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CHAPTER 17

Dynamics of nutrients, dissolved organic matter and exopolymers in sea ice

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17.1 Introduction

Sea ice is not a static medium. It provides a seasonal to multi-year reservoir for particulates and solutes, and supports various ecosystem processes that cycle nutrients and organic matter, driving polar marine biogeochemistry (Vancoppenolle et al., 2013a). Sea ice consists of a dynamic matrix of pure ice, brine-filled interstices and gas bubbles (Chapter 1). Coupled physical, chemical and biological processes affect the pools as well as the cycling and fate of dissolved nutrients and dissolved organic matter (DOM) in sea ice. In general, initial concentrations of solutes in sea ice are controlled by the composition of the water from which the sea ice forms. Therefore, solutes initially behave conservatively with salinity. Boundary fluxes, both across ice–ocean as well as atmosphere–snow/ice interfaces, additionally affect solute concentrations in sea ice (Nomura et al., 2010; Vancoppenolle et al., 2010; Saenz & Arrigo, 2012; Figure 17.1). Dissolved inorganic and organic nutrient pools are then modified within the ice, and may become depleted or enriched when compared with salinity (Gleitz et al., 1996; Thomas et al., 2010). Upon ice melt, dissolved and particulate nutrients and organic matter are released into the water column where they can impact on pelagic processes, or contribute to particle export (Riebesell et al., 1991; Norman et al., 2011; Boetius et al., 2013; Lannuzel et al., 2013; Niemi et al., 2014).

In contrast to classical concepts of conservative incorporation of dissolved constituents into sea ice, recent research on dissolved organic carbon and so-called exopolymeric substances (EPS) have shown preferential incorporation of these substances into newly forming

sea ice in the field and laboratory (Riedel et al., 2007a; Ewert & Deming, 2011; Müller et al., 2013; Zhou et al., 2014, 2016), and also demonstrated their effect on physical sea ice properties with implications for sea ice biogeochemistry and habitability (Krembs & Deming, 2008; Krembs et al., 2011). In addition, advancing from simple salt rejection and constant diffusive transport theory, new concepts for the exchange of solutes across the ice–ocean interface and solute transport between sea ice layers with different porosity, temperature and brine salinity have been developed. These include new measurements of sea ice permeability thresholds and the application of mushy-layer and thermohaline convection theory (Notz & Worster, 2009; Hunke et al., 2011; Loose et al., 2011). In turn, these new physical concepts have significantly improved and informed emerging sea ice biogeochemical and primary production studies and modelling efforts (Saenz & Arrigo, 2012, 2014; Tedesco & Vichi, 2014; Chapters 14 and 20). A number of recent summary articles have highlighted the importance of sea ice biogeochemistry and ecology for polar marine systems (Loose et al., 2011; Underwood et al., 2013; Vancoppenolle et al., 2013a; Arrigo, 2014; Meier et al., 2014) and also provide recommendations for best-practice sampling methodologies (Eicken & Salganek, 2010; Miller et al., 2015).

Building on these previous reviews, this chapter aims to provide an overview of the current understanding of the sources and sinks of biologically important inorganic and organic solutes in sea ice. Our focus will be on physical, chemical and biological processes that influence the pools of dissolved inorganic macronutrients, the micronutrient iron and DOM in sea ice. In addition, we discuss the dynamics and role of sea ice EPS,

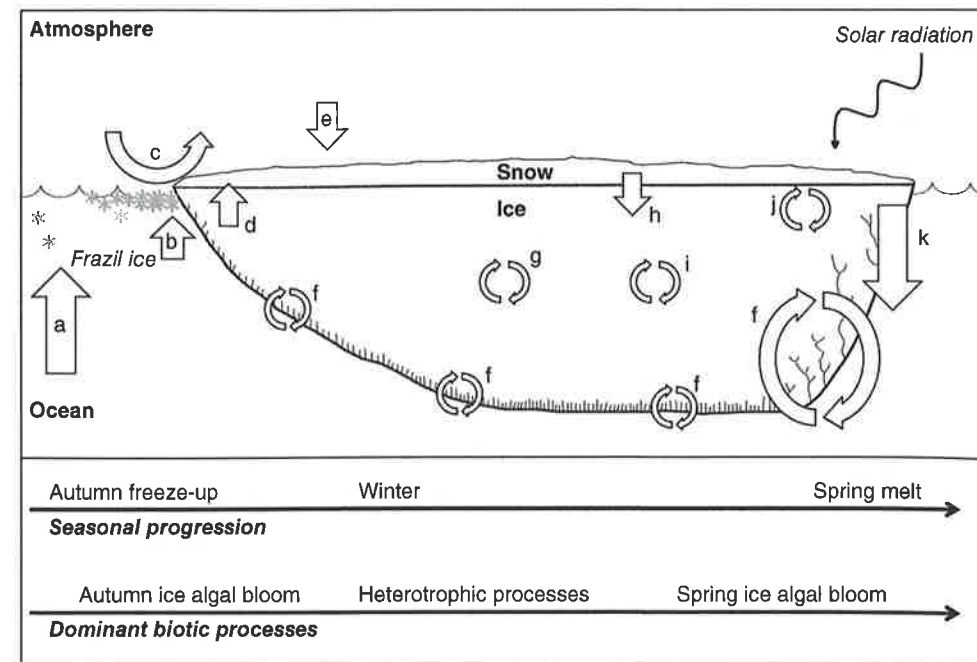


Figure 17.1 Schematic of the sea ice growth, melt cycle and processes affecting dissolved and particulate matter pools in sea ice. a, scavenging of lithogenic and biogenic material by frazil crystals; b, sieving of particulates by newly forming and young sea ice due to wave-field pumping and convection; c, aerosol formation due to wind erosion and outgassing; d, brine expulsion; e, atmospheric deposition; f, brine convection in permeable sea ice layers; g, chemical/physical solubilization of lithogenic/biogenic particulate matter; h, snow ice formation; i, freeze-concentration and coagulation of dissolved organic precursor materials into gels; j, photochemical processes affecting both organic and inorganic solute pools; and k, melt water flushing. For details see text.

including exopolymeric gels and particles. The chapter includes a general overview of processes occurring in Arctic, Antarctic and lower-latitude sea ice. Finally, it provides a brief outlook for sea ice biogeochemical and ecosystem research needs in response to an increasingly altered climate. Current and future changes in sea ice environments (Chapters 10–12) will be accompanied by significant changes to biogeochemical cycles, highlighting the need for an improved understanding of the coupled physical–chemical–biological processes of ice-covered oceans in both hemispheres.

17.2 Definitions and biogeochemical importance of solutes in sea ice

17.2.1 Macronutrients

In marine science, the term ‘macronutrients’ generally refers to the inorganic chemical elements that algae take up in the largest quantities. These include dissolved

inorganic nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), phosphate (PO_4^{3-}) and silicic acid ($\text{Si}(\text{OH})_4$). Bulk concentrations of nutrients in sea ice are generally low when compared with seawater (Vancoppenolle et al., 2013a), and in the absence of biological uptake or remineralization, are proportional to salinity and more or less follow so-called theoretical dilution lines (Figure 17.2). Nutrient concentrations in sea ice may limit ice algal growth at times of high ice algal productivity and/or restricted external input. Observations and modelling studies suggest that ice algal growth in both hemispheres can be limited by nitrate as well as silicic acid (Lavoie et al., 2005; Gradinger, 2009; Saenz & Arrigo, 2014). Silicic acid limitation particularly affects sea ice diatoms, often the dominant taxonomic group in algal communities. Sea ice communities in the brackish northern Baltic Sea have been shown to be phosphate-limited, with total seasonal ice-associated primary production strongly influenced by the nutrient concentration of the water from which the sea ice

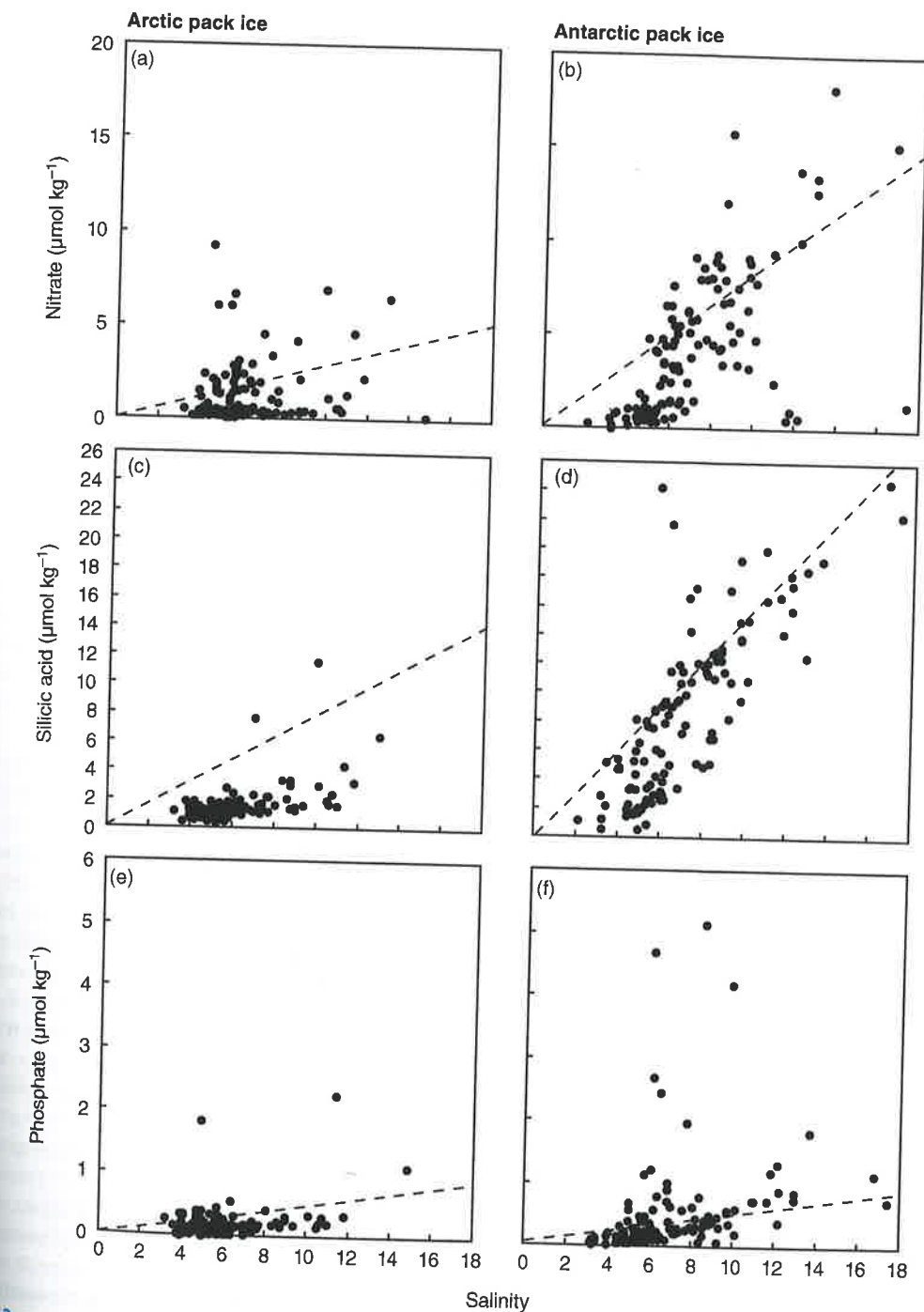


Figure 17.2 Concentrations of dissolved nutrients versus bulk ice salinity in Arctic (a, c, e) and Antarctic (b, d, f) pack ice. Dashed lines (theoretical dilution lines; for details see text) indicate nutrient concentrations to be expected from mean surface water values if the respective nutrient behaved conservatively with salinity. Arctic data are from the Beaufort Sea (Circumpolar Flaw Lead study, March 2007–June 2008, C. Michel, unpubl. data); Antarctic data were collected in September–October 2007 off East Antarctica (Meiners et al., 2011).

formed (Chapter 27). Nutrient limitation affects ice algal physiology and metabolism, impacting carbon, lipid and fatty acid content of cells, with associated effects on the fate of ice algae due to changes in aggregation potential, sinking rates and food quality for herbivores (e.g. Riebesell et al., 1991; Leu et al., 2010).

17.2.2 Dissolved iron

Iron is a key limiting micronutrient controlling phytoplankton production in the ocean, in particular in so-called high-nutrient-low-chlorophyll areas where macronutrients are high but phytoplankton biomass is low due to iron limitation (Boyd et al., 2007). Dissolved iron in Antarctic sea ice can be enriched by one to three orders of magnitude relative to iron-deplete seawater (Lannuzel et al., 2007, 2010; van der Merwe et al., 2011; de Jong et al., 2013), making sea ice an important iron reservoir. The release of this micronutrient during ice melt in spring – in combination with increasing light levels and surface ocean meltwater stratification – is thought to contribute to the development of Antarctic ice-edge blooms. While initial studies focused on the atmospheric supply of iron, i.e. by snow deposition (Edwards & Sedwick, 2001), more recent research has shown that marine iron sources are more important (Lannuzel et al., 2007, 2010; van der Merwe et al., 2009; de Jong et al., 2013).

Studies from the northern hemisphere have reported high dissolved iron concentrations in sea ice in the Bering Sea as well as in the Sea of Okhotsk, where iron released from melting sea ice may also significantly contribute to phytoplankton production (Aguilar-Islas et al., 2008; Tovar-Sánchez et al., 2010; Kanna et al., 2014). Iron is released from melting sea ice together with organic ligands, which may affect its residence time and bioavailability in the water column (van der Merwe et al., 2009). Although sea ice algae generally show large cell sizes (Arrigo et al., 2010), indicating a high iron demand (Sunda & Huntsman, 1995), ice algal communities are generally not considered to be iron-limited due to overall high dissolved iron concentrations within the sea ice brine channel network (Pankowski & McMinin, 2008; Lannuzel et al., 2014).

17.2.3 Dissolved organic matter

Dissolved organic matter is a diverse pool of complex organic compounds that is defined to be smaller than 0.2 μm . In practice, DOM is often operationally defined

as material that passes through glass-fibre filters with a nominal pore size of 0.7 μm (Thomas et al., 2010). Sea ice DOM pools consist of carbohydrates, amino acids as well as more complex substances such as humic acids. Sea ice DOM can also contain high levels of dissolved organosulphur compounds, including the climate-relevant dimethylsulphoniopropionate (Chapter 18). DOM remains poorly characterized at the molecular level and can range in size from monomers to large polymers. Molecular size can be indicative of the bioavailability of compounds and DOM is often grouped into biolabile and refractory fractions. Sea ice DOM includes material that has been produced *in situ* through biological release from organisms living in sea ice (autochthonous; Underwood et al., 2010; Aslam et al., 2012a) as well as material trapped during sea ice formation (allochthonous; Stedmon et al., 2007). The former can be orders of magnitude higher than the latter and can reach concentrations of up to 2.5 mmol L^{-1} (Thomas et al., 2001; Riedel et al., 2008). Understanding the incorporation of DOM into sea ice, as well as its fate, is an active area of research and current studies indicate that some DOM can be enriched into newly forming sea ice relative to salinity (Müller et al., 2011, 2013; Zhou et al., 2014, 2016).

Dissolved organic matter is most commonly measured as dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) (Thomas et al., 2010). Sea ice DOC concentrations are generally enriched when compared with the seawater from which the ice has formed (Figure 17.3). In Antarctic sea ice, DOC and DON concentrations are generally correlated, although DOC/DON ratios are both relatively high and highly variable (Thomas et al., 2001; Norman et al., 2011). Even higher DOC/DON ratios, increasing with total DOC concentration, have been reported from Arctic sea ice (Thomas et al., 2001, 2010) and are probably a result of DOC-rich riverine supply. The high carbon content of sea ice DOM has also been attributed to high concentrations of biologically produced sea ice carbohydrates, which may be a result of high concentrations of sea ice EPS (Underwood et al., 2010, 2013). Recent experimental results show that the release of sea ice DOM at the time of ice melt can stimulate prokaryotic activity in surface water microbial communities (Niemi et al., 2014). Importantly, DOM can be chromophoric, and so-called coloured DOM (CDOM) absorbs light at the ultraviolet radiation (UVR) and photosynthetically active radiation

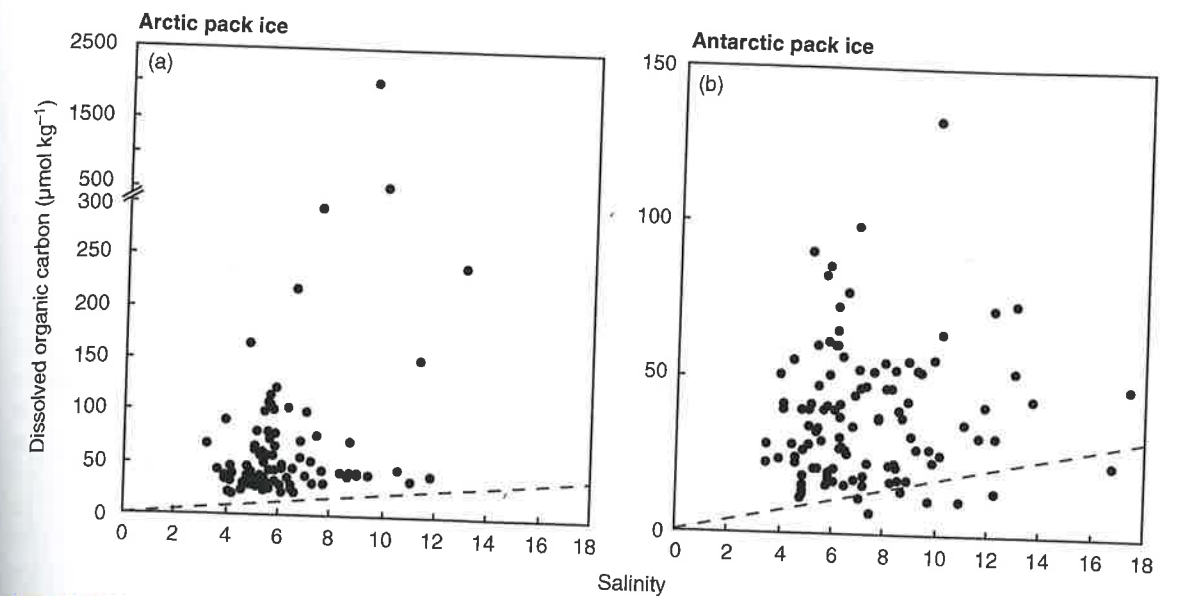


Figure 17.3 Concentrations of dissolved organic carbon (DOC) versus bulk ice salinity in Arctic (a) and Antarctic pack ice (b). Dashed lines (theoretical dilution lines; for details see text) indicate concentrations to be expected from mean surface water values if DOC behaved conservatively with salinity. Note the different y-axes and axis break. Arctic data are from the Beaufort Sea (Circumpolar Flaw Lead study, March 2007–June 2008, C. Michel, unpubl. data); Antarctic data were collected off East Antarctica (Norman et al., 2011).

(PAR) wavelength bands, therefore affecting the energy budget of sea ice as well as the exposure of ice-associated organism to UVR and PAR (Belzile et al., 2000; Uusikivi et al., 2010).

Upon ice melt, Antarctic sea ice-derived CDOM has been suggested to affect the optical properties and phytoplankton production of surface waters via UV protection and attenuation of visible light (Norman et al., 2011). This effect might be somewhat reduced in the Arctic Ocean, due to already high DOM concentrations in surface waters from riverine sources. There is growing evidence that sea ice CDOM is strongly affected by photochemical processes, and this may be particularly true in the surface layers of sea ice floes exposed to high irradiances (Uusikivi et al., 2010; Beine et al., 2012). Photochemical degradation of DOM can lead to direct remineralization of DOM to CO and CO₂, but also to the formation of biolabile organic compounds that can fuel sea ice microbial food webs (Thomas et al., 2010; Norman et al., 2011). DOM cycling in sea ice needs to be considered as a function of physico-chemical, in particular photochemical, and microbial processes acting in parallel.

17.2.4 Exopolymeric substances

Marine and ice-associated microbial EPS exist in a dynamic equilibrium and along a size continuum from dissolved polysaccharides to complex gel-like and particulate EPS (retained on 0.2–0.4 μm filters) that can form aggregates at the millimetre to centimetre scale (Krembs et al., 2011; Underwood et al., 2013). EPS are produced by algae and bacteria and can differ widely in chemical composition and structure (Aslam et al., 2016). However, in general, EPS are rich in carbohydrates, resulting in a high carbon:nitrogen ratio of the material. Exopolymers are characterized by polysaccharides that have carbon backbones of high molecular weight, typically carrying carboxylic acid groups such as uronic acids, which give EPS a predominantly poly-anionic nature. Exopolymeric gels can self-assemble from dissolved precursors and the process is facilitated by divalent cations like calcium and magnesium ions that can cross-link negatively charged groups (Verdugo, 2012).

Exopolymeric substances can also contain other chemical substances, including sulphates, lipids, proteins and nucleic acids that may strongly affect sea ice EPS chemical properties (Mancuso Nichols et al., 2005;

Ewert & Deming, 2011). The use of different analytical methods to quantify EPS in sea ice makes comparisons difficult, but they coherently indicate that EPS contribute a significant fraction to sea ice carbon pools in both the Arctic and Antarctica (Meiners et al., 2003, 2004; Riedel et al., 2006; Collins et al., 2008). Moreover, recent evidence of a consistent contribution of uronic acids to dissolved EPS across a variety of ice types, seasons and locations in both hemispheres points to broad-scale predictability of carbohydrates in sea ice (Underwood et al., 2013).

Exopolymeric substances play multiple ecological roles in serving marine bacteria and diatoms in adhesion to surfaces, locomotion, supporting sequestration of dissolved nutrients and providing a protective buffer against unfavourable environmental changes such as shifts in ionic, osmotic, pH, desiccation and toxic-metal conditions. In sea ice, EPS may serve particularly as protectant against hyper- and hypo-osmotic conditions as well as against mechanical damage from growing ice crystals (Krembs & Deming, 2008).

The stickiness of EPS affects incorporation of organisms into newly forming sea ice and also their retention within the sea ice during ice melt, thereby affecting cryopelagic coupling processes (Meiners et al., 2003; Riedel et al., 2006; Juhl et al., 2011). Krembs et al. (2011) highlighted the role of EPS in altering physical properties of sea ice. These authors showed that high concentrations of EPS affect sea ice bulk salinity and sea ice brine pocket complexity by EPS-clogging of brine channel micropores, reducing brine drainage (Figure 17.4). This increases sea ice habitable pore space, and the EPS coatings also maintain an aqueous environment around cells that may facilitate retention of excrete compounds, including extracellular enzymes and ice-binding proteins (Ewert & Deming, 2013). The overall result of EPS enrichment is a sea ice structure and brine channel environment that is more favourable for microbial communities. Information on the fate of sea ice EPS remains poor, although particulate EPS in sea ice can be considered as a hotspot for biogeochemical cycling, e.g. by harbouring high numbers of bacteria that may contribute to its degradation and by serving as a carbon source for heterotrophic protists (Meiners et al., 2004, 2008; Riedel et al., 2007b).

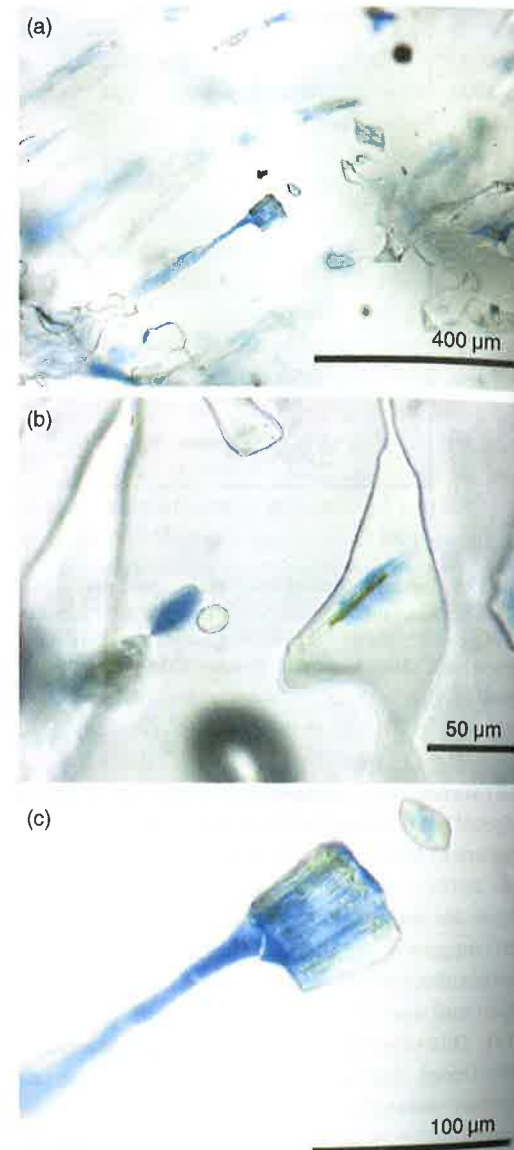


Figure 17.4 Photomicrographs of sea ice thin sections containing biological material. Images show sea ice pore structure (a), sea ice diatoms (a–c) and exopolymeric gels (stained with Alcian Blue). Note the plug-like exopolymeric substance matrix (darker blue colours) in (c). Source: Images provided by G. Krembs. Image (c) from Krembs et al., 2011. [Reproduced with permission from the Proceedings of the National Academy of Science (USA)].

17.3 Physical sources and sinks

17.3.1 Incorporation and exchange of dissolved solutes

Salt and inorganic solute concentrations in sea ice are generally much lower than in the seawater from which the ice has formed. Salts and solutes are mainly rejected from ice crystals and therefore become concentrated in interstitial brines. A notable exception is NH_4^+ which can be trapped within ice crystals during freezing (Weeks, 2010) and/or can also be biologically produced in newly formed sea ice (Riedel et al., 2007a). Neglecting gas inclusions and precipitation of some salts, sea ice remains a mixture of solid ice and liquid salty brines during all stages of growth and melt. Assuming equilibrium conditions, brine salinity is a function of ice temperature and brine volume is a function of temperature and sea ice bulk salinity (Chapter 1). The brine volume of sea ice controls its permeability, i.e. its ability for fluid transport (Golden et al., 1998). Above a brine volume fraction of 0.05 ($\text{volume}_{\text{brine}}/\text{volume}_{\text{ice}}$), brine pockets coalesce and form brine channels and sea ice with a columnar structure, i.e. ice formed by congelation growth, becomes permeable for fluid transport. The ~0.05 brine volume fraction corresponds to a bulk ice salinity of 5 and temperature of -5°C ('the rule of fives'; Golden et al., 1998). It has been suggested that the permeability of granular ice, formed by frazil ice accumulation, may be smaller than the permeability of columnar ice at a given porosity (Golden et al., 1998; Saenz & Arrigo, 2012). This can be explained by a more random, less aligned distribution of brine pockets and channels in granular sea ice (Chapter 1).

Classically five processes have been suggested to contribute to salt and solute release from the sea ice cover: initial solute rejection at the ice–water freezing interface; diffusion of solutes; brine expulsion; gravity drainage; and flushing (Notz & Worster, 2009; Hunke et al., 2011). New laboratory experiments and field research in conjunction with improved understanding of the multi-phase behaviour of sea ice through application of mushy layer theory (Feltham et al., 2006; Notz & Worster, 2009; Loose et al., 2011) have now identified gravity drainage and flushing by meltwater as the key drivers of salt loss (Notz & Worster, 2009; Hunke et al.,

2011) and these must therefore also be recognized as the major physical processes controlling macronutrients in sea ice.

Gravity drainage results from atmospheric cooling of sea ice. The temperature decrease towards the ice surface increases brine salinity, leading to an unstable density gradient in brine columns, which causes convective overturning in connected brine channels and, ultimately, the release of high saline brine from permeable sea ice layers into the water column. The lost brine is replaced by less saline and generally nutrient-replete seawater. This resupply of nutrients is considered to be important for high algal accumulation in sea ice bottom and interior layers during spring when the sea ice warms and permeability increases, and also during autumn when surface cooling destabilizes brine stratification in an existing and generally porous sea ice cover allowing convective overturning. Convective resupply of iron has been hypothesized to transport dissolved iron into the bottom layers of sea ice where it is enriched into the particulate fraction due to ice algal uptake, i.e. bioaccumulation (van der Merwe et al., 2009). Vancoppenolle et al. (2010) have captured these processes in detail in a model combining brine convection and silicic acid uptake by an ice algal community.

Forced convection, i.e. convection induced by under-ice currents, may additionally enhance transport of nutrients into the ice and may be a key driver of high biomass accumulations observed in many landfast ice regimes open to coastal currents and tidal influence (Cota et al., 1987; Lavoie et al., 2005; Vancoppenolle et al., 2013a). Overturning convection of sea ice brines throughout the entire ice column can also be the result of the refreezing of so-called surface slush layers (Vancoppenolle et al., 2010; Saenz & Arrigo, 2012). These layers are a significant and widespread feature of Antarctic sea ice and originate from submersion of the snow–ice interface due to snow-loading or result from melting of near-surface sea ice due to warmer summertime surface temperatures, amongst other processes (Ackley et al., 2008). Surface slush layers can be enriched in nutrients supplied from seawater, and these nutrients can be supplied to sea ice interior layers by convection induced by refreezing. In contrast, surface

melting of snow, slush and ice results in the flushing out of nutrients due to meltwater percolation through the sea ice. The percolation of freshwater through the sea ice results in a loss of solute-rich brine and is primarily observed during advanced melt stages, i.e. in highly permeable sea ice (Petrich & Eicken, 2010; Chapter 1). Surface melt is a key feature of Arctic sea ice, where melt ponds can cover a significant area of the ice surface (Polashenski et al., 2012).

While nutrients trapped into the ice during formation provide an initial pool, brine convection controlled by sea ice porosity and brine density gradients is important in providing new, i.e. non-recycled, nutrients to sea ice microbial communities. The capacity of sea ice layers for gravity drainage can be quantified in a mushy-layer Rayleigh number which expresses the ratio between negative buoyancy in brines and dissipation (Vancoppenolle et al., 2013b). This concept can be applied to determine convectively active regions in the sea ice cover (Vancoppenolle et al., 2013b; Zhou et al., 2013, 2014, 2016).

17.3.2 Enrichment of solutes in newly forming sea ice

A small number of studies have observed enrichment of inorganic solutes into new sea ice formed from natural seawater, with non-conservative enrichment of specific trace metals as well as macronutrients (Granskog et al., 2004; Zhou et al., 2014, 2016). This enrichment may be attributed to biogeochemical processes that do not completely stop during ice formation as well as undefined physico-chemical processes. Various mechanisms for iron enrichment in sea ice have since been discussed. They are dependent on the mode and timing of ice formation, ice cover duration and sea ice carbon content and ice algal biomass (van der Merwe et al., 2009, 2011; Lannuzel et al., 2010; de Jong et al., 2013).

Several studies have shown that DOM and EPS can be enriched in newly forming artificial and natural sea ice, and suggest that incorporation is related to physico-chemical processes (Giannelli et al., 2001; Riedel et al., 2007a; Ewert & Deming, 2011). Recent field and laboratory evidence show that freezing can modify the quality of DOM. Examples of such are an enrichment of chromo- and fluorophoric DOM and changes in the size distribution of EPS and DOM (Aslam et al., 2012b; Müller et al. 2011, 2013). Ewert and Deming (2011) demonstrated that EPS produced by the

cold-adapted marine gammaproteobacterium, *Colwellia psychrerythraea*, a species found in cold sea water and sea ice, is enriched in sea ice produced experimentally. The retention of the *Colwellia*-produced EPS was attributed to a heat-labile fraction, suggesting that the responsible component is a protein with ice-affinity properties. Antarctic sea ice bacterial EPS has been shown to contain a high fraction of protein (Mancuso Nichols et al., 2005). So-called ice binding proteins that attach to and change the structure of ice crystals are produced by sea ice bacteria as well as sea ice diatoms (Janech et al., 2006; Raymond et al., 2007).

In addition to the direct binding of molecules to ice crystals, other processes for selective retention of organic solutes in sea ice have been suggested. These include coagulation of DOM, facilitated by increased cation and dissolved precursor concentrations in brines. Spontaneous self-assembly and coagulation of gels has been reported from marine environments and is influenced by cation concentrations (e.g. Verdugo, 2012), but – to the best of our knowledge – has not yet been observed in sea ice. Orellana et al. (2011) demonstrated that in the high Arctic, marine gels (<1 µm in diameter) have unique physico-chemical characteristics that originate in the organic material produced by ice algae and ice-associated surface plankton. The polymers in this dissolved organic pool assembled faster and with higher micro-gel yields than at lower latitudes. After initial coagulation of DOM, small colloids and aggregates may further serve as sites for selective binding of additional DOM through hydrogen and ionic bonds (Verdugo, 2012; Müller et al., 2013).

In summary, the mechanisms for non-conservative uptake of biogeochemically active solutes into sea ice remain largely unresolved. They must be considered as a result of complex interactions of biological activity, brine dynamics and physico-chemical processes affecting constituents in solution and at ice crystal interfaces. Quantitatively and qualitatively differential solute loading of parent sea waters with DOC and nutrients is expected to influence bulk concentrations of these constituents in young sea ice, both along onshore-offshore gradients in the Arctic and, in particular, in between hemispheres. As a result, there could be distinct biogeochemical cycling of matter in Arctic and Antarctic sea ice, but comparative studies remain scarce (Underwood et al., 2013; Fripiat et al., 2014a; Zhou et al., 2014, 2016).

17.3.3 Dissolution of particulate precursors

Particulates including biogenic (algae and detritus) and lithogenic material can be incorporated into sea ice through various processes, including nucleation where marine particles serve as ice-condensation nuclei; scavenging of particles, also referred to as suspension freezing, by frazil ice crystals rising through the water column; and sieving of particle-containing seawater through layers of newly forming or established sea ice, trapping particles into the sea ice matrix (Ackley & Sullivan, 1994; Spindler, 1994; Gradinger & Ikävalko, 1998). Once embedded in the sea ice, particulate matter is exposed to high salinities as well as mechanical stress through ice crystal growth, potentially enhancing particle solubilization. Incorporation of algal material from autumn blooms into sea ice and entrainment of resuspended sediments are therefore considered to affect not only the particulate but also the dissolved nutrient loading of sea ice. These processes are considered to be particularly relevant for particulate and dissolved iron accumulation in Antarctic landfast ice (Grotti et al., 2005; de Jong et al., 2013) and are also important in offshore pack ice (Lannuzel et al., 2010).

High concentrations of dissolved macronutrients [NO_2^- , PO_4^{3-} , $\text{Si}(\text{OH})_4$] have been reported in association with organic-rich sediment layers from sea ice in the Sea of Okhotsk, indicating strong remineralization of particulate matter in association with 'turbid' sea ice (Nomura et al., 2010). The layers were depleted in NO_3^- , suggesting that they may also serve as sites for denitrification (Nomura et al., 2010). The understanding of the mechanisms and quantitative importance of remineralization processes of allochthonous particulate material in sea ice remains poor. However, the widespread occurrence of sediment inclusions in Arctic sea ice (Eicken et al., 2000) may significantly affect the spatiotemporal distribution and cycling of dissolved macronutrients and trace metals in the Arctic Ocean (Measures, 1999). Due to low sediment loading of Antarctic sea ice (Chapter 1), the process is assumed to be less important in Southern Ocean environments. There, the generally dynamic conditions during sea ice formation result in a large contribution of frazil ice to Antarctic sea ice (Chapter 1), indicating a high potential for scavenging of biogenic particles and ice-associated remineralization (e.g. Lannuzel et al., 2010).

17.3.4 Sea ice surface processes and atmospheric deposition

Frost flowers, due to their unique growth process and chemical composition, provide an important link in the ocean-ice-atmosphere system in polar regions (Bowman & Deming, 2010; Douglas et al., 2012). Brine expulsion can transport highly saline brine to the sea ice surface, where expelled brines may contribute to the formation of frost flowers, i.e. vapour-deposited crystals that wick brines from the sea ice surface. Precipitation of snow results in the wicking of brine into surface snow layers, resulting in so-called brine-wetted snow. Incorporation of brine EPS and other solutes into frost flowers and brine-wetted snow has been reported from laboratory experiments and Arctic first-year sea ice (Bowman & Deming, 2010; Aslam et al., 2012b; Ewert et al., 2013). Material enriched in frost flowers and snow can be transported into the atmosphere by wind (Shaw et al., 2010). This part of the 'marine' aerosol pool may then affect atmospheric chemistry and cloud properties or, after redistribution, be again deposited into sea ice or open water surface layers (Alvarez-Aviles et al., 2008; Bowman & Deming, 2010; Orellana et al., 2011).

The deposition of atmospheric aerosols can also provide a nutrient source to sea ice. Granskog et al. (2003) found that nitrogen-rich snow metamorphosing into snow-ice provides an important nitrogen pool in Baltic Sea ice. High nitrate and ammonium concentrations have also been reported in snow ice in the Sea of Okhotsk (Nomura et al., 2010).

In the Southern Ocean, deposition of aerosol iron can contribute to the trace metal load of pack ice (Edwards & Sedwick, 2001), although marine sources are considered to be more important for the total (vertically integrated) iron content of Antarctic pack ice (Lannuzel et al., 2007, 2010). Studies on Antarctic landfast sea ice indicate that deposition of iron-rich dust from ice-free regions can be an important source to the particulate iron load of coastal sea ice (e.g. de Jong et al., 2013). Importantly, and as a function of geographic location, atmosphere-derived nutrients accumulate in sea ice during its entire growth season and can be redistributed through wind events or sea ice drift, but are generally released to the water column during a relatively short melt period in a localized area. This collation of material over time and space, followed by a more focused release, constitutes a sea ice 'funnelling' effect. Iron released from sea ice in this way has been suggested to

be an important driver of productivity in the Antarctic marginal ice zone (Lancelot et al., 2009).

17.4 Chemical sources and sinks

High and variable concentrations of solutes in sea ice brines provide a dynamic environment for chemical processes. Concentrations are controlled by freeze-concentration and melting cycles over a range of temporal and spatial scales. Chemical processes within the brine-filled interstices, including photochemical processes, constitute key drivers in sea ice nutrient and organic matter cycling (Thomas et al., 2010). Chemical reactions associated with the polycrystalline ice matrix, i.e. occurring on ice grain surfaces and in veins, nodes and pre-melted layers, may also impact bulk concentrations of biogeochemical solutes, but are not the focus of this chapter. For more details on ice microphysics and their impacts on chemical processes in environmental ice, we refer to the recent reviews by Wettlaufer (2010) and McNeill et al. (2012) (and citations therein).

17.4.1 Effects of freeze-concentration and salt precipitation

Hyper-saline brines generated during the freezing of seawater undergo changes with respect to their mineral-liquid thermodynamic equilibrium and are conducive to sequential mineral precipitation (Marion, 2001), e.g. calcium carbonate as ikaite (Papadimitriou et al., 2007, 2012; Dieckmann et al., 2008). The freezing process also leads to changes in ion concentration and composition and increases encounter rates of molecules. In the absence of biology, sea ice brine pH evolution is considered to be primarily controlled by the carbonate system, i.e. the brine CO_2 concentration, which in turn is affected by freeze concentration, outgassing, ikaite precipitation and brine drainage (Miller et al., 2011; Papadimitriou et al., 2012; Rysgaard et al., 2013). Direct measurements of the pH of sea ice are scarce, but indicate strong positive and negative deviations from seawater values due to combined abiotic (as discussed earlier) as well as biotic processes (photosynthesis, respiration), which are influenced by the age of the ice as well as the vertical position of microhabitats within the ice cover (Gleitz et al., 1995; Hare et al., 2013). While only limited information is available for sea ice, pH changes have been shown to strongly influence marine

biogeochemical processes in various ways, including effects on micro- and macronutrient availability and algal physiology (Shi et al., 2009; McMinn et al., 2014).

Changes in pH as well as the concentrations of cations affect the solubility of DOM and EPS and phase transitions among the dissolved, colloidal or particulate phases (Verdugo, 2012; Ewert & Deming, 2013). The extent to which reversible gel self-assembly might occur in sea ice brine channels, where precursor concentrations are high and pH and cation concentrations are conducive to self-coagulation, has not yet been studied. An initial study on natural ice cores kept frozen for several months indicated limited self-assembly (Krembs et al., 2002), but both Arctic and Antarctic sea ice harbour high concentrations of EPS aggregates with diameters $> 2 \mu\text{m}$, suggesting the potential for chemically driven changes in the hydration phases of micro-gels and EPS aggregation in addition to biological production. The closely linked changes in brine temperature, salinity and volume are therefore expected to have both direct and indirect effects on the composition and fractionation of organic matter pools in sea ice (Meiners et al., 2003; Ewert & Deming, 2013). As DOM pools also include chelating agents that influence the bioavailability of metals, in particular iron, freezing as well as dilution of brines may additionally affect micronutrient availability in sea ice and, during ice melt, in ice-associated surface waters.

17.4.2 Photochemical degradation processes

Photochemical transformation of dissolved organic and inorganic matter, driven in particular by high-energy radiation in the UVR and blue wavelength ranges, can degrade sea ice dissolved matter and lead to the formation of reactive products, such as radicals (Thomas et al., 2010; Norman et al., 2011). Photodegradation of DOM can produce labile nitrogen, mainly ammonium (photoammonification), as well as phosphate, which may contribute to biological production in marine environments (Stedmon et al., 2007, 2011; Xie et al., 2012). Significant photochemical production of carbon monoxide and carbon dioxide from DOM has been observed in Arctic first-year sea ice (Xie & Gosselin, 2005) and OH^\cdot radical production due to oxidation of hydrogen peroxide (H_2O_2) and nitrate has been reported in Antarctic sea ice (King et al., 2005).

Increased absorption in the UVR wavelength range of EPS associated with bacterial communities in the surface

layer of Arctic winter sea ice suggests that EPS may also be susceptible to photochemical processes (Ewert & Deming, 2013). High concentrations of DOM that strongly absorb UV radiation have been reported from Arctic, Antarctic and Baltic sea ice (Belzile et al., 2000; Uusikivi et al., 2010; Norman et al., 2011), indicating that significant photo-oxidation of the material may occur. High concentrations of CDOM in sea ice surface layers can also significantly modulate UVR exposure of ice algal communities and under-ice phytoplankton. As both sea ice and snow effectively attenuate UVR and PAR, photochemical processes most likely occur in sea ice layers exposed to high and increasing irradiance levels, e.g. surface ice layers with thin and melting snow covers during spring. Other factors influencing photochemical reactions in sea ice include ambient precursor concentrations and composition (e.g., DON:DOC ratios) as well as environmental controls such as pH, iron and oxygen concentrations, as discussed earlier (e.g. Xie et al., 2012).

Improved understanding of the photochemical processes affecting CDOM pools in sea ice is tightly linked to gaining a better knowledge of CDOM quality, in particular its molecular composition. The recent application of DOM fluorescence spectroscopy to sea ice environments has proven a powerful tool for quantifying different sea ice DOM fractions and characterizing their individual dynamics (Stedmon et al., 2011; Müller et al., 2011, 2013). The combination of classical DOC and DON measurements via combustion and chemical analysis, CDOM absorption measurements and fluorescence spectroscopy may provide a way forward to tease out the complex interplay of physical, chemical and biological sources and sinks of DOM and CDOM in sea ice habitats. Time-series experiments as well as spatial studies are needed to characterize the behaviour of DOM and CDOM during the seasonal ageing of sea ice and to characterize different DOM sources, e.g., riverine versus open ocean, and their impact on organic matter cycling in sea ice.

17.5 Biological cycling of nutrients, dissolved carbon and EPS

Sea ice communities consist of organisms that use different energy sources and comprise multiple trophic levels, including chemoautotrophic bacteria and archaea;

photosynthetic bacteria and algae; and heterotrophic bacteria, archaea, protists, fungi and metazoans, which are all involved in the biogeochemical cycling of nutrients, dissolved organic carbon and EPS (Thomas & Dieckmann, 2010; Chapters 13–16). Major biological processes in the cycling of matter between the dissolved and particulate phase include nutrient uptake by algae and bacteria, excretion of intracellular compounds and extracellular remineralization of particulate or DOM through release of exoenzymes. Complete remineralization of organic compounds is frequently mediated by several organisms or bacterial groups with different metabolic pathways, often requiring diverse environmental conditions, such as aerobic and anaerobic micro-zones, for existence and growth (Rysgaard & Glud, 2004; Ewert & Deming, 2013; Fripiat et al., 2014a).

17.5.1 The role of bacteria

The elemental composition of substrates that bacteria grow on differs from that of bacterial biomass, so heterotrophic bacteria need the capacity to both take up and release inorganic nutrients in order to maintain steady-state elemental composition. The critical role of heterotrophic bacteria in sea ice environments is considered to be recycling, i.e. providing a biological source of inorganic nutrients through remineralization of organic matter (Riedel et al., 2007b). For example, high accumulations of PO_4^{3-} in older sea ice have been linked to bacterial remineralization (Thomas et al., 2010). Remineralization rates of silicate in sea ice are generally believed to be slow due to low temperatures (Thomas et al., 2010), although recent evidence of high silica dissolution:production ratios (range 0.4–0.9) from Si isotope measurements in Arctic and Antarctic sea ice suggests otherwise (Fripiat et al., 2014b).

High bacterial biomass and respiration rates occurring in the semi-confined sea ice environment may result in the development of anaerobic micro-zones (Rysgaard & Glud, 2004; Glud et al., 2014). These conditions are favourable for nitrogen cycling through NO_3^- to NO_2^- reduction and potential further reduction to N_2 (denitrification), as well as anaerobic ammonium oxidation (anammox). Bacterial groups involved in these processes have been identified in Antarctic sea ice (Staley & Gosink, 1999), and denitrification, i.e. significant losses of fixed nitrogen through production of molecular nitrogen (N_2), has been suggested for both

polar and temperate regions (Rysgaard et al., 2008; Arrigo et al., 2014; Chapter 27).

Using a stable isotope approach, Fripiat et al. (2014a) suggest that nitrification, an aerobic process, may provide an important source of oxidized nitrogen (NO_3^-) for primary production in Antarctic pack ice. The first step of nitrification, e.g. NH_4^+ to NO_2^- oxidation, has been measured in Antarctic fast ice (Priscu et al., 1990), and nitrification has also been inferred from significant NO_2^- accumulations in sea ice (e.g. Arrigo et al., 1995). This indicates that some of the NO_3^- , generally assumed a 'new' nutrient, may in fact be a 'regenerated' nutrient in sea ice (Fripiat et al., 2014a). In summary, there is now strong evidence for complex nitrogen cycling in sea ice including N assimilation, N remineralization, denitrification and nitrification (Rysgaard & Glud, 2004). However, the relative importance of these processes, their spatial distribution across sea ice micro-zones, as well as their seasonal patterns still remain poorly constrained (Rysgaard et al., 2008; Fripiat et al., 2014a).

Bacterial uptake of DOM produced by ice algae is a key process in sea ice microbial food webs and considered the main pathway for the transfer of DOM into the particulate fraction. Bacterial biomass in turn serves as a food source for heterotrophic protists that link microbial to metazoan food webs. Seasonal shifts in carbon cycling also take place, as exemplified by an Arctic first-year carbon budget showing that DOC and/or EPS consumption is required to supplement bacterivory to meet heterotrophic carbon requirements during, but not prior to, the ice algal bloom period (Riedel et al., 2007b). Bacterial uptake of DOM combined with extracellular breakdown of dissolved matter may also mediate the release of essential micro- and macronutrients as well as vitamins, providing positive feedback for ice algal primary production. Limited information on viruses in sea ice indicates high viral abundance and high virus–bacteria contact rates (Wells & Deming, 2006; Deming, 2010). Research in pelagic environments suggests that DOC released by viral lysis of bacterial host populations can serve as a substrate for the growth of non-infected bacterial populations. This effect may be enhanced in the semi-enclosed brine channel system of sea ice, highlighting the potential role of viruses for sea ice–brine biogeochemical cycling, although DOC standing stocks are generally high and the relative contribution of lysate DOC might be small. Unravelling bacteria- and virus-mediated DOC dynamics

in sea ice remains a major challenge (Deming, 2010; Chapter 13).

To our knowledge, no *in situ* bacterial EPS production rates have been measured in sea ice habitats so far. Crude estimates, calculated through a combination of cell-specific rates of temperate organisms corrected for temperature effects and abundance data from sea ice habitats, indicate that in sea ice, bacterial EPS production is generally low compared with algal EPS production (Meiners et al., 2003, 2004). However, in distinct habitats, e.g. surface horizons in winter sea ice, bacteria may provide the dominant source of sea ice-associated EPS (Collins et al., 2008). Temperature has been shown to affect not only the yield of EPS production of an Antarctic sea ice bacterial isolate of *Pseudoalteromonas*, but also the uronic acid content of the produced material (Mancuso Nichols et al., 2005). Furthermore, the EPS produced by *Pseudoalteromonas* is poly-anionic and may bind cations such as trace metals (Mancuso Nichols et al., 2005). EPS produced by sea ice bacteria may therefore affect trace metal availability (van der Merwe et al., 2009), but interactions remain poorly understood. Sea ice EPS may also serve as substrate for bacterial growth (Meiners et al., 2004, 2008) and have been shown to increase NH_4^+ production, probably a result of grazing by heterotrophic protists (Riedel et al., 2007b).

17.5.2 The role of algae

Ice algae utilize carbon dioxide and inorganic nutrients contained in sea ice brine and are the most important producers of autochthonous DOC and EPS in sea ice systems. However, they can also take up DOC and EPS under both light and dark conditions and may contribute to the degradation of DOM (Rivkin & Putt, 1987; Palmisano & Garrison, 1993), but information on ice algal facultative heterotrophy remains extremely sparse.

Highest ice algal biomass generally occurs in microenvironments that are coupled to the underlying water column and exhibit stable growth conditions, e.g. bottom horizons and porous freeboard layers that are easily infiltrated with seawater (Arrigo et al., 2010; Meiners et al., 2012). Growth of ice algae requires acquisition of C, N and P and a host of micronutrients such as iron, as well as Si for diatoms. Ice algae can serve as a reservoir for nutrients, and biomass-rich bottom ice layers have been described as a 'capacitor' for nutrients due to their ability

to seasonally bio-accumulate macronutrients as well as iron in particulate biogenic fractions contained in sea ice (van der Merwe et al., 2009; Vancoppenolle et al., 2010; Noble et al., 2013). Key limiting nutrients for sea ice algal communities are NO_3^- and Si(OH)_4 , and some studies have shown positive relationships between sea ice and under-ice water nutrient concentration and algal biomass (Rózanska et al., 2009).

Nutrient stress affects algal physiology and metabolism and is often accompanied by a release of DOC from the cells by both passive (leakage) and active processes (exudation). A strong increase in the production of extracellular organic carbon fractions (both DOC and EPS) by sea ice algae under environmental stress has been reported (Aslam et al., 2012a; Ugalde et al., 2013). Moreover, field studies have shown strong relationships between the distribution of ice algae and EPS concentrations, with EPS quality and complexity influenced by environmental conditions such as ice temperature and brine salinity (Underwood et al., 2010, 2013). These findings are underpinned by laboratory experiments indicating that the sea ice diatom *Fragilariopsis cylindrus* responds to freezing, high-saline growth conditions and raised pH with an increase in the production of EPS, and that EPS yields of ice algae vary as function of growth rate (Aslam et al., 2012a; Ugalde et al., 2013). Coupled physical (e.g. temperature, salinity) and chemical drivers (e.g. macronutrient concentration, pH) are therefore assumed to regulate the extracellular carbon (both DOC and EPS) production of ice algae.

17.5.3 Heterotrophic protists and metazoans

The principal biogeochemical role of brine channel-dwelling heterotrophic protists and metazoans (for details see Chapter 16) is ingestion of particulate organic carbon (e.g. particulate EPS, bacteria and algae) and remineralization of inorganic nutrients through excretion. The limited number of studies on sea ice microbial food webs indicates the existence of a functional microbial loop, with bacterial standing stocks generally linked to high DOC and EPS concentrations, and grazed upon, but generally not controlled, by heterotrophic protists (Riedel et al., 2007b, 2008). Estimates of the grazing impact and carbon demand of in-ice herbivores are low, constituting only a few percent of ice algal primary production (Gradinger, 1999; Nozais et al., 2001; Michel et al., 2002), with most of the organic

carbon produced in sea ice released during ice melt, thereby contributing primarily to pelagic food webs and particle export (Michel et al., 2006; Juul-Pedersen et al., 2008). While the overall importance of heterotrophic protists and metazoans for carbon transfer is estimated to be small, they may contribute significantly to nutrient – in particular nitrogen – cycling, but information remains sparse. Sea ice food web dynamics remain challenging to study and must be considered as distinctly different from those observed in the pelagic realm due to the spatial complexity of the brine channel habitat, including attachment and association of organisms with internal surfaces, e.g. brine channel walls and particle surfaces, as well as clogging of brine channels by EPS (Krembs et al., 2000; Riedel et al., 2007b; Deming, 2010; Ewert & Deming, 2013).

17.6 Summary and future challenges

We have provided a brief overview on the various sources, sinks and processes involved in the cycling of a selected suite of biogeochemically relevant solutes in sea ice. We highlighted the fact that sea ice not only provides an important reservoir for macro- and micronutrients, DOC and EPS in the coupled ocean–sea ice–atmosphere systems of both hemispheres, but importantly it also serves as a dynamic interface in the cycling of these substances.

Cross-disciplinary field and laboratory (including large-scale ice tank) studies that simultaneously measure physical, chemical and biological properties and provide the basis for integrated analyses have been – and will be – key in furthering our understanding of sea ice biogeochemical processes. Recent development and application of new *in situ* (micro-) sensors, robust and automated sea ice observatories, and advances in under-ice platforms and vehicle technology provide promising new tools for measuring various sea ice properties (and their variability) on large scales. Multidisciplinary approaches on increasing temporal (seasonally to multi-year) and spatial (10s of metres to 100s of kilometres) scales, and across different ice regimes, are needed to improve the representation of biogeochemical processes in numerical sea ice models. Refined identification and parameterization of physical drivers of sea ice biogeochemical processes are particularly needed to improve sea ice primary production

models and predict future trends in polar marine ecosystem function. This in turn will improve assessments of the impacts of changing sea ice conditions on polar marine systems and beyond.

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CHAPTER 18

Gases in sea ice

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18.1 Introduction

18.1.1 Environmental and climatic role of gases in sea ice

The interest of the scientific community in gases in sea ice dates back to the early 1960s, with the pioneering work of Japanese scientists (Miyake & Matsuo, 1963; Matsuo & Miyake, 1966). Sea ice acquires its initial gas content from the pool of dissolved gases in the surface ocean. This is controlled by exchange of gaseous components of the atmosphere with the surface oceanic water, biological activity and inorganic reactions, such as photochemical oxidation and ionization. Much like the dissolved ions in seawater, dissolved gases will also be subject to solute rejection and physical concentration in the residual brine that forms during seawater freezing and is trapped – the small part of it that escapes gravity drainage to the underlying ocean – as inclusions in thermal equilibrium with the ice crystal matrix in sea ice. Again like the dissolved ionic species, the concentrated dissolved gases will be further subject to biological and abiotic reactions, including most prominently the aqueous–gaseous phase transition via gas bubble nucleation controlled by gas solubility, a thermodynamic property of gas interaction with electrolyte solutions. Such reactions will modulate the concentration of the dissolved gases in the sea ice brines away from the effect of the physical concentration mechanism.

The gas content and gas composition of sea ice have become a subject of intense investigation by the glaciological and oceanographic communities on account of their potential feedback into the climate system via the influence of gas bubbles on the sea ice albedo due

to their specific optical properties (see Chapter 4) and on account of exchange of greenhouse gases with the atmosphere. Reports of exchange of greenhouse gases between sea ice and the atmosphere in the last decade have defied the traditional view of sea ice as an inert and impermeable barrier for gas exchange and have raised interest in gas dynamics within sea ice. The investigation of gases is also an important component in biogeochemical studies of sea ice on account of gas transformations by biological activity (sympagic primary and secondary production) and physical-chemical processes (brine concentration–dilution and degassing–gas solvation). The diversity of ice types within the sea ice cover of polar and sub-polar surface waters (snow ice, superimposed ice, frazil ice, columnar ice, platelet ice – see Chapter 1) and the versatility of its surface properties in the course of its growth–decay cycle (bare ice, fresh snow cover, wet snow cover, melt ponds) result in a large range of total gas content (gaseous in gas bubbles plus dissolved in sea ice brine) and also in the variable fractional contribution of each of the individual gaseous species to the total gas content of sea ice. This high temporal and spatial variability in the phase distribution of gas species in sea ice is conveyed on the albedo of its surface, which is still a major challenge for climate modelling. Further, the amount of light that will penetrate the sea ice cover and reach the ice–water interface will also be quite variable, with potential implications for the photosynthetic activity and light sensitivity of the sympagic algal communities. Also, the density of sea ice will vary considerably, with known complications for the development of the algorithms used to derive sea ice thickness information from satellite laser

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