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Abundance and Dynamics of Dissolved Organic Carbon in Glacier Systems

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Abstract

The biogeochemical cycling of organic carbon (OC) has important implications for aquatic system ecology because the abundance and molecular characteristics of OC influence contaminant transport and bioavailability, and determine its suitability as a substrate for microbial metabolism. There have been few studies of OC cycling in glacier systems and questions remain regarding the abundance, provenance, and biogeochemical transformations of OC in these environments. To address these questions, the abundance and fluorescence characteristics of dissolved organic carbon (DOC) were investigated at John Evans Glacier and Outre Glacier, Canada, and Victoria Upper Glacier, Antarctica. These systems are characterized by different thermal and hydrological regimes, and have different potential DOC sources. Where possible, samples of supraglacial runoff, glacier ice and basal ice, and subglacial meltwater were collected. The DOC concentration in each sample was measured (high-temperature combustion and non-dispersive IR detection), and emission and/or synchronous fluorescence spectroscopy were used to characterize the DOC from each environment. DOC exists in detectable quantities (0.06–46.6 ppm) in all of these glacier systems. The fluorescence characteristics of DOC vary between glaciers, between environments at the same glacier, and over time within a single environment. These results suggest that quality of available OC and glacier hydrological flow routing influence the characteristics of DOC, and that microbial cycling of OC may be active in glacier systems.

Introduction

Advancing glaciers often override soils, sediment, and vegetation. Dissolved and particulate organic carbon (OC) from these sources may be incorporated into glacial sediments and basal ice (debris-rich ice formed at the glacier sole). OC may also enter the subglacial environment from sources on the glacier surface (supraglacial) and areas surrounding the glacier (ice-marginal) by transport in glacier ice or runoff. Potential supraglacial OC sources include wind-blown material and microbial populations that exist in the surface snowpack, cryoconite holes, and meltwater streams. The subglacial OC pool may provide a substrate for metabolism by microbial populations and is thus a potential source of CO₂ and acidity for subglacial weathering mechanisms. Subglacial microbial metabolism may alter the quality of OC such that OC released from glaciers in runoff may have different properties from the OC that enters the subglacial environment. The microbial alteration of OC has potentially important implications for downstream aquatic ecology because OC abundance and properties (e.g., reactivity) influence nutrient and contaminant transport and bioavailability, and determine its suitability as a substrate for microbial metabolism.

Fluorescence spectroscopy has been used to characterize dissolved organic carbon (DOC) in soil solutions (e.g., Fraser et al., 2001), and in lacustrine (e.g., McKnight et al., 1994), fluvial (e.g., Stedmon et al., 2003) and oceanic (e.g., Parlanti et al., 2000) environments. Fluorescence arises when fluorescing species (fluorophores) that have been irradiated with electromagnetic energy relax from an excited electronic state to a lower energy state (Penzer, 1980). The spectral characteristics of this fluorescence are related to the molecular structure of the relaxing molecule. The emission fluorescence technique excites a molecule at a predetermined wavelength with an excitation monochromator and monitors its fluorescent emission over a predetermined spectral interval with an emission monochromator. Emission scanning is used for samples with only one fluorophore or

where the fluorescing conditions of the fluorophore of interest are known. The synchronous fluorescence technique involves synchronously scanning a sample with both the excitation and emission monochromators with a predetermined interval between the two monochromators. Synchronous fluorescence scanning has the advantage of reducing the spectral overlap in a sample that contains more than one fluorophore, such as DOC (e.g., Cabaniss and Shuman, 1987), thereby providing better spectral resolution for each individual fluorophore.

As an analytical technique, fluorescence spectroscopy has the advantage of being more sensitive and requiring a less concentrated sample than other techniques such as ¹³C–nuclear magnetic resonance (NMR), Fourier-transform infrared (FTIR), or electron paramagnetic resonance (EPR) spectroscopy. Furthermore, very little sample preparation is required prior to fluorescence spectroscopic analysis.

The majority of DOC in natural waters is comprised of humic material (Aiken et al., 1985). Fulvic acids are the fraction of humic material that is water soluble at any pH. Previous investigations have shown that the position of the fluorescent emission peak of fulvic acids (400–600 nm at an excitation of 370 nm) is indicative of organic matter provenance. Fluorescence emission peaks at shorter wavelengths are indicative of fulvic acids that are derived from microbial biopolymers, while peaks at longer wavelengths are indicative of fulvic acids that are derived from terrestrial sources (e.g., plant and leaf litter biopolymers) (McKnight et al., 2001). Due to their predominantly lignin-based precursor material, terrestrially derived fulvic acids contain more aromatic carbon (25–30% of total carbon) than microbial fulvic acids (12–17% of total carbon) (McKnight et al., 2001). This shift in the fulvic acid region of the spectrum is also found in whole water samples (Donahue et al., 1998). Two DOC end members are commonly cited and used as standards for microbially and terrestrially derived humic substances (e.g., Mobed et al., 1996; Donahue et al., 1998; McKnight et al., 2001). Lake Fryxell (microbial) DOC displays a fluorescent emission peak at 443 nm, while Suwannee River (terrestrial) DOC has its emission peak at 462 nm.

The presence of emission peaks at specific wavelengths of a synchronous spectrum indicates the existence of electron donating fluorophores that can be used to characterize the DOC in a sample. For example, emission peaks in the range 250–300 nm (with an 18 nm difference between excitation and emission monochromators [$\lambda_{em} = \lambda_{ex} + 18$ nm]) have been attributed to the presence of proteins (De Souza Sierra et al., 1994) that are indicative of compounds of recent biological origin (which are potentially relatively labile), whereas peaks in the range 400–500 nm are indicative of humic material (Miano et al., 1988; Chen et al., 2003), which is a more recalcitrant form of DOC.

As there have been few studies of DOC cycling in glacial environments (e.g., Lafreniere and Sharp, 2004), the sources, distribution, and biogeochemical transformations of DOC in these settings are poorly understood. We therefore investigated the abundance and fluorescence characteristics of DOC in three glacier systems with contrasting thermal and hydrological regimes and different potential DOC sources. The purpose of this paper is to quantify DOC abundance in a range of glacial sub-environments, and to characterize the DOC using emission and synchronous fluorescence spectroscopy.

Field Sites and Methodology

FIELD SITES

This paper presents results from the analysis of samples collected from three glacier systems: John Evans Glacier, Ellesmere Island, Canada (79°49'N, 74°00'W); Outre Glacier, British Columbia, Canada (56°14'N, 130°01'W); and Victoria Upper Glacier in the McMurdo Dry Valleys of Antarctica (77°16'S, 161°29'E).

John Evans Glacier is a polythermal glacier that overlies, and is surrounded by, predominantly carbonate bedrock and sediments in a region with sparse arctic tundra vegetation. Outflow of subglacial meltwater (meltwater flowing from beneath the glacier) is confined to the period between late June and early August each year. The first subglacial water that emerges each year is solute-rich, suggesting a long subglacial residence time (Skidmore and Sharp, 1999). The solute concentrations in the subglacial meltwater decrease rapidly following the onset of subglacial outflow due to dilution by new surface meltwaters that are routed to the bed via moulins and crevasses (Boon and Sharp, 2003). Subglacial and supraglacial meltwater (water flowing over the glacier surface) samples were collected once a day at John Evans Glacier during the 2001 ablation season (late June–late July). We attempted to monitor the water level in the subglacial channel as it emerged from beneath John Evans Glacier using a pressure transducer, but continuous bank erosion and stream migration prevented an accurate record from being obtained.

Outre Glacier is a temperate glacier in the coastal mountains of northern British Columbia that currently terminates below treeline in temperate rainforest. During its Little Ice Age advance it likely overran OC in forest soils and vegetation. Outre Glacier has retreated approximately 700 m during the last century, but its terminus is still located below treeline, so it may have a large subglacial OC pool that is characterized by both labile (e.g., microbially derived and non-vascular plant-derived biopolymers) and recalcitrant (e.g., vascular plant-derived biopolymers) organic matter. To allow comparison of the characteristics of DOC from glacierized and non-glacierized catchments, a small stream in a non-glacierized catchment located to the south of Outre Glacier was also sampled. Water samples from Outre Glacier were collected at approximate daily flow minima and maxima during the 2002 ablation season (early July–late August). Water from the non-glacial stream was sampled approximately once every two weeks over the same period. Outre Glacier basal ice was sampled once late in the field season and stored frozen until analysis. Subglacial

stream water level was monitored continuously using a Levellogger (Solinst, Canada) pressure transducer that was fixed to a stable frame.

Victoria Upper Glacier is a cold-based glacier in a polar desert environment and is adjacent to a proglacial ice-covered lake, which may be a significant source of labile (e.g., algal) OC to the glacier if it has overrun lake sediment or water in the past. While soil OC concentrations in the Dry Valleys are low (<0.1%; Horowitz et al., 1972), DOC concentrations as high as 30 ppm have been reported in Dry Valley lakes and have been attributed to algal production (McKnight et al., 1991). Victoria Upper Glacier terminates in an ~50-m-high ice cliff, the lower ~15 m of which is composed of basal ice. Souchez et al. (2004) proposed a mechanism by which the upward flow of pore water (and associated DOC) through saturated subglacial sediment allows freezing onto the sole of the bed of cold-based glaciers forming basal ice sequences such as those observed in Dry Valley glaciers. A pro-glacial accumulation of glacier ice that has calved from the glacier terminus has produced an apron which extends to an elevation of ~10–15 m and permits the sampling of both meteorically derived glacier ice and ~1–5 m of basal ice in the vicinity of the glacier ice/basal ice contact. Glacier and basal ice samples from Victoria Upper Glacier were collected in January 2003.

The thermal regime of glaciers determines the routing of water through them. Subglacially and supraglacially derived meltwaters circulate along the bed of both temperate and polythermal glaciers. Liquid water in cold-based glaciers is limited to thin films around entrained sediment (Cuffey et al., 1999) and gas bubbles (Dash et al., 1995) and at ice grain boundaries (Price, 2000). Glacier meltwater routing controls the distribution of water, oxygen, and nutrients in the subglacial environment and will thus influence subglacial microbial activity and determine the type of microbe that colonizes a particular subglacial site (Tranter et al., 2005). Similarly, the physical and chemical characteristics of the ice mass will influence the distribution and chemical characteristics of liquid water within the ice. Thus, the quality and spatial distribution of available nutrients would also be expected to exert a significant influence on subglacial and englacial (within the ice) microbial activity. For example, a subglacial heterotrophic microbial population in a temperate glacier could use OC in both subglacially routed supraglacial meltwater and subglacial sediment for metabolism. Some of the OC flushed from the glacier surface into the subglacial environment would be expected to consist of microbial exudates produced by algal communities in the supraglacial snowpack. The subglacial sediment would be expected to consist of OC from overridden soils and vegetation. The overridden OC may be more widely distributed across the glacier bed than the supraglacially derived OC and may be quantitatively more significant and, therefore, potentially important to subglacial microbial communities. However, the overridden OC may contain a large percent per volume of recalcitrant lignin-derived biopolymers (from overridden vascular plant material) that may not be efficiently used for subglacial microbial metabolism. Additionally, some of this OC may be located in areas of the subglacial environment that are oxygen limited and therefore not conducive to heterotrophic metabolism by some microbes. Though less widely distributed and less quantitatively significant, the more labile supraglacially derived algal exudates that are transported in more oxygenated supraglacially derived meltwater may represent the more significant source of OC to subglacial heterotrophic communities. Thus, we hypothesize that in addition to glacier water flow routing, the characteristics and distribution of subglacial OC will influence subglacial microbial processes and influence the characteristics and abundance of DOC both within, and exported from, the glacier system. The choice of field sites, as described above, provides the opportunity to quantify and characterize OC in glaciers with different hydrological regimes and different sources, distribution, and methods of entraining OC.

TABLE 1
DOC abundance.

Site	Location	Mean DOC (ppm)	DOC range (ppm)	Sample type	<i>n</i>	Sampling duration
John Evans Glacier (subglacial)	79°49'N, 74°00'W	0.225	0.124–0.427	water	48	18 June–30 July 2001
John Evans Glacier (supraglacial)		0.252	0.114–0.471	water	35	
Outre Glacier (subglacial)	56°14'N, 130°01'W	0.100	0.057–0.175	water	72	6 July–25 August 2002
Outre Glacier (supraglacial)		0.188	0.328–0.111	water	3	
Outre Glacier (non-glacial)		0.151	0.099–0.211	water	5	
Outre Glacier (basal ice)		0.303	0.301–0.305	ice	2	
Victoria Upper Glacier	77°16'S, 161°29'E	5.897	1.783–46.66	ice		January 2003

SAMPLING

Whenever possible, supraglacial meltwater, glacier ice, basal ice, and subglacial meltwater were sampled at each site (Table 1). Liquid samples were collected in pre-rinsed amber glass bottles and filtered immediately through pre-combusted 0.7 µm GF/F filter papers using a pre-rinsed glass filtration apparatus. The filtrate was decanted in duplicate into acid washed and pre-combusted amber glass vials and stored in the dark at ~4°C until analysis. Ice samples were collected using ethanol-bathed and flame-sterilized chisels and aluminum collection trays, melted in the field, and filtered as described above.

ANALYSIS

One of each pair of duplicate samples was analyzed for DOC concentration by high-temperature combustion and non-dispersive infrared detection using a Shimadzu TOC-5000A Total Organic Carbon Analyzer equipped with a high-sensitivity platinum catalyst. Prior to analysis, each DOC sample was acidified to pH 2 using trace metal grade HCl and sparged for 5 min with TOC grade air to remove dissolved carbonate species from the sample. Each sample was analyzed in triplicate. Five replicates were analyzed if the coefficient of variation exceeded 2%. The detection limit was 0.05 ppm (Miller and Miller, 1988). Sample dilution with UV-sterilized and deionized water was required to measure the concentration of DOC when concentrations exceeded 2.4 ppm.

The second of each pair of duplicate samples was analyzed by either emission (John Evans Glacier) or synchronous (Outre Glacier and Victoria Upper Glacier) fluorescence spectroscopy. Synchronous spectroscopy was employed more frequently because of the broader range of information that the technique provides. Emission spectra were measured using a Shimadzu RF-1501 spectrofluorometer with a Xenon lamp as an excitation source. Synchronous spectra were obtained using a SPEX Fluorolog-3 spectrofluorometer equipped with both excitation and emission monochromators and a Xenon lamp. Scans were performed at 1 nm increments with a 0.1 s integration period using a 10 nm bandwidth and an 18 nm offset between monochromators (for synchronous scans). All samples were scanned at room temperature using a quartz glass cuvette with a 10 mm path length. All spectra were Raman corrected by subtracting the spectrum for deionized water under identical scanning conditions. Scans were dark corrected, and instrument output was normalized to the water Raman spectra to correct for lamp fluctuation (<0.08% over the course of the analysis). No inner filter corrections were applied for DOC concentrations below 2.4 ppm. In the event that sample DOC concentrations exceeded 2.4 ppm, the diluted sample that was used for DOC determination was used for spectroscopic analysis. All fluorescence spectra were normalized to the sample fluorescence peak spectral maximum to facilitate the comparison of sample fluorophore peak location between samples. Fluorescence spectra were also smoothed with a 12 point running average to reduce spectrofluorometer signal noise and facilitate

fluorophore peak identification. Peaks were identified by calculating the first derivative of the spectrum and identifying the point on the ascending slope where values equaled zero. No drift in fluorescent peak position was observed between replicate sample analyses.

Where possible, the fluorophores revealed in the spectra from John Evans Glacier, Outre Glacier, and Victoria Upper Glacier were identified by comparison with spectra reported in the literature, for which accompanying fluorophore identification has been provided (e.g., Ferrari and Mingazzini, 1995). This information can potentially be used to better understand the characteristics of DOC variability in glacier systems.

Results and Discussion

JOHN EVANS GLACIER

Meltwater samples taken from John Evans Glacier during the 2001 melt season (18 June–29 July 2001) were analyzed for DOC concentration (Table 1, Fig. 1a) and fluorescence emission spectra (Fig.

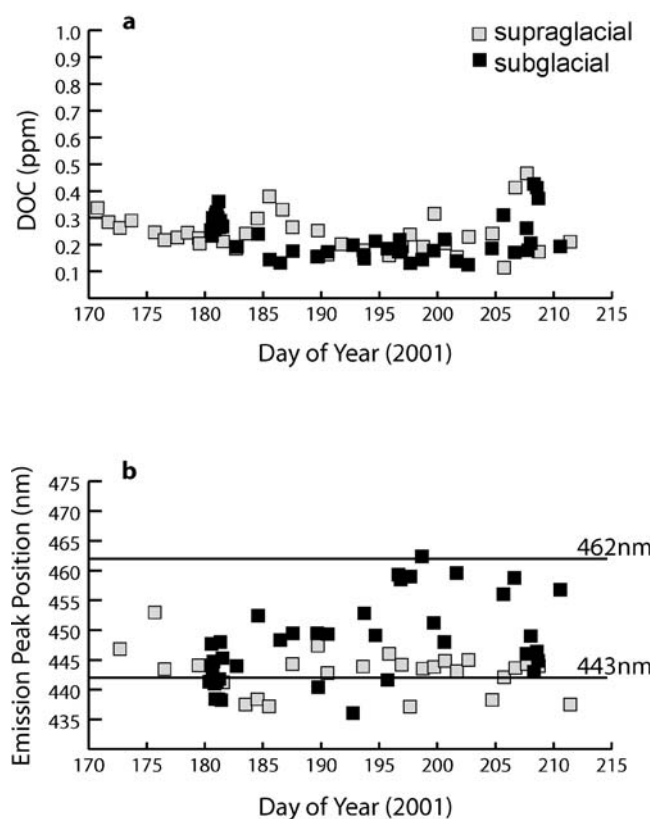


FIGURE 1. (a) Dissolved organic carbon concentrations, and (b) emission fluorescence spectra peaks for subglacial and supraglacial water samples from John Evans Glacier, 2001.

1b). Supraglacial and subglacial meltwaters contained an average of 0.256 ppm (SD = 0.096, $n = 35$) and 0.225 ppm (SD = 0.075, $n = 48$) DOC, respectively (Table 1). These mean concentrations are lower than the 0.44 ppm reported by Lafreniere and Sharp (2004) for a glacial stream flowing from an alpine glacier in the Canadian Rocky Mountains, and considerably lower than the 4.4 ppm that has been reported as an average for river waters in North America (Aiken et al., 1985). This is not unexpected because of the poorly developed soils and sparse vegetation (thus low abundance of OC) that characterize the arctic tundra biome.

The position of the emission fluorescence peak of DOC is less variable in samples from the supraglacial stream than in samples from the subglacial stream (Fig. 1b). In supraglacial samples, the peak position is typically located between 442 nm and 446 nm, values that are usually associated with microbially derived DOC (McKnight et al., 2001). DOC concentrations in the supraglacial stream rose noticeably above the mean concentration on three occasions (Fig. 1a). During the first of these (Days 183–187; maximum DOC concentration of 0.403 ppm), the fluorescence emission peak values were relatively low (437–438 nm) (Fig. 1b). On the second occasion (Day 199), DOC concentrations of 0.315 ppm were associated with an emission peak at 444 nm. On the final occasion (Days 206–207), the maximum DOC concentration was 0.466 ppm and the emission peak varied between 443 and 444 nm. These results indicate that supraglacially derived DOC is microbial in character (McKnight et al., 2001) and that periodic increases in the DOC concentration may be the result of flushing of microbially derived DOC from the snowpack and supraglacial cryoconite holes. Cryoconites are produced by the melting of wind-blown sediment into the surface of a glacier, and the resulting meltwater pool has been found to host microbial communities (Christner et al., 2003). DOC from cryoconite holes has an emission peak at ~443 nm (mean = 442.7 nm, SD = 0.339, $n = 5$) (data not shown). The similarity between the cryoconite fluorescence and the fluorescence during the second and third events indicates that these events result from the flushing of cryoconite holes, while the first event is likely the result of flushing of microbially derived DOC from the snowpack (mean = 436.3 nm, SD = 6.278, $n = 5$) (data not shown). This is consistent with the progressive removal of the seasonal snowpack and exposure of glacier ice surfaces that are pockmarked by cryoconite holes over the course of the melt season.

The peak position for the subglacial stream DOC shifts from shorter wavelengths (~438 nm) to longer wavelengths (~458 nm) as the melt season progresses (Fig. 1b). This represents a statistically significant shift (t -test, $P < 0.05$) from predominantly microbially derived DOC to predominantly terrestrially derived DOC (McKnight et al., 2001). There is no consistent relationship between concentration and fluorescence emission peak position for subglacial stream DOC. Increases in subglacial DOC are accompanied by shifts to longer fluorescence peak wavelengths on Day 180, but to shorter wavelengths on Day 207 (Figs. 1a and 1b). The shortest (436 nm) and longest (462 nm) peak wavelengths in the subglacial stream record occur on Days 192 and 198, and correspond to DOC concentrations of 0.197 ppm and 0.144 ppm, respectively. While the fluorescence peak positions on these days are exceptional within the subglacial stream record, the corresponding DOC concentrations are not. This indicates that separate subglacial pools of microbial and terrestrial DOC can be accessed by the subglacial drainage system. The minimum and maximum peak positions of the DOC in subglacial water (e.g., Days 192 and 198, respectively) fall outside the range of peak values observed in the supraglacial meltwater at any time during the melt season, indicating that supraglacial meltwater is not the only source of DOC in subglacial meltwater. While these pools do not contribute enough DOC to increase DOC concentrations in the bulk subglacial meltwater flow significantly above background levels, their contribution is detected in

the fluorescence record. The amount of variability in subglacial peak position also increases with time (Fig. 1b), suggesting that the predominant fluorescence characteristics of DOC in subglacial meltwater become more variable as the melt season progresses.

These results indicate that various pools of DOC with distinct microbial and terrestrial characteristics are accessed by the bulk subglacial flow during the melt season. This is most likely a consequence of seasonal development of the glacier drainage system coupled with discharge-related variations in the routing of meltwaters across the glacier bed (Bingham et al., 2005). The first subglacial meltwater to be released is extremely solute-rich, and the DOC within it has a strongly microbial fluorescence signature (Fig. 1b). This water has likely experienced prolonged storage in an environment where subglacial microbial communities are active. As the melt season progresses and the character of the subglacial drainage system evolves from distributed to more channelized in form (Bingham et al., 2005), a shift in fluorescent peak positions indicates that subglacially routed meltwaters gain access to a source of terrestrial DOC, such as vascular plant biopolymers (e.g., lignin) at the glacier bed. As the channelized system develops, intermittent hydrologic connections between the main conduits and the residual distributed system may permit the flushing of previously isolated pools of subglacially stored water, with microbial fluorescence characteristics, into the bulk flow.

OUTRE GLACIER

DOC concentrations in Outre Glacier runoff are low (subglacial mean = 0.1 ppm, $n = 72$) and stable (SD = 0.08) relative to those observed at John Evans Glacier (Table 1, Fig. 2a). Outre Glacier likely overran rainforest soils and vegetation during its Little Ice Age advance and so may have a large subglacial OC pool. The low DOC concentrations in the subglacial meltwater at Outre Glacier (Table 1, Fig. 2a), however, indicate that if such a pool exists it is not normally accessed by bulk subglacial meltwaters.

Ferrari and Mingazzini (1995) identified fluorophores with peaks at 270 nm and 370 nm in synchronous fluorescence spectra, which they interpreted as indicating the presence of proteins and fulvic material, respectively. Proteins are labile, and the presence of proteinaceous material in DOC has been interpreted as evidence of active microbial synthesis (De Souza Sierra et al., 1994). Fulvic material results from secondary abiotic humification reactions (Sylvia et al., 1999) and is recalcitrant. The ratio between the heights of the fluorescent peaks at 270 nm and 370 nm (270/370 nm) is therefore used here as a basis for discriminating between the contributions from primary material of recent origin and secondary altered material to the DOC in a sample.

The average synchronous spectra from the supraglacial and subglacial streams at Outre Glacier are the most similar in shape, and different from the spectra from the non-glacial stream and basal ice (which are also different from each other) (Figs. 2b and 2c). The range of relative emission intensities recorded in the synchronous spectra of the DOC from the subglacial stream encompasses the average supraglacial spectrum (Fig. 2d) suggesting that, on some occasions, the synchronous spectra of subglacial meltwater may be identical to those of supraglacial meltwater. There is, however, a difference in the mean 270/370 nm between supraglacial (1.87) and subglacial (1.58) streams (Fig. 2b), which suggests that the relative contribution from fulvic material is greater in the subglacial stream than in the supraglacial stream. The 270/370 nm in the average synchronous spectrum of DOC in the non-glacial stream (1.59) is similar to the value for the subglacial stream, while the spectrum from basal ice indicates an enrichment in proteinaceous material relative to fulvic material (270/370 nm = 3.66) (Fig. 2c). These results suggest that there is a subglacial source of fulvic DOC. DOC in supraglacial meltwater is proteinaceous in

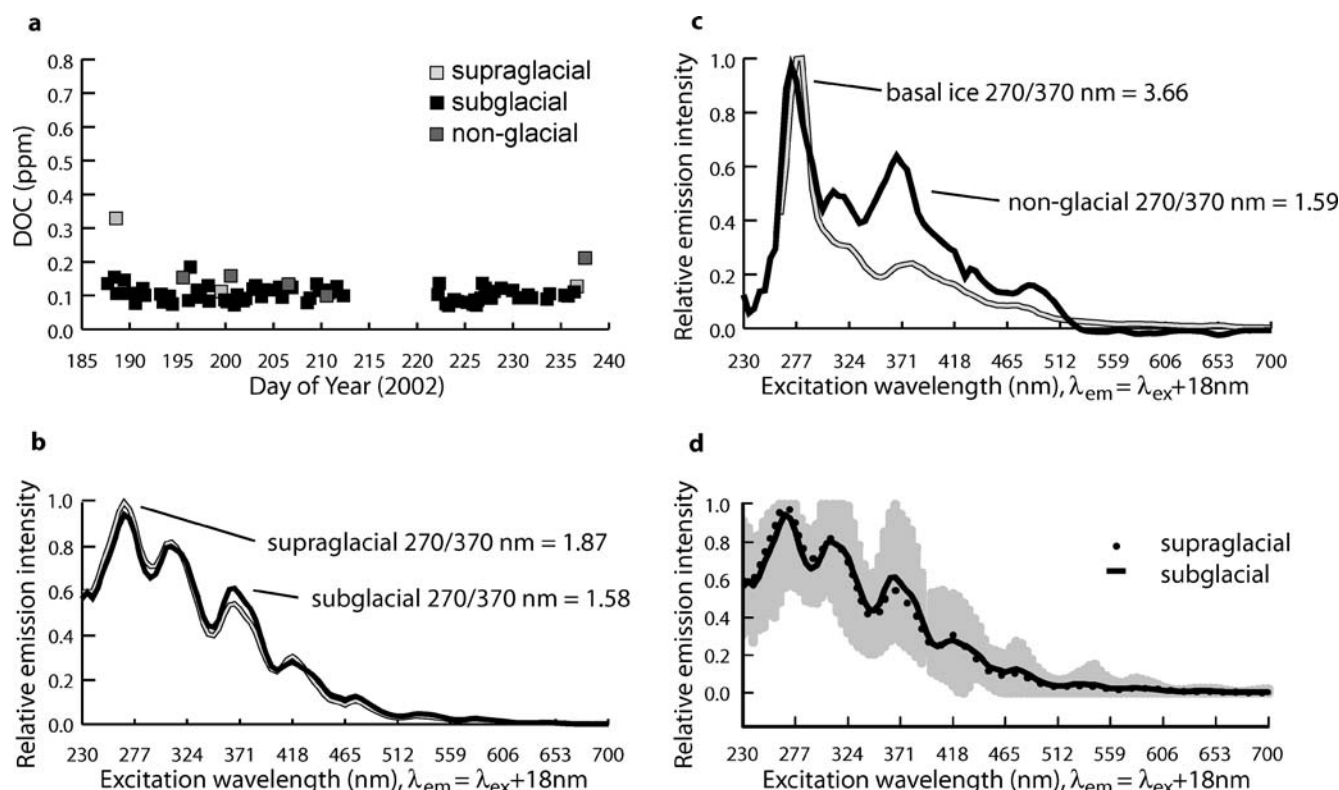


FIGURE 2. (a) Dissolved organic carbon concentrations for subglacial, supraglacial, and non-glacial samples from Outre Glacier, 2002. (b) Synchronous spectra for averaged subglacial, supraglacial, and (c) basal ice and non-glacial stream samples from Outre Glacier, 2002. (d) Average subglacial and supraglacial synchronous spectra. The shaded area indicates the range of relative emission intensities for each wavelength during the monitoring period for the subglacial stream. Note that the subglacial and non-glacial stream samples were taken from the same elevation.

character, which suggests active microbial DOC synthesis. Likewise, active microbial synthesis also appears to occur in basal ice.

The 270/370 nm of synchronous spectra from the DOC in the subglacial stream changes diurnally, with higher 270/370 nm occurring on the rising limb of the discharge hydrograph and lower 270/370 nm occurring during decreasing discharge (Figs. 3a and 3b). This indicates a more significant contribution by the proteinaceous fluorophore to the fluorescence spectra during periods of rising discharge in the subglacial stream than during periods of decreasing discharge. A higher resolution sampling of subglacial meltwater shows that this variation in 270/370 nm occurs throughout the day and that it follows the trend in the subglacial stream discharge (Fig. 3b).

Several subglacial meltwater channels are incised into bedrock (N-channels) in the proglacial area of Outre Glacier, and the current subglacial stream occupies an N-channel at the glacier terminus. It is therefore likely that much of the subglacial flow at Outre Glacier is confined to subglacial N-channels and that water passing through these channels is isolated from areas of the glacier bed where OC may still be found. The similarity between subglacial and supraglacial DOC concentrations at Outre Glacier (Table 1, Fig. 2a) supports this hypothesis and could be taken to indicate that under most flow conditions supraglacially derived DOC is transported directly through a subglacial N-channel network to the terminus. The similarity between the average subglacial and supraglacial fluorescence spectra (Figs. 2b and 2d) is also consistent with this suggestion. However, the diurnal change in the fluorescence spectra of DOC in the subglacial meltwater, as indicated by changes in 270/370 nm (Figs. 2b, 3a, and 3b), suggests that there is also a subglacial source of more recalcitrant DOC. The diurnal change in subglacial DOC 270/370 nm (Figs. 3a and 3b) suggests that water is diverted from the major channels into a distributed subglacial drainage system as discharge and channel water pressures rise, and returned to

the major channels as discharge and channel water pressures fall (e.g., Hubbard et al., 1995). Under these circumstances, the distinctive spectra of DOC exported from the glacier during declining discharges may reflect an input of DOC from areas of the bed drained by a distributed drainage system that is isolated from the major drainage channels at times of high flow. During periods of surface melt, proteins produced supraglacially by microbes in the snowpack (e.g., algae) will be flushed and routed to the glacier bed through crevasses and moulins, and supraglacially derived meltwater will dominate subglacial flow. During declining discharges, when water pressure in the main channels decreases and flow from the distributed system contributes to the bulk subglacial flow, fulvic material, which is likely derived from glacially overridden terrestrial organic matter, is detected. However, the DOC concentration in the bulk subglacial meltwater is relatively constant throughout the melt season. This suggests that the contribution of DOC from the distributed system to the bulk flow is small, though still identifiable by the change in the fluorophores found in the subglacial stream DOC.

The fact that the overall shape of the fluorescence spectra of the DOC flushed from Outre Glacier differs from that of the DOC in the adjacent non-glacial stream (Figs. 2b and 2c) indicates either that the source of DOC beneath Outre Glacier differs from that of the DOC in the non-glacial stream, or that biogeochemical processes acting on DOC in the subglacial environment are different from those occurring in proximal non-glacial environments. For example, the peaks at 270 nm and 370 nm are most prominent in the non-glacial stream fluorescence spectra, and 270/370 nm in the average non-glacial stream spectrum is very similar to that of the average subglacial stream spectrum. The peak at 320 nm (indicative of two condensed ring systems; Ferrari and Mingazzini, 1995) is more prominent in the subglacial stream fluorescence spectra than in the non-glacial stream

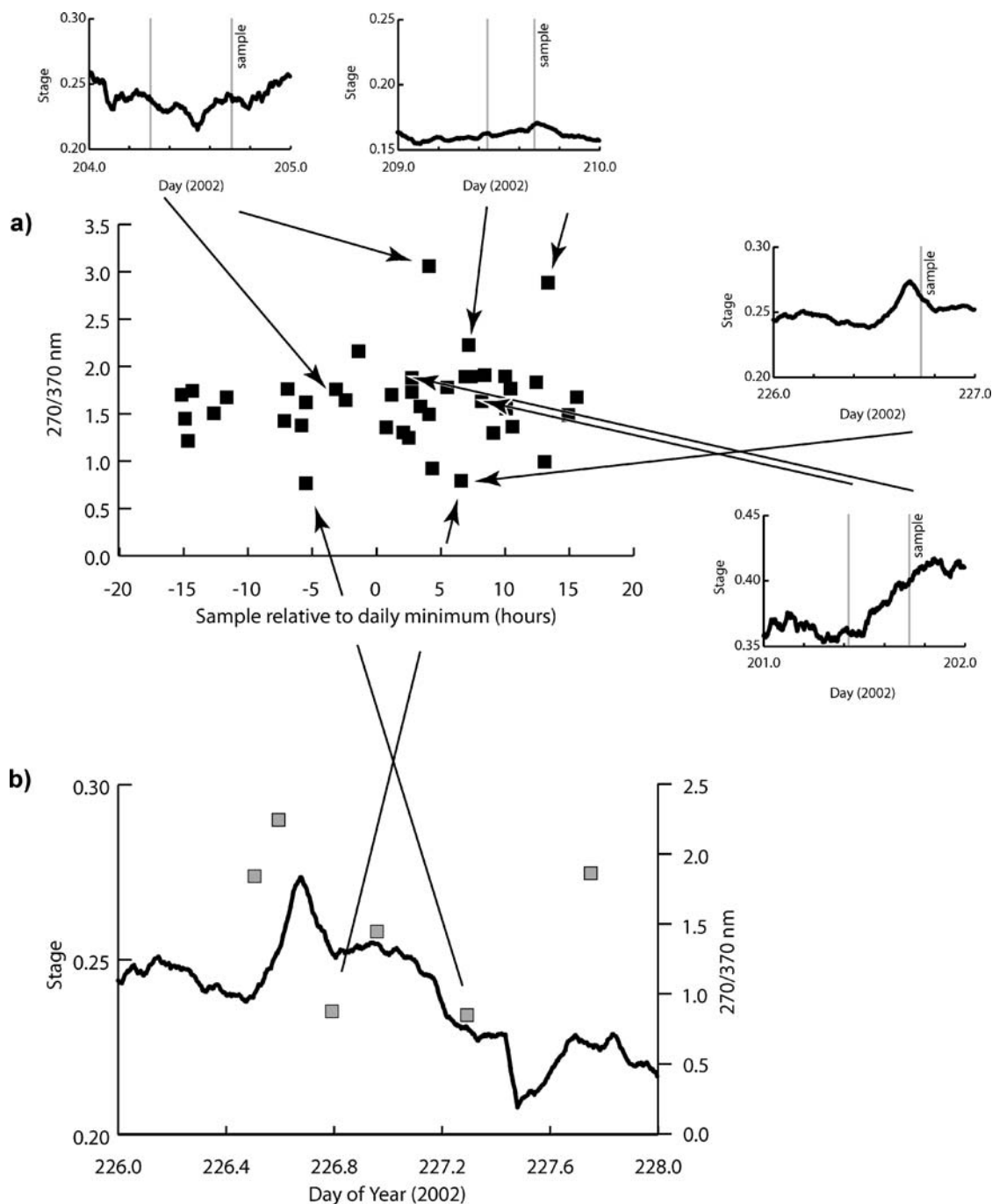


FIGURE 3. (a) Plot of 270/370 nm relative to the time of the daily minimum flow for the subglacial stream at Outre Glacier. Accompanying hydrographs show that higher 270/370 nm occur on ascending limbs of the subglacial stream discharge hydrograph, while lower 270/370 nm occur on descending limbs. (b) A higher resolution plot of 270/370 nm over with the associated subglacial stream discharge hydrograph.

spectra. This observation indicates that either the fluorescence peaks resulting from the production of proteins and fulvic acids in the non-glacial stream DOC overwhelms the peak at 320 nm, that the production of the fluorophore at 320 nm is the result of a supraglacial process, or that subglacial biogeochemical conditions favor the preservation of molecules that fluoresce in this region of the spectrum, relative to the non-glacial stream.

VICTORIA UPPER GLACIER

Evidence of differences in the fluorescence characteristics of DOC in the distributed and channelized drainage systems beneath Outre

Glacier and in the supraglacial and subglacial meltwater systems at John Evans Glacier suggests that DOC properties vary spatially within glacial environments. If this is true, spatial variations in the abundance and properties of DOC within and between glacier ice and basal ice might also be expected due to differences in DOC source. For example, subglacially accreted basal ice might be expected to incorporate DOC from subglacial sources, whereas meteorically derived glacier ice might be expected to incorporate DOC from supraglacial sources.

DOC concentrations vary along a vertical transect across the boundary between glacier ice and basal ice at Victoria Upper Glacier, with a zone of particularly high DOC concentration located immediately above the glacier ice/basal ice contact (Fig. 4). The fluorescence

spectra of the DOC also change through the profile (Fig. 5). The only consistent fluorescent peaks in DOC from glacier ice occur at 276 nm and 317 nm. The 317 nm peak becomes dominant as the basal ice contact is approached. Minor peaks at 370 nm and 526 nm appear sporadically throughout the glacier ice transect. The basal ice spectra also contain peaks at 276 nm and 317 nm, but show stronger peaks than the glacier ice spectra at 370 nm and 526 nm, and a unique peak at 417 nm. The peak at 317 nm does not feature as prominently in the basal ice spectra as it does in the glacier ice spectra from 0–8 cm above the basal ice contact.

The heterogeneity of DOC characteristics and concentrations observed in the ice of Victoria Upper Glacier could reflect a range of possible DOC sources and incorporation mechanisms including atmospheric deposition, overriding of lake ice or lake sediment during past advances, or basal freeze-on of DOC-rich lake water (e.g., Souchez et al., 2004). To resolve this uncertainty, one would need to characterize individual fluorophores as carbon functional groups.

The peak at 276 nm indicates proteins (Ferrari and Mingazzini, 1995) and suggests recent biological productivity (De Souza Sierra et al., 1994). The fact that the protein peak in Victoria Upper Glacier ice occurs at longer wavelengths than the protein peak in Outre Glacier subglacial meltwater suggests that the protein at Victoria Upper Glacier is more conjugated and/or contains condensed ring systems. The sporadic peaks at 417 and 526 nm indicate the presence of humic material in the ice (Ferrari and Mingazzini, 1995). Like fulvic material, humic material is formed by abiotic secondary condensation reactions and would be expected to be older and more recalcitrant than proteinaceous material. The most likely source of this humic material at Victoria Upper Glacier is overridden sediment, and the fact that the basal ice has stronger peaks at these wavelengths supports this hypothesis. The 276/370 nm (note that the ratio has been changed relative to that used for Outre Glacier to accommodate the protein peak position at Victoria Upper Glacier) through the transect at Victoria Upper Glacier indicates that, relative to protein, fulvic material contributes more to the fluorescence spectra in the basal ice than in the glacier ice (Fig. 6). The occasional detection of these peaks in the glacier ice may be the result of wind-blown deposition of sediment on the surface of the glacier.

The ubiquitous peak at 276 nm in the fluorescence spectra of both glacier and basal ice at Victoria Upper Glacier indicates the presence of proteinaceous material. The fact that the protein peak can occur in the absence of the fulvic (370 nm) or humic (>417 nm) peaks suggests that the presence of the protein is not a consequence of wind-blown sediment deposition (in the case of glacier ice) or the incorporation of overrun sediment (in the case of basal ice), but that it may indicate biological production within the ice itself.

The peak at 317 nm, which features so prominently near the glacier ice/basal ice contact, indicates the presence of two condensed ring systems (Ferrari and Mingazzini, 1995) which shift the fluorescence to longer wavelengths. For example, the amino acid tryptophan, which contains a two condensed ring system as an indole substituent on the β carbon, fluoresces at 291 nm, while the amino acid tyrosine, which has only one condensed ring (as a phenol), fluoresces at 277 nm (Ferrari and Mingazzini, 1995). Given the provenance of proteinaceous fluorophores in the ice at Victoria Upper Glacier, and the evidence of protein conjugation, a possible explanation for the peak at 317 nm is the presence of condensed ring systems in association with proteinaceous material. Why this fluorophore becomes dominant at the glacier ice/basal ice interface is unclear.

Summary and Conclusions

The concentration and fluorescence characteristics of DOC were measured in ice and meltwaters from three glaciers with different thermal and hydrological regimes, and with different potential sources

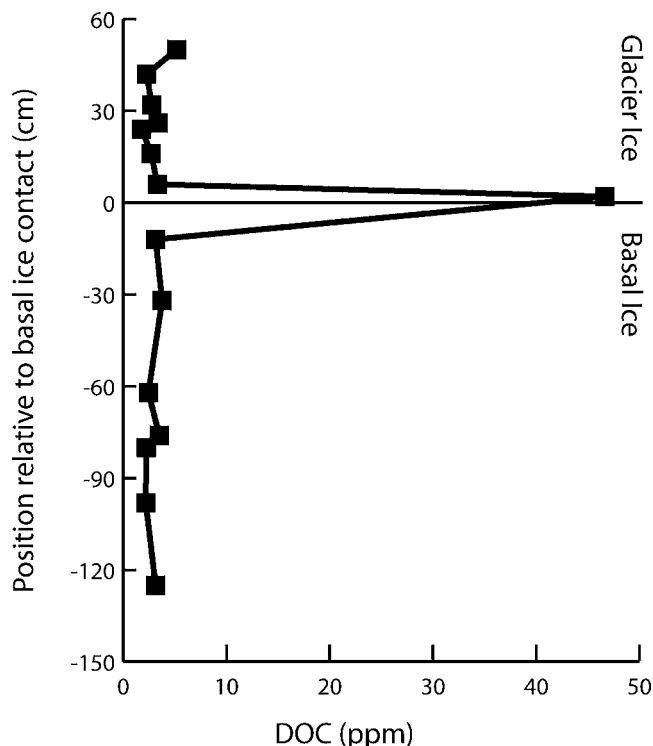


FIGURE 4. Dissolved organic carbon concentrations in ice along a transect from glacier ice to basal ice at Victoria Upper Glacier.

of OC. The average DOC concentrations in subglacial and supraglacial meltwaters do not differ significantly at the sites investigated. This might be taken as evidence of a lack of subglacial OC sources. However, fluorescence analyses indicate that the fluorescence characteristics of the DOC in bulk subglacial meltwater can differ from those of the DOC that enters the glacier via its surface. The nature of these differences suggests that there are sources of DOC in the subglacial environment that have both microbial and terrestrial provenance. The mobilization and export of subglacial DOC in glacier meltwater is dependent on meltwater flow routing. The results from analyses of DOC in ice at Victoria Upper Glacier indicate that DOC abundance and properties can vary spatially within the glacier itself.

Proteins and proteinaceous material, such as amino acids, fluoresce at different wavelengths depending on their molecular structure. The proteinaceous fluorophore in the ice at Victoria Upper Glacier fluoresces at wavelengths that have been attributed to the amino acid tyrosine (Ferrari and Mingazzini, 1995), whereas the proteinaceous fluorophore in the subglacial meltwater at Outre Glacier may be a tyrosine precursor, such as phenylalanine, which fluoresces at shorter wavelengths (Yamashita and Tanoue, 2003). The ubiquitous presence of tyrosine-like fluorescence within glacier and basal ice, independent of fulvic fluorescence, suggests *in situ* protein production.

While fluorescence spectroscopy is useful for detecting changes in DOC characteristics, one must currently rely on published reports to explain which fluorophores are responsible for the fluorescence response that is detected, or resort to techniques such as ^{13}C -NMR, FTIR, and EPR to identify the functional groups that are present in the sample. The overall form of the synchronous spectra reported here differs from that of spectra previously published for other environments (e.g., Parlanti et al., 2000). It is recognized that synchronous spectra from different environments are unique (for example soil vs. marine synchronous spectra; Lombardi and Jardim, 1999) due to the combination of unique DOC sources and unique biogeochemical processes that transform the characteristics of DOC in each

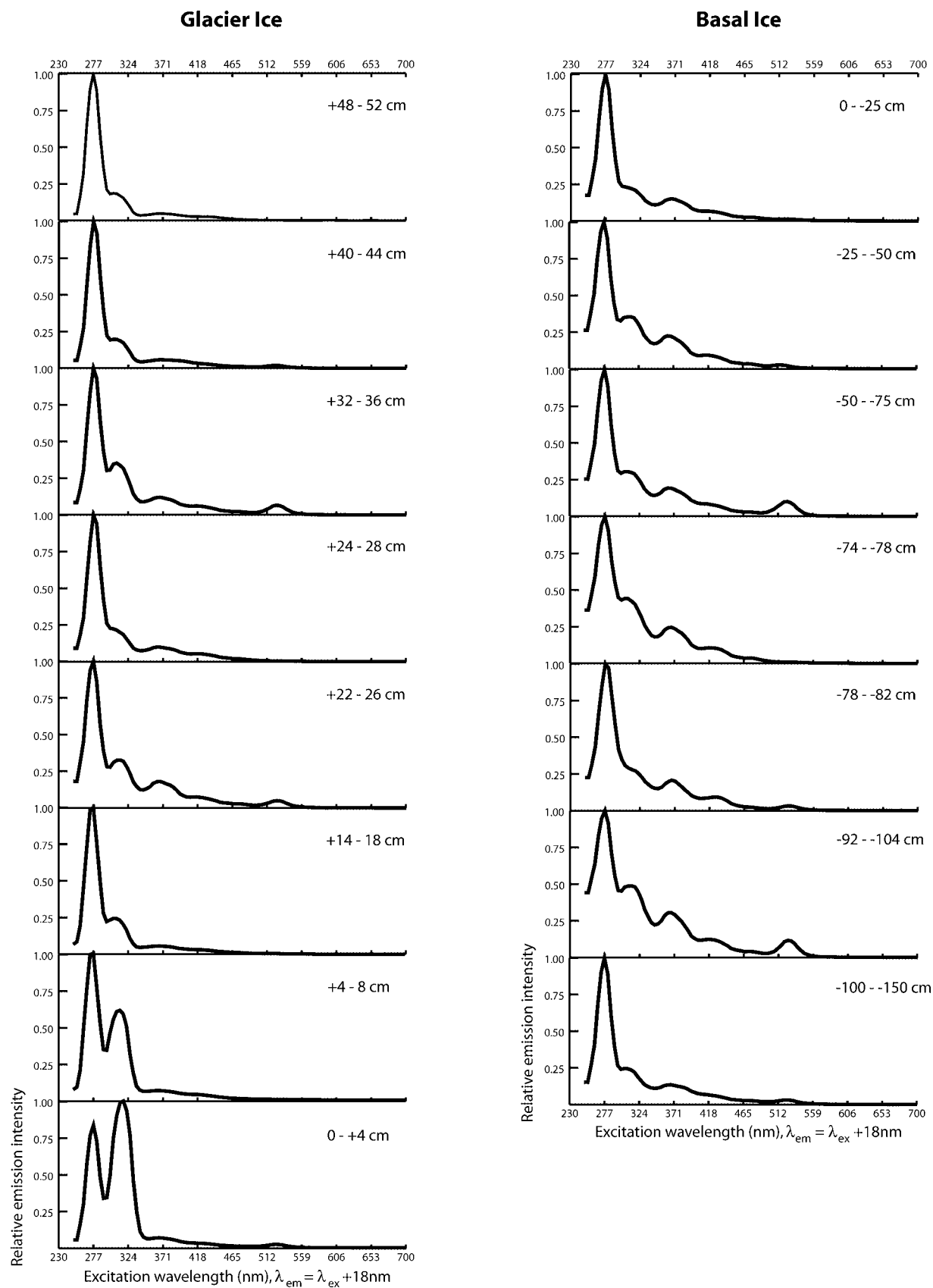


FIGURE 5. Synchronous spectra from ice samples at Victoria Upper Glacier. All distances are relative to the glacier ice/basal ice contact. Spectra have been corrected to represent intensity relative to the maximum intensity in the spectrum.

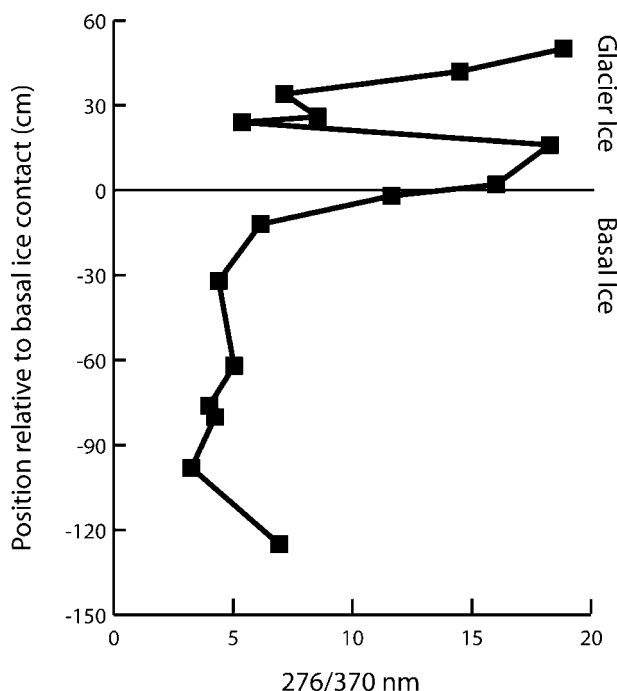


FIGURE 6. The 270/370 nm ratio in ice along a transect from glacier ice to basal ice at Victoria upper Glacier. The difference between the 270/370 nm in basal ice and glacier ice is statistically significant (t -test, $P < 0.05$).

environment. The unique fluorescence spectra reported here (e.g., Outre subglacial vs. non-glacial spectra) suggest that the dominant biogeochemical processes responsible for the synchronous spectra of glacially derived DOC may differ from those in adjacent non-glacial environments. In order to identify the fluorophores and biogeochemical processes that occur in glacial environments, techniques that identify specific carbon functional groups in glacier samples will be needed. For example, FTIR analysis would be useful for characterizing the fluorophore that is associated with the 317 nm peak in the fluorescence spectra at Victoria Upper Glacier. Such information may provide insight into the biogeochemical processes that may be modifying the proteinaceous material in the ice and help to resolve the unanswered question of why the 317 nm peak is prominent at the glacier ice-basal ice transition at Victoria Upper Glacier.

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