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## RESEARCH ARTICLE

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## Key Points:

- The subglacial waters of temperate ice have pH and alkalinities consistent with partial atmospheric gas exchange during chemical weathering
- Closed system sulfur oxidation following atmospheric gas exchange typically explains high  $p\text{CO}_2$  values found in subglacial waters
- Drawdown of atmospheric  $\text{CO}_2$  through silicate weathering typically exceeds  $\text{CO}_2$  flux from organic matter decomposition in subglacial systems

## Supporting Information:

- Supporting Information S1
- Data Set S1

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## Calculating the balance between atmospheric $\text{CO}_2$ drawdown and organic carbon oxidation in subglacial hydrochemical systems

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**Abstract** In order to constrain  $\text{CO}_2$  fluxes from biogeochemical processes in subglacial environments, we model the evolution of pH and alkalinity over a range of subglacial weathering conditions. We show that subglacial waters reach or exceed atmospheric  $p\text{CO}_2$  levels when atmospheric gases are able to partially access the subglacial environment. Subsequently, closed system oxidation of sulfides is capable of producing  $p\text{CO}_2$  levels well in excess of atmosphere levels without any input from the decay of organic matter. We compared this model to published pH and alkalinity measurements from 21 glaciers and ice sheets. Most subglacial waters are near atmospheric  $p\text{CO}_2$  values. The assumption of an initial period of open system weathering requires substantial organic carbon oxidation in only 4 of the 21 analyzed ice bodies. If the subglacial environment is assumed to be closed from any input of atmospheric gas, large organic carbon inputs are required in nearly all cases. These closed system assumptions imply that order of  $10\text{ g m}^{-2}\text{ y}^{-1}$  of organic carbon are removed from a typical subglacial environment—a rate too high to represent soil carbon built up over previous interglacial periods and far in excess of fluxes of surface deposited organic carbon. Partial open system input of atmospheric gases is therefore likely in most subglacial environments. The decay of organic carbon is still important to subglacial inorganic chemistry where substantial reserves of ancient organic carbon are found in bedrock. In glaciers and ice sheets on silicate bedrock, substantial long-term drawdown of atmospheric  $\text{CO}_2$  occurs.

**Plain Language Summary** Two things can happen beneath a glacier or ice sheet: atmospheric carbon dioxide can be captured through chemical reactions with the underlying rock and carbon can be released to the atmosphere by decaying organic matter. This study finds that, in most cases, more carbon dioxide is captured than produced under ice. Carbon dioxide is a long-lived, heat-trapping gas whose influence on climate makes it a major controller in the growth and collapse of ice sheets over time. Glaciers that consume carbon dioxide through chemical weathering are helping maintain glacial conditions on Earth, whereas those that release carbon dioxide from organic matter are limiting them. This paper synthesizes data from 21 glaciers, analyzing the balance of atmospheric and organic carbon in each. Our analysis suggests that under most glaciers, more carbon dioxide is leaving the atmosphere through chemical weathering than entering from the decay of organic matter, but the scale of this effect depends on the type of rock underlying the ice. This differs from previous scientific work that postulated a more important role for organic carbon decay.

### 1. Introduction

Studies of subglacial hydrochemistry have examined the role of glaciers and ice sheets in geochemical processes since the 1970s. Past syntheses of chemical data from subglacial waters suggest substantial drawdown of atmospheric  $\text{CO}_2$  into dissolved inorganic carbon in subglacial environments [e.g., *Hodson et al.*, 2000]. Because of the discovery of substantial microbial populations in subglacial waters [*Sharp et al.*, 1999], recent studies have suggested that microbial oxidation of organic matter (rather than atmosphere  $\text{CO}_2$ ) may be the primary source of dissolved inorganic carbon in subglacial waters [*Ryu and Jacobson*, 2012; *Wadham et al.*, 2010]. Microbial mediation of chemical reactions explains the oxidation of sulfides and organic matter under such low-temperature conditions [*Sharp et al.*, 1999; *Skidmore et al.*, 2010]. Under laboratory conditions, microbial processes increase rates of silicate and carbonate dissolution [*Montross et al.*, 2013]. However, the magnitude of microbial decomposition of organic matter under ice bodies remains an area of active research, with large ranges of estimates for the microbial flux of  $\text{CH}_4$  and  $\text{CO}_2$  potentially emerging from glaciers and ice sheets [*Stibal et al.*, 2012; *Wadham et al.*, 2012, 2008]. This

study aims to constrain whether the drawdown of atmospheric  $\text{CO}_2$  under ice bodies typically exceeds  $\text{CO}_2$  fluxes from the decomposition of organic matter. Since chemical weathering is the main process by which  $\text{CO}_2$  is removed from the ocean-atmosphere system over long time scales [Berner *et al.*, 1983; Gaillardet *et al.*, 1999], the effect of glaciation on the carbon balance of weathering reactions is relevant to the chemical controls on glacial-interglacial cycles [e.g., Kump and Alley, 1994].

In most glacier and ice sheet systems, bicarbonate ( $\text{HCO}_3^-$ ) is the dominant anion in subglacial and discharging waters [Graly *et al.*, 2014; Hodson *et al.*, 2000; Thomas and Raiswell, 1984]. Bicarbonate, carbonate ( $\text{CO}_3^{2-}$ ) and carbonic acid ( $\text{H}_2\text{CO}_3$ ) are the three components of dissolved inorganic carbon and represent the dissolved carbon pool that can readily exchange with the atmosphere. These components form from three principal sources: atmospheric  $\text{CO}_2$ , carbonate minerals, and organic carbon. These three sources are importantly different in their effect on the Earth's  $\text{CO}_2$  budget. Atmospheric carbon is drawn out of the Earth's atmosphere through carbonation reactions, which alter  $\text{CO}_2$  to bicarbonate or carbonate. If Ca- and Mg-bearing silicates are dissolved through these carbonation reactions, precipitation of carbonate minerals in the oceans commensurately increases, providing a carbon sink on the time scale of the residence time of Ca in the oceans ( $10^6$  years) [Berner *et al.*, 1983]. Where bicarbonate is produced from carbonate minerals, the additions of carbon and Ca + Mg to the oceans are balanced by carbonate precipitation and there is no long-term effect on the carbon budget of the ocean/atmosphere system. Where organic matter decays to carbon dioxide in the subglacial environment, this carbon ultimately evades into the ocean/atmosphere system (if not fixed by other weathering processes).

Organic carbon can enter a glacial system either from the subglacial substrate or from organic matter accumulating on the surface of the ice sheet. Surface snow and ice accumulates organic matter from autotrophic, carbon fixing biological activity [Anesio *et al.*, 2009] and from aerosol soot [Stubbins *et al.*, 2012]. In mountain settings, various geomorphic processes can flux organic matter to the glacier from the surrounding slopes. Buried soils and ancient organic carbon in sedimentary rocks also provide carbon that can be physically or chemically removed during glacier-bed interactions. This carbon can enter the glacial system as either dissolved or particulate organic compounds. In most glacial systems, the supraglacial influx of dissolved organic matter approximately balances with its outflux in runoff [Hood *et al.*, 2015]. Particulate organic matter is not as well studied, but proglacial outflux appears to substantially exceed supraglacial influx in one Greenland Ice Sheet setting [Bhatia *et al.*, 2013]. This flux of organic material is only relevant to the carbon balance of subglacial hydrochemical chemical systems if it is oxidized into the inorganic carbon pool. Organic carbon can also enter the dissolved inorganic pool as methane, but typically at concentrations that are at least an order of magnitude lower than carbon dissolved as carbonic acid, bicarbonate, and carbonate [e.g., Boyd *et al.*, 2010].

The net effect of subglacial weathering on long-term atmospheric  $\text{CO}_2$  drawdown depends on the relative contribution of organic and atmospheric carbon to the dissolved load and the proportion of Ca and Mg cations released through silicate weathering (Table 1). The high abundance of fresh mineral surfaces produced by glacial comminution allows the rapid release of silicate-derived cations from feldspars and micas: alteration of silicate minerals to clays will occur over longer time scales [Drever and Hurcomb, 1986; Graly *et al.*, 2014; Tranter *et al.*, 2002]. If the addition of carbon into subglacial waters from organic processes exceeds this production of Ca and Mg from silicates, the subglacial environment is a net long-term carbon source. If Ca and Mg silicate weathering exceeds the addition of carbon from organic sources, subglacial processes effectively act as a sink (through the commensurate increase of the ocean carbonate sink). Accurate accounting of the sources of bicarbonate and major cations is therefore essential to understanding the role of ice bodies in the Earth's climate system.

### 1.1. Assessments of Carbon Balance

Past assessment of organic, atmospheric, and mineral contributions to dissolved inorganic carbon have relied on bulk chemistry alone and have not considered stable or radiogenic isotope tracers [e.g., Wadham *et al.*, 2010]. Though  $\delta^{13}\text{C}$  differs substantially between mineral, atmospheric, and organic sources [Wadham *et al.*, 2004], stable isotope measurements have not been performed in most studies. This may be because  $\delta^{13}\text{C}$  measurements do not resolve the problem unambiguously, as three isotopic signatures mix to form a single value. It is also likely that some glacial hydrochemical systems have sufficiently

**Table 1.** Weathering Reactions for Subglacial Environments

	Description	Equation	Kinetics	Notes	Longterm CO <sub>2</sub> effect
Silicate Weathering	Anorthite surface weathering	$\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{Al}_2\text{Si}_2\text{O}_8 + \text{Ca}^{2+} + 2\text{HCO}_3^-$	Fast	Limited to fresh feldspar surfaces	50% of $\text{HCO}_3^-$ precipitates as calcite in oceans
	At high pH	$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{Al}_2\text{Si}_2\text{O}_8 + \text{Ca}^{2+} + \text{CO}_3^{2-}$	Fast	Requires high pH	100% of $\text{CO}_3^{2-}$ precipitates as calcite in oceans
	Anorthite weathering to clays	$\text{CaAl}_2\text{Si}_2\text{O}_8 + (2-x)\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+} + (2-2x)\text{HCO}_3^- + x\text{CO}_3^{2-}$	Slow	x represents the proportion of carbonate	50–100% of carbon anions precipitate in proportion to bicarbonate / carbonate ratio
	Albite/K-feldspar weathering	$(\text{Na, K})\text{AlSi}_3\text{O}_8 + (1-0.5x)\text{H}_2\text{CO}_3 + 0.5y\text{H}_2\text{O} \rightarrow (1-y)\text{HAlSi}_3\text{O}_8 + 0.5y\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2y\text{SiO}_2 + (\text{Na, K})^+ + (1-x)\text{HCO}_3^- + 0.5x\text{CO}_3^{2-}$	Fast surficial / slow to clays	y represents the proportion of weathering to clays (versus surficial weathering)	None: $\text{HCO}_3^-$ alters to $\text{CO}_2$ and is released to the ocean / atmosphere system during marine clay alteration reactions.
Carbonate Weathering	Biotite weathering	$\text{K}(\text{Mg, Fe})_3\text{AlSi}_3(\text{OH})_2 + (1-0.5x)\text{H}_2\text{CO}_3 + 0.25y\text{O}_2 \rightarrow (1-y)\text{H}(\text{Mg, Fe})_3\text{AlSi}_3(\text{OH})_2 + y(\text{Mg, Fe})_3\text{AlSi}_3(\text{OH})_2 + \text{K}^+ + (1-x)\text{HCO}_3^- + 0.5x\text{CO}_3^{2-} + 0.5y\text{H}_2\text{O}$	Slow		50–100% of carbon anions precipitate in proportion to bicarbonate / carbonate ratio
	Amphibole weathering	$\text{Ca}_2(\text{Fe, Mg})_4\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2 + 12(1-0.5x)\text{H}_2\text{CO}_3 + 5\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5\text{H}_4\text{SiO}_4 + 2\text{Ca}^{2+} + 4(\text{Mg, Fe})^{2+} + 12(1-x)\text{HCO}_3^- + 6x\text{CO}_3^{2-} + (\text{Ca, Mg})\text{CO}_3 + \text{H}_2\text{CO}_3 \leftrightarrow (\text{Ca, Mg})^{2+} + 2\text{HCO}_3^-$	Fast		None: Released mineral carbonate is re-precipitated in oceans.
Oxidation Reactions	Sulfide oxidation	$\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$	Oxidation and reduction reactions are potentially fast when mediated by biological processes but are otherwise slow or non-existent under subglacial conditions.		None ( $\text{H}^+$ may weather Ca-Mg silicates)
	Organic oxidation	$\text{FeS}_2 + 3.75\text{O}_2 + 3.5\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$ $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{H}_2\text{CO}_3$			
Anoxic Processes	Sulfate reduction	$2\text{H}^+ + \text{SO}_4^{2-} + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{CO}_3$			$\text{CO}_2$ released into ocean / atmosphere system (Carbonic acid produced may weather Ca-Mg silicates)
	Nitrate reduction	$2\text{H}^+ + 2\text{NO}_3^- + 2.5\text{CH}_2\text{O} \rightarrow \text{N}_2 + \text{H}_2\text{O} + 2.5\text{H}_2\text{CO}_3$			$\text{CO}_2$ released into ocean / atmosphere system (Weathering only likely to occur if carbonic acid production exceeds proton consumption)
	Iron reduction	$2\text{H}^+ + \text{Fe}(\text{OH})_3 + 0.25\text{CH}_2\text{O} \rightarrow \text{Fe}^{2+} + 2.5\text{H}_2\text{O} + 0.25\text{H}_2\text{CO}_3$	Slower than oxidation	Requires biological mediation	$\text{CO}_2$ and $\text{CH}_4$ released into ocean / atmosphere system
	Organic fermentation	$\text{CH}_2\text{O} \rightarrow 0.5\text{CO}_2 + 0.5\text{CH}_4$			

short time scales of water-rock interaction that stable isotopes do not fully equilibrate [Skidmore *et al.*, 2004]. Radiocarbon would also have unique values for atmosphere, mineral, and sufficiently young organic sources, and while radiocarbon has been used to assess the source of glacial dissolved organic carbon [e.g., Stubbins *et al.*, 2012], it has not (to our knowledge) been employed in tracing the source of dissolved inorganic carbon in glaciers.

In presenting a synthesis of the water chemistries of several outlet glaciers, Wadham *et al.* [2010] argue that the linear correlation between bicarbonate and sulfate concentrations found that in many glacial outlet streams can be leveraged to estimate the source of bicarbonate within the subglacial system. This method assumes that the linear increase of bicarbonate with sulfate represents sulfide-mediated dissolution of carbonate and the intercept of the correlation on the bicarbonate axis represents bicarbonate produced from either atmospheric or organic sources. It also assumes that the contribution of atmospheric CO<sub>2</sub> to subglacial bicarbonate is limited to 220 μM, and intercepts higher than this value imply the addition of carbon from microbial decay of organic matter. The value of 220 μM derives from assuming carbonate reactions run to saturation prior to any substantial production of acid by sulfide oxidation [Tranter *et al.*, 2002]. Wadham *et al.* find bicarbonate axis intercepts suggestive of substantial subglacial organic carbon contribution in the glaciers of Svalbard but do not observe such trends in Haut Glacier, d'Arolla, Switzerland, or in the ice sheets of Greenland and Antarctica.

More recent measurements from the Greenland Ice Sheet [Graly *et al.*, 2014; Ryu and Jacobson, 2012] find substantially higher proportions of bicarbonate to sulfate than was observed in the glacial data compiled by Wadham *et al.* [2010]. Alkalinity and pH measurements of the Greenland Ice Sheet's lateral outlet streams indicate dissolved CO<sub>2</sub> concentrations exceeding atmospheric partial pressures several fold. Ryu and Jacobson [2012] argue that the excess is sourced from microbial decay of organic matter beneath the ice sheet.

In this study, we develop a more complete analysis of the sources of inorganic carbon within subglacial systems, without a priori assumptions that may not hold for all glacial systems. Our analysis also assesses the potential flux of microbially oxidized organic carbon into the Earth's atmosphere compared to the drawdown of atmospheric carbon through chemical weathering. This new analysis of subglacial water chemistry treats pH and alkalinity as principal metrics.

## 2. Analysis

Our analysis assumes that the pH of subglacial water is controlled by a bicarbonate buffer. It is therefore not appropriate for systems where alkalinity is not produced in the glacial hydrochemical system [e.g., Fortner *et al.*, 2011; Yde *et al.*, 2008] or where alkalinity is predominately in the form of a sulfate or phosphate buffer (i.e., an evaporate bed). The analysis makes two key distinctions. First, we are reviving the distinction between chemical processes that occur in an open and closed system. In an open system, gases can freely enter and leave the subglacial weathering environment in exchange with a body of air of approximately atmospheric composition. In a closed system, gas can neither enter nor leave the subglacial weathering environment. The differing effects of open and closed systems on pH and alkalinity have long been known [Garrels and Christ, 1965; Langmuir, 1971] and have been previously considered in the context of subglacial waters [Raiswell, 1984]. However, more recent work has assumed closed system dynamics a priori [Tranter *et al.*, 2002; Wadham *et al.*, 2010]. Second, we are distinguishing between silicate and carbonate weathering environments. Carbonate reactions can add mineral sourced carbon to the subglacial geochemical system, whereas silicate reactions involve only atmospherically and organically sourced carbon. Carbonate and silicate open systems do not differ substantially in their effects on pH and alkalinity, as the additional mineral carbon can exchange with the atmosphere along with carbon derived from other sources. This leaves three frameworks with which to analyze the pH and alkalinity of subglacial weathering reactions: open system, closed system silicate, and closed system carbonate. Our analysis is developed from Langmuir's [1997] treatment of carbonate-buffered geochemical systems and differs from Raiswell's [1984] treatment of subglacial systems in that it includes the effects of the CO<sub>3</sub><sup>2-</sup> ion at high pH and considers the effects of oxidation reactions.

### 2.1. Weathering by Carbonic Acid

Three key constants control the weathering of Earth materials by dissolved CO<sub>2</sub>: The Henry's law constant for dissolution of CO<sub>2</sub> in water (K<sub>H</sub>) and the first and second dissociation constants of carbonic acid (K<sub>1</sub> and K<sub>2</sub>). These are defined as follows:

$$K_H = \frac{[\text{H}_2\text{CO}_3]}{p\text{CO}_2}, \quad (1a)$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}, \text{ and} \quad (1b)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}. \quad (1c)$$

Values of these constants have been empirically determined for temperatures of 0°C [Plummer and Busenburg, 1982].

In the discussion that follows we assume that activities equal concentrations, both represented by the symbol [ ]. This is reasonable for the generally dilute waters under consideration. From our assumption of a dominantly bicarbonate buffer, we assume that alkalinity (Alk) is approximately equivalent to [HCO<sub>3</sub><sup>-</sup>] + 2 [CO<sub>3</sub><sup>2-</sup>]. Substituting this definition of alkalinity into equations (1a)–(1c), we can express the concentration of each of the three principal carbon species in terms of measured pH and alkalinity and known constants:

$$[\text{H}_2\text{CO}_3] = \text{Alk} \frac{[\text{H}^+]^2}{K_1[\text{H}^+] + 2K_1K_2}, \quad (2a)$$

$$[\text{HCO}_3^-] = \frac{\text{Alk}}{1 + \frac{2K_2}{[\text{H}^+]}} \text{, and} \quad (2b)$$

$$[\text{CO}_3^{2-}] = \frac{\text{Alk}}{2 + \frac{[\text{H}^+]}{K_2}}. \quad (2c)$$

These definitions and equations require that

$$\text{Alk} = p\text{CO}_2 K_H \frac{K_1}{[\text{H}^+]} \left( 1 + \frac{2K_2}{[\text{H}^+]} \right). \quad (3)$$

In an open system, *p*CO<sub>2</sub> will be at atmospheric values, and equation (3) will describe the possible range of pH and alkalinity values that can be maintained while CO<sub>2</sub> is at saturation with the atmosphere. When contact between the water and atmosphere ceases, a closed system will continue to evolve from initial conditions controlled by this open system line. If no carbonate or bicarbonate is produced by the weathering reactions (or from organic matter), the total concentration of dissolved carbon species in the system (C<sub>i</sub>) will remain constant. Under these closed system silicate weathering conditions, the alkalinity of the system will evolve as pH changes:

$$\text{Alk} = \frac{C_i \left( 1 + \frac{2K_2}{[\text{H}^+]} \right)}{1 + \frac{[\text{H}^+]}{K_1} + \frac{K_2}{[\text{H}^+]}} \quad (4a)$$

where C<sub>i</sub> is the sum of dissolved CO<sub>2</sub>, bicarbonate, and carbonate and can be calculated via equations (2a)–(2c) using the values for alkalinity and pH when contact with the atmosphere ceases.

If carbonate minerals are being weathered in a closed system, every mole of carbonic acid produces 2 mol of bicarbonate (Table 1). If carbonic acid is consumed only in carbonate weathering reactions, closed system pH and alkalinity evolve according to the following:

$$\text{Alk} = \frac{(2C_i - \text{Alk}_i) \left( 1 + \frac{2K_2}{[\text{H}^+]} \right)}{1 + \frac{[\text{H}^+]}{K_1}}, \quad (4b)$$

where Alk<sub>i</sub> is the alkalinity when contact with the atmosphere ceases.

In most subglacial geochemical systems, increases in pH and alkalinity will be limited by calcite saturation. Saturation is reached when

$$K_c = [\text{Ca}^{2+}][\text{CO}_3^{2-}], \quad (5)$$

where  $K_c$  is the empirically determined equilibrium constant for calcite precipitation. In a system where carbonate and bicarbonate are the dominant anions, we can assume that

$$\text{Alk} = \frac{2[\text{Ca}^{2+}]}{\alpha}, \quad (6a)$$

where  $\alpha$  is the proportion of  $\text{Ca}^{2+}$  in equivalents among the cations produced by the subglacial weathering reactions. Substituting equations (2c) and (6a) into equation (5),

$$\text{Alk} = \sqrt{\frac{2K_c}{\alpha} \left( 2 + \frac{[\text{H}^+]}{K_2} \right)}. \quad (6b)$$

Equation (6b) describes calcite saturation in pH-alkalinity space. In subglacial environments where calcite weathering dominates,  $\alpha$  approaches 1. Where silicate weathering dominates,  $\alpha$  may vary considerably with the Ca content of the minerals undergoing weathering. For example, if the mineral substrate consists only of Ca-pyroxenes ( $\alpha = 1$ ), calcite saturation in an open system would be reached at pH 8.25 and alkalinity of  $\sim 1400 \mu\text{M}$ , whereas if granitic material were weathered ( $\alpha = 0.1$ ), open system calcite saturation would be obtained at pH 8.58 and alkalinity of  $\sim 3000 \mu\text{M}$  (Figure 1).

In an open system, alkalinity and pH increase linearly in log-log space as weathering reactions proceed (Figure 1). The initial pH of 5.5 originates from the pH of pure water that equilibrates with atmospheric  $\text{CO}_2$  at  $\sim 0^\circ\text{C}$ .

On the premise that glacial systems may initially weather material in an open system before contact with the atmosphere ceases, closed system trajectories are drawn as originating from any place along the open system line (Figure 1). The closed system has less alkalinity at a given pH than the open system. Any sample of subglacial water that plots to the right of the open system line in a pH versus alkalinity diagram has likely weathered some amount of material while closed off from the atmosphere. If waters plot below the bottom closed system line (originating at pH = 5.5 on the open system line), it suggests that a portion of the subglacial water never equilibrated with the atmosphere (i.e., englacial or basal melting).

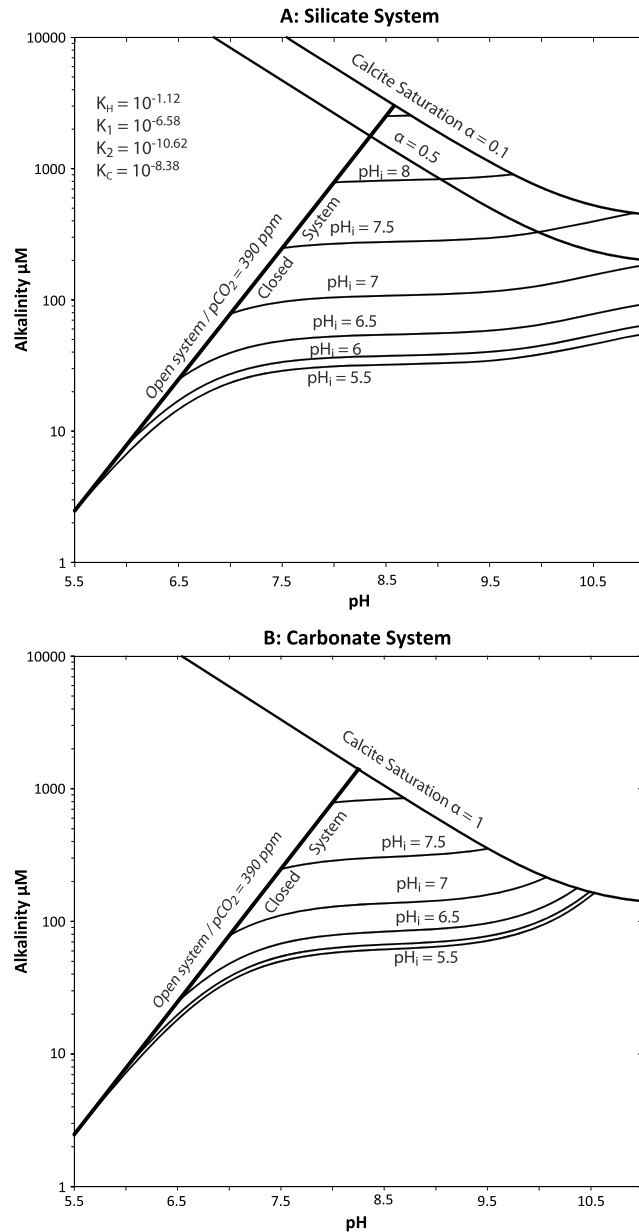
## 2.2. Effect of Oxidation of Sulfides and Organic Matter

In most subglacial waters, dissolved  $\text{O}_2$  is capable of reacting either with sulfide minerals or with organic carbon-bearing material, producing either sulfuric acid or carbonic acid as a product (Table 1). In a bicarbonate-buffered system, sulfuric acid can quickly exchange  $\text{H}^+$  with bicarbonate, producing sulfate and carbonic acid. In open systems, an increase of carbonic acid concentration creates partial pressures of  $\text{CO}_2$  higher than atmosphere values, allowing the excess gas to evade. In a closed system,  $\text{CO}_2$  can accumulate within the subglacial water and only evade upon its discharge from the glacier. If this  $\text{CO}_2$  accumulates faster than it is consumed in silicate weathering reactions, alkalinities will plot above the open system line (Figure 2).

We can modify the silicate closed system trajectory in equation (4a) to account for the addition of carbonic acid from organic carbon oxidation:

$$\text{Alk} = \frac{(C_i + C_{\text{org}}) \left( 1 + \frac{2K_2}{[\text{H}^+]} \right)}{1 + \frac{[\text{H}^+]}{K_1} + \frac{K_2}{[\text{H}^+]}} \quad (7a)$$

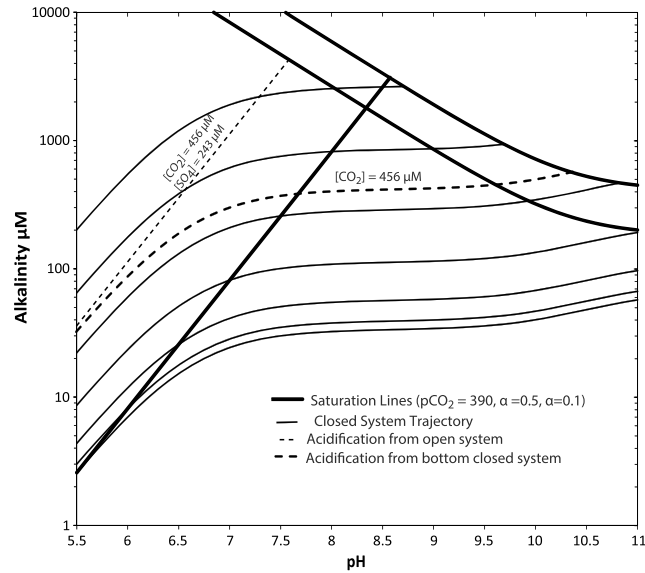
where  $C_{\text{org}}$  is the total molarity of organic carbon oxidized into the dissolved inorganic carbon pool. No term for sulfate appears, because the alteration of bicarbonate to carbonic acid by sulfuric acid maintains the same total of carbon species in the system. Under sulfide oxidation, the decrease in pH will cause a decrease in alkalinity via equation (7a). Weathering of subglacial silicate material will continue concurrently with sulfide and organic carbon oxidation reactions. In a closed silicate system, water compositions will run toward the high pH side of the open system line if silicate weathering occurs faster than oxidation and toward the high alkalinity side if oxidation occurs faster than silicate weathering.



**Figure 1.** Evolution of pH versus alkalinity following the input of atmospheric carbon into open and closed systems, resulting in (a) silicate dissolution and (b) carbonate dissolution. The open system line is drawn using equation (3). The closed system trajectories are drawn using equations (4a) and (4b) in Figures 1a and 1b, respectively. These lines represent the pathway over which pH and alkalinity would evolve were contact with atmospheric gases to cease at the initial point depicted on the open system line. The initial alkalinity and total carbon species for the closed system are derived from equations (3) and (2a)–(2c), respectively, using the initial pH shown. The calcite saturation lines are drawn with equation (6b), using various values for  $\alpha$ . In Figure 1a,  $\alpha$  values of 0.5 and 0.1 are used (representing 50% and 10% Ca cations in the subglacial waters). In Figure 1b, an  $\alpha$  value of 1 is used (representing 100% Ca cations in the subglacial waters). Once calcite saturation is reached, further changes in pH and alkalinity from silicate or carbonate weathering are unlikely. The values for  $K_H$ ,  $K_1$ ,  $K_2$ , and  $K_C$  are for 0° C [Plummer and Busenbarg, 1982].

Except near calcite saturation, sulfide and organic carbon oxidation is unlikely to proceed faster than carbonate mineral dissolution. In a closed system where calcite is abundant and Fe remains in an oxidized state, sulfate production will result in the weathering of 2 mol of calcite for every mole of sulfate produced (Table 1). If equation (4b) is modified to account for this, we can assess the effects of both carbonation and oxidation on a carbonate weathering via





**Figure 2.** Evolution of pH versus alkalinity during oxidation of organic carbon or sulfide in a closed system, coupled with silicate dissolution. The closed system trajectories (equation (4a)) continue above the open system when the rate of sulfide oxidation exceeds the rate of silicate weathering. The maximum possible acidification from the open system is calculated from assuming  $O_2$  is limited to what would be dissolved in supraglacial waters and employing equations (11a) and (11b). An identical result is obtained for both carbon and sulfur oxidation. The thick dashed line is calculated from equation (7a) and represents the maximum alkalinity of a system in which no open system behavior occurred and all the oxygen was consumed in the oxidation of organic carbon. The system would remain on the bottom closed system trajectory if oxygen was consumed in sulfide oxidation.

$$Alk = \frac{(2C_i - Alk_i + 2C_{org} + 2[SO_4^{2-}]) \left(1 + \frac{2K_c}{[H^+]}\right)}{1 + \frac{2[H^+]}{K_1}} \quad (7b)$$

Following the assumption that calcite dissolution is faster than oxidation, evolution of the system by equation (7b) keeps alkalinities below the open system line prior to saturation.

As sulfate production contributes to silicate weathering but does not contribute to alkalinity (equation (3)), our equation that assesses alkalinity in terms of Ca weathering (6a) should be modified to include the effects of  $Ca^{2+}$  produced by sulfide oxidation:

$$Alk = \frac{2[Ca^{2+}]}{\alpha} - 2[SO_4^{2-}]. \quad (8a)$$

If equations (8a) and (2c) are substituted into the equation for calcite saturation (5), the carbonate saturation line in a system where sulfate is being produced is described:

$$Alk = \frac{1}{2} \sqrt{4([SO_4^{2-}])^2 + \frac{8K_c}{\alpha} \left(2 + \frac{[H^+]}{K_2}\right)} - [SO_4^{2-}]. \quad (8b)$$

The evolution of calcite-saturated waters as oxidation continues can be determined by setting equations (7b) and (8b) equal to each other:

$$(2C_i - Alk_i + 2C_{org} + 2[SO_4^{2-}]) \frac{K_1[H^+] + 2K_1K_2}{2[H^+]^2 + K_1K_2} = \frac{1}{2} \sqrt{4([SO_4^{2-}])^2 + \frac{8K_c}{\alpha} \left(2 + \frac{[H^+]}{K_2}\right)} - [SO_4^{2-}]. \quad (9)$$

Equation (9) has an analytic solution (fifth-order polynomial).

Once closed from atmospheric interaction, the ability of oxidation reactions to affect the chemistry of subglacial water is limited by the quantity of dissolved oxygen in the system. At  $0^\circ C$ , dissolved oxygen is limited to  $\sim 456 \mu M$  and will be smaller at higher elevation sites [Langmuir, 1997]. This is not necessarily an absolute limit

of oxidized products in the subglacial system. Oxidation that occurs in an open system will add oxidized products without necessarily depleting dissolved  $O_2$ . Additionally, glacial ice typically has abundant air bubbles. It is also conceivable that air may become trapped in subglacial water as a result of the turbulent mixing of water and air in large moulins, effectively allowing supersaturation of dissolved gases once the system closes.

In ice formed by the compaction of dry firn by overlying snow,  $100 \text{ cm}^3$  of air per kilogram of ice is typical [Berner *et al.*, 1977]. If such ice melts in a closed system, the molar concentration of dissolved  $O_2$  can be calculated by the following:

$$[O_2] = \frac{\rho v p O_2}{m}, \quad (10)$$

where  $\rho$  and  $v$  are the density and volume of air and  $pO_2$  and  $m$  are partial pressure of  $O_2$  and molar mass of  $O_2$ . Using the density of air at standard pressure and  $0^\circ\text{C}$ ,  $\sim 934 \mu\text{M}$  of  $O_2$  result from  $100 \text{ cm}^3$  of air per kilogram of ice.

In a closed silicate system,  $[H^+]$  will increase only as far as there is  $O_2$  available to fuel sulfide oxidation. We can modify equation (2a) to calculate the  $[H^+]$  expected if all the  $O_2$  initially dissolved in supraglacial water is depleted through oxidation reactions without any further weathering reactions. In the case where sulfide is oxidized, alkalinity will decrease as carbonic acid is formed, so the  $[H^+]$  formed from sulfide oxidation in a closed system can be calculated:

$$(\text{Alk}_i - \beta[O_2])[H^+]^2 - ([H_2CO_3]_i + \beta[O_2])K_1[H^+] - ([H_2CO_3]_i + \beta[O_2])2K_1K_2 = 0, \quad (11a)$$

where  $\text{Alk}_i$  and  $[H_2CO_3]_i$  are the initial values when contact with atmosphere ceased,  $[O_2]$  is the total oxygen consumed through oxidation reactions, and  $\beta$  is the ratio of  $O_2$  consumed to  $[H^+]$  produced in the sulfide oxidation reaction.  $\beta$  is 16/15 if iron remains oxidized or 4/7 if iron is reduced (Table 1). In the case where organic material is oxidized, alkalinity will remain constant, and the  $[H^+]$  formed in a closed system is calculated:

$$\text{Alk}_i[H^+]^2 - ([H_2CO_3]_i + [O_2])K_1[H^+] - ([H_2CO_3]_i + [O_2])2K_1K_2 = 0. \quad (11b)$$

The alkalinity associated with this new pH is calculated via equation (7a), creating a limit to the degree that sulfide oxidation can theoretically increase alkalinity above the open system line (Figure 2). Because of the  $C_m$  term in equation (7a), sulfide and organic carbon oxidation plots in identical pH-alkalinity space (Figure 2).

In the carbonate system, we can assess the effect of dissolved oxygen by substituting an  $[O_2]$  term into equation (9):

$$(2C_i - \text{Alk}_i + \beta[O_2]) \frac{K_1[H^+] + 2K_1K_2}{2[H^+]^2 + K_1K_2} = \frac{1}{2} \sqrt{4([\text{SO}_4^{2-}])^2 + \frac{8K_c}{\alpha} \left(2 + \frac{[H^+]}{K_2}\right)} - [\text{SO}_4^{2-}]. \quad (9b)$$

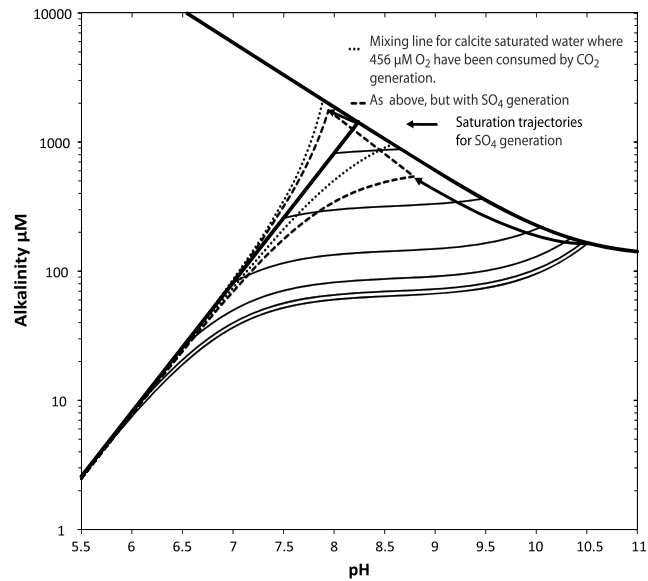
In the carbonate system case,  $\beta$  is 2 for organic matter oxidation, as additional alkalinity will form from carbonate dissolution as carbonic acid dissociates (Table 1). The maximum range for equation (9b) can be determined by assuming initial conditions consistent with an open system until saturation; a minimum by assuming initial conditions consistent a system that closes at 5.5 pH. End-member states are calculated by assuming that all dissolved  $O_2$  is microbially oxidized to either  $\text{CO}_2$  or  $\text{SO}_4$  (Figure 3).

### 2.3. Mixing

The tendency for subglacial systems to evolve toward carbonate saturation and oxygen depletion can be countered by heterogeneous glaciological processes that introduce new waters saturated in dissolved gases and depleted of dissolved minerals. In such mixing situations, the concentrations of dissolved products including alkalinity are a weighted average of the various sources. pH will evolve from the mixture of multiple sources for which the proportion is known via

$$[H^+] = \frac{K_1 \sum w_j [H_2CO_3]_j}{\sum w_j [HCO_3^-]_j}, \quad (12)$$

where  $w_j$  is the proportion of water mixing from each of  $j = 1 \dots n$  sources.



**Figure 3.** Evolution of pH and alkalinity during oxidation in a closed system, coupled with carbonate dissolution. Saturation states are calculated using equation (8b) with  $[O_2] = 456 \mu M$  and with end-member values for  $C_i - Alk_i$ . The mixing of saturated waters with supraglacial waters is shown using equations (13a)–(13c).

If water at calcite saturation and unaltered surface water are assumed to be the only components of the mixture, the composition of the saturated water can be calculated via

$$[SO_4^{2-}]_{sat} = \frac{[SO_4^{2-}] - w[SO_4^{2-}]_{surf}}{1 - w}, \tag{13a}$$

$$Alk_{sat} = \frac{Alk - wAlk_{surf}}{1 - w}, \tag{13b}$$

$$(1 - w)Alk_{sat}[H^+]_{sat}^2 + [wK_1[H_2CO_3]_{surf} - w[H^+][HCO_3^-]_{surf} - (1 - w)[H^+]Alk_{sat}][H^+]_{sat} + 2wK_1K_2[H_2CO_3]_{surf} - 2wK_2[H^+][HCO_3^-]_{surf} = 0, \tag{13c}$$

where sat indicates the value at calcite saturation, surf indicates the value in surface water, and  $w$  is the proportion of surface water mixing with calcite-saturated water. The system of equations can be fully solved when equations (8a) and (8b) is included to constrain the values at saturation and the surface composition is known or assumed.

Two principal sources of dilute water for mixing are supraglacial water (where melting ice exchanges gases with the atmosphere) and ice melted within the closed glacial system. Supraglacial water will have a composition that plots on the lower reaches of the open system line; subglacial ice is typically largely devoid of dissolved  $CO_2$  or bicarbonate, as its total carbon content reflects the atmospheric gases trapped therein. Some glacial ice will have gas composition similar to that of supraglacial water due to ice forming from firn with abundant melting and refreezing processes [Berner *et al.*, 1977].

The mixing of ice melt water into the system generally reduces alkalinity through dilution, with a more modest effect on pH (equation (12)). However, as ice melt water is oxygen rich, some of the lost alkalinity can be regained either through oxidation of organic C coupled with any mineral dissolution or through sulfide oxidation coupled with carbonate dissolution. In net effect, ice melt water must have more  $O_2 +$  non-mineral C than the water with which it is mixing in order to potentially increase the alkalinity of the water. Assuming  $100 \text{ cm}^3$  of air per kilogram of ice, waters that diverge from the open system line at  $pH < 7.77$  can potentially see alkalinity increase through mixture with ice melt waters. Ice with  $> \sim 125 \text{ cm}^3$  of air per

kilogram can increase the alkalinity of calcite-saturated water with atmospheric  $p\text{CO}_2$  levels, subject to some variation controlled by the elevation and temperature at which the air is trapped in ice.

The mixing of supraglacial water and calcite-saturated water will diverge substantially from the open system line at  $\text{pH} \sim 7.5$ , representing mixtures that are greater than  $\sim 20\text{--}40\%$  calcite-saturated water (Figure 3). The upper mixing line represents the maximum amount of alkalinity possible where carbonate saturation was reached in an open system and all available oxygen was consumed through oxidation of organic carbon. Any alkalinity above this line would have to be accounted for by fermentation of organic material or oxygen supersaturation.

#### 2.4. Anoxic Processes

In a closed system depleted of atmospherically sourced dissolved  $\text{O}_2$ , oxidant species may employ redox reactions to further oxidize organic carbon. The effect of these processes on alkalinity and  $\text{pH}$  depends on the species in question. If the redox reaction consumes more protons than it produces carbonic acid, weathering is suppressed; if carbonic acid production exceeds proton consumption, additional weathering is possible. The most commonly abundant oxidants in glacial waters are sulfate, nitrate, and ferric oxyhydroxides. Of these, sulfate reduction consumes  $\text{H}^+$  and produces carbonic acid in equal proportions, nitrate reduction produces 5 mol of carbonic acid per 4 mol of  $\text{H}^+$  consumed, and iron reduction produces 1 mol of carbonic acid per 8 mol of  $\text{H}^+$  consumed (Table 1). Only nitrate reduction can potentially exceed the limits on  $\text{pH}$  and alkalinity space set by equations (9), (11a), and (11b) (Figures 2 and 3), and then only by 0.25 times the quantity of nitrate reduced. Other redox reactions that oxidize organic carbon or sulfides without consuming  $\text{H}^+$  are possible but are likely to rely on compounds that are rare or kinetically slow in subglacial environments [Tranter *et al.*, 2002].

In the absence of further redox agents, organic carbon can continue to decay through fermentation reactions (Table 1). Such reactions can run as long as organic matter remains available for fermentation. This can increase the  $C_{\text{org}}$  term in equations (7a), (7b), and (9) to an indefinitely large quantity. The methane produced by such reactions may be an important climate amplifier [Wadham *et al.*, 2008].

#### 2.5. Estimating Carbon Sources

This analytic framework can be used to partition the total carbon in a subglacial environment between mineral, atmospheric, and organic sources. Mineral carbon can be estimated from other features of the bulk chemistry, with moles of carbon from carbonate being approximately equal to the moles of Mg and Ca dissolved in water, less Mg and Ca from silicate minerals. The relative contribution of atmospheric and organic carbon depends largely on whether closed or open system assumptions are employed.

Some past workers have estimated Ca and Mg silicate contribution to subglacial waters from typical ratios of Ca and Mg to Na and K found in global rivers [Hodson *et al.*, 2000; Sharp *et al.*, 1995]. This method suggests approximately 1.2 mol of silicate-derived  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  per mole of  $\text{Na}^+$  and  $\text{K}^+$ . In many of the silicate-bedded glaciers analyzed, this calculation would suggest more Ca and Mg from silicate than there is in total. Furthermore, weathering mechanisms differ considerably between subglacial and subaerial environments, with glacial environments promoting the exchange of cations on fresh mineral surfaces over complete alteration of silicate minerals to clays [Drever and Hurcomb, 1986; Graly *et al.*, 2014; Tranter *et al.*, 2002]. These surface exchange processes occur readily on micas and feldspars but do not occur on amphiboles or pyroxenes in the  $\text{pH}$  range typically of subglacial waters [Schott *et al.*, 2012]. As amphiboles and pyroxenes have high Ca and Mg to Na and K ratios, this allows a greater proportion Na and K in glacial waters than is found in average rivers.

Here we estimate the proportion of silicate weathering by considering the stoichiometry of local lithology [i.e., Anderson *et al.*, 2000; Yde *et al.*, 2008]. In most settings, silicate  $\text{Na}^+$  comes predominantly from feldspars.  $\text{Ca}^{2+}$  derived from feldspar weathering can therefore be calculated from the  $\text{Na}^+$  content (less Na derived from halite dissolution) and the Ca:Na ratio in the underlying feldspars.  $\text{Mg}^{2+}$  can derive either from dolomite or from mafic silicate minerals (i.e., amphiboles and pyroxenes). The attribution of Mg weathering to dolomite can be strongly inferred in settings where sedimentary carbonate is present in

the bedrock. But in silicate bedrock settings, dolomite (unlike calcite) is unlikely to be a major bedrock component [White *et al.*, 2005]. In silicate settings, we estimate Ca and Mg silicate contribution via

$$[\text{Ca}^{2+}]_{\text{Silicate}} + [\text{Mg}^{2+}]_{\text{Silicate}} = \frac{\text{Ca}_{\text{Feld}}}{1 - \text{Ca}_{\text{Feld}}}([\text{Na}^+] - \gamma[\text{Cl}^-]) + \frac{\text{Ca}_{\text{Amph}} + \text{Mg}_{\text{Amph}}}{\text{Mg}_{\text{Amph}}}[\text{Mg}^{2+}], \quad (14a)$$

where  $\text{Ca}_{\text{Feld}}$  is the molar proportion of Ca in the setting's typical bedrock feldspar,  $\text{Ca}_{\text{Amph}}$  and  $\text{Mg}_{\text{Amph}}$  are the molar quantities of Ca and Mg in typical amphiboles, and  $\gamma$  is the proportion of  $[\text{Cl}^-]$  that entered the system in conjunction with  $[\text{Na}^+]$ .  $\gamma$  does not necessarily reflect the Na composition of sea water, as Cl often enters glacial hydrologic systems from fluid inclusions or other mineral sources. This estimate assumes no dolomite in silicate settings and approximately even proportions of Ca and Mg between amphibole and other mafic minerals and therefore may not be appropriate in settings where  $\text{Mg}^{2+}$  represents a large portion of the dissolved load. The estimate may underestimate Ca derived from mafic minerals where Mg remains in secondary phases (such as chlorite). It may also underestimate Ca derived from feldspars due to preferential leaching of calcic feldspars over sodic ones.

In carbonate settings, we use

$$[\text{Ca}^{2+}]_{\text{Silicate}} + [\text{Mg}^{2+}]_{\text{Silicate}} = \frac{\text{Ca}_{\text{Feld}}}{1 - \text{Ca}_{\text{Feld}}}([\text{Na}^+] - \gamma[\text{Cl}^-]). \quad (14b)$$

This assumes that all Mg comes from dolomite and is inappropriate in settings that have both carbonate and mafic silicate rocks. In most of the analyzed ice bodies, the underlying mineralogy is not sufficiently constrained to put in precise values these variables, and we insert high and low estimates based on general geology descriptions (e.g., 0.4–0.6  $\text{Ca}_{\text{Feld}}$  for basalt).

To determine the contribution of mineral carbon, we subtract the equations (14a) and (14b) values for  $[\text{Ca}^{2+}]_{\text{Silicate}} + [\text{Mg}^{2+}]_{\text{Silicate}}$  from the total Ca and Mg in the waters. The remaining carbon must either be atmospheric or organic in origin. A minimum estimate for organic carbon oxidation is calculated in a silicate system by the following:

$$C_{\text{Org}} = \text{Max}(0, [\text{CO}_2]_s - p\text{CO}_2K_H), \quad (15a)$$

where  $[\text{CO}_2]_s$  is the concentration of dissolved  $\text{CO}_2$  corrected for sulfide oxidation and  $p\text{CO}_2$  represents atmospheric levels.  $[\text{CO}_2]_s$  is calculated using equation (2a), substituting  $\text{Alk} + 2*[\text{SO}_4^{2-}]$  for alkalinity and  $[\text{H}^+]$  calculated by equation (4a) using  $\text{Alk} + 2*[\text{SO}_4^{2-}]$  in place of alkalinity. This assumes open system behavior without organic carbon or sulfide oxidation prior to closure and no silicate weathering after closure. In a carbonate system, minimum organic carbon oxidation is calculated via

$$C_{\text{org}} = \text{Max}[0, (1 - w)([\text{CO}_2]_s^* - p\text{CO}_2K_H)], \quad (15b)$$

where  $[\text{CO}_2]_s^*$  is the concentration of  $\text{CO}_2$  calculated at saturation via equations (13a)–(13c) and corrected for sulfide via equation (9).

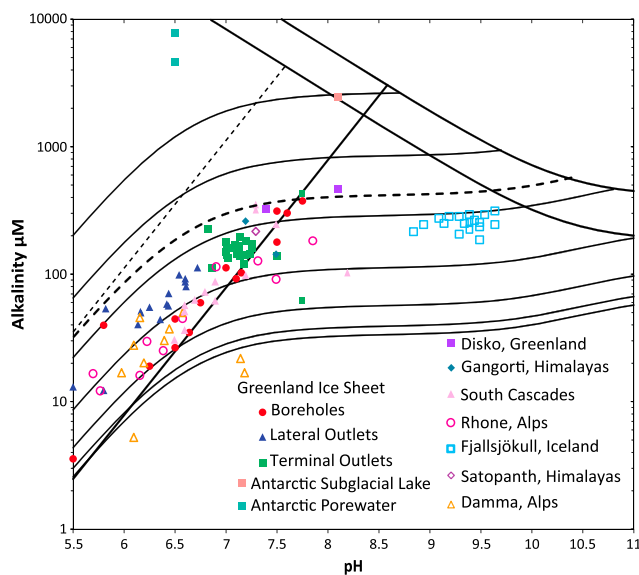
A maximum estimate for oxidized organic carbon in a glacial system can be calculated by assuming that no atmospheric  $\text{CO}_2$  is added to the system after the equilibration of surface water with the atmosphere (i.e., an entirely closed system). This is calculated as follows:

$$C_{\text{org}} = C_T - [\text{Ca}^{2+}]_{\text{Carbonate}} - [\text{Mg}^{2+}]_{\text{Carbonate}} - p\text{CO}_2K_H, \quad (16)$$

where  $C_T$  is the total amount of carbon ( $\text{CO}_2$ , bicarbonate, and carbonate) inferred from pH and alkalinity via equations (2a)–(2c). This formulation does not account for closed system mixing with basal or englacial ice melt water (that would be nearly devoid of atmospheric carbon) or the unconstrained quantities of organic  $\text{CO}_2$  that could flux to the atmosphere in an open system.

### 3. Comparison to Published Data

In order to examine which of the chemical pathways outlined in section 2 are most prevalent in nature, we plot the pH and alkalinity of waters collected from samples of subglacial or outlet stream waters from several glaciers and ice sheets. In principle, comparisons of pH and alkalinity to stable isotopes of carbon and sulfur would also be useful for distinguishing the mixing of multiple sources of material [Deines and Langmuir, 1974; Michaelis, 1992; Schaefer and Usdowski, 1992]. However, such data have thus far only been reported for a



**Figure 4.** Alkalinity and pH in subglacial waters compared to theoretical curves for silicate-bedded glaciers and ice sheets.

These sites have relatively high sea-salt-corrected ratios of Na and K to Ca and Mg, indicating that carbonate dissolution does not dominate the chemistry. Sites underlain by carbonates and sites with a varied or unknown carbonate presence are plotted as carbonate rocks if Ca makes up a large percentage (typically >80 mol %) of the cations. Some of these are in settings where the bedrock contains considerable silicates.

### 3.1. Silicate-Bedded Glaciers

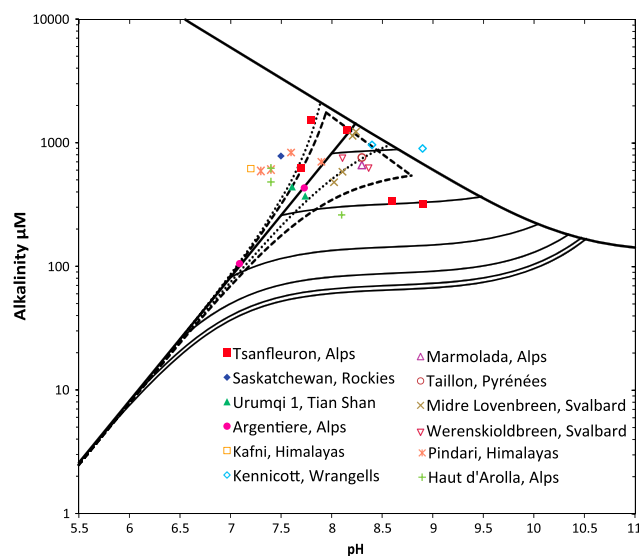
#### 3.1.1. Alpine Glaciers

Data from several silicate-bedded alpine glaciers are plotted in Figure 4. Data are plotted either from individual measurements or from season-long averages, depending on which were available in the published source. Most of the data plot near the  $p\text{CO}_2 = 390$  ppm line, implying predominately open system behavior in most of the glaciers examined. The data are also within the range explainable by oxidation of sulfide or organic carbon in a closed system (Figure 4). However, the proximity of most data to the open system line renders complete closed system behavior implausible. Waters with lower values for alkalinity and pH tend to have  $p\text{CO}_2$  greater than atmospheric levels, whereas higher pH waters tend to be below atmospheric levels. Disko, Greenland [Yde *et al.*, 2005], Rhone Glacier, Switzerland [Hosein *et al.*, 2004], South Cascade Glacier, USA [Reynolds and Johnson, 1972], Gangort, Himalaya [Singh *et al.*, 2012], and Satopanth, Himalaya [Singh and Hasnain, 2002], all have water chemistries that plot on both sides of the open system line. The chemistry of Fjallsjökull, Iceland [Raiswell and Thomas, 1984], diverges substantially from the open system line, implying closed system depletion of  $\text{CO}_2$ . But its high alkalinity suggests substantial open system behavior occurred before closure. Fjallsjökull may represent a unique subglacial environment due to the presence of volcanic activity. Damma Glacier, Switzerland [Hindshaw *et al.*, 2011] mostly has chemistries that indicate closed system acidification of waters after only minimal open system dynamics, with a few samples that plot below the open system line, suggesting completely closed system behavior. The samples from Damma were taken at the terminus of a dead ice zone detached from the main glacier [Hindshaw *et al.*, 2011] and therefore may represent an atypical subglacial environment.

#### 3.1.2. Greenland Ice Sheet

Samples from the Greenland Ice Sheet display similar characteristics to silicate alpine glaciers (Figure 4), with higher pH samples plotting somewhat below and lower pH samples plotting somewhat above the open system line. Nearly all samples taken from ablation zone boreholes [Graly *et al.*, 2014] plot on or near the line. Samples from outlet streams [Graly *et al.*, 2014; Ryu and Jacobson, 2012] generally have greater than atmospheric  $p\text{CO}_2$  values, though most have sufficient sulfate to account for the  $\text{CO}_2$  through acid-producing sulfide oxidation, which alters bicarbonate to carbonic acid. The samples requiring organic carbon

single subglacial setting and not in conjunctions with pH or alkalinity measurements [Wadham *et al.*, 2004]. The ice bodies selected in this study have generally either been studied over the entire melt season, so that average annual conditions can be assessed, or represent difficult-to-acquire samples, collected directly from the glacial bed. Such borehole samples can represent more hydrologically isolated portions of subglacial water than the hydrologically integrated waters that emerge from glacial termini [Graly *et al.*, 2014; Tranter *et al.*, 2002]. Samples from field sites where the bedrock does not contain substantial carbonate formations are plotted using diagrams for silicate rocks. While some carbonate dissolution is still expected in these settings from accessory or secondary minerals,



**Figure 5.** Alkalinity and pH in subglacial waters compared to theoretical curves for carbonate-bedded glaciers.

far exceed levels that could source from dissolved  $O_2$  [Christner *et al.*, 2014; Skidmore *et al.*, 2010]. In the case of Antarctic subglacial waters, open system behavior is unlikely as no moulines exist to bring to surface water and air to the ice-bed interface. The source of oxidized products such as bicarbonate and sulfate must either be evaporites, such as are often found in Antarctic soils [e.g., Bockheim, 1980], freeze-on processes that concentrate the solution, or oxidation pathways relying on the reduction of silicate or oxide-sourced species, such as  $Fe^{3+}$  [Skidmore *et al.*, 2010]. The residence times of Antarctic subglacial lakes can be greater than  $10^4$  years [e.g., Bell *et al.*, 2002], while residence times for subglacial water produced by supraglacial melt is often on the scale of days, even in ice sheet systems [Chandler *et al.*, 2013]. The production of oxidized products through kinetically slow processes that do not require dissolved oxygen may be significant in Antarctic subglacial environments but are not likely to occur at appreciable levels in meltwater systems of the Greenland Ice Sheet or in alpine glacier environments.

### 3.2. Carbonate-Bedded Glaciers

Samples from carbonate alpine glaciers tend to have high pH values ( $>7.5$ ) and generally are near but not at calcite saturation (Figure 5). This is consistent with a mixture of calcite-saturated waters and supraglacial waters that have had minimal interaction with the ice-bed interface. Data from Tsanfleuron, Switzerland [Fairchild *et al.*, 1994; Zeng *et al.*, 2012], plot on both sides of the  $pCO_2 = 390$  ppm line, with some samples requiring closed system organic carbon/sulfide oxidation after calcite saturation is reached in an open system, some samples consistent with complete open system conditions, and others requiring incomplete oxygen consumption and closure from atmospheric interaction at  $<7.5$  pH. Marmolada, Italian Dolomites [Fairchild *et al.*, 1994], Taillon-Gabiétous, French Pyrénées [Brown *et al.*, 2006], Kennicott River, Alaska [Anderson *et al.*, 2003], Werenskioldbreen, Svalbard [Stachnik *et al.*, 2016], and the “quick flow” waters of Midre Lovenbreen, Svalbard [Wynn *et al.*, 2006], require exchange between subglacial waters and atmospheric gases prior to carbonate saturation. Urumqi Glacier No.1, Tian Shan [Feng *et al.*, 2012], Argentière, French Alps [Thomas and Raiswell, 1984], and the “delayed flow” waters of Midre Lovenbreen, are consistent with a predominantly open system (though similar values can be obtained through  $O_2$  consumption in closed system waters).

Pindari, Himalaya [Pandey *et al.*, 2001], Kafni, Himalaya [Singh *et al.*, 1998], Saskatchewan Glacier, Alberta [Fairchild *et al.*, 1994], and Haut d'Arolla, Switzerland [Tranter *et al.*, 2002], have chemistries whose alkalinity is in excess of what could be produced by calcite saturation in an open system followed by complete consumption of typical levels of dissolved  $O_2$  in a closed system. Of these, Haut d'Arolla and Pindari have substantial sulfate, implying that sulfide oxidation proceeded in excess of normal values for dissolved  $O_2$ . This suggests  $O_2$  supersaturation by either the melting of air-rich ice or the mixing of air and subglacial water,

decomposition are all taken from waters originating from lateral glacial outlets (located near the end of the access road from Kangerlussuaq to the ice). These outlets have little discharge compared to terminus locations and may be more strongly influenced by soil-percolated groundwater than most subglacial or terminal outlet sites.

#### 3.1.3. Antarctic Subglacial Waters

Samples from Antarctic subglacial lakes [Christner *et al.*, 2014] and pore waters in the till beneath Antarctic ice streams [Skidmore *et al.*, 2010] are at or near calcite saturation and have far greater alkalinities than could be explained by dissolved  $O_2$  acting in a closed system (Figure 4). These samples also have very high concentrations of  $SO_4^{2-}$ , which also

or possibly some role for silicate or oxide-driven oxidation processes. Kanfi and Saskatchewan both have very low sulfate concentrations. Their alkalinity levels must therefore have been formed either through oxidation of organic carbon in an oxygen-supersaturated setting or through fermentation of organic carbon. Both glaciers are located in settings containing schistose sedimentary rocks. Such rocks likely contain high levels of ancient organic carbon.

#### 4. Discussion

In glacial hydrologic systems across a range of geographic and geologic settings, the pH and alkalinity of subglacial waters imply dissolved  $\text{CO}_2$  concentrations that are at or near equilibrium with the atmosphere. Such results are consistent with subglacial systems that are largely able to exchange gases with the atmosphere or switch regularly between open and closed system dynamics [Raiswell, 1984]. However,  $\text{CO}_2$  saturation can also be achieved through closed system processes. In most of the carbonate-based glaciers, this would require either supersaturation of dissolved  $\text{O}_2$  (through the melting of air-rich ice) or the fermentation of organic carbon (Figure 5).

We calculated the maximum and minimum estimates for the input of microbially oxidized organic carbon into subglacial systems using average data from the analyzed glaciers and ice sheets (Table 2 and supporting information). Where average values were provided in the source manuscripts, those values are used to solve equations (14a), (14b), (15a), (15b), and (16), where the source manuscript provided multiple data points, those values were averaged. We also compare these maxima and minima to the long-term  $\text{CO}_2$  drawdown predicted by the weathering of Ca and Mg silicates.

If closed system assumptions are employed, most subglacial water compositions imply hundreds of micromolars of organic C oxidation into the dissolved inorganic carbon pool (Table 2). For most glaciers, this is well above the long-term carbon drawdown from Ca or Mg silicate weathering. Thus, in most settings, closed system assumptions require substantial  $\text{CO}_2$  evasion from ice bodies on a long-term basis.

If open system assumptions are employed, most glacial systems do not require any addition of organic carbon to explain their chemistries. The only settings that flux substantial organic carbon under open system assumptions are glaciers with substantial sedimentary organic carbon in the substrate (Saskatchewan and Kafni) and the Greenland lateral stream (that may have soil groundwater input). In many silicate glaciers and in some areas of the Greenland Ice Sheet, open system assumptions imply atmospheric drawdown into long-term marine carbonate storage at volumes of order of  $100 \mu\text{M}$  (Table 2). Fixing of atmospheric  $\text{CO}_2$  is negligible in carbonate glaciers, as carbonate deposition is paired with carbonate weathering.

The annual flux of  $\text{CO}_2$  derived from organic matter can be estimated from the molarity of organically sourced carbon in discharge waters multiplied by the average volume of water delivered to the glacier-bed interface. In practice, most ablation zone melt is delivered to the bed through moulins and crevasses, whereas melt in the accumulation zone mostly refreezes in the firn layer [e.g., Cox *et al.*, 2015]. We therefore limit our consideration of glacier-bed interaction to the ablation zone, both as the region of melt and as the region where surface water reaches the bed to perform chemical weathering. In the Greenland Ice Sheet, ablation zone melt averages 2–4 m per year [Hanna *et al.*, 2005]. Temperate alpine glaciers typically have higher values [e.g., Oerlemans *et al.*, 2009]. If we assume  $4 \text{ m}^3$  of runoff per square meter of the ablation zone ice bed and use the values for oxidized organic carbon derived from closed system assumptions, 2–18 g of organic carbon per  $\text{m}^2/\text{yr}$  would be removed from subglacial environments (Table 2). Through fluxes of dissolved organic carbon originating from glacial surfaces are much smaller—on the order of  $0.5 \text{ mg C per l}$  [Hood *et al.*, 2015], providing  $2\text{--}3 \text{ g C m}^{-2} \text{ yr}^{-1}$  in a typical melt season. And since surface inputs of dissolved organic carbon approximately balance meltwater outputs [Hood *et al.*, 2015], only a fraction of this through flux could be contributing to the dissolved inorganic carbon pool. We therefore infer that closed system assumptions would require a minimum removal of order of  $10 \text{ g C m}^{-2} \text{ yr}^{-1}$  from the subglacial substrate in most of the analyzed settings.

Unless organic C is sourced from sedimentary rocks, microbially oxidized subglacial carbon is sourced from soils built up during previous interglacial periods. A synthesis of soil data suggests that over the course of order of  $10^4$  years, high alpine soils build up 15–22 kg of organic carbon per square meter [Egli *et al.*, 2012]. A power law relationship between organic carbon content and age in younger alpine soils suggests



**Table 2.** Long-Term Fluxes of Carbon Into Subglacial Weathering Systems With Open and Closed System Assumptions

Glacier	Bedrock Type <sup>a</sup>	Total Carbon (μM)	Mineral Carbon (μM)	Closed System Organic Carbon Flux			Open System Drawdown of Atmospheric CO <sub>2</sub>					
				Short Term (μM)	Long Term <sup>b</sup> (μM)	Long Term <sup>c</sup> (g m <sup>-2</sup> a <sup>-1</sup> ) <sup>c</sup>	Short Term (μM)	Long Term <sup>d</sup> (μM)	Short Term (g m <sup>-2</sup> a <sup>-1</sup> ) <sup>c</sup>	Long Term (g m <sup>-2</sup> a <sup>-1</sup> ) <sup>c</sup>		
Greenland <sup>e</sup>	Grandiorite Gneiss (S)	299	0–50	219–270	70	11.73	3.38	0	249–299	149–199	13.16	8.35
Silicic Boreholes												
Greenland <sup>e</sup> Alkali Boreholes	Grandiorite Gneiss (S)	232	20–28	174–183	147	8.57	7.05	0	204–213	27–36	10.00	1.52
Greenland <sup>e</sup> Intermediate Boreholes	Grandiorite Gneiss (S)	106	6–11	65–71	58	3.26	2.79	5	85–90	2–7	4.21	0.23
Greenland <sup>e</sup> Terminus Boreholes	Grandiorite Gneiss (S)	212	26–40	142–157	105	7.18	5.04	0	172–186	38–52	8.61	2.14
Greenland <sup>e</sup> Lateral	Grandiorite Gneiss (S)	164	8–10	124–127	116	6.02	5.57	64	27–29	–55 to –52	1.34	–2.59
Disko	Basalt (S)	426	0–37	359–396	259	18.12	12.44	0	389–426	100–137	19.55	5.68
Rhone	Gneiss (S)	90	10–12	48–50	44	2.35	2.10	7	63–65	–3 to –1	3.08	–0.10
Damma	Granite (S)	102	10–13	59–62	54	2.92	2.58	16	57–60	–11 to –8	2.79	–0.44
Satopanth	Granite/ Metasediment (S)	263	58–75	159–175	123	8.01	5.91	0	188–205	35–52	9.44	2.09
Gangoti	Granite/ Metasediment (S)	247	51–109	108–165	–22	6.55	–1.06	0	138–195	130–187	7.98	7.61
Fjallsjökull	Basalt (S)	218	0–48	140–188	54	7.88	2.60	0	170–218	86–134	9.31	5.28
South Cascade	Diorite/Greenstone (S)	165	61–70	65–74	60	3.33	2.89	0	95–104	5–14	4.76	0.44
Haut d'Arolla A Boreholes	Greenschist (C)	713	498–511	173–186	168	8.61	8.04	2	199–212	3–17	9.87	0.48
Haut d'Arolla B Boreholes	Greenschist (C)	552	349–361	161–173	156	8.03	7.51	0	191–203	5–17	9.46	0.52
Haut d'Arolla C Boreholes	Greenschist (C)	267	109–121	116–129	111	5.86	5.34	0	146–158	5–17	7.29	0.53
Tsanflueran	Limestone (C)	846	497–500	316–319	314	15.23	15.08	0	346–349	2–5	16.66	0.15
Marmalada	Dolostone (C)	667	375	263	263	12.62	12.62	0	0	0–0	14.05	0.00
Argentiere	Gneiss (C)	299	132–135	134–136	130	6.48	6.24	0	164–166	4–6	7.91	0.24
Tallion	Sandy Limestone (C)	768	480	258	258	12.38	12.38	0	0	0–0	13.81	0.00
Kennicott	Limestone (C)	926	532–558	338–364	328	16.85	15.76	0	368–394	10–35	18.28	1.09
Saskatchewan	Impure Limestone (C)	871	467–469	372–374	370	17.91	17.76	51	300–301	–49 to –47	14.42	–2.31
Midre Lovenbreen (Delayed Flow)	Phyllite Schist (C)	1179	934–966	183–215	138	9.54	6.64	0	213–244	44–76	10.97	2.90
Werenskioldbreen	Meta-sedimentary (C)	696	447–485	181–219	178	9.59	8.53	0	210–249	3–41	11.02	1.06
Urumqi 1	Dolomite-bearing Schist (C)	438	373–381	27–35	25	1.49	1.20	0	57–65	2–10	2.92	0.29
Pindari	Gneisses and Schists (C)	760	708–715	15–22	13	0.90	0.60	0	45–52	3–10	2.33	0.30
Kafni	Schist and Marble (C)	765	351–369	367–384	360	18.04	17.26	116	166–183	–108 to –91	8.37	–4.77

<sup>a</sup>(S) denotes analysis using the silicate system; (C) denotes analysis using the carbonate system.

<sup>b</sup>Less Ca and Mg weathering from silicates (which will drawdown CO<sub>2</sub> as ocean carbonate).

<sup>c</sup>Assuming ablation zone averages of 4 m melt.

<sup>d</sup>Weathering of Ca and Mg silicates less organic carbon flux.

<sup>e</sup>All Greenland Ice Sheet samples were collected from the Kangerlussuaq sector.

2–3 kg m<sup>-2</sup> in thousand year old soils and <0.5 kg m<sup>-2</sup> in hundred year old soils [Egli *et al.*, 2012]. Removal of 10 g C m<sup>-2</sup> yr<sup>-1</sup> would deplete fully developed alpine sediments of their organic matter on a thousand-year time scale. These closed system rates of organic carbon removal also far exceed rates of microbial decomposition of subglacial organic matter found in laboratory experiments, which suggest multiple millions of years to remove the organic carbon present in sediments from Greenland and high arctic settings [Stibal *et al.*, 2012].

It is possible that some soil organic matter could have remained frozen under cold-based ice, which has recently turned warm as glaciers shrink and ablation zones expand. However, to produce the levels of organic carbon decay implied by closed systems assumptions (Table 2), the newly contacted organic matter would need to be released into subglacial system as dissolved inorganic carbon at rates of multiple kg m<sup>2</sup>/yr. Such rates could be obtained from the melting of clathrate hydrates [Wadham *et al.*, 2008] but not from the decay of intact organic matter. While the transient melting of long-stored clathrates would maintain closed system assumptions across the range of analyzed glacial settings, we consider open system input of atmospheric carbon more plausible.

Existing stable isotope data are also not consistent with the results of the closed system assumptions. Reported  $\delta^{13}\text{C}$  values range from –10 to –4‰, only a few per mill below values expected from the closed system mixing of atmospheric CO<sub>2</sub> and mineral carbonate [Wadham *et al.*, 2004]. The mosses and lichens that dominate polar and high alpine environments are C3 plants that have  $\delta^{13}\text{C}$  signatures in the range of –27 to –25‰ [Teeri, 1981]. Kerogen from sedimentary rocks measured in Svalbard has a  $\delta^{13}\text{C}$  signature ranging from 22 to 25‰ [Wadham *et al.*, 2004]. These values allow at most 10–20% of dissolved carbon to source from organic matter; the proportions of organic carbon implied under closed system assumptions are substantially higher (Table 2).

Closed system assumptions imply more microbially mediated carbon gas production than can be explained from interglacial soil development, a higher proportion of organic carbon than available stable isotope data suggest and are inconsistent with the general trend of the data to be near atmosphere pCO<sub>2</sub> values. This implies that most glacial hydraulic systems in arctic and alpine settings have some continued interaction with the atmosphere beyond the chemistry that occurs in surface waters and that silicate-bedded glaciers and ice sheets draw CO<sub>2</sub> out of the atmosphere on a long-term basis. Decay of organic carbon is nevertheless an important process under glaciers and ice sheets; both Saskatchewan and Kafni glaciers have chemistries that require substantial organic carbon input, and we expect that other glaciers that overlie sedimentary bedrock rich in ancient organic carbon would similarly oxidize substantial quantities of the organic matter beneath. But in most other systems, glacial hydrochemistry can be explained without substantial organic input.

## 5. Conclusions

Analysis of the chemical dynamics of subglacial waters using both closed and open system assumptions can explain the pH and alkalinity of arctic and alpine subglacial waters while requiring appreciable flux from the oxidation of organic matter only in limited circumstances. Subglacial water samples from a wide range of glaciers and ice sheets have pH and alkalinity values that are near atmospheric pCO<sub>2</sub> levels, consistent with a large portion of subglacial weathering occurring in open exchange with the atmosphere. While such chemical compositions could be explained through closed system weathering and mixture with surface waters, such pathways would require implausibly large levels of organic matter decay. Future analyses of glacial hydrochemistry should not presume that the system is closed from atmospheric interaction or attribute elevated pCO<sub>2</sub> values to organic processes a priori.

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