



Role of sea ice in global biogeochemical cycles: emerging views and challenges



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ABSTRACT

Observations from the last decade suggest an important role of sea ice in the global biogeochemical cycles, promoted by (i) active biological and chemical processes within the sea ice; (ii) fluid and gas exchanges at the sea ice interface through an often permeable sea ice cover; and (iii) tight physical, biological and chemical interactions between the sea ice, the ocean and the atmosphere. Photosynthetic micro-organisms in sea ice thrive in liquid brine inclusions encased in a pure ice matrix, where they find suitable light and nutrient levels. They extend the production season, provide a winter and early spring food source, and contribute to organic carbon export to depth. Under-ice and ice edge phytoplankton blooms occur when ice retreats, favoured by increasing light, stratification, and by the release of material into the water column. In particular, the release of iron – highly concentrated in sea ice – could have large effects in the iron-limited Southern Ocean. The export of inorganic carbon transport by brine sinking below the mixed layer, calcium carbonate precipitation in sea ice, as well as active ice-atmosphere carbon dioxide (CO₂) fluxes, could play a central role in the marine carbon cycle. Sea ice processes could also significantly contribute to the sulphur cycle through the large production by ice algae of dimethylsulfoniopropionate (DMSP), the precursor of sulphate aerosols, which as cloud condensation nuclei have a potential cooling effect on the planet. Finally, the sea ice zone supports significant ocean–atmosphere methane (CH₄) fluxes, while saline ice surfaces activate springtime atmospheric bromine chemistry, setting ground for tropospheric ozone depletion events observed near both poles. All these mechanisms are generally known, but neither precisely understood nor quantified at large scales. As polar regions are rapidly changing, understanding the large-scale polar marine biogeochemical processes and their future evolution is of high priority. Earth system models should in this context prove essential, but they currently represent sea ice as biologically and chemically inert. Palaeoclimatic proxies are also relevant, in particular the sea ice proxies, inferring past sea ice conditions from glacial and marine sediment core records and providing analogues for future changes. Being highly constrained by marine biogeochemistry, sea ice proxies would not only contribute to but also benefit from a better understanding of polar marine biogeochemical cycles.

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1. Introduction

Past and on-going climatic changes are amplified in the polar regions (Holland and Bitz, 2003). Current climate changes, associated with large-scale anthropogenic emissions of greenhouse

gases, involve a warming of the ocean, changes in its chemical composition, as well as a dramatic sea ice retreat in the Arctic (Comiso, 2010). Future changes in the polar seas and continued sea ice retreat (Arzel et al., 2006) will affect future marine biogeochemistry, with important feedbacks on climate and consequences for marine ecosystems, some of which have already been observed (e.g., Montes-Hugo et al., 2009; Wassmann et al., 2011). Palaeoclimate studies indicate that past climatic and atmospheric composition changes were associated with extensive modifications in the polar oceans, in terms of circulation, sea ice cover and chemical composition (Crosta et al., 1998; Sarnthein et al., 2003; de Vernal et al., 2005; Sigman et al., 2010). While a seasonal ice cover should subsist in the future (Armour et al., 2011), the future large-scale biogeochemical dynamics of the polar oceans and in particular the contribution of sea ice are difficult to predict.

Ocean biogeochemistry exerts a large control on atmospheric chemistry and climate by absorbing about a fourth of anthropogenic carbon dioxide (CO₂) emissions (Sabine et al., 2004), the ocean dampens global warming. The polar and sub-polar oceans are of central importance as they support most of the oceanic CO₂ uptake (Takahashi et al., 2009). Air–sea carbon exchanges are ultimately driven by two main categories of processes: the solubility and biological pumps. The solubility pump is the ensemble of physical and chemical processes driving CO₂ dissolution and outgassing. The biological pump is driven by (i) the fixation of inorganic carbon into organic matter and its export to depth by sinking plankton material and (ii) the formation of calcium carbonate (CaCO₃) via calcification, releasing CO₂ (Sigman et al., 2010). While the natural carbon cycle is largely driven by the biological pump (Sarmiento and Gruber, 2006), the uptake of anthropogenic carbon can be, so far, almost entirely explained by physical and chemical processes (Prentice et al., 2001). The oceanic CO₂ absorption capacity decreases with increasing oceanic CO₂ burden, but may also be reduced because of future anthropogenic climate change (decreasing solubility and increased upper ocean stratification), hence amplifying global warming (Friedlingstein et al., 2006). The ocean suffers from the increase in its CO₂ burden: more dissolved CO₂ acidifies the ocean (Doney et al., 2009), threatening sensitive and essential marine species, with potential consequences for entire marine food webs. Besides absorbing CO₂, the ocean is also a preferential site for dimethylsulfide (DMS) emissions. In the atmosphere, DMS acts as a precursor of acidic aerosol sulfates which as cloud condensation nuclei have a potential cooling effect on the planet (Charlson et al., 1987; Watson and Liss, 1998).

Sea ice – the ice forming from the freezing of seawater (WMO, 1970) – is one of the largest known biomes on Earth (Dieckmann and Hellmer, 2010), covering about 7% of the World Ocean, with remarkable seasonal variations seen in both hemispheres (see Comiso, 2010, for a review). The Arctic sea ice pack has lost about 30% of its summer coverage over the last thirty years (e.g., Comiso, 2010) with a spectacular culmination in 2012. This could lead to a summer ice-free Arctic Ocean by the middle of this century (e.g., Massonnet et al., 2012). The Antarctic sea ice extent has slightly increased over the last thirty years (~1% per decade). However, regional variability is large: increases in the Ross and Weddell Sectors exceed the strong retreat in the Amundsen–Bellingshausen regions (Stammerjohn et al., 2012). In addition, the Antarctic sea ice extent is consistently projected to significantly decrease by the end of this century (Arzel et al., 2006). The implications of sea ice retreat on the future oceanic capacity to absorb CO₂ and emit DMS, as well as the consequences for climate change, ocean acidification and marine ecosystems, are poorly understood.

Focussing on sea ice processes relevant to polar marine biogeochemistry (see Fig. 1) is first motivated by the *potentially significant influence of sea ice on air–sea gas exchanges*. Seen as an

impervious cap, sea ice would drastically reduce air–sea CO₂ exchange (Stephens and Keeling, 2000). However this is hardly the case in practice, because of the presence of open water within the pack (leads and polynyas), providing pathways for atmosphere–ocean gas exchanges (Morales Maqueda and Rahmstorf, 2002). Sea ice itself is permeable when warm enough (e.g., Golden et al., 1998), supporting gas exchanges (e.g., Delille et al., 2007; Nomura et al., 2010; Papakyriakou and Miller, 2011) and acts as a source for some gases, for example DMS (Zemmelink et al., 2008) and potentially Bromine Oxide (BrO) (e.g., Simpson et al., 2007). Until now, the research community has mainly been interested in the study of biogenic and climatically significant gases (i.e., N₂O, O₂, CO₂, DMS) (e.g., Delille et al., 2007), although there is growing interest in research on other gases such as Br components, which influence polar atmospheric chemistry (e.g., Simpson et al., 2007) and methane (CH₄), a strong greenhouse gas that is present in gas bubbles released from anoxic sediments to the water column and sea ice (Shakhova et al., 2009). A second process of interest is the *sinking to depth of CO₂-rich brine* (e.g., richer than seawater), *released into the surface ocean during sea ice formation* (Rysgaard et al., 2007). This process should be among the important mechanisms contributing to the ocean CO₂ sink, not only today (Rysgaard et al., 2011), but also during the Last Glacial Maximum (Bouttes et al., 2010).

In addition, mounting field observations show *dynamic biogeochemical processes in the sea ice zone* (Thomas and Dieckmann, 2010), with potential impacts on open ocean biogeochemistry and atmospheric composition. Sea ice microbial communities are present, and often thrive, in a network of liquid saline brine inclusions distributed within a pure ice matrix (see Fig. 2), providing a habitat that is both stable and ventilated by nutrient-rich seawater, depending on the complex brine flow through the ice (e.g., Vancoppenolle et al., 2010). Organic carbon is produced by ice algae via photosynthesis in specific light, nutrient and temperature conditions, to which the organisms are usually adapted and acclimated. Ice algae can also produce copious amounts of dimethylsulfoniopropionate (DMSP), the precursor of DMS, an osmotic regulator and a cryoprotectant (e.g., Tison et al., 2010). Finally, iron concentrations in sea ice can be much higher than in the ocean and sea ice can act as a seasonal reservoir in the Southern Ocean (Lannuzel et al., 2007, 2011): growing sea ice incorporates large amounts of iron, later released into surface waters when the ice melts. This seasonal process may temporarily relieve iron limitation on phytoplankton growth, notably in the Southern Ocean (Lancelot et al., 2009), a key player in the marine carbon cycle (Sarmiento and Gruber, 2006; Sigman et al., 2010), but also in the Bering Sea (Aguilar-Isilas et al., 2008)

Sea ice proxies integrate information from biological, chemical and physical processes occurring in the polar oceans in an attempt to reconstruct past sea ice conditions (see Armand and Leventer, 2010, for a review). Many sea ice proxies rely on assumptions related to the biogeochemical properties of the polar oceans, as recorded in marine sediment or glacial ice cores. For instance, changes in diatoms and dinoflagellates community composition, attributed to the open ocean–sea ice zone transition, are used to reconstruct past sea ice characteristics. Crosta et al. (2008), de Vernal et al. (2005) and Müller et al. (2009), based on marine sediment core data, use diatom frustules, dyncocysts and biomarkers specifically produced by sea ice-associated diatoms and open water phytoplankton, respectively. Curran et al. (2003) and Wolff et al. (2006) use the concentration of methane-sulphonic acid (MSA), an atmospheric by-product of DMS emission in the sea ice zone; and sea salt sodium from glacial ice core data, respectively. However, Hezel et al. (2011) – in an attempt to model the sulphur cycle in the Southern Ocean – find that the presence of sea ice does

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