



Proglacial freshwaters are significant and previously unrecognized sinks of atmospheric CO₂

Kyra A. St. Pierre^{a,1}, Vincent L. St. Louis^a, Sherry L. Schiff^b, Igor Lehnerr^c, Paul G. Dainard^b, Alex S. Gardner^d, Pieter J. K. Aukes^b, and Martin J. Sharp^e

^aDepartment of Biological Sciences, University of Alberta, Edmonton, AB T6G 2E9, Canada; ^bDepartment of Earth and Environmental Sciences, University of Waterloo, Waterloo, ON N2L 3G1, Canada; ^cDepartment of Geography, University of Toronto Mississauga, Mississauga, ON L5L 1C6 Canada; ^dJet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109; and ^eDepartment of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB T6G 2E3 Canada

Edited by Andrea Rinaldo, Swiss Federal Institute of Technology in Lausanne, Lausanne, Switzerland, and approved July 18, 2019 (received for review March 21, 2019)

Carbon dioxide (CO₂) emissions from freshwater ecosystems are almost universally predicted to increase with climate warming. Glacier-fed rivers and lakes, however, differ critically from those in nonglaciated catchments in that they receive little terrestrial input of organic matter for decomposition and CO₂ production, and transport large quantities of easily mobilized comminuted sediments available for carbonate and silicate weathering reactions that can consume atmospheric CO₂. We used a whole-watershed approach, integrating concepts from glaciology and limnology, to conclusively show that certain glacier-fed freshwater ecosystems are important and previously overlooked annual CO₂ sinks due to the overwhelming influence of these weathering reactions. Using the glaciated Lake Hazen watershed (Nunavut, Canada, 82°N) as a model system, we found that weathering reactions in the glacial rivers actively consumed CO₂ up to 42 km downstream of glaciers, and cumulatively transformed the High Arctic's most voluminous lake into an important CO₂ sink. In conjunction with data collected at other proglacial freshwater sites in Greenland and the Canadian Rockies, we suggest that CO₂ consumption in proglacial freshwaters due to glacial melt-enhanced weathering is likely a globally relevant phenomenon, with potentially important implications for regional annual carbon budgets in glaciated watersheds.

glacial meltwaters | carbon | biogeochemistry | freshwater

Most inland freshwater systems, such as lakes, rivers, ponds, and reservoirs, are net emitters of CO₂ to the atmosphere on an annual basis (1). Biological and abiotic processes leading to CO₂ supersaturation and resultant emissions from surface waters include net heterotrophy (2), catchment inputs of dissolved inorganic carbon (DIC) (3, 4), photochemical mineralization of organic matter (5, 6), and calcite precipitation (7). Glacier-fed rivers and lakes have hitherto been overlooked in studies of CO₂ cycling, despite their rapid expansion after enhanced glacier melt (8, 9). CO₂ cycling in glaciated watersheds differs critically from what is observed in other northern, temperate, and tropical systems due to both little export of organic carbon (OC) from sparsely vegetated landscapes, an important subsidy of heterotrophy (2, 10), and an abundance of freshly eroded and reactive sediments susceptible to rapid chemical weathering. Together, these characteristics mean that chemical weathering controls on CO₂ fluxes in glacier-fed freshwaters could overwhelm the typical biological and abiotic processes that dominate in most nonglaciated watersheds.

Subglacial chemical weathering has been described extensively (e.g., refs. 11 to 13), but comparatively little is known about the extent of such weathering in proglacial freshwaters (12). Both carbonate and silicate weathering reactions (Eqs. 1 and 2 in Fig. 1) have the potential to consume atmospheric CO_{2(g)} dissolved in water (CO_{2(aq)}), but can be limited subglacially due to a lack of CO_{2(g)} exchange with the atmosphere (11), and supraglacially due to a lack of comminuted sediments (14). Although the possibility of atmospheric CO₂ consumption by chemical weathering in proglacial

freshwaters has been proposed (15, 16), in-depth studies of proglacial freshwater networks have been limited (17–20), with very few in situ measurements of CO_{2(aq)}, despite its importance as an indicator of both freshwater ecosystem function and mineral weathering reactions.

Here we extend the study of chemical weathering beyond the glaciers themselves to the proglacial freshwater drainage network (Fig. 1), using the Lake Hazen watershed (81.8°N, 71.4°W; 7,516 km², 40.9% glaciated) in Quttinirpaaq National Park on Ellesmere Island, Nunavut, Canada, as a model system (*SI Appendix*, Fig. S1). Ultra-oligotrophic Lake Hazen (544 km², maximum depth = 267 m) is fed by 11 glacial rivers (4.6 to 42 km long) originating from the southeastern outlet glaciers (6 to 1,041 km²) of the Northern Ellesmere Icefield. We sampled 7 glacial rivers across the Lake Hazen watershed to quantify changes in CO₂ fluxes and river chemistry throughout the ablation season (June, July, August [JJA]). Along 3 of the rivers (Blister, Snow Goose, Gilman), we conducted transects between the glacier termini and their deltas along the Lake Hazen shoreline to assess changes in CO₂ fluxes over space. At 2 of these rivers (Blister, Snow Goose), we also conducted biweekly surveys at their deltas to assess changes in CO₂ fluxes over time. To elucidate the impact of glacial inputs on CO₂ fluxes within Lake Hazen itself, we extended these biweekly surveys to lake

Significance

Glacier melt is one of the most dramatic consequences of climate change in high-latitude and high-altitude environments. As meltwaters move across poorly consolidated landscapes, they transport vast quantities of highly reactive comminuted sediments prone to chemical weathering reactions that may consume atmospheric CO₂. Using a whole watershed approach in the Canadian High Arctic, combined with additional dissolved CO₂ measurements in glacial rivers in Greenland and the Canadian Rockies, we show that certain glacier-fed freshwater ecosystems are significant and previously unrecognized annual CO₂ sinks due to chemical weathering. As many of the world's rivers originate from glacial headwaters, we highlight the potential importance of this process for contemporary regional carbon budgets in rapidly changing high-latitude and high-altitude watersheds.

Author contributions: K.A.S.P., V.L.S.L., S.L.S., and I.L. designed research; K.A.S.P., V.L.S.L., S.L.S., I.L., P.G.D., A.S.G., and P.J.K.A. performed research; K.A.S.P., P.G.D., A.S.G., and M.J.S. analyzed data; and K.A.S.P. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

Published under the PNAS license.

¹To whom correspondence may be addressed. Email: kyra2@ualberta.ca.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1904241116/-DCSupplemental.

Published online August 19, 2019.

$$\text{DIC} = \sum \text{CO}_{2(\text{aq})} + \text{HCO}_3^-_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})}$$

$$\text{DIC} = \text{terrestrial inputs} + \text{net respiration} + \text{chemical weathering} + \text{CO}_2 \text{ influx}$$

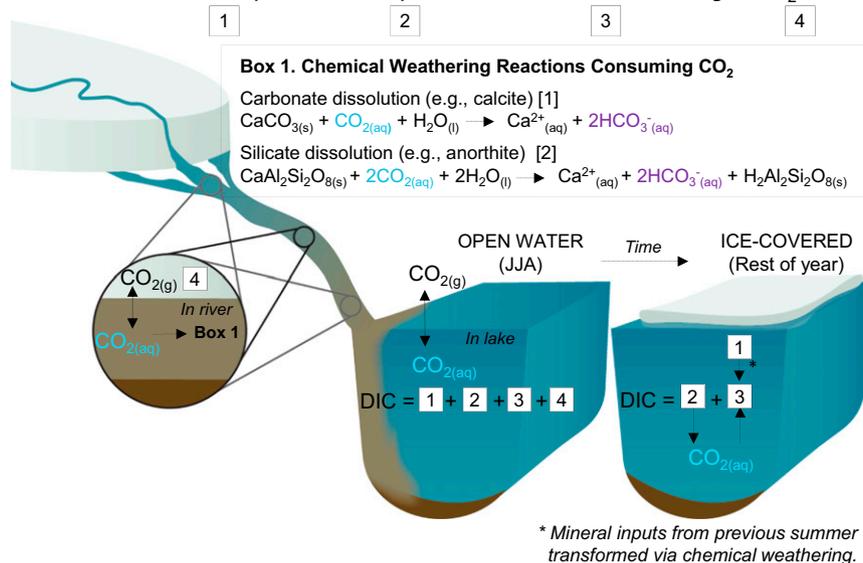


Fig. 1. Theoretical model of glacial meltwater impacts on downstream freshwater $\text{CO}_{2(\text{aq})}$ cycling. Minerals highlighted in Box 1 are shown for illustrative purposes with equations from ref. 11. During the open water season (JJA), glacial rivers flow into the downstream lake and lake ice melt enables the surface exchange of CO_2 . As ice forms on the lake, this surface exchange is minimized and glacial inputs from the previous summer are processed within the lake.

waters along the northwestern shoreline between the Blister and Snow Goose rivers. Detailed depth profiles of the lake were conducted during the ablation season and under the ice in spring to determine seasonal changes in lake CO_2 dynamics, with and without glacial inputs (Fig. 1). We then compared the measured freshwater CO_2 fluxes with CO_2 fluxes from the adjacent terrestrial environment (polar desert and nonglacial wetlands and ponds) (21, 22) to understand the relative importance of glacier-fed freshwater CO_2 cycling in watershed CO_2 budgets.

$\text{CO}_{2(\text{aq})}$ Consumption in Glacial Inflows to Lake Hazen. In situ concentrations of $\text{CO}_{2(\text{aq})}$ across the 7 glacial rivers were below atmospheric equilibrium at all but one of the sites sampled (% CO_2 saturation range: 15.2% to 102%, mean \pm SD: $70.4 \pm 22.7\%$; *SI Appendix, Fig. S2*). In contrast, concentrations of dissolved oxygen ($\text{O}_{2(\text{aq})}$) were at or above atmospheric equilibrium at all sites ($101 \pm 4.10\%$), showing that turbulent proglacial river waters were well mixed with the atmosphere, and precluding any significant anoxic subglacial contributions. $\text{CO}_{2(\text{aq})}$ saturation decreased with increasing distance from the glaciers with a concomitant increase in dissolved inorganic carbon (DIC), cations, and silica (Fig. 2), suggesting the existence of a weathering-dominated system (Box 1, Fig. 1) (23).

If chemical weathering were the predominant mechanism behind the observed CO_2 undersaturation, we would expect $\delta^{13}\text{C-DIC}$ to be depleted relative to atmospheric equilibrium because of the kinetic fractionation that occurs after rapid carbonate and silicate weathering (24). Indeed, $\delta^{13}\text{C-DIC}$ was highly depleted in the proglacial rivers relative to atmospheric equilibrium, ranging between -7.32‰ and 0.40‰ (mean, -2.92‰ ; *SI Appendix, Table S1*) and positively correlated with $\text{CO}_{2(\text{aq})}$ concentrations (Pearson product-moment: $r = 0.43$; $t = 2.43$; $P < 0.05$), such that $\delta^{13}\text{C-DIC}$ became more depleted at lower $\text{CO}_{2(\text{aq})}$. Aside from rapid carbonate and silicate weathering, the only other mechanism that could have resulted in the depletion of $\delta^{13}\text{C-DIC}$ is OC oxidation. However, dissolved organic carbon concentrations in all glacial rivers were extremely low (mean, $0.4 \pm 0.2 \text{ mg}\cdot\text{L}^{-1}$; *SI Appendix, Table S1*), precluding OC oxidation from significantly influencing $\delta^{13}\text{C-DIC}$, and OC respiration would have resulted in

the oversaturation, not undersaturation, of $\text{CO}_{2(\text{aq})}$. As such, rapid mineral weathering within the rivers is the most likely process to account for increasing DIC and declining $\text{CO}_{2(\text{aq})}$ concentrations over the river lengths, as well as low $\delta^{13}\text{C-DIC}$ values.

Across the proglacial drainage network, geological formations are poorly consolidated after glacial retreat, such that glacial meltwaters can easily erode riverbed sediments and bank deposits (*SI Appendix, Fig. S3*). This leads to increasing concentrations of suspended mineral sediments capable of weathering in river waters with increasing distance from the glaciers. Indeed, peak glacial river runoff in late July coincided with minimum $\text{CO}_{2(\text{aq})}$ and $\delta^{13}\text{C-DIC}$ (Fig. 3).

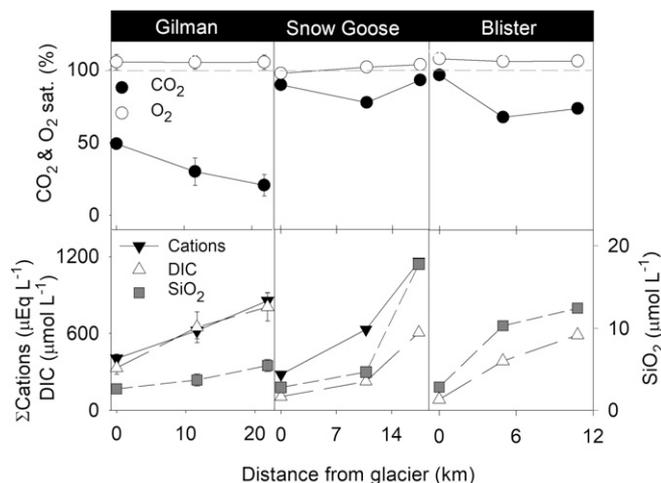


Fig. 2. Transects of dissolved gas ($\text{CO}_{2(\text{aq})}$, $\text{O}_{2(\text{aq})}$), cation (sum of Ca^{2+} , Mg^{2+} , Na^+ , K^+), DIC, and silicon (Si) concentrations with increasing distance from the glaciers along the Gilman (mean of 2 transects, 11 July and 1 August 2016, ± 1 SD), Snow Goose (1 August 2016) and Blister (19 July 2016) rivers. Discharge is assumed to be constant between the glacier and river delta.

As weathering reactions consume $\text{CO}_{2(\text{aq})}$ in the rivers, $\text{CO}_{2(\text{aq})}$ is constantly being replenished from the atmosphere (Fig. 1), but much more slowly than the weathering reactions can consume it (24). As such, in situ $\text{CO}_{2(\text{aq})}$ concentrations in proglacial rivers represent the balance between the rate of consumption by chemical weathering and the resupply from the atmosphere. To quantify the capacity for weathering reactions to consume $\text{CO}_{2(\text{aq})}$ in the absence of atmospheric exchange at the time of sampling (termed instantaneous weathering potential $\text{CO}_{2(\text{aq})}$), unfiltered river water samples were collected in pre-evacuated serum bottles containing a KCl preservative to prevent biological activity (25). The mean instantaneous weathering potential $\text{CO}_{2(\text{aq})}$ saturations were $29.5 \pm 35.3\%$, which is markedly more undersaturated than that measured in situ in the flowing rivers (SI Appendix, Table S1). These potential $\text{CO}_{2(\text{aq})}$ concentrations conclusively showed that CO_2 consumption was actively occurring in the rivers and was not primarily a result of primary productivity, and that equilibrium with the atmosphere had not been reached at the time of sampling.

Net DIC accumulation along the length of rivers was used as a measure of realized CO_2 consumption within the glacial rivers. This approach was adopted in lieu of using $\text{CO}_{2(\text{aq})}$ concentrations and

calculated gas transfer coefficients (k), the latter of which are extremely variable in rivers, especially braided ones, such as those studied here (26, 27). In the absence of detailed river morphology and water velocities, which were impossible to obtain in our remote High Arctic watershed, the derivation of k from traditional scaling relationships (e.g., refs. 3 and 28) was logistically unfeasible and fraught with uncertainty, necessitating an alternative approach. By relating the increases in cations and silica concentrations to weathering stoichiometry (Eqs. 1 and 2 in Fig. 1), we were able to attribute all ($125 \pm 13.6\%$) of the increase in DIC concentration between the glacier termini and river deltas to weathering (Fig. 2 and SI Appendix, Fig. S4), thus further excluding biological processes as important contributors to CO_2 dynamics within the glacial rivers.

We estimate that the glacial rivers in the Lake Hazen watershed consumed $1,020 \pm 496 \text{ Mg C-CO}_2 \text{ y}^{-1}$ through chemical weathering, making the glacial rivers an important and previously overlooked CO_2 sink at the watershed scale (Table 1). On an areal basis, the glacial rivers consumed $0.376 \pm 1.20 \text{ g C-CO}_2 \text{ m}^{-2}\cdot\text{d}^{-1}$, by far the largest flux (source or sink) in the watershed. This is in stark contrast to rivers globally, which are almost ubiquitously considered net sources of C to the atmosphere ($0.66 \pm 0.11 \text{ g C-CO}_2 \text{ m}^{-2}\cdot\text{d}^{-1}$ (29)). In fact, during the 2016 ablation season (a relatively low melt year), the glacial rivers in the Lake Hazen watershed consumed, on a per square meter basis, about half as much carbon daily ($0.085 \pm 0.187 \text{ g C-CO}_2 \text{ m}^{-2}\cdot\text{d}^{-1}$; calculated from refs. 30 and 31). During the 2015 ablation season, when glacial melt was ~ 3 times that in 2016, CO_2 consumption rates in the glacial rivers were, on average, twice that of the Amazon rainforest, with maximum daily rates of up to 40 times higher on a per square meter basis ($6.14 \text{ g C-CO}_2 \text{ m}^{-2}\cdot\text{d}^{-1}$).

Impact of Glacial Inputs on Net CO_2 Consumption in Proglacial Lakes.

Similar to other Arctic and alpine glacier-fed lakes, the chemistry of ultra-oligotrophic Lake Hazen is particularly sensitive to geochemical inputs from its catchment (10, 32). Coincident with the start of watershed inputs to the lake in early June, when the lake is still ice-covered, an open-water moat forms around the periphery of Lake Hazen. As the region warms, lake ice melts, and the surface area available for exchange with the atmosphere increases gradually until complete ice off, if it occurs, in late July or early August. Whereas the lake rarely went ice-free before the early 2000s, a late summer ice-free lake is now commonplace (33).

To understand the influence of glacial inputs on CO_2 fluxes in nearshore waters of Lake Hazen, we measured in situ $\text{CO}_{2(\text{aq})}$ concentrations in nearshore waters and used the wind-speed-derived gas exchange coefficient (k_{CO_2}) to calculate surface CO_2 fluxes (34). After lake ice melt in 2015 (26 July), $\text{CO}_{2(\text{aq})}$ concentrations in waters near the shore of Lake Hazen between the inflows of the Blister and Snow Goose rivers ranged between 19.7 and 25.2 μM (mean, $21.8 \pm 1.07 \mu\text{M}$). The lake surface was a net CO_2 sink during the same period, with instantaneous CO_2 consumption from lake surface waters averaging $27.1 \pm 18.1 \mu\text{mol m}^{-2}\cdot\text{h}^{-1}$. Maximum CO_2 consumption occurred overnight, likely due to a general increase in wind speed during this time (SI Appendix, Fig. S5). CO_2 fluxes in waters near the shore of Lake Hazen were significantly influenced by glacial runoff ($r^2 = 0.21$; $F = 9.54$; $P < 0.001$), such that these waters became a progressively greater CO_2 sink as glacial melt intensified (SI Appendix, Fig. S6). Chlorophyll *a* concentrations ranged from below detection to only $0.04 \mu\text{g L}^{-1}$, suggesting little, if any, primary production in these turbid nearshore waters. As in the glacial rivers, instantaneous weathering potential $\text{CO}_{2(\text{aq})}$ concentrations in nearshore waters were significantly lower than in situ $\text{CO}_{2(\text{aq})}$ concentrations (paired *t* test: $t = 4.73$; $P < 0.001$), further excluding CO_2 consumption by primary producers as the main cause of CO_2 undersaturation.

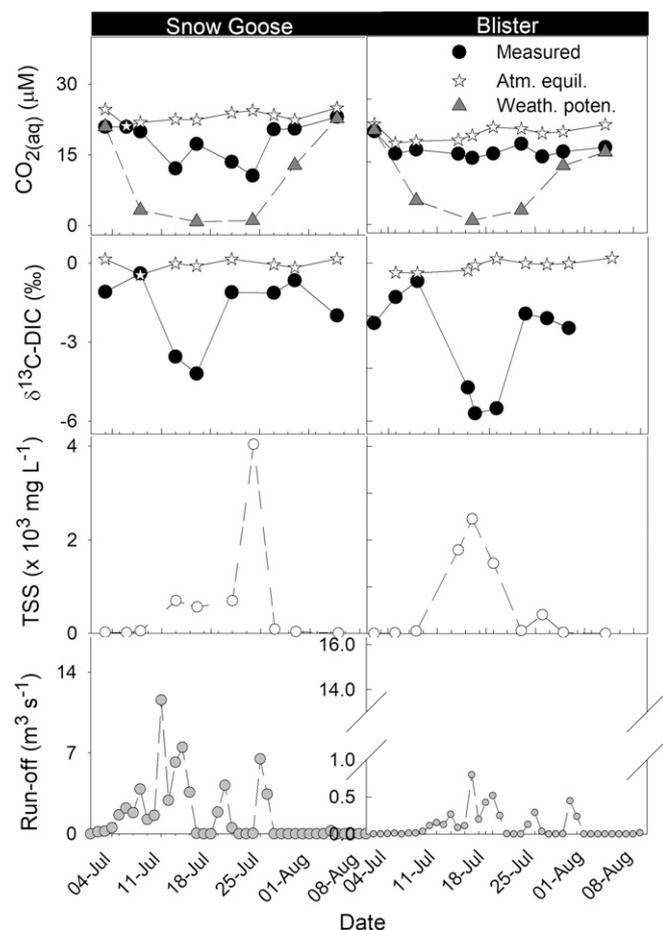


Fig. 3. Temporal variability in $\text{CO}_{2(\text{aq})}$ concentrations, $\delta^{13}\text{C-DIC}$, total suspended solids and modeled daily mean instantaneous glacial runoff in the Snow Goose and Blister rivers between 2 July and 9 August 2016. Atmospheric equilibrium $\text{CO}_{2(\text{aq})}$ and $\delta^{13}\text{C-DIC}$ was calculated from ambient water temperature and barometric pressure. Instantaneous weathering potential $\text{CO}_{2(\text{aq})}$ was measured on unfiltered samples preserved with KCl in a closed system. The $\delta^{13}\text{C-DIC}$ of closed system weathering of CaCO_3 with atmospheric CO_2 at the observed pH is in the range of -5% to -4% . Runoff was modeled for the glacier surface using a surface mass balance approach.

Table 1. Mean annual Lake Hazen watershed CO₂ budgets

Landcover classification	Area, km ² (%)	g C-CO ₂ m ⁻² d ⁻¹ (±SE)	Mg C-CO ₂ y ⁻¹ (±SE)
Aquatic			
Small lakes and ponds*	145(1.93)	+0.045 ± 0.180	+598
Glacial rivers [†] This study,†	91(1.21)	-0.376 ± 0.038	-1,020 ± 496
Lake Hazen surface [‡] This study,‡	544(7.23)	+0.003 ± 0.001	+47.7 ± 19.8
Lake Hazen internal [§] This study	—	—	-1,340 ± 516
Net aquatic total	780(10)		-1,710 ± 1,030
Terrestrial			
Polar semidesert [§]	3,742(49.8)	+0.016	+22,100
Meadow wetland [§]	130 (1.73)	-0.139	-6,580
Glacial ice [¶]	3,074(40.9)	N/A	N/A
Net terrestrial total	6,946(92)		+15,500
Watershed totals	7,516 [#] (100)	—	+13,800

Terrestrial and upland aquatic data from 2008 to 2012 are scaled to the watershed area determined here (7,516 km²). Positive fluxes denote a net source of CO₂ to the atmosphere; negative fluxes denote a net CO₂ sink

*Ref. 21, net annual flux calculated from mean flux multiplied by scaled area.

†The glacial river CO₂ flux calculations presented are means of both 2015 and 2016, across the 7 glacial rivers studied, given that they represent 84% of the watershed glacierized area.

‡Seasonal flux determined from ice-free area of lake surface, as such these estimates are less than those in ref. 21.

§Ref. 22, daily flux calculated from annual fluxes of 5.9 g C m⁻² (polar semidesert) and -50.6 g C m⁻² (wetland).

¶Glacial ice may actively cycle CO₂ (51), but this is beyond the scope of the present study.

#Because of rounding, individual components, as presented here, do not add up to the watershed area (7,516 km²), but the difference is only ~1%.

By applying daily ice-free areas on the lake delineated using the MODIS snow cover product (MOD10A1) to the mean daily nearshore CO₂ fluxes during the continuous measurement period (7 July to 2 August 2015), we estimated a mean daily surface CO₂ consumption rate (sum of hourly fluxes, $n = 14$ d with 24-h records) of $2,570 \pm 603$ kg C-CO₂ d⁻¹, translating to an estimated cumulative surface drawdown of 66.7 ± 11.5 Mg C-CO₂ during the measurement period. However, as glacial inputs to Lake Hazen slowed in August, turbulent mixing in the nearshore region was reduced. The respiration of OC and subsequent production of CO_{2(aq)} therefore became a relatively more important contributor to net CO₂ fluxes during the shoulder seasons than chemical weathering processes. Thus, when adding the early and late season fluxes measured in 2016 (*SI Appendix, Fig. S6*) onto the primary open water season, Lake Hazen surface waters were a marginal (<1% of the total annual budget) CO₂ source, emitting 47.7 ± 19.8 Mg C-CO₂ to the atmosphere (Table 1).

At the center of the lake, 4.5 kilometers away from the direct influence of the nearest glacial inflows (*SI Appendix, Fig. S1*), surface waters were likewise undersaturated in CO_{2(aq)} during the summer ($84.5 \pm 3.34\%$; *SI Appendix, Fig. S7*). Even at 250 m depth, CO_{2(aq)} concentrations were 19.4 μM (August 2015) and 24.8 μM (August 2016), corresponding to CO_{2(aq)} saturations of 72.9% and 93.9%, respectively (O_{2(aq)} saturation: 101% and 98.2%). CO_{2(aq)} undersaturation or even equilibrium at depth are highly atypical for large deep lakes, where light penetration and primary productivity are limited to the upper reaches of the water column (35). As dense, sediment-laden glacial river waters flowed into Lake Hazen, they formed turbid underflows, transporting fine particulates and waters with high O_{2(aq)} and low CO_{2(aq)} from river deltas to the depths of the lake (*SI Appendix, Fig. S7*). The magnitude of summer melt was thus the primary control on water column CO_{2(aq)} concentrations, as the greater glacial melt volume in 2015 was associated with greater CO_{2(aq)} undersaturation at depth. The observation of CO_{2(aq)} undersaturation at depth was particularly striking, given that springtime CO_{2(aq)} concentrations in bottom waters were up to 476% oversaturated (121 μM). Indeed, summertime oxygenation and CO_{2(aq)} undersaturation of Lake Hazen bottom waters were historically rare and are believed to be a direct consequence of

the intensification of glacial melt in the watershed with a resultant change in lake mixing (36).

To quantify CO₂ consumption by chemical weathering within Lake Hazen as a whole, we calculated annual DIC mass balance budgets for the lake by subtracting DIC inputs from all major water sources (glacial and snow melt waters) from DIC exports out the Ruggles River (36). We then used water column δ¹³C-DIC to attribute net DIC exports from Lake Hazen to respiration or chemical weathering. Lake Hazen was annually a source of DIC ($3,150 \pm 3,870$ Mg C-CO₂ y⁻¹) to the Ruggles River, of which only 12.9% could be attributed to respiration. Given that the remaining DIC must then have originated from chemical weathering, of which half comes from the dissolved CO₂ and the remainder from the comminuted sediments delivered to the lake during the previous summer (Eq. 1 in Fig. 1), we roughly estimated that 43.6% of DIC exports in each year originated from the consumption of CO₂ by carbonate dissolution. Combining these estimates of CO₂ produced by respiration and CO₂ consumed by chemical weathering, we calculated a net CO₂ consumption for the Lake Hazen water column of $1,330 \pm 1,160$ (2015; high melt year) or 606 ± 524 Mg C-CO₂ y⁻¹ (2016; low melt year). Due to the dynamic nature of CO₂ production and consumption within lakes, these estimates are approximations of a potentially important process distinct to proglacial lakes, which warrants greater research efforts in the future.

Internal CO_{2(aq)} consumption within Lake Hazen was thus approximately equal to or greater than CO_{2(aq)} consumption within the glacial rivers in a given year. Together, these estimates show not only that the influence of the glacial rivers extends far beyond the river channels themselves but also that the magnitude of this net CO₂ uptake due to chemical weathering varies interannually, depending on the volume of meltwaters discharging from the glaciers, such that there would be greater erosion and CO₂ consumption during high-melt years, and less erosion and CO₂ consumption during low-melt years. We also highlight the Ruggles River as a potentially important vector for the delivery of weathering products even further downstream. By summing estimates of net CO₂ consumption in glacial rivers and Lake Hazen itself, we calculate a net aquatic CO₂ uptake within the Lake Hazen watershed of $1,710 \pm 1,030$ Mg C-CO₂ season⁻¹ (Table 1). Although this aquatic flux is less than that of the more

extensive terrestrial ecosystems that actively produce or consume CO₂ throughout the year, the addition of the glacier-fed ecosystems to the budget increased the overall CO₂ sink in the watershed by 35% and transformed the summed aquatic components from being a net CO₂ source to a net CO₂ sink, an important development in our understanding of carbon cycling in these rapidly changing watersheds.

Projected Global Glacial Melt and Downstream Freshwater CO₂ Cycling. By 2050, global (non-ice-sheet) glacier volume could decline by between 28% and 44% (37) with coincident near-term changes in glacial river runoff (38). At high latitudes, glacial runoff is expected to increase at least until the middle of the century (38, 39), with yet unknown consequences for the biogeochemistry of receiving aquatic ecosystems (40). Although Lake Hazen is an unusually large body of water for the High Arctic, and thus theoretically more resilient than smaller systems to short-term (seasonal) perturbations (41), we show that the lake is still annually transformed into a CO₂ sink by glacial river inputs. Inputs of large volumes of water from projected glacial melt could thus conceivably radically transform the biogeochemistry of smaller, more common freshwater systems.

While the Lake Hazen watershed is underlain by a diverse, carbonate-rich geology (42), transient CO₂ consumption by weathering processes in glacial meltwaters has also been inferred beneath glaciers in areas dominated by basalt and metamorphic rocks (15, 43), an effect which should extend into the proglacial freshwater network. Although studies directly quantifying the downstream impacts of glacial melt on CO₂ are few, CO_{2(aq)} undersaturation has been observed at other sites in Greenland, Svalbard, Central Europe, and Western Canada (*SI Appendix, Table S3*). For example, CO_{2(aq)} concentrations in rivers fed by the Kiattuut Sermiat (Greenland, 61°11.8'N, 45°20.4'W) and Saskatchewan (Alberta, Canada, 52°10.2'N, 117°4.6'W) glaciers, measured using the same technique as in the Lake Hazen watershed, were only 22% and 35% saturated with respect to atmospheric CO₂ at locations 2.5 and 5 km downstream of the glaciers, respectively. This strongly suggests that the effects of freshwater CO_{2(aq)} consumption by sediment-laden glacial meltwaters observed in the Lake Hazen watershed could be relevant across divergent geologies, glacier thermal regimes, and climates.

Understanding the effect of glacier mass loss on carbon cycling in downstream freshwater ecosystems, however, remains challenging. Due to the dynamic relationship between proglacial systems and fluctuating glacier dynamics (44), there exists no published estimate of either the number of proglacial rivers and/or area of proglacial lakes globally, hampering our ability to understand the extent of glacial influence on downstream systems. Our results highlight the importance of glacially fed freshwater systems to the carbon cycle at the watershed scale. We suggest that the effect of glacial melt on CO₂ consumption in downstream ecosystems reported here is not limited to the High Arctic (*SI Appendix, Table S3*) but, rather, is potentially a globally relevant phenomenon meriting greater in-depth study, given future climate change predictions in glacierized regions. On the basis of our results, projected increases to glacial melt imply not only a short- to medium-term increase in water fluxes to downstream ecosystems, but also an increase in the amount and intensity of weathering of highly reactive comminuted sediments being transported downstream, with a concomitant uptake of atmospheric CO₂ that has important implications for regional carbon budgets in certain glacierized catchments.

Methods

Study Area. Lake Hazen, located within Quttinirpaaq National Park on northern Ellesmere Island, Nunavut, Canada, is the world's most voluminous lake entirely above the Arctic Circle (*SI Appendix, Fig. S1*). Runoff from the outlet glaciers of the Northern Ellesmere Icefield occurs primarily through

supraglacial and ice-marginal channels, although subglacial water has been detected for the Henrietta Nesmith Glacier (45). Ice from the Northern Ellesmere Icefield retreated from Lake Hazen ~5,000 y ago (46), exposing a diverse geology dominated by the Cambrian Grant Land formation (quartzite, sandstone, schist) to the northwest and the Silurian Danish River formation (sandstone, carbonate, shale) to the southwest, along the Hazen Plateau (42).

The glacial rivers surveyed in this study drained 2,568 km² or 84% of the total glacierized watershed area, and extended between 4 and 42 km along defined river valleys before flowing into Lake Hazen. The annual ablation season on northern Ellesmere Island currently extends from early June to late August. Total modeled glacial runoff volumes for the Lake Hazen watershed were 0.98 km³ and 0.29 km³ in 2015 and 2016, respectively (2001 to 2016 mean = 0.47 ± 0.44 km³), with the most important contributions coming from the Henrietta Nesmith, Very, and Gilman glaciers. The Ruggles River (28.8 km) flows year-round, connecting Lake Hazen to Chandler and then Coneybear fjords on the northeastern coast of Ellesmere Island. The Lake Hazen watershed is located within the continuous permafrost zone, and although active layer thaw occurs, it is hydrologically insignificant. Total precipitation for the nonglacierized area of the Lake Hazen watershed is ~95 mm (47).

Snowmelt on the landscape and lake ice surface occurs in late May/early June, followed by a short decrease in runoff before melt from the glacierized area begins in late June. Rainfall during the summer (JJA) ablation season has been previously recorded as only ~34 mm (2008 to 2012 mean) (21). During summer, snowfall within the watershed outside of the icefield is rare. During the period of this study, the ablation seasons extended from ~2 June to 17 August (2015), and 5 June to 28 August (2016). No meltwaters are discharged from the glaciers outside of this period. Mean annual air temperatures for 2015 and 2016 at Alert (82.5°N, 62.3°W) and Eureka (80.0°N, 85.9°W), the closest permanent weather stations, were -14.8 ± 1.3 °C and -17.5 ± 0.8 °C, respectively (Environment and Climate Change Canada).

Water samples were collected during summers 2015 (6 July to 2 August) and 2016 (2 July to 8 August), focusing on Lake Hazen itself in 2015 and on the glacial rivers in 2016. In so doing, we surveyed the entirety of the arctic freshwater continuum from the glacier termini through to the receiving freshwater ecosystems (river and lake). Details on sample collection and analysis can be found in the *SI Appendix*.

Glacial Rivers.

CO₂ consumption calculations. Proglacial CO_{2(g)} fluxes were calculated for the glacial rivers, using the changes in DIC concentrations along the transects of the Blister, Snow Goose, and Gilman rivers ($n = 5$) and relating these changes to weathering stoichiometry (11). Every 1 mol increase in Ca²⁺ and Mg²⁺ between the glacier terminus and the river delta consumes 1 mol CO_{2(aq)} via carbonate dissolution (Eq. 1 in Fig. 1), with Ca²⁺ concentrations corrected for the increase in SO₄²⁻ over the same distance. Further, a 1 mol increase in SiO_{2(aq)} consumes 2 mol CO_{2(aq)} via silicate dissolution (Eq. 2). Although this latter ratio inherently assumes stoichiometric dissolution, which does not always occur (20), silicate weathering conservatively accounted for only 1.50 ± 0.65% of the DIC increase across all transects. Using this approach, we accounted for 125 ± 13.6% of the DIC increase over the length of the glacial rivers (*SI Appendix, Fig. S4*), validating our use of the change in DIC concentration along the river lengths as a metric of CO₂ consumption by dissolution. To estimate DIC concentrations at the glacier termini on rivers and days for which transects were not completed, we applied a mean DIC change of 0.045 ± 0.008 mg L⁻¹ per 1 m elevation difference between the glacier terminus and the river delta at Lake Hazen, a remarkably consistent factor across all 5 transects, likely reflecting the dependence of lotic gas transfer on slope (28). Assuming no additional water sources to the rivers downstream of the glaciers, we subtracted the daily modeled DIC load at the glacier from the DIC load at the delta (*SI Appendix, Table S4*). We attributed this change in DIC load to dissolution reactions (CO_{2(aq)} consumption and consequent HCO₃⁻/DIC production) in the rivers. The difference was then halved to account for the fact that 1 product HCO₃⁻ results from the CO_{2(aq)} and the other from the mineral (CaCO₃ in Eq. 2).

Lake Hazen (Surface).

CO₂ flux calculations. Gas fluxes from the surface of Lake Hazen were calculated (48) using the wind-speed derived gas exchange coefficient (k_{CO_2}) (34), corrected for chemically enhanced CO₂ influx at high pH (49, 50):

$$Flux (\mu\text{mol m}^{-2} \text{h}^{-1}) = k_{CO_2} \alpha \Delta CO_{2(aq)},$$

where k_{CO_2} is the gas exchange coefficient calculated from mean hourly wind speed (in m s⁻¹), α is the enhancement factor of CO₂ diffusion at high pH, and $\Delta CO_{2(aq)}$ is the difference between the CO₂ concentration measured in situ and the CO₂ concentration that would occur if the waters were at atmospheric equilibrium, calculated using Henry's Law, and in situ temperature

and barometric pressure. To calculate enhanced fluxes when there was no associated pH measurement, we applied a median enhancement factor of 18% ($n = 356$) to the uncorrected flux, a conservative estimate based on the mean (25%) and range of enhancement factors observed (2% to 97%). Net ablation season CO_2 exchange from the Lake Hazen surface in both 2015 and 2016 was estimated from the measured daily flux multiplied by the daily ice-free area, extracted from the MODIS snow cover product (MOD10A1) (33). For days when net daily fluxes were not measured, we used the mean of the previously and subsequently measured daily fluxes. To extrapolate the data outside of the measurement period, either the first (2 July) or last (8 August) measured fluxes from 2016 were applied to the periods before or after measurement, respectively. Values for 2016 were also applied to the shoulder seasons in 2015, when a shorter field campaign was undertaken.

Lake Hazen Water Column (Internal).

CO_2 consumption within Lake Hazen. CO_2 consumption within the Lake Hazen water column was calculated by constructing a DIC mass balance budget for Lake Hazen in both 2015 and 2016. Briefly, hydrological inputs of DIC to the lake were the sum of glacial river (described here, using the surface mass balance approach and LOADEST log-linear models) and snow meltwater inputs (described in detail in ref. 36), while the sole hydrological output of DIC from

the lake was via the Ruggles River. Ruggles River discharge was estimated as the sum of all hydrological inputs to the lake. The difference between DIC inputs and outputs thus reflects processes occurring within the water column itself, where DIC is produced by chemical weathering and heterotrophic respiration, or consumed by primary productivity, which is negligible in ultra-oligotrophic Lake Hazen. We then used $\delta^{13}\text{C}$ -DIC and DIC concentrations in the Lake Hazen water column to account for respiration contributions to DIC accumulation in the water column: only 12.9% of bottom water DIC (or 210 μM of the 1,630 μM of DIC accumulated in the water column in spring 2012, based on $\delta^{13}\text{C}$ -DIC = -3.8‰ and $\delta^{13}\text{C}$ -OC of organic matter = -29.0‰) could be attributed to heterotrophic respiration, with the balance of DIC presumably originating from weathering processes. We applied this respiration constant and weathering stoichiometry (Fig. 1) to the net DIC production in Lake Hazen DIC to constrain the contribution from mineral weathering.

ACKNOWLEDGMENTS. Financial and in-kind support for the study were provided by the Natural Science and Engineering Research Council of Canada, ArcticNet Network Centre of Excellence, Natural Resources Canada (Polar Continental Shelf Program) and Parks Canada. R. Elgood (University of Waterloo) and staff at the Biogeochemical Analytical Service Laboratory (University of Alberta) provided analytical support.

- J. J. Cole *et al.*, Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems* (N. Y.) **10**, 172–185 (2007).
- C. M. Duarte, Y. T. Prairie, Prevalence of heterotrophy and atmospheric CO_2 emissions from aquatic ecosystems. *Ecosystems* (N. Y.) **8**, 862–870 (2005).
- P. A. Raymond *et al.*, Global carbon dioxide emissions from inland waters. *Nature* **503**, 355–359 (2013).
- G. A. Weyhenmeyer *et al.*, Significant fraction of CO_2 emissions from boreal lakes derived from heterotrophic inorganic carbon inputs. *Nat. Geosci.* **8**, 933–936 (2015).
- R. M. Cory, C. P. Ward, B. C. Crump, G. W. Kling, Carbon cycle. Sunlight controls water column processing of carbon in arctic fresh waters. *Science* **345**, 925–928 (2014).
- D. Vachon, J.-F. Lapierre, P. A. del Giorgio, Seasonality of photochemical dissolved organic carbon mineralization and its relative contribution to pelagic CO_2 production in northern lakes. *J. Geophys. Res. Biogeosci.* **121**, 864–878 (2016).
- R. Marcé *et al.*, Carbonate weathering as a driver of CO_2 supersaturation in lakes. *Nat. Geosci.* **8**, 107–111 (2015).
- C. Song, Y. Sheng, L. Ke, Y. Nie, J. Wang, Glacial lake evolution in the southeastern Tibetan Plateau and the cause of rapid expansion of proglacial lakes linked to glacial-hydrogeomorphic processes. *J. Hydrol. (Amst.)* **540**, 504–514 (2016).
- M. Peltó, “Alpine glacier change summary” in *Recent Climate Change Impacts on Mountain Glaciers*, (John Wiley & Sons Ltd., 2017), pp. 211–214.
- J. T. Crawford, M. M. Dornblaser, E. H. Stanley, D. W. Clow, R. G. Striegl, Source limitation of carbon gas emissions in high-elevation mountain streams and lakes. *J. Geophys. Res. Biogeosci.* **120**, 952–964 (2015).
- M. Tranter *et al.*, Geochemical weathering at the bed of Haut Glacier d’Arolla, Switzerland: A new model. *Hydrol. Processes* **16**, 959–993 (2002).
- M. Tranter, J. L. Wadham, “7.5—geochemical weathering in glacial and proglacial environments” in *Treatise on Geochemistry*, H. D. Holland, K. K. Turekian (Elsevier, ed. 2, 2014), pp. 157–173.
- J. A. Graly, J. I. Drever, N. F. Humphrey, Calculating the balance between atmospheric CO_2 drawdown and organic carbon oxidation in subglacial hydrochemical systems. *Global Biogeochem. Cycles* **31**, 709–727 (2017).
- R. Raiswell, Chemical models of solute acquisition in glacial melt waters. *J. Glaciol.* **30**, 49–57 (1984).
- M. J. Sharp, M. Tranter, G. H. Brown, M. Skidmore, Rates of chemical denudation and CO_2 drawdown in a glacier-covered alpine catchment. *Geology* **23**, 61–64 (1995).
- S. P. Anderson, Biogeochemistry of glacial landscape systems. *Annu. Rev. Earth Planet. Sci.* **35**, 375–399 (2007).
- R. J. Cooper, J. L. Wadham, M. Tranter, R. Hodgkins, N. E. Peters, Groundwater hydrochemistry in the active layer of the proglacial zone, Finsterwalderbreen, Svalbard. *J. Hydrol. (Amst.)* **269**, 208–223 (2002).
- J. L. Wadham, R. Hodgkins, R. J. Cooper, M. Tranter, Evidence for seasonal subglacial outburst events at a polythermal glacier, Finsterwalderbreen, Svalbard. *Hydrol. Processes* **15**, 2259–2280 (2001).
- S. P. Anderson, J. I. Drever, C. D. Frost, P. Holden, Chemical weathering in the foreland of a retreating glacier. *Geochim. Cosmochim. Acta* **64**, 1173–1189 (2000).
- A. Hodson, M. Tranter, G. Vatne, Contemporary rates of chemical denudation and atmospheric CO_2 sequestration in glacier basins: An arctic perspective. *Earth Surf. Process. Landf.* **25**, 1447–1471 (2000).
- C. A. Emmerton *et al.*, The importance of freshwater systems to the net atmospheric exchange of carbon dioxide and methane with a rapidly changing high Arctic watershed. *Biogeosciences* **13**, 5849–5863 (2016).
- C. A. Emmerton *et al.*, Net ecosystem exchange of CO_2 with rapidly changing high Arctic landscapes. *Glob. Change Biol.* **22**, 1185–1200 (2016).
- I. J. Fairchild, J. A. Killawee, B. Hubbard, D. Wolfgang, Interactions of calcareous suspended sediment with glacial meltwater: A field test of dissolution behaviour. *Chem. Geol.* **155**, 243–263 (1999).
- M. Skidmore, M. Sharp, M. Tranter, Kinetic isotopic fractionation during carbonate dissolution in laboratory experiments: Implications for detection of microbial CO_2 signatures using $\delta^{13}\text{C}$ -DIC. *Geochim. Cosmochim. Acta* **68**, 4309–4317 (2004).
- J. D. Hamilton, C. A. Kelly, J. W. M. Rudd, R. H. Hesslein, N. T. Roulet, Flux to the atmosphere of CH_4 and CO_2 from wetland ponds on the Hudson Bay lowlands (HBLs). *J. Geophys. Res.* **99**, 1495–1510 (1994).
- P. A. Raymond, J. J. Cole, Gas exchange in rivers and estuaries: Choosing a gas transfer velocity. *Estuaries* **24**, 312–317 (2001).
- M. B. Wallin *et al.*, Spatiotemporal variability of the gas transfer coefficient (k_{CO_2}) in boreal streams: Implications for large scale estimates of CO_2 evasion. *Global Biogeochem. Cycles* **25**, GB3025 (2011).
- P. A. Raymond *et al.*, Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. *Limnol. Oceanogr. Fluids Environ.* **2**, 41–53 (2012).
- T. J. Battin *et al.*, Biophysical controls on organic carbon fluxes in fluvial networks. *Nat. Geosci.* **1**, 95–100 (2008).
- F. D. B. Espírito-Santo *et al.*, Size and frequency of natural forest disturbances and the Amazon forest carbon balance. *Nat. Commun.* **5**, 3434 (2014).
- R. J. W. Brienen *et al.*, Long-term decline of the Amazon carbon sink. *Nature* **519**, 344–348 (2015).
- P. B. Hamilton, K. Gajewski, D. E. Atkinson, D. R. S. Lean, Physical and chemical limnology of 204 lakes from the Canadian Arctic Archipelago. *Hydrobiologia* **457**, 133–148 (2001).
- I. Lehnher *et al.*, The world’s largest High Arctic lake responds rapidly to climate warming. *Nat. Commun.* **9**, 1290 (2018).
- R. Wanninkhof, J. R. Ledwell, W. S. Broecker, Gas exchange-wind speed relation measured with sulfur hexafluoride on a lake. *Science* **227**, 1224–1226 (1985).
- R. G. Wetzel, *Limnology* (Academic Press, 2001).
- K. A. St Pierre *et al.*, Contemporary limnology of the rapidly changing glacierized watershed of the world’s largest High Arctic lake. *Sci. Rep.* **9**, 4447 (2019).
- B. Marzeion, G. Kaser, F. Maussion, N. Champollion, Limited influence of climate change mitigation on short-term glacier mass loss. *Nat. Clim. Chang.* **8**, 305–308 (2018).
- A. Bliss, R. Hock, V. Radic, Global response of glacier runoff to twenty-first century climate change. *J. Geophys. Res. Earth Surf.* **119**, 717–730 (2014).
- M. Huss, R. Hock, Global-scale hydrological response to future glacier mass loss. *Nat. Clim. Chang.* **8**, 135–140 (2018).
- M. J. Sharp *et al.*, “Mountain glaciers and ice caps” in *Snow, Water, Ice and Permafrost in the Arctic* (Arctic Monitoring and Assessment Programme, 2011), pp. 7.33–7.42.
- S. R. Carpenter, K. L. Cottingham, Resilience and restoration of lakes. *Conserv. Ecol.* **1**, 2 (1997).
- R. L. Christie, “Bedrock geology” in *Operation Hazen: Narrative and Preliminary Reports for the 1957 Season*, G. Hattersley-Smith, Ed. (Defence Research Board Canada, 1958), pp. 16–18.
- S. R. Gíslason *et al.*, Direct evidence of the feedback between climate and weathering. *Earth Planet. Sci. Lett.* **277**, 213–222 (2009).
- J. L. Carrivick, F. S. Tweed, Proglacial lakes: Character, behaviour and geological importance. *Quat. Sci. Rev.* **78**, 34–52 (2013).
- J. Gray, Using multiple RADARSAT InSAR pairs to estimate a full three-dimensional solution for glacial ice movement. *Geophys. Res. Lett.* **38**, L05502 (2011).
- I. R. Smith, Late quaternary glacial history of lake Hazen basin and eastern Hazen Plateau, northern Ellesmere Island, Nunavut, Canada. *Can. J. Earth Sci.* **36**, 1547–1565 (1999).
- W. Thompson, “Climate” in *Resource Description and Analysis: Ellesmere Island, National Park Reserve* (National Resource Conservation Selection, Prairie and Northern Region, Parks Canada, Department of Canadian Heritage, 1994), p. 78.
- P. S. Liss, P. G. Slater, Flux of gases across air-sea interface. *Nature* **247**, 181–184 (1974).
- B. Jähne, G. Heinz, W. Dietrich, Measurement of the diffusion coefficients of sparingly soluble gases in water. *J. Geophys. Res. Oceans* **92**, 10767–10776 (1987).
- R. Wanninkhof, M. Knox, Chemical enhancement of CO_2 exchange in natural waters. *Limnol. Oceanogr.* **41**, 689–697 (1996).
- J. Wang, H. Han, S. Zhang, Carbon dioxide flux in the ablation area of Koxkar glacier, western Tien Shan, China. *Ann. Glaciol.* **55**, 231–238 (2014).