MEASURING CO_2 IN SEA ICE: CAVEATS AND IMPROVEMENTS.

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Why measuring the partial pressure of CO_2 (pCO_2) in sea ice ?

The impact of sea ice on the physical interactions between the atmosphere, the ocean and the biosphere is well know in the polar area. However, sea ice has been assumed to be an impermeable and inert barrier to air-sea exchanges.
But, Golden and al. (1998) showed that sea ice is a highly permeable medium for gases under some conditions (T = -5°C, Bulk salinity = 5).
Accordingly, uptake of atmospheric CO_2 over the sea ice cover in the Arctic and Southern Ocean were recently reported.

Development of a new analytical method

Data on gas composition in sea ice are scarce.
Unfortunately, conventional analytical for continental freshwater ice methods cannot be applied for CO_2 in sea ice since CO_2 is mainly found in seawater media in dissolved carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) forms that cannot be measured by a simple vacuum extraction.
We use a new method that overcomes this issue. The backbone idea is that the ice sample is equilibrated during 4 hours at the in situ temperature with a standard atmosphere of know concentration in CO_2. After the equilibration, the pCO_2 of the headspace is measured by gas chromatography (Chrompack CP9001).

Manufacture of standard sea ice

We aimed to asses the reproducibility of the method. A prerequisite was to find a method to produce a standard ice with reproducible and homogeneous physical properties. We use an ice-cream maker to create a slush. During this process the slush is equilibrated with the external atmosphere to keep the pCO_2 of this ice constant. This slush is squeezed with an hydraulic press in a cold room *(fig. 1)*.
Measurements of pCO_2 are carried out on this standard sea ice and compared to assess the reproducibility of the measurement.

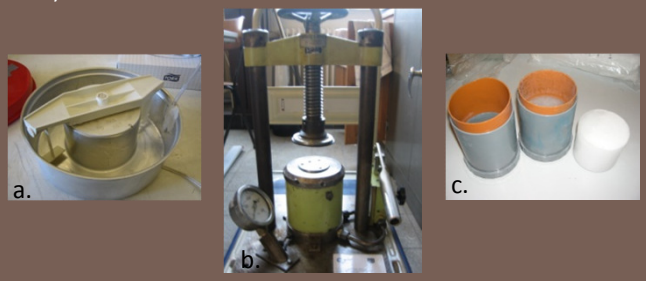

fig. 1. - a. ice-cream maker, b. hydraulic press, c. different steps in sea ice fabrication.

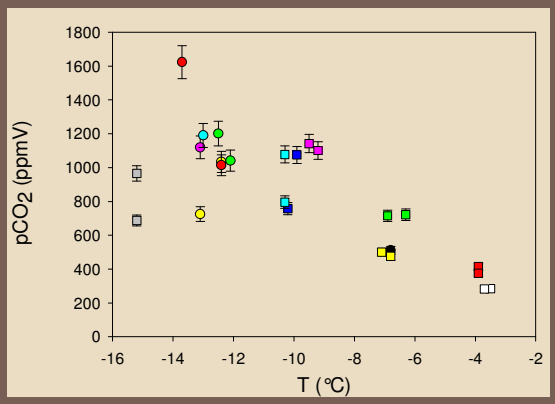

fig. 2. - Evolution of pCO_2 of standard sea ice.
Round and square show different time of analysis and each color represent 2 samples from the same block of sea ice.

Results

Above -8°C, the measures are linearly correlated with the temperature within 14%. Measurement carried out at the same temperature on the same block of standard sea ice are consistent, margin of error less than 5%. pCO_2 measurements carried out on different sea ice block are also consistent (*fig. 2*).
At temperature lower than -8°C, we observed a large scattering of pCO_2, probably due to an insufficient equilibration.

Conclusions

The reproducibility of the method is lower than 14% at temperature above -8°C, giving some confidence in the overall method. However, at temperature lower than -8°C, reduced permeability and counteracts the equilibration. The method then requires some improvements at low temperature.

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