

Can sea ice-specific biogeochemical processes support significant air-ice CO₂ fluxes ?



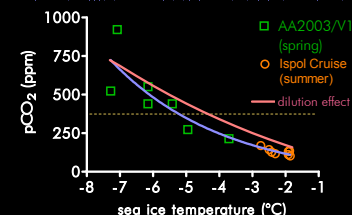
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Sea ice exchanges CO₂ with the atmosphere. Today our best estimate of uptake of CO₂ by compact Antarctic sea ice edge (ice concentration above 65%) ranges from 0.015 to 0.024 PgC (from September to January). This represents 6% to 9% of the uptake of the Southern Ocean south of 50°S. However we surmise this is lower end of the spring and summer uptake of CO₂ by Antarctic sea ice edge since we do not take into account contribution of surface communities. This highlights the significance of CO₂ flux at the air-sea ice interface but raises the need to thoroughly verify if sea ice-specific processes can support such CO₂ fluxes.

Temperature: a key parameter

We carried out first **direct measurements** of pCO₂ within sea ice brines using conventional underway pCO₂ equilibration techniques, during two sea ice surveys (AA2003/V1 cruise onboard the RV *Aurora Australis* during spring 2005 and Ispol cruise onboard the RV *Polarstern*, during summer 2005).

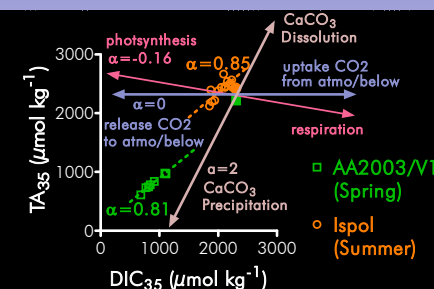
By controlling sea ice porosity, and subsequently gas transfer and nutrients supply, **temperature appears to be one of the main controlling factors** on the CO₂ dynamics. Ice below the temperature **threshold of about -5°C** (winter type stations) displays the higher pCO₂ values, whilst the warmer, more porous, ice ("spring" type station) favours the set up of primary production and hence, shows the lowest pCO₂ values.



Precipitation/dissolution of carbonate minerals

Precipitation of CaCO₃ in sea ice as a result of drastic increase of salinity in brines is subject to a long-lived debate. Numerous laboratory experiments showed that precipitation of CaCO₃ occurs during sea ice formation, but to date has not been verified in the field.

However, low values of normalized DIC and TA (DIC₃₅ and TA₃₅, respectively) in brines collected in early spring in Antarctic pack ices are a conspicuous indication that CaCO₃ precipitation had taken place within sea ice brines prior to the cruise. The impact of this precipitation is very marked, leading to a **removal of 60% of DIC₃₅ from brines**. Precipitation of CaCO₃ produces CO₂ during sea ice growth as brine salinity increases dramatically. On the opposite, as sea ice is melting in spring, subsequent dissolution of CaCO₃ likely matches and enhances the decrease of pCO₂ due to the dilution with meltwater.



The plot of normalized DIC to a constant salinity of 35 (DIC₃₅) against normalized TA (TA₃₅) gives some insights on the processes occurring within sea ice (with the notable exception of temperature change and concentration/dilution of brines that do not affect DIC₃₅ and TA₃₅) both prior and during our surveys. Open squares and open circles denote, respectively, spring and summer samples; slope of the corresponding regression line is reported as "α". Full square and circle denote mean values of the underlying water in spring and summer, respectively. Arrows represent the theoretical variation of DIC₃₅ and TA₃₅ according to specific biogeochemical processes.

Potential CO₂ transfer from the atmosphere

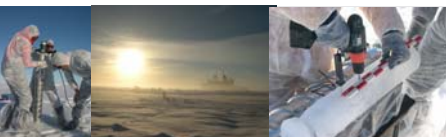
We attempted to assess the potential maximum impact of each main spring and summer physical and biogeochemical processes on pCO₂ observed during both cruises. We consider the dilution associated to the increase of temperature and subsequent melting of ice crystal (T° increase from -7.2° to -1.3 corresponding to a salinity decrease from 117 to 23), the spring dissolution of carbonate minerals trapped within sea ice, and assessed that primary production ranges between Chl a and POC changes of standing stocks (upper table).

The potential air-ice CO₂ transfers related to sea ice physical and biogeochemical processes were assessed by considering a homogeneous 90 cm thick sea ice cover in equilibrium with the atmosphere and without exchanges with the underlying layer. We assumed that sea ice was initially in equilibrium with the atmosphere, we applied the biogeochemically driven DIC and TA changes observed during both cruises (upper table) and computed the CO₂ transfer from the atmosphere necessary to restore the equilibrium (lower table).

Depending on the assessment of primary production, based on either Chl a or POC change of stock, the overall CO₂ uptake from the atmosphere ranges from, respectively, **125 to 146 mmol m⁻²**. Taking into account a mean value for the Antarctic sea ice surface area of 16×10⁶ km², the corresponding overall CO₂ uptake account for **0.024 and 0.028 PgC** which represent additional CO₂ sinks of, respectively, **9.3 and 10.9 % to the current consensual assessment of the uptake of CO₂ by the Southern Ocean south of 50°S (0.26 PgC yr⁻¹)**.

	temperature (°C)	salinity brines	TA (µmol kg ⁻¹ of bulk ice)	DIC (µmol kg ⁻¹ of bulk ice)	TA (µmol kg ⁻¹ of brines)	DIC (µmol kg ⁻¹ of brines)	pCO ₂ (ppm)
temperature increase and related dilution	5.9	-94	0	0	-2125	-1918	-662
CaCO ₃ dissolution	0	0	157.2	78.6	4075	2038	-625
Chl a build up	0	0	1.4	-8.8	36	-227	-425
POC build up	0	0	4.9	-30.7	128	-776	-672

	related CO ₂ transfer from the atmosphere (mmol m ⁻²)
temperature increase and related dilution	-60
CaCO ₃ dissolution	-56
Chl a build up	-8
POC build up	-30



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