in situ 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 pCO$_2$$_{2}$, and rapidly increased pH during CO$_2$$_{2}$ outgassing at its site 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 pCO$_2$$_{2}$, and rapidly lowered their pH values to achieve equilibrium upon entering the atmosphere, as observed at Gornergletscher during July and August 1981. Gornergletscher summer proglacial stream waters, sometimes show pH increases from rock weathering, with the rate limited by the transfer rate of CO$_2$ across the air-water interface to drive the weathering reactions. Throughout the year, any water parcel at equilibrium with atmospheric CO$_2$ is generally at an equilibrium pH value, if filtration prohibits solution enrichment. For these reasons, laboratory pH measurements are unacceptable for quantitative studies of melt-water chemistry and should be discontinued.


FIELD pH DETERMINATIONS IN GLACIAL MELT WATERS

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**INSTRUMENTS & METHODS**

**FIELD pH DETERMINATIONS IN GLACIAL MELT WATERS**

Abstract. Laboratory pH analyses of glacial melt waters are unrepresentative of in situ values, due primarily to CO$_2$ gas exchange between the sample and the atmosphere, and solute enrichment from chemical reaction with sediment and ground water, 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.

Throughout the year, any water parcel at equilibrium with atmospheric CO$_2$ is generally at an equilibrium pH value, if filtration prohibits solution enrichment. For these reasons, laboratory pH measurements are unacceptable for quantitative studies of melt-water chemistry and should be discontinued.

**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 pCO$_2$ and pH are crucial inputs to modern models of subglacial precipitation and ice formation during regulation sliding at the glacier bed, pH values "contaminated" by CO$_2$ in Arctic ice melt are a significant error, and 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 CO$_2$ transport.

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 CO$_2$, 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°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 a near-neutral pH value to an increase of pH with time for initial spring melt water leaving the Gornergletscher terminus. Noise at 25 min was caused by convection during thermometer insertion and at 64 min by vibration from a nearby avalanche.

FIG. 1. Field d(pH)/dt experiment of 28 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 38 min.

Noise at 25 min was caused by convection during thermometer insertion and at 64 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 dm⁻³ 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 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).

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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(CO2). 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 over-saturated, with respect to atmospheric p(CO2) approach equilibrium pH values faster than samples in equilibrium with atmospheric p(CO2).

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 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(pH)/dt analysis of CO2 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 CO2 gas entering or leaving the sample while approaching equilibrium with atmospheric CO2. Ek (1964, p.140) and Metcalf (unpublished; 1979, p.235) used pH and titration alkalinity, and pH and carbonate saturation measurements, respectively, to show that summer melt waters were often severely undersaturated (by one to two orders of magnitude) with respect to atmospheric p(CO2). 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 CO2 content towards the glacier terminus. As Hallet (1976, p.1005) noted, melt water from such ice will be significantly undersaturated with respect to atmospheric CO2. If all of the CO2 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 CO2 needed to be in equilibrium with atmospheric CO2 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(CO2) at 0°C.

Figure 5 shows an example of the pH changes associated with CO2 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 July-August 1981. An iterative computer calculation available from the author, assuming constant alkalinity during CO2 uptake, was employed to back-calculate CO2 partial pressures from the carbonate equilibria. This approximation was verified by comparison with atmospheric p(CO2) at equilibrium pH and with a replicate analysis after the solution had reached equilibrium (Fig. 5).

A second crucial assumption that CO2-species control the pH of the tested sample has been verified by W.E. Gordon (personal communication 1982). Gordon (1979; 1982) has described the computational procedure used to evaluate pKw 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 HCO3 (61±2, 59±3 \( \mu \)mol dm\(^{-3} \)), the free acid is CO2, and the measured pKw value for the H2CO3/HCO3 conjugate pair is about 6.3. Details of the p(CO2) 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 serpentine grains 3-5 \( \mu \)m 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 CO2 transfer from the air. A measurement with an
Fig. 5. Field d(pH)/dt measurements of 7 August 1981 showing: CO₂ gas uptake in melt water beginning 1 min after sample collection from a supraglacial englacial stream (Curve 1), and CO₂ equilibrium in a replicate sample measured 240 min after collection (Curve 2).

Concurrent with the d(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 m³ s⁻¹ discharge and 0.3 - 0.5 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 CO₂ outgassing. pH experiments showing identical d(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 CO₂ outgassing was observed using an electrode sensitive to CO₂, 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 CO₂ 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; Statt, unpublished). One cannot quantitatively predict the size of pH change that will occur unless the CO₂ 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, CO₂ gas saturation...
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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REFERENCES


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. Adequate filtration at the time of collection and sediment or colloidal minerals will increase 110 tails of this process may be explained by the large colloidal suspensions by Jenny and others (1950).

Temperature and pressure changes

At 0°C, the error from inadequate temperature compensation is only 0.0037 pH unit per Celsius degree error with water 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 solubilities transfer species in equilibrium with H2CO3 and H2SO4. These two acids controlling pH in most glacier ice melt (Koerner and Fisher, 1982).

Determine melt-water properties

Numerous studies of CO2 transfer across the air-water interface show that high wind (Hoover and Berkshia, 1969; Liss, 1973) or turbulence (Kawisher, 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 hypolimnetic 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 the 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 shielded cable, make instrumental loss probable.

For a constant addition of CO2 to solutions of constant volume, Kawisher (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 Gornner Gletscher in 1981.


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