared and travelled a curved path of 25 - 30 cm upward in 0.2 - 0.45 s as they left the glacier terminus, in non-turbulent flowing waters of $0.1 - 0.2 \text{ m}^3 \text{ s}^{-1}$ discharge and $0.3 - 0.5 \text{ m s}^{-1}$ velocity (Metcalf, in press). These bubbles are considered proof of outgassing in these otherwise quiet waters. The increase of pH with time shown in Figure 2 is therefore interpreted as CO_2 outgassing. pH experiments showing identical $d(\text{pH})/dt$ curves for two to five separate samples seem unlikely to originate from the same amount of rock weathering going on in each separate sample, although that is possible. Finally, the qualitative trend of CO_2 outgassing was observed using an electrode sensitive to CO_2 , which is protected from interference from rock-weathering solutes by a gas-permeable membrane separating it from the sample.

For the reasons above, it is proposed here that CO_2 gas transfer is the primary reason for the more acid laboratory pH values usually measured in summer melt waters compared with field values (Ek, 1964; 1966; Slatt, unpublished). One cannot quantitatively predict the size of pH change that will occur unless the CO_2 gas saturation and titration alkalinity at the time of sampling are known. Since melt water has many different origins, travel paths, and consequent cumulative erosional histories, CO_2 gas saturation

and the magnitude of pH changes after sampling would be expected to vary widely, as is observed. Unfortunately, any unfiltered colloidal rock particles may contribute to sample pH, masking pH changes caused by CO₂. Thus, there is no simple correction for laboratory-measured pH values; they are considered unrepresentative of the *in situ* water chemistry.

Suspended sediment

The present study has shown that solute enrichment from chemical reactions between glacial melt water and sediment or colloidal minerals will increase sample pH by about 0.1 to 0.3 pH units in unfiltered water, at *in situ* temperatures and pressures. These complications may be at least partly avoided by adequate filtration at the time of collection.

High suspended sediment concentrations in summer melt-water streams can present problems for electrodes placed directly in the stream. A phenomenon termed "abrasion pH" by Stevens and Carron (1948) may be observed when charged "ionic shells" on mineral grains influence the electrode from a true pH value. The details of this process may be explained by the large liquid-junction potentials (10 to 100 mV) observed in colloidal suspensions by Jenny and others (1950). Metcalf (unpublished) found this effect could increase pH by up to 0.4 pH units at Nisqually Glacier, Washington, U.S.A. The "abrasion pH" effect is avoided by making measurements in filtered samples outside the stream.

Temperature and pressure changes

At 0°C, the error from inadequate temperature compensation is only 0.0037 pH unit per Celsius degree error with a reading 1.0 pH unit from standardization (Westcott, 1978, p.25). In glacial waters, the main influence on sample pH values of pressure and temperature changes is gas transfer to and from solution - specifically CO₂, H₂S, and SO₂. These volatiles transfer species in equilibrium with H₂CO₃ and H₂SO₄, the two acids controlling pH in most glacier ice melt (Koerner and Fisher, 1982).

Intrinsic melt-water properties

Numerous studies of CO₂ transfer across the air-water interface show that high wind (Hoover and Berkshire, 1969; Liss, 1973) or turbulence (Kanwisher, 1963) will increase the CO₂ transfer rate. Reynolds and Johnson (1972) and Metcalf (unpublished, 1979) have observed down-stream alkaline pH changes in pro-glacial streams from enhanced chemical weathering driven by resupply of atmospheric CO₂ into the turbulent water. This natural aeration is very efficient, causing pH increases in pro-glacial streams of 1.0 to 1.8 pH units within 400 m of leaving the glacier terminus.

Water velocity will cause a rather small (about 0.1 - 0.2 pH unit) change in measured pH due to the high liquid-junction potential created ("streaming potential"). However, turbulent stirring promotes faster electrode response and homogenization of the sample. Thus, in winter and early spring, pH measurements may be made directly in the stream, but the previously discussed noise caused by probe movement is a great problem. In summer, the additional problem of suspended sediment makes direct measurement unacceptable. Besides, saltation boulder impacts, and rapid water-level changes greater than the length of the electrode's short, shielded cable, make instrumental loss probable.

For a constant addition of CO₂ to solutions of constant volume, Kanwisher (1963, p.200) has shown that the change in p(CO₂) in equilibrium with a given water sample is much greater for waters of low ionic strength than for waters of high ionic strength. Thus, the purest glacial melt water will show the largest pH changes, for a given CO₂ gas saturation, as it approaches equilibrium with the atmosphere, due to its low buffer capacity. This was confirmed by field observation at Gornergletscher in 1981.

PRECISION OF METHOD

Mean precision for five replicate pairs in the field is -0.04 pH unit with a standard deviation of 0.01 pH unit. This probably includes slight CO₂ gas uptake past the operationally defined "20 minute equilibrium end point" because *all* replicate pairs were slightly more acid, ranging from -0.02 to -0.05 pH units lower for the second sample compared to the first.

CONCLUSIONS

Laboratory pH analyses of glacial melt waters are usually very unrepresentative of *in situ* values and should be discontinued since there is no simple correction that will approximate field values. CO₂ gas transfer and solute enrichment from rock particles are the two main sources of error for pH measurements performed at *in situ* temperatures and pressures. The method described yields final melt-water pH values in equilibrium with atmospheric p(CO₂), and is reproducible to within 0.04 pH units. Future work should concentrate on developing hermetically sealed, insulated filtrate containers, which will make gas transfer between the sample and the atmosphere impossible, facilitating stable field pH measurements representative of *in situ* values.

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