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Review

Biomolecular Composition of Sea Ice Microalgae and Its Influence on Marine Biogeochemical Cycling and Carbon Transfer through Polar Marine Food Webs

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Abstract: Microalgae growing on the underside of sea ice are key primary producers in polar marine environments. Their nutritional status, determined by their macromolecular composition, contributes to the region's biochemistry and the unique temporal and spatial characteristics of their growth makes them essential for sustaining polar marine food webs. Here, we review the plasticity and taxonomic diversity of sea ice microalgae macromolecular composition, with a focus on how different environmental conditions influence macromolecular production and partitioning within cells and communities. The advantages and disadvantages of methodologies for assessing macromolecular composition are presented, including techniques that provide high throughput, whole macromolecular profile and/or species-specific resolution, which are particularly recommended for future studies. The directions of environmentally driven macromolecular changes are discussed, alongside anticipated consequences on nutrients supplied to the polar marine ecosystem. Given that polar regions are facing accelerated rates of environmental change, it is argued that a climate change signature will become evident in the biochemical composition of sea ice microalgal communities, highlighting the need for further research to understand the synergistic effects of multiple environmental stressors. The importance of sea ice microalgae as primary producers in polar marine ecosystems means that ongoing research into climate-change driven macromolecular phenotyping is critical to understanding the implications for the regions biochemical cycling and carbon transfer.

Keywords: sea ice; sympagic microalgae; lipid; protein; carbohydrates; biochemistry; trophic transfer; sea ice microalgae

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1. Introduction

Ice-covered seas account for approximately 10% of the global ocean surface area (34×10^6 km^2) annually, with the seasonal formation and decay of sea ice playing a key role in global ocean turnover. Sea ice forms during the dark winter months reaching its maximum extent as spring commences. Therefore, in the Arctic, the maximum extent of sea ice (~15.2×10^6 km^2) occurs in March, while in the Antarctic, sea ice extent reaches a maximum (~18.5×10^6 km^2) in September [1] (Figure 1). Despite their asynchrony, combined, these two regions form a significant biome, providing essential habitat for many marine organisms, including diverse communities of bacteria, protists, and meiofuana [2,3].

The organisms that thrive in these vast expanses of frozen seawater, underpin polar marine biodiversity and biochemistry. In particular, photosynthetic microalgae, which become engrained into the ice as it forms (Figure 1), support polar marine food webs, and, together with heterotrophic bacteria, are principal players in the biochemical cycling of elements within the marine and sea ice environments [2]. Sea ice primary productivity and nutrient cycling is important for understanding the dynamics of seawater biochemistry, as the biomolecular composition of sea ice microalgae and the cycling of nutrients that occurs within sea ice microbial communities influences the biochemistry of seawater [4,5].

However, biochemical components can be sensitive to physical processes, including photooxidation from UV, which is determined by ice thickness or mixing depth [6,7], potentially reshaping the biochemical signature of the seawater [8,9].

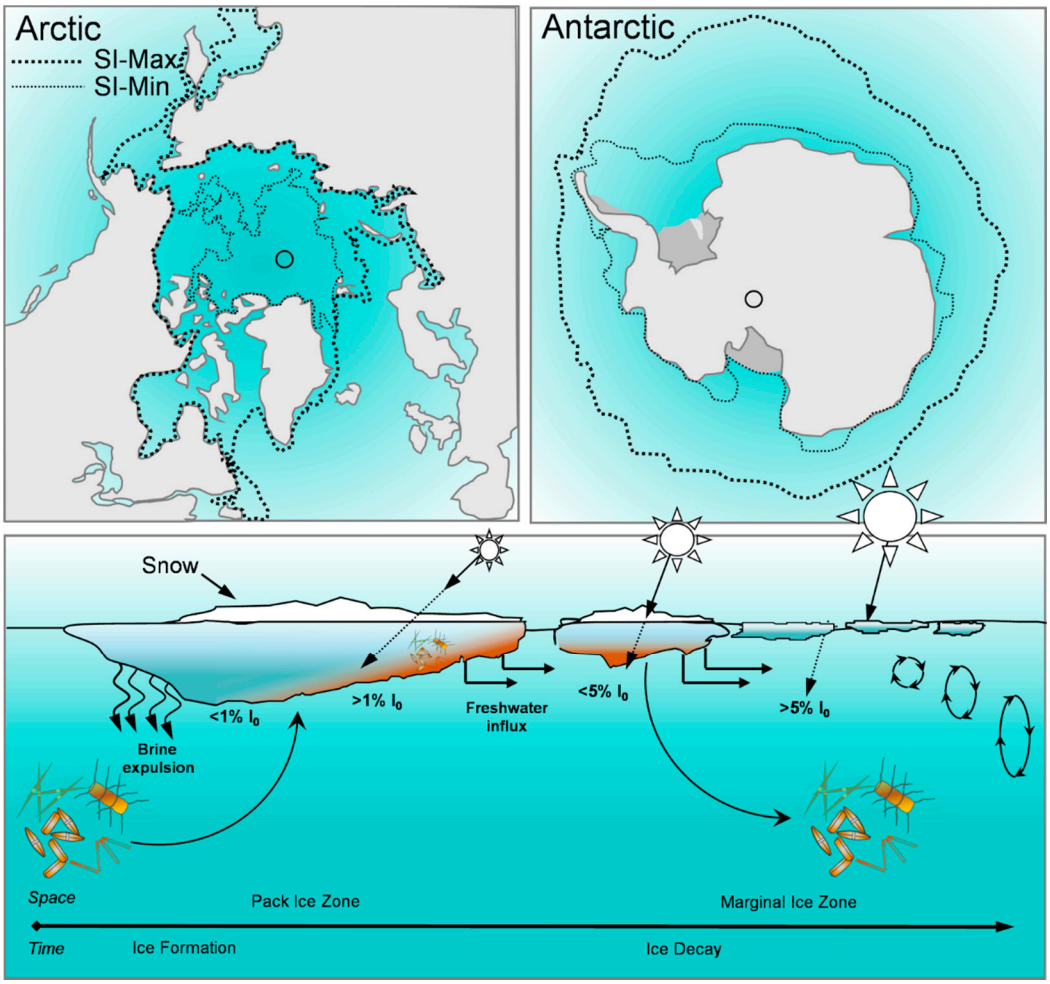

Figure 1. Sea ice zones in both polar regions. Stippled lines indicate the maximum (SI-Max) and minimum (SI-Min) extent of sea ice in the Arctic (**top left**) and Southern Ocean (**top right**). Black open circles indicate the poles. Schematic of the spatial and temporal evolution and decay of sea ice in polar marine ecosystems. Arrows indicate seasonal changes in salinity from brine extrusion and freshwater melt, as well as light attenuation, solar angle, and mixing depth. The entrainment of microalgae into the sea ice as it forms, its proliferation and re-release into the water column during melt is also shown. I_0 = percent incident irradiance.

The ecological importance of sea ice microalgae is attributed to their role in primary production during the frozen winter and in spring as the ice begins to melt. During the early spring, sea ice microalgae grow within the brine channel network under very low irradiances [10,11], and as the solar angle increases, spring blooms commence, marked by an increase in biomass on the underside of the ice [10,11]. The total biomass that accumulates depends on the amount of light transmitted and therefore the thickness of the ice and snow cover, as well as the duration of the growth season, with substratum melt and ice breakup ultimately forcing the end of the sea ice algae growth season [12,13].

Sea ice microalgal communities can make significant contributions to primary production in polar regions, accounting for up to 25% of total primary production in seasonally ice-covered waters and up to ~60% in perennially ice-covered Arctic waters [14–17]. However, their precise contribution to primary production varies depending on time of year and geographic location. For example, sea ice algae contributed as little as <1% to primary

production in Young Sound, Greenland in 2002 [18] yet contributed ~70% of primary production in Barrow, Alaska in 2003 [19]. Whilst the contribution of sea ice microalgae to total primary productivity is generally less than that of pelagic phytoplankton, the divergence in their timing and distribution means that the sea ice microalgae subsist as an important source of nutrients and energy to the marine food web [17,20]. Indeed, their presence extends biological production in polar waters by up to three months [12], because they are the primary source of organic carbon for pelagic consumers during the ice-covered winter [15,21,22]. Specifically, sea ice microalgae form a critical food source for copepods, amphipods, and euphausiids [23,24], where the availability and nutritional quality of the microalgae have been shown to play an important role in the timing of zooplankton reproduction and, therefore, the quantity and quality of secondary production [25–27]. As the ice begins to melt, the ecological function of sea ice microalgae extends to seeding phytoplankton blooms in the marginal ice zone [28–33]. Through shaping the initial phytoplankton community [13,30] and influencing the timing of the pelagic bloom and secondary production [32], sea ice microalgae can strongly influence pelagic processes, and thus exert significant influence over food web dynamics and biochemical cycling in the polar marine environment.

As primary producers, sea ice microalgae convert solar energy into carbon via photosynthesis, making light a principal driver of sea ice productivity. Photosynthates are converted into a variety of biochemical components including proteins, lipids, and carbohydrates; biomolecules that make up the majority of the cell biomass. The allocation of the photosynthetically derived carbon is largely determined by environmental conditions and is therefore dynamic, whereby the biomolecular composition of the microalgal cell reflects its physiological status [34]. Shifts in biochemical composition in response to environmental conditions, while important for the physiology and nutritional status of the sea ice microalgae itself, also strongly influence the productivity and nutritional value of primary consumers. For example, sea ice microalgae have been shown to contribute up to ~146% of the energy budget of Antarctic krill during the winter [35]. Similarly, adequate lipid supply has been shown to be critical to the survival and reproduction of zooplankton [36,37]. Over winter, large lipid reserves are particularly important for zooplankton when pelagic primary production is low [38–40]. The biomolecular stores of primary producers are therefore the cornerstone of productive marine ecosystems, and changes in the partitioning of these critical biomolecules contained in microalgae inevitably alters the supply of energy and essential compounds to higher trophic levels.

Planetary warming is causing polar environments to change rapidly [41], and the significant decline in sea ice is of major ecological concern [1,42]. For the past four decades, the most profound and consistent sea ice decline has been measured in the Arctic [1,41,43], which has experienced a decline in average September sea ice extent of ~10.1% per decade [44,45]. Concomitant with the decline in extent is a dramatic loss of thicker multi-year ice, increasing the expanse of open water in summer, with predictions of sea ice-free summers within decades [43,46,47]. The situation in the Antarctic is more nuanced, as the southern hemisphere sea ice extent experienced a gradual rate of increase between 1981 and 2014, after which it has been experiencing a precipitous rate of decline [48] amounting to a 27% reduction between 2010 and 2017 [45]. Given that the growing season for sea ice microalgae is already constrained to within a few months each year and seems likely to be further shortened as oceans warm and ice extent continues to decline [12,43,49], it is probable that in the future we will see reduced accumulation of biomass, disrupting the critical early-season food supply for the region's primary consumers. Furthermore, as polar regions warm, light climate under the sea ice is expected to change, influencing productivity. A reduction in snow cover and declining sea ice thickness would result in higher under-ice light intensity [11]; conversely, where precipitation is expected to increase (more snow), light transmission may decline. In addition, sea surface temperatures are rising [50], polar oceans are acidifying [41,51], and there is an increase in freshwater input due to glacial retreat and run off [52]. These shifts in ecosystem condition will influence future

community composition [53,54] and biomolecular partitioning of sea ice microalgae [55–60]. Therefore, accurate assessment of the direction and magnitude of these cellular changes is necessary to better understand the impact on marine biogeochemistry and carbon transfer through the polar marine food web.

2. Biomolecular Composition of Sea Ice Algae from Polar Regions

Microalgae are the primary source of biomolecules (protein, lipids, and carbohydrates) in marine ecosystems. In cells, proteins play a key role in all enzymatic processes and growth, while lipids and carbohydrates are essential components of cell membranes and form important energy reservoirs [34,38,61]. Particular to sea ice microalgae, lipids and antifreeze amino acids such as proline have been important evolutionary adaptations to tolerating the freezing and hypersaline conditions of the ice matrix [62,63]. The biomolecular composition of sea ice microalgae in both absolute amounts and relative proportions vary between species, making community composition a strong determinant of overall nutritional status of primary producers.

Lipids are the most energy-rich biomolecules and, as such, contain much of the energy that is transferred among trophic levels [38]. Carbohydrates, which contribute less to energy transfer [38], have an important role in supplying the cellular carbon pool [64], and are integral for protein synthesis [65]. Proteins are the predominant source of amino acids [66] and form a cellular nitrogen reservoir [61]. They are a key source of nutrition for higher trophic levels [38]. In terms of carbon transfer through trophic webs, proteins have the highest relative efficiency [34,67,68], thus making protein rich species of potentially greater value in supporting secondary production. However, specific to polar regions, microalgae with high lipid content have been shown to be important for zooplankton fecundity [25,26,69].

Investigations into the biochemical composition of pelagic phytoplankton from the two polar regions have revealed differences in biomolecular characteristics, with Arctic waters shown to be dominated by lipid-rich cells [70,71], possibly a result of low nitrogen status. In contrast, Antarctic phytoplankton are generally found to be rich in protein [72–74]. The high protein production by these primary producers, is likely supported by the high nitrogen concentrations in the seawater [75,76], resulting in a nitrogen-rich food source for primary consumers and thus able to support a highly productive ecosystem. One study however, found high concentrations of carbohydrates during a summer bloom in the Amundsen Sea [77]. This was attributed to high densities of the haptophyte *Phaeocystis antarctica*, which is a common bloom-forming species in Antarctic waters [77,78]. It is important to note, however, that while these patterns highlight differences between the Arctic and Antarctic, these general trends for pelagic phytoplankton are derived from only a few studies, representing low temporal and spatial coverage, and thus may not capture any potential seasonal and spatial variability. While numerous studies have investigated the biomolecular composition of sea ice microalgae from both polar regions (Table 1), to date, no similar overall patterns have been observed for sea ice microalgae. However, given the propensity for sea ice microalgae to seed pelagic blooms, similar differences in key biochemical characteristics may exist for the ice communities from the two regions.

One of the strongest determinants of biomolecular composition is taxonomic composition. Phylogenetically distinct microalgal groups have been shown to vary in their proportional allocation of biomolecules. Diatoms (Orcophyta: Bacillariophyceae), for example, generally have higher lipid and lower carbohydrate content than other microalgal phyla, such as the Chlorophytes and Haptophytes [61]. More specifically, pennate diatoms within the sea ice have been shown to have higher lipid, fatty acid, and carbohydrate content than the centric diatoms from the same community [60]. Similarly, diatoms with a smaller cell volume (such as pennate diatoms) have been shown to have higher carbohydrate content than larger volume diatoms [79]. At the taxonomic level of species, differentiation is more subtle, but nevertheless has been shown [57,60,80,81]. However, by far most knowledge on species-specific biomolecular profiles is derived from single-species

culture studies, providing a poor representation of what may be true for natural mixed communities. It is therefore important that studies on natural communities start to discriminate biomolecular profiles of individual taxa within a community if we are to improve our understanding of taxonomic biomolecular diversity.

Table 1. Compilation of studies that have measured biomolecules in sea ice microalgae in the Arctic and Antarctic.

	Study	Taxa	Location	Latitude, Longitude	Sampling Date	Biomolecules Investigated
Antarctica	An et al., 2013	*Chlamydomonas* sp. ICE-L	Zhongshan Research Station	69° S, 77° E	N/A	Fatty acids
	Cade-Menun & Paytan 2010	*Fragilariopsis curta*, *Fragilariopsis cylindrus*, *Nitzschia subcurvata*, *Phaeocystis Antarctica*, *Thalassiosira weissflogii*, *Dunaliella tertiolecta*, *Synechoccus* sp.	Culture	N/A	N/A	Lipid, protein, carbohydrate
	Gleitz & Kirst 1991	Diatom-dominated mixed community, primarily *Nitzschia* sp., *Chaetoceros* sp., *Navicula* sp., *Corethron* sp., *Rhizosolenia* sp., *Amphiprora* sp., *Dactyliosolen* sp., *Synedropsis* sp., *Tropidoneis* and *Phaeocystis pouchetii*	Weddell Sea	58–63° S, 55–45° W	1988/1989	Lipid, amino acid, carbohydrate
	Mock & Kroon 2002a	*Fragilariopsis curta*, *Navicula gelida var.-antarctica*, *Nitzschia medioconstricta*	Weddell Sea	70°02′ S, 06°00′ W	March–May 1999	Lipid, protein
	Mock & Kroon 2002b	*Fragilariopsis curta*, *Navicula gelida var.-antarctica*, *Nitzschia medioconstricta*	Weddell Sea	70°02′ S, 06°00′ W	March–May 1999	Lipid, protein
	Palmisano & Sullivan 1985	Diatom-dominated mixed community, primarily *Pleurosigma* sp., *Nitzschia stellata*, *Berkeleya* sp., *Amphiprora kuferathii*, *Phaeocystis* sp. and small centrics.	McMurdo Sound	77° S, 166° W	November–December 1983	Lipid, protein, polysaccharide
	Teoh et al., 2004	*Chlamydomonas* sp. and *Navicula* sp.	Windmill Islands	66°17′ S, 110°29′ E	N/A	Lipid, protein, carbohydrate, fatty acids
	Sackett et al., 2013	*Fragilariopsis cylindrus*, *Chaetoceros simplex* and *Pseudo-nitzschia subcurvata*	Southern Ocean and Prydz Bay	66° S, 147° E, 68° S, 73° E	N/A	Lipid, protein, carbohydrate, fatty acids, amino acids
	Xu et al., 2014	*Chlamydomonas* sp. ICE-L	Zhongshan Research Station	69° S, 77° E	N/A	Lipid, fatty acids
Arctic	Lee et al., 2008a	Mixed community dominated by large chain-forming diatoms	Barrow, Alaska	71°20′ N, 156°39′ W	April–June 2003	Lipid, protein, polysaccharide
	Lee et al., 2008b	Mixed community dominated by large chain-forming diatoms	Barrow, Alaska	71°20′ N, 156°39′ W	February–June 2003	Lipid, protein, polysaccharide
	Leu et al., 2006b	*Thalassiosira antarctica* var. *borealis*	Ny-Ålesund, Svalbard	78°55′ N, 11°56′ E	May–June 2004	Fatty acids

Table 1. *Cont.*

Study	Taxa	Location	Latitude, Longitude	Sampling Date	Biomolecules Investigated
Leu et al., 2010	Diatom-dominated mixed community, primarily *Nitzschia frigida*, *Navicula septentrionalis* and *Fragilariopsis cylindrus.*	Ripfjorden, Svalbard	80° N, 22° E	March–July 2007	Fatty acids
Lund-Hansen et al., 2020	Mixed diatom-dominated community. Primarily *Nitzschia frigida*, *Nitzschia longissima* and *Thalassiosira* sp.	Kangerlussuaq West Greenland	66°57′ N, 50°57′ W	March 2016	Fatty acids
Mock & Gradinger 2000	Mixed community dominated by *Nitzschia* sp., *Fragilariopsis* sp. and *Chaetoceros* sp.	Barents Sea	77°10′ N, 34°04′ E	May–June 1997	Lipid, protein, polysaccharides
Pogorzelec et al., 2017	*Nitzschia frigida*, pennate ribbon colonies and *Attheya* sp.	Dease Strait, Nunavut, Canada	69°1′ N, 105°19′ W	March–May 2014	Lipid, protein
Smith et al., 1987	Mixed community	Resolute Passage, Canada	74°41′ N, 95°50′ W	April–June 1985	Lipid, protein, polysaccharides
Smith et al., 1989	Diatom-dominated mixed community, primarily *Nitzschia frigida* and *Nitzschia grunowii*	Central Canadian Arctic	74°40′ N, 94°54′ W	April–May 1985; 1986	Lipid, protein, amino acid, polysaccharide
Smith et al., 1993	Diatom-dominated mixed community	Resolute Passage, Canada	74°41′ N, 95°50′ W	March–June 1989	Lipid
Smith & Herman 1992	Diatom-dominated mixed community	Resolute Passage, Canada	74°41′ N, 95°50′ W	May 1987, May–June 1988	Lipid, protein, polysaccharide
Søreide et al., 2010	Diatom-dominated mixed community	Ripfjorden, Svalbard	80°27′ N, 22°29′ E	March–July 2007	Fatty acids
Torstensson et al., 2013	*Nitzschia lecointei*	Amundsen Sea	N/A	January 2011	Fatty acids
Torstensson et al., 2019	*Nitzschia lecointei*	Amundsen Sea	N/A	N/A	Lipid, protein carbohydrate, fatty acids

3. Measuring Biochemical Composition in Microalgae

Quantification of the biomolecular composition of sea ice microalgae is central to assessing biochemical cycling and carbon transfer through the polar marine food web. Numerous studies have quantified the principal constituents of cells, including lipids, carbohydrates, and proteins in sea ice microalgae, using a variety of methods (Table 2). Chromatography techniques, including High Performance/Thin Layer Chromatography (HPTLC/TLC) and Gas Chromatography (GC), are popular in sea ice microalgal studies because they are accurate, reproducible, sensitive, and rapid methods to separate and measure components within a given sample. The predominant method used in earlier studies of sea ice microalgal nutrition was HPTLC/TLC [56,82–85]; however GC, which is more widely available, is generally favored now [55,86–92]. These methods have both been used to measure proteins, lipids, carbohydrates, and fatty acids (Table 2). A more detailed analysis of fatty acid content (i.e., polyunsaturated (PUFA), monounsaturated (MUFA), and saturated fatty acids (SFA)) is commonly included in sea ice microalgal studies, because fatty acids can be characteristic for specific taxonomic groups and can therefore be used as

trophic markers [87]. Determining the proportion of PUFAs within microalgae is important for the polar food webs, as they are synthesized de novo only by photosynthetic organisms, yet are essential for many primary and secondary consumers [93], playing a key role in successful egg production, hatching and larval development of zooplankton [55,93,94]. Therefore, one of the major advantages of these chromatographic methods is their ability to determine specific fatty acid composition. Another significant advantage of these chromatographic methods is the capacity to measure carbon isotope signatures of individual lipids, specifically those with enhanced ^{13}C values, such as sterols and highly branched isoprenoid alkenes [4,95–97]. The signature of these specific lipids can then be used to determine the biochemical contribution of sea ice algae to the water column [4,5].

Radioisotope labelling is a relatively easy and reliable method to measure lipid, protein, polysaccharides, and amino acid content, and has been used extensively in sea ice microalgal studies [98–101]. However, this method requires biomolecular classes to be extracted prior to analysis [102] and only provides information on the proportion of primary productivity allocated to a particular biomolecular pool, and not absolute concentrations, making it less quantitative than chromatographic methods.

Table 2. Summary of the various analytical techniques that have been used to measure biomolecules (proteins and amino acids, lipids, and fatty acids, carbohydrates, and polysaccharides) in sea ice microalgae, their advantages, and disadvantages.

Method	Biomolecules Investigated	Advantages	Disadvantages	Example Studies with Sea Ice Algae
High Performance/Thin Layer Chromatography (HPTLC/TLC)	Lipid Fatty acid Amino Acid Carbohydrate	Rapid and easy to run multiple samples in parallel. Useful for complex lipids (therefore most marine lipids). Can be used for small quantity of sample.	Reproducibility can be unreliable. Temperature gradients can exist across the plate resulting in partial distillation of the sample. The silica plate is not reusable.	Gleitz & Kirst 1991 Smith et al., 1993 Henderson et al., 1998 Mock & Kroon, 2002a,b
Gas Chromatography (GC)	Lipid Fatty acid Protein Carbohydrate	Highly sensitive Accurate and reproducible. Easy to couple with detection and quantification techniques. Can analyze all biomolecular classes at once. Effective with a very small amount of sample.	Requires sample to be volatile and therefore lipids need to be derivatized into Fatty Acid Methyl Esters (FAMEs).	Nichols et al., 1989 [103] Teoh et al., 2004 Leu et al., 2006a,b; 2007 [104]; 2010 Søreide et al., 2010 An et al., 2013 Xu et al., 2014 Lund-Hansen et al., 2020 Torstensson et al., 2013; 2019
Mass Spectrometry (MS)	Lipid Protein Polysaccharide	Sensitive Accurate and reproducible.	Less sensitive than GC. Requires coupling with another technique, e.g., HPLC or radioisotope labelling	Lee et al., 2008a,b
Radioisotope Labelling	Lipid Protein Amino Acid Polysaccharide	Highly sensitive Accurate and reproducible. Rapid and easy to run multiple samples in parallel.	Requires additional measurements to determine absolute concentrations. Requires extraction of biomolecular classes. Requires correction for quenching. Requires training and precautions due to radioactive materials	McConville et al., 1985 [105] Palmisano & Sullivan 1985 Smith et al., 1987 Palmisano et al., 1988 Smith & Herman 1992 Mock & Gradinger 2000
Fluorescent Dye (BIODIPY 505/515)	Lipid	Rapid Inexpensive Performed in vivo Has lipid specificity, only binding to lipid bodies and chloroplasts and no other cytoplasmic compartments.	Does not stain all microalgae successfully. Can be issues associated with fading (i.e., fluorescence extinction)	Xu et al., 2014

Table 2. *Cont.*

Method	Biomolecules Investigated	Advantages	Disadvantages	Example Studies with Sea Ice Algae
Sulpho-phospho-vanillin (SPV) reaction	Lipid	Rapid High throughput Relatively easy to implement. Relatively cheap Requires a small amount of sample.	Requires a reference standard Color intensity varies between different lipids Requires a two-step reaction	Smith et al., 1989
Lowry and Smith Assays	Protein	Highly sensitive Produces a linear response curve. Low protein-to-protein variation meaning higher accuracy in unknown protein samples. Widely used and well characterized.	Susceptible to interference by some common chemicals present in samples. Time sensitive during analysis. Lowry is more complicated with more steps than the Smith Assay. Destructive to proteins.	Smith et al., 1989 Mock & Kroon 2002a Torstensson et al., 2019
Phenol-Sulfuric Acid Method	Carbohydrate	Rapid Relatively easy to implement. Accurate and reproducible. Widely used and well characterized.	Phenol is a toxic compound posing health risks Non-stoichiometric method, meaning a calibration curve using a series of standards must be generated, limiting the analysis of more complex carbohydrates.	Smith et al., 1989 Torstensson et al., 2019
Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR) Spectroscopy	Lipid Protein Carbohydrate	Can analyze all biomolecular classes at once. Provides intramolecular detail.	Low sensitivity Long duration of analysis.	Cade-Menun & Paytan 2010
FTIR-microspectroscopy	Lipid Fatty acid Protein Amino acid Carbohydrate	Highly sensitive Can be used to analyze single cells giving species-specific results. Nondestructive. Ability to obtain data at multiple wavelengths simultaneously. Can analyze all biomolecular classes at once. Effective with a very small amount of sample.	Small size mounting chamber. Synchrotron light source is not readily available and is expensive.	Sackett et al., 2013 Pogorzelec et al., 2017 Sheehan et al., 2020

Spectroscopic techniques have been broadly used in sea ice microalgal research for determining lipid, protein, and carbohydrate contributions, as they have the advantage of being inexpensive and easy to use. In some cases, it may be necessary to extract the biomolecule prior to spectroscopy, for example, with the Sulpho-phospho-vanillin (SPV) reaction employed to measure lipid content [106]. A potentially easier and more effective way to measure lipid content in vivo is by utilizing fluorescent dyes, such as BODIPY 505/515 [91]. This form of live staining, however, has not been used for determination of protein or carbohydrate content in sea ice microalgae, which are instead routinely measured using the Lowry and Smith assay [85,90,106] and phenol-sulfuric acid method [90,106], respectively. Spectroscopy techniques are limited, however, in that they are unable to determine specific fatty acid contributions. However, with ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy, a quantitative measure of all biomolecules within the sample simultaneously can be obtained, with the added benefit of providing finer detail on the types of lipids, proteins, and carbohydrates present [107]. Due to its low sensitivity however, this technique has not been widely used in sea ice microalgal biochemical studies [107].

As with NMR and GC analyses, Fourier Transform Infrared (FTIR) microspectroscopy is a technique that measures the whole biomolecular profile at once, enabling each sample to be spectrally defined based on a biochemical fingerprint [108]. This spectroscopic approach has the benefits of being sensitive, high throughput, quantitative, and rapid [57,58,108–111]. Coupled with a Synchrotron light source, FTIR microspectroscopy becomes more sensitive and can deliver much higher resolution (~3 μm) spectral imaging [112]. This technique has the significant advantage that it can be performed on individual cells and subcellular

compartments, allowing for unique insight into the response of individual taxa within a natural community. Moreover, with micrometer resolution, it can be used to localize and measure specific organelles within larger cells or tissues. The ability to understand specifically which species within the community is affected by environmental change and in what way is unique to this biomolecular method. In nonpolar marine microalgae, it has been used widely to investigate biomolecular responses to environmental change [108,113–115]. To date however, very few studies have looked at the nutritional value of natural sea ice assemblages at the species level, with only two studies investigating the effects of light on biomolecular composition of Arctic diatoms [59,116] and one describing the biomolecular profiles of four Antarctic sea ice diatoms [60]. Synchrotron-based FTIR-microspectroscopy has been used successfully to investigate changes in biomolecular composition as a result of ocean acidification in Antarctic diatoms [81] and biomolecular changes as a result of iron enrichment in Antarctic microalgae [117]. As the only biochemical method that delivers species-level resolution, it is an attractive technique for resolving questions related to response diversity within natural communities and tracking potential shifts in trophic carbon transfer.

4. Environmental Factors That Influence Bioomolecular Composition

The sea ice environment exposes microorganisms that live within it to strong gradients in temperature, salinity, and light [62,63,118]. From the extreme hypersaline brine channels (salinities up to 145 ppt), freezing temperatures (−2–−20 °C) and high light conditions (>100 μmol m^{-2} s^{-1}) near the ice surface [119], to the relatively mild and stable conditions for the microalgae living at the ice–water interface (temperature: ~1.8 °C; irradiance: 3.5–40 μmol m^{-2} s^{-1}) [12,120]. These steep environmental gradients, which vary over the seasonal formation and decay of the ice, mean that the organisms living and thriving in this habitat have evolved specialized physiological strategies, including biomolecular adjustments, to cope with rapid and extreme changes in their living conditions [63]. It is worth noting that growth rate is also expected to influence biomolecular storage; however, this is not explored further below as it cannot be measured or controlled for within natural community studies.

Temperature: At the ice–water interface, temperature generally remains around −1.8 °C throughout spring, however as sea surface temperatures rise with the onset of ocean warming [50], it is possible that warmer temperatures will alter the biochemical composition of the algae, drive an earlier ice melt, and ultimately inhibit sea ice microalgal growth completely [11,43]. Limited work has been completed on the effects of temperature on the biochemical composition of sea ice algae, but from these few studies some patterns have emerged. Extreme subzero temperatures (−20 °C) have been associated with a decline in fatty acids, especially PUFA content [88]. A decline in fatty acids has been observed also under moderate temperature increases (from −1.8 °C to 3 °C), as well as in temperature increases well beyond the natural range (~15 °C) [86,88–90] (Figure 2A). In several Antarctic sea-ice diatoms, an increase in relative protein content and decrease in carbohydrate content have been observed with exposure to warmer (up to 3 °C) temperatures [90], including temperatures well above (~20 °C) the natural range for sea ice microalgae [86]. These data indicate that optimal temperatures for maximum fatty acid content lies around −1.8 °C, and that increases in temperature will likely see reductions in PUFA and carbohydrate content but increases in protein.

Salinity: Salinity within sea ice follows a steep gradient, from hyper-saline conditions within the brine channels (>70 ppt) to seawater and meltwater (~30 ppt) salinity levels at the ice–water interface. In hypersaline environments, such as sea ice brine channels, lipid and amino acid content have been shown to be higher than at lower salinity (~35 ppt) [57]. On the other hand, decreasing salinity (i.e., 10–20 ppt, compared to ambient levels) have resulted in increased protein [82], amino acid [57], fatty acid [90], and carbohydrate content [90] (Figure 2B). These changes in response to hyposaline conditions provide insight into some of the possible changes to nutritional status of microalgae with increased fresh-

ening from ice melt and glacial runoff. Whilst further research is needed, these results suggest that ongoing ocean freshening [121,122] may lead to a decline in lipid, yet increase in protein and carbohydrate content.

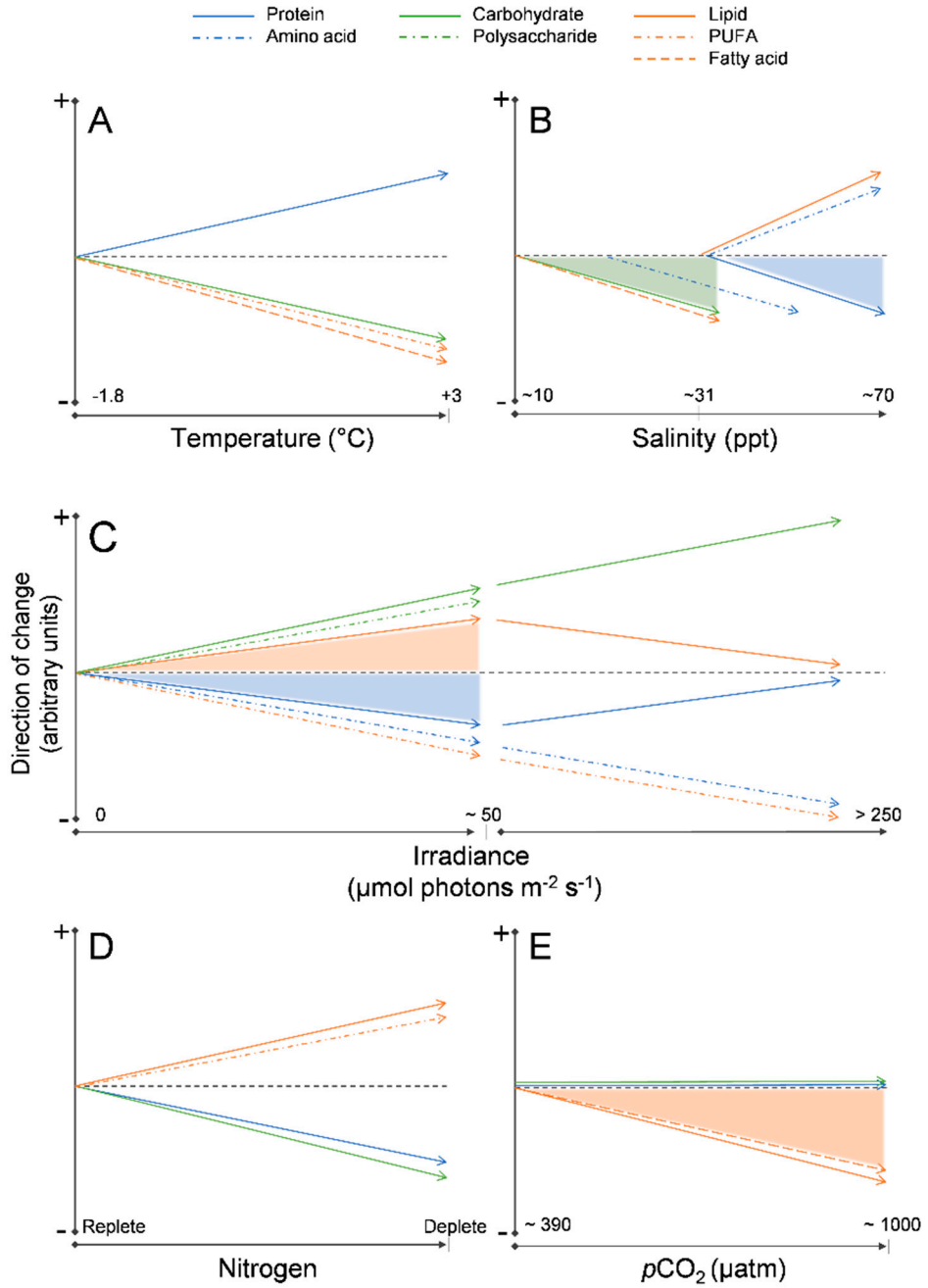

Figure 2. Schematic showing the direction of change (increase or decrease) in biomolecules in sea ice microalgae exposed to variations in (**A**) temperature, (**B**) salinity, (**C**) irradiance, (**D**) nitrogen concentration, and (**E**) pCO_2. Changes are not indicative of magnitude. The different biomolecules are coded by color and line type as described in the legend. Shaded areas indicate where results from studies have revealed both a change and no change with environmental perturbation. Data were obtained from the studies listed in Table 1.

Light: Being photosynthetic organisms, light transmittance is one of the key factors driving sea ice microalgal community productivity and composition [11,12], playing a defining role in the commencement of the spring under ice bloom. It has been shown repeatedly to determine the nutritional quality in sea ice microalgae, although the direction

of change in biomolecular composition varies depending on the magnitude of change in light intensity (Figure 2C). Primarily, a seasonally relevant change in light intensity as a result of low and high snow cover [59,106,116] and through naturally manipulated light levels [123], have been found to increase lipid synthesis over the duration of the spring bloom [19,83,99,100], with one study finding no significant correlation [98]. On the other hand, light intensity beyond the expected natural range (>100 μmol m^{-2} s^{-1}) has been found to cause a decrease in lipid content [82,107] possibly due to photoinhibition limiting photosynthetic energy production and thereby biomolecular synthesis. In contrast to the general overall lipid response, PUFAs have consistently been found to decline with increasing light intensity (Figure 2C). Decline in PUFAs have been observed in natural sea ice microalgal communities with increase in irradiance, with minimal and dense snow cover [56], when exposed to in situ light manipulation [92] and experimentally, using a unialgal culture of *Thalassiosira antarctica* var. *borealis* [124] or when light adjusted sea ice algae are subjected to continuous darkness [91]. In Arctic open water phytoplankton communities, PUFAs have also been observed to decline with increasing light during the spring period [87].

Changes in irradiance have also been shown to influence protein, amino acid, and carbohydrate content (Figure 2C). In mixed microalgae communities, protein and amino acids have generally been found to decrease with increasing light intensity over a realistic spring light range (3.5–40 μmol m^{-2} s^{-1}), largely concomitant with an increase in lipid content [19,98,99,106,123]. Declines in protein have also been observed at light levels exceeding those expected in situ (40–100 μmol m^{-2} s^{-1}; [82]); however, at higher light levels (125–250 μmol m^{-2} s^{-1}), protein allocation has been shown to increase [107]. Importantly however, some studies found no effect on protein and amino acid content in response to increasing irradiance [55,59,100]. For carbohydrates, sea ice microalgae have been shown to increase their allocation of carbon to carbohydrates in response to natural environmental increases in irradiance [106], controlled incubations within the natural light range [55,99] and to higher than naturally expected under-ice light intensities (42–106 μmol m^{-2} s^{-1}, compared with 3–19 μmol m^{-2} s^{-1}; [82]), with only one study finding no significant effect on carbohydrate content as a result of increasing light intensity [19].

Nutrient limitation: Another key factor well known for shaping sea ice microalgal biomolecular composition is nutrient availability. Nutrient limitation can occur within the narrow brine channels, where the microalgae can exhaust some or all of the available nutrients. This may partly explain why some lipids measured in sea ice microalgae are enriched with ^{13}C [24,125]. Nutrient limitation is less of a problem at the ice–water interface, where nutrients are continually replenished from the seawater. However, nitrogen limitation, which is a defining constraint on growth and development [11,126,127] and is expected to intensify with increasing ocean stratification [128,129], commonly leads to increased lipid and decreased protein content in microalgae (e.g., [130–133]). This is because nutrient stress induces the algae to favor energy storage in lieu of growth and photosynthetic efficiency [113,134–136]. These trends have been observed in sea ice microalgae, which were shown to increase in relative lipid [85,101] and PUFA content [85], concomitant with a decline in protein and carbohydrate allocation [85,101] (Figure 2D) with nitrogen limitation. Given that vast expanses of the Arctic are nitrogen poor, it is possible that this low nitrogen environment, which underpins the lipid-rich sea ice microalgae [70,71], is partially responsible for driving an evolutionary dependence on lipids for the successful egg hatching and reproduction of arctic zooplankton [25,137].

pH: With ocean warming, nutrient limitation will likely occur heterogeneously; carbon availability, however, from atmospheric CO_2 uptake by seawater, is increasing ubiquitously. Ocean acidification poses a real and imminent threat to marine life in the polar regions, including microalgae [41,138,139]; however, limited work has been undertaken to understand its effect on sea ice microalgal growth and biochemical composition. To date few studies have compared biochemical composition of sea ice microalgae under current pCO_2 levels (~390 μatm) and those projected for 2100 (~1000 μatm; [140]). Elevated pCO_2

levels (~1000 µatm) over a period of ≥14 days resulted in reduced lipid [91] and fatty acid content [89], whilst shorter exposure (6 days) at the same pCO_2 levels was found to have no significant effect on protein, fatty acid, or carbohydrate content [90], suggesting that length of exposure influences physiological response (Figure 2E). A recent study on Antarctic coastal diatoms found that high pCO_2 levels resulted in a decrease in lipid content for the two largest taxa and an increase in protein content across all five taxa investigated [81]. Although conducted on polar pelagic algae, this study indicates that species-specific responses likely exist within sea ice communities, which has the potential to affect food web dynamics and carbon transfer in polar regions.

5. Sea Ice Microalgae Biochemistry and Carbon Transfer through the Polar Marine Food Web with Climate Change

Climate change has the potential to alter biodiversity and, therefore, ecosystem functioning. Multi-species assemblages are considered more resilient to environmental fluctuations, as the differences in the individuals' phenotypic plasticity and tolerance, as well as the inherent complexity of species interactions, result in greater response diversity within the community. For natural phytoplankton communities, biodiversity has been shown to be important for maintenance of overall ecosystem functioning in variable environments [141], meaning that a reduction in biodiversity may reduce ecosystem productivity and resilience. We know from studies looking at biomolecular profiles of individual sea ice diatoms that there is considerable diversity in cellular carbon allocation between species [58–60]. Similarly, while exploring the role of climate change on biomolecular partitioning, it has been shown that CO_2 enrichment of natural Antarctic diatom communities resulted in species-specific biochemical responses [81]. These studies highlight the potential importance of species richness and response diversity within sea ice microalgal communities for the resilience of the polar ecosystem to climate change. Natural community studies on the nutritional value of sea ice algae have primarily been completed on whole communities, which is valuable in that it can show an overall shift in food quality, but only by investigating individuals within a community, such as with synchrotron-based FTIR microspectroscopy, is it possible to determine the diverse taxon-specific responses, thereby elucidating the strength and direction of change and determining the winners and losers of environmental change.

There are indications that with the ongoing ecosystem changes in the polar regions, microalgal communities will shift toward smaller taxa and no longer be dominated by larger diatoms. This has already been observed in both Arctic and Antarctic communities in response to ocean acidification [142,143], ocean freshening [143–145], reduced sea ice extent [146,147], and sea surface warming [143]. Such a shift is anticipated to have a significant effect on trophic energy transfer, where a community dominated by smaller cells would generally mean a reduction in grazing efficiency by zooplankton [144,148–150]. There is also evidence of climate change altering taxonomic dominance, for example, increased light transmittance has been shown to favor diatoms over flagellates [127], specifically favoring centric rather than pennate diatoms [151]. In under ice and pelagic phytoplankton blooms, nanoflagellate dominance has been observed along with ocean freshening [144,147,152] and post-bloom meltwater conditions [127]. While these shifts in microalgal community composition will be heterogeneous and geographically dependent, any persistent changes or losses in species will invariably have trophic and biogeochemical implications. For example, shifts that favor taxa of poorer nutritional quality, such as species with reduced lipid or protein content, would result in less energy available for transfer through the marine food web. Specifically, a decline in lipid content may alter the growth and reproduction of primary and secondary consumers [25,137,153]. Similarly, environmental conditions that favor one taxonomic group such as a shift toward nanoflagellate dominated communities at the expense of diatoms, may see strong alterations to regional carbon and silicon cycling [61,154,155]. It is clear, therefore, that as communities change or become less complex, we can expect to see altered marine biochemistry and ecosystem functioning.

Geographic variation in climate change effects means that changes to community composition and, therefore, biochemical composition of primary producers at the community level cannot be expected to be uniform. Since the 1970s, Arctic landfast ice regions have seen a much more rapid decline in sea ice extent of 10.5% per decade, compared to 5.2% per decade for Arctic seas [156], and recent studies have revealed similar trends of accelerated landfast ice retreat in Antarctica [157,158]. As such, these coastal areas will likely experience an increased reliance on open water pelagic phytoplankton blooms sooner than perennial multi-year ice regions [159,160]. While we have seen a ~3 month increase in annual sea-ice free period since 1980 at both polar regions, the change is occurring in different ways. In the Arctic, sea ice retreat is occurring on average two months earlier, with the advance one month later, whilst the Antarctic Peninsula is experiencing the average sea ice retreat one month earlier and the advance two months later [161]. With predictions of ice-free periods becoming more prolonged [46,162] we may see increases in total primary production [128,129,160,163]. However, there are concerns that a heavily reduced sea ice season will result in a timing mismatch between the primary producers and the consumers who rely on the earlier sea ice microalgal bloom for reproduction [25,26,164–167]. In addition, for both the Arctic and Antarctic, reduced sea ice production and increased glacial melt has amplified ocean freshening particularly in enclosed fjordic systems [121,122,168], altering phytoplankton community composition [144,146,152]. Taken together, broad changes in sea ice microalgal community structure, phenology, and species-specific carbon allocation, could significantly alter carbon transfer and biochemical characteristics of polar marine ecosystems.

6. Conclusions

Knowledge of sea ice microalgal biochemical composition and understanding the influence of environmental factors on their cellular carbon partitioning is critical to determining the nutritional quality of primary production in polar regions and the broader effects on energy transfer through the marine food web. As light is a primary driver of sea ice microalgae primary productivity, many studies to date have focused on the effect of irradiance on biomolecular composition, with trends indicating that an increase in total irradiance dose would drive an increase in lipid and carbohydrate content but a decrease in PUFA and protein content. Studies have also shown, however, that warmer temperatures will increase protein content, and nitrogen limitation will enhance lipid and PUFA production at the expense of all other biomolecules. Across the environmental effects considered here, changes in response to different environmental factors were not unidirectional, and as such, the overall direction of change likely to occur in the ecosystem under future conditions remains unclear. Further research is therefore recommended to better tease apart discrete and synergistic effects on sea ice microalgal biochemistry. While understanding any degree of change across sea ice microalgal communities is important, biochemical changes appear to have a degree of species specificity, and, therefore, future studies would benefit also from employing methodologies that allow for the determination of species-specific biomolecular characterization. With the accelerated pace of climate change rapidly reshaping the physical and chemical marine environment (warmer temperatures causing reductions in sea ice extent, thickness and longevity, ocean stratification and increasing atmospheric CO_2 concentrations causing seawater acidification), it is anticipated that changes to sea ice microalgal community structure and biochemical composition will ensue. As shown here, these changes will likely alter the allocation of carbon to different biomolecules by sea ice microalgae resulting in significant shifts in biochemical cycling and carbon transfer through polar marine food webs, the effects of which could have far-reaching consequences for polar marine ecosystems.

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