Biogas (O_2, CO_2 and DMS) dynamics within and below sea ice during coastal sea ice edge retreat

B. Delille[(1)] , D. Delille[(2)], B. Jourdain[(3)], M.Legrand[(4)], S. Ferrón Smith[(1)] and M. Frankignoulle[(1)]

Fig. 1: Sampling

In order to collect sea ice brine, holes were drilled into the ice using 10 cm (internal diameter) ice auger to a depth of 50 cm. As soon as 1l of brine had accumulated at the bottom of the core hole (usually 10-15 min), sampling commenced. After complete drilling of the ice cover, subsurface seawater samples were collected at 0 m (the platelet ice layer) and 1m depth. Attention has been paid to avoid degassing and freezing during sampling and return to the laboratory.

Approach

- In spite of the **high biological activity** of the sea ice environment, biogeochemical cycles within and below sea ice receive less attention that they actually deserve. In spite of the singular interest of biogeochemistry in such an environment submitted to extreme physico-chemical constrains, little is known of the **impact of the biogeochemical processes specific to the sea ice environment** at larger scale for the whole marginal ice zone. We present here the first joint measurements of dissolved oxygen (O_2), carbon dioxide (CO_2) and dimethylsulfide (**DMS**) **within and below sea ice.**
- We focused on the dynamic of these three biogas in relation to chlorophyll a abundance during spring breaking of coastal fast ice. Three specific environments - **brine**, **platelet layer** and **underlying** have been sampled.

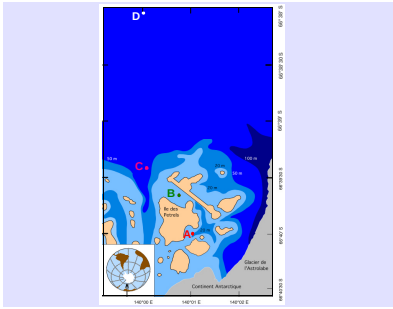

Fig. 2: Site

The study was carried out from November to December 1999 during the sea ice edge retreat in Terre Adélie, Antarctica (66°40'S, 140°01 E). Samples were collected weekly at four stations (denoted A, B, C, D) located in the vicinity of the Dumont d'Urville base.

Analytical methods

For study area and sampling strategy , please refer to fig.1 and 2

- The inorganic carbon speciation was calculated from pH and total alkalinity (TAlk) measurements. pH was measured using commercial combination electrodes calibrated on to the total hydrogen scale using Tris and Amp buffers according to Dickson (1993). Attention has been paid to carry out pH measurement as soon as possible after return to the laboratory (typically less than 3 hours after sampling) and to make calibration between 1 and 3°C using buffers prepared at salinity of 30, 35, 40 and 80. CO_2 speciation was calculated using the CO_2 acidity constants of Roy et al. (1993) and assumption have been made that these latters are valid for salinity up to 90. The accuracy of pH measurements was 0.01 pH units. TAlk was measured using the classical Gran electrotitration method on 100ml GF/F filtered samples. The accuracy of TAlk measurements was 4 µeq.kg^{-1} thus the errors in pCO_2 and DIC were 14 µatm and 9 µmole.kg^{-1} respectively. TAlk and DIC have been normalized at salinity 35 ($TAlk_{35}$ and DIC_{35})
- Phytoplankton was studied using chlorophyll a concentration. Samples were filtered by gentle vacuum filtration of 1l of seawater through a Whatman GF/F glass-fiber filter. The measurements of chlorophyll a were carried out following the recommendations of Arar and Collins (1997). Fluorescence was measured on a Turner Designs TD 700 spectrofluorometer.
- Sampling for dissolved DMS was realised by flushing seawater through a glass fibre filter (Whatman GF/F, Ø47 mm) into 20 mL polyethylene vials. DMS analyses were performed in the field during the four hours following the sampling using a gas chromatograph equipped with a flame photometric detector (HP 6890, 393 nm). DMS was then cryogenically trapped at -60°C on a tenax GC 80 loaded tube maintained in a bath of ethanol cooled by a Cryocool CC100 device. DMS was subsequently transferred to the gas chromatograph by thermal desorption of the tenax trap (boiling water) as detailed by Nguyen et al. (1990). Working chromatographic conditions applied here were an oven temperature of 95°C, a detector temperature of 200°C, and a flow rate at the flame of 30 mL.min^{-1} of helium (carrier gas), 80 mL.min^{-1} of air, and 55 mL.min^{-1} of hydrogen. Calibration range was typically from 1.18 to 3.54 ng of DMS. The detection limit was found to be close to 0.2 ng of DMS, leading to a DMS detection limit under 0,3 nmol.L^{-1} for 10 mL of sea-water.

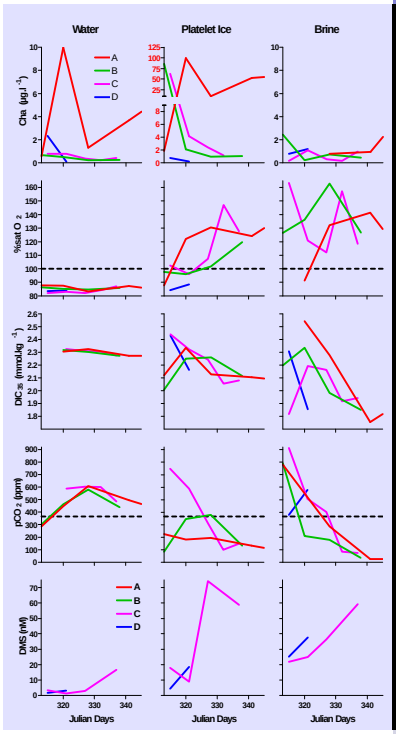

Fig. 3: Temporal changes of Chlorophyll a concentration (Cha), Oxygen saturation (O_2 sat), Normalized Dissolved Inorganic Carbon (DIC_{35}), partial pressure of CO_2 (pCO_2) and Dimethylsulfide (DMS) in sea ice underlying water, platelet layer and brine

Station D has been poorly sampled due to the early ice edge retreat at the most offshore site.

O_2 saturation, and pCO_2 cover a large range of values and thereafter exhibit large temporal changes. Furthermore all the parameters are contrasted between the three environments . However each environment examined individually shows conspicuous and similar trends at all stations.

DMS concentrations in the underlying layer is in the range of previous observations in the Southern Ocean. In platelet layer and brine, three times higher concentrations can be expected.

Main results

- **Underlying water** exhibited (Fig.3) both O_2 undersaturation (around 85%) and pCO_2 oversaturation (up to 600 µatm). Moderate chlorophyll a content (less than 4 µg/l) leads to the decrease of DIC_{35} while **DMS concentration increases but remains below 20 nM**. The **observed persistent undersaturation of pCO_2** could be related at first sight to winter hydrodynamical processes or organic matter decay, as indicated by undersaturation of oxygen. However, comparison of normalised DIC and TAlk shows that **precipitation/dissolution of $CaCO_3$** (Fig.4) occurred below the sea-ice.

Precipitation of $CaCO_3$ can be written as: $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$. As a result, the carbonate system shifts to higher CO_2 levels so that precipitation of $CaCO_3$ in the underlying water promotes the increase of pCO_2 and subsequent oversaturation.

- In the **platelet layer**, O_2 saturation level increased, from undersaturation to oversaturation up to 130 % owing to **high chlorophyll a content (up to 85 µg l^{-1}).** Accordingly, **pCO_2 decreased down to 150 µatm** while the magnitude of DIC_{35} changes was about 400 µmol kg^{-1} month^{-1} and **DMS concentration increased up to 75 nM.**

- In **brine**, in spite of **lower chlorophyll a content**, O_2 and CO_2 changes were enhanced and **O_2 oversaturations over 160 %** were observed, while **pCO_2 decreased from a high oversaturation above 800 µatm to undersaturation down to 30 µatm**, with associated decrease of DIC around 700 µmol kg^{-1} month^{-1}. Accordingly, **DMS increased up to 60 nM**. Thus, in spite of moderate chlorophyll a content, brine appeared to be very productive probably due to enhanced light availability.

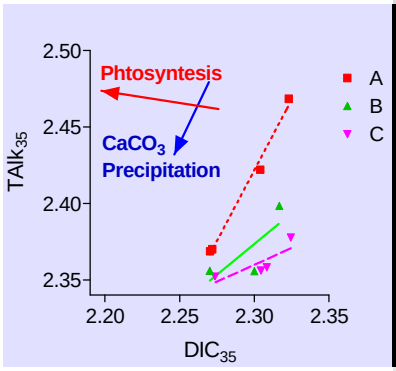

Fig. 4: CO_2 release from $CaCO_3$ precipitation in the underlying water

DIC_{35} plotted against $TAlk_{35}$ at stations A, B and C in the underlying water. Blue arrow indicates the changes of DIC_{35} and $TAlk_{35}$ owing to $CaCO_3$ precipitation (reverse side corresponds to $CaCO_3$ dissolution) while red arrow indicates changes due to photosynthesis (reverse side indicates mineralization).
It appears that DIC_{35} and $TAlk_{35}$ changes at stations B and C are due to $CaCO_3$ precipitation/dissolution superimposed to photosynthesis. This tendency becomes acute at the shallower station A where inorganic carbon dynamics in the underlying layer appears to be mainly driven by $CaCO_3$ precipitation/dissolution.

To conclude…

Hence, brine and platelet layer environments appears to be highly dynamic in spring in terms of production of O_2 and DMS and uptake of CO_2 in contrast with the persistent O_2 undersaturation and pCO_2 oversaturation observed in the underlying water. Magnitude of temporal changes of O_2 saturation, pCO_2 and DMS concentration in brine and platelet layer reflect the leading influence of biological activity, while underlying layer appears to be influenced by chemical processes as $CaCO_3$ dissolution/precipitation superimposed to hydrodynamical and biological processes.

Thereafter arises the question of the gas exchanges between sea-ice and neighbouring environments (i.e. water column and atmosphere).

EGS-AGU-EUG Joint Assembly
Nice, France, 06 - 11 April 2003

www.ulg.ac.be/oceanbio/co2/

Acknowledgements:
Office for Scientific, Technical and Cultural affairs (A4/DD/B14 and EV/12/7E)
IPEV

[1] Université de Liège, MARE, Unité d'Océanographie Chimique, Belgium (Bruno.Delille@ulg.ac.be)
[2] UMR 7621 , Observatoire Océanologique de Banyuls, France
[3] Laboratoire Chimie Environnement, Université de Provence, Marseille, France
[4] CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement, St Martin d'Hères, France