TNA User Report

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Project title	Kinetic isotopic fractionation of the $\delta^{13}C$ signature of methane during sea ice formation and melt
Name of the accessed chamber	RvG-ASIC (formerly ASIBIA)
Number of users in the project	2
Project objectives (max 100 words)	This study was designed to trace the effect of the kinetic isotopic fractionation on the $\delta^{13}C$ signature of methane along the pathways of methane into, within and out of sea ice in both directions, i.e. water and air during the freeze and the melt cycle. This study seeks to simulate under laboratory conditions in detail processes common on Arctic shelves: Methane released from shelf sources induces super-saturated shelf water in summer. Later in autumn during sea ice formation, super-saturated brine is created which either might be released during further freeze processes in winter or during the melt in spring again.
Description of work (max 100 words):	We carried out four experiments to induce methane circulation between sea ice, sea water and air under various conditions. Before starting the experiments the ice chamber was cleaned to inhibit bacterial growth. Thereafter the chamber was filled with artificial seawater and subsequently spiked with methane. Two of the experiments were just related to the freeze process, i.e. fast and slow freeze and was interrupted when sea ice had grown. The following two experiments were associated to the melt process, i.e. slow and fast melt each after fast freezing conditions. During and after the experiments samples from all compartments were taken.

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[1] Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

[2] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.

[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

[4] Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Ellen Damm
Chamber name and location: RvG-ASIC (formerly ASIBIA), University of East Anglia, Norwich
Campaign name and period: November 6th, until December 5th 2017
Text:

Introduction and motivation

Methane is a greenhouse gas and increasing atmospheric concentrations contribute to trigger global warming. The most severely impacted region is the Arctic. Here, temperature changes may quickly enhance methane emissions, due to large natural sources. This so-called Arctic amplification of global warming (i.e., warming feeds warming), affects sea ice retreat, thus enhancing sea-air gas exchange (IPCC, 2013). In addition, there is growing evidence that sea ice itself is crucial in Arctic methane cycling as enhanced near-surface atmospheric methane concentrations over open leads and regions with fractional sea-ice cover point to unexpected feedbacks (Kort et al, 2012, Damm et al, 2015 and 2018). On one side, sea ice is likely a potential driver in sizable shifts between methane sources and sinks. On the other side, sea ice formation and melt might induce alterations in the isotopic composition of methane along the pathways, mainly by the kinetic isotopic fractionation effect. Those processes might initiate modifications in the isotopic signature compared to the initial source-signature. As the isotopic signature is commonly used to identify different sources of Arctic emissions (AMAP 2015), those processes also encourage a misinterpretation and finally misleading source identification. In summary, the innovative aspect of the planned experiment is to supply a first data set about the effect of kinetic fractionation on methane along pathways coupled to various sea ice formation conditions.

Scientific objectives

This study investigates the methane pathways during sea ice formation and melts under laboratory conditions under special consideration of the kinetic isotopic fractionation effect on the $\delta^{13}C$ signature of methane along these pathways, i.e. into, within and out of sea ice in both directions from sea water to sea ice and from sea ice back into sea water or into air.

Reason for choosing the simulation chamber/ calibration facility

The Roland von Glasow Air-Sea-Ice Chamber (RvG-ASIC) at the University East Anglia (UEA) was selected, as this chamber disposes the facilities simulating an enclosed ocean-sea ice-atmosphere system. The chamber is temperature controlled from -55 to 33°C and enables getting samples from all compartments i.e., sea water, sea ice and air. Further the tank supports to work exclusively with the physical processes mediated of the isotopic fractionation without considering any biological activities. In 2016 a first pre-experiment has been successfully running in this chamber, in collaboration with Prof. Jan Kaiser and Dr. James France.

Method and experimental set-up

Experimental set up

A total of four experiments simulating different conditions were conducted in the RvG-ASIC. A 3500L glass tank “ocean” (length × width × depth= 2.4 m x 1.4 m x 1.1 m) was used with a removable FEP film-enclosed “atmosphere” above (2.4 m × 1.4 m × (0.1–1 m); 0.3 to 3.3 m^3 air volume). In addition, the “ocean” was equipped with a wave generator and circulation pump. Temperature and conductivity in sea water and ice during the four experiments were measured using a Sea-Bird MicroCAT CTD-sensor, located 20 cm above the base tank. Los Gatos Research instrument measured methane concentration in air every 5 minutes when the experiments were running. Before the experiments started the chamber was cleaned to minimize bacterial growing and subsequently, filled with artificial sea water to obtain a salinity of ca. 29.6. Additionally, CH_4 100% were added into the water bath (dissolved in 350 ml artificial sea water in a gas tight bag and equilibrated for at least 3 hours), making sure the signal will be clear above the background concentration afterwards. Samples from sea water prior (blank) and after (T0) spiking were collected to follow each step.

1. First experiment simulated a “*fast freezing condition*”. The room temperature was kept constant during the experiment at -33°C for four days. Sea water samples were collected twice per day (mornings and afternoons) until 16 cm of sea ice thickness was reached. When this ice thickness was reached, the experiment was stopped and six sea ice cores were taken. A cube of ice was taken as well and kept it in -40°C for three days, to retain as much brine as possible and to compare those values with the sea ice cores afterwards.
2. The second experiment simulated a “*slow freezing condition*”. The room temperature was kept constant at -15°C for seven days reaching 16 cm of sea ice thickness at the seventh day. Sea water samples were taken once per day (mornings) until the experiment was finished. Once the ice thickness was reached, nine ice cores were taken. A cube of ice was also taken following the same procedure as the experiment 1.
3. The third experiment simulated a “*slow melting followed by a fast freezing condition*”.

The room temperature was set to -33°C for three days. After that, the room temperature was increased from -33°C to -2°C for 2 days, ending the experiment with 3 days at 5°C. Sea water samples were also taken twice per day, but no ice was sampled.

4. The fourth experiment simulated a "*fast melting followed by a fast freezing condition*". The room temperature was set to -33°C for three days followed by two days at 10°C. Sea water samples were taken twice per day.

Sea water sampling

Sea water and sea ice samples for CH_4 concentration and stable carbon isotopic composition were collected during the four experiments.

Discrete sea water samples were collected with 60 ml syringes in triplicates, twice per day (mornings and afternoons or depending the experiments conditions) by two lines (Tygon tubing) connected into the ice tank (one at the surface and the other one 10 cm above the tank bottom) (Fig 1). Bubble free samples were taken in 120 ml glass vials, sealed directly with rubber stoppers and crimped with aluminum caps. The samples were kept in cold room (4°C) and in darkness until the measurements were done at the lab. For methane concentration, 5 ml of N_2 was added into the vials, and then equilibrated for 1 hour at room temperature. 1.5 ml of sample was injected into a gas chromatograph (Agilent 8900) with a flame ionization detector (FID). For gas chromatographic separation a packed column (Porapac Q 80/100 mesh) was used. The GC was operated isothermally (60°C) and the FID was held at 250°C. 1.665, 4.99, 10, 24.97 and 50.09 ppm standards gas mixture were used for calibration. $\delta^{13}C$-CH_4 values were determined using a Delta XP plus Finnigan mass spectrometer. The extracted gas was purged and trapped with PreCon equipment (Finnigan) to pre-concentrate the sample. All isotopic ratios were given in a δ -notation relative to the Vienna Pee Dee Belemnite (VPDB) standard using conventional δ -notation.

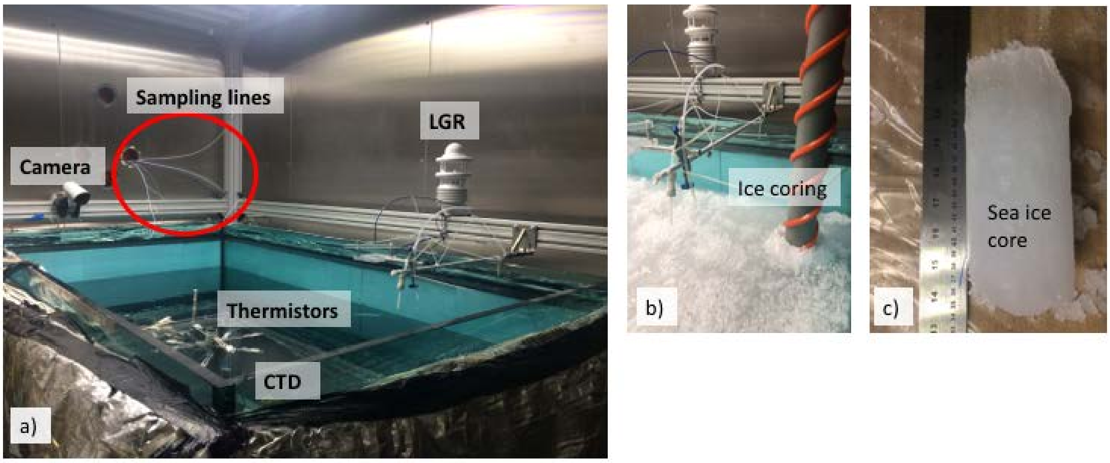

Figure 1: a) Sea ice tank filled with artificial sea water with different instruments on it. CTD for conductivity-temperature-depth measurements in sea water; Thermistors measuring temperature in sea ice, LGR (Los Gatos Research) for CH_4 concentration in air; two sampling lines (red circle) for sea water collecting in two depths (sea ice underneath and 10 cm above the base tank) and a camera. b) ice coring at the end of experiment 1 (fast freezing conditions). c) Sea ice core roughly 16 cm thick.

Sea ice sampling

Sea ice cores were taken with an ice coring. Ice from experiment 1 was cut into two pieces (TOP and BOTTOM), and for experiment 2 was cut into four pieces, to have a better sampling resolution. After the ice was cut, the sea ice samples were transferred immediately into gas tight bags avoiding contact with the atmosphere. The bags were quickly closed and vacuumed. Sea ice samples were melted in 4°C cold room and in darkness for 48 hours. 120 ml glass vials were carefully filled up with the melted water and following the same procedure for the sea water sampling. In addition to the ice cores, a cube of sea ice in both experiments (1 and 2) was taken and kept frozen in -40°C for 3 days to retain as much brine as possible. The cube of sea ice was cut into 4 pieces (ca. 4.4 cm each piece) and brought it into tight air bags, following the same procedure of the ice cores sampling.

Air sampling

Gas tight bags (1 and 3L) were filled with air from the tank using a vacuum pump, every day during all experiments. Methane concentration and methane isotopic composition were measured by GC and MS, respectively, as was previously described in methodology.

Preliminary results and conclusion

1. *Experiment 1: Fast freezing*

Sea water temperature decreases from -1.08 to -1.77°C and salinity increased from 29.6 to 33.05 when sea ice was growing. The temperature decreases quickly down to -1.64°C (first 20 hours) and later slowly until the end of the experiment. Once the experiment started, sea ice grows exponentially reaching 16 cm of ice at the end of the experiment. Salinity in sea water increased during ice growth, reflecting brine rejection into the sea water. This coincided with the appearance of ice crystal in the upper centimeters of the ice tank. On the other side, methane concentration shows a sharply decrease until 44 hours and then it remains slightly invariable for the rest of the experiment. Taken together, this results suggest that sea ice is potentially catching up the methane from sea water into sea ice. In regards to methane isotopic fractionation in sea water, the change in $\delta^{13}C$ of methane was about 6.5‰.

2. *Experiment 2: Slow freezing*

Sea water temperature slowly decreases from -1.00 to -1.77°C and salinity increased from 29.36 to 33.43 during the slow sea ice growing rate (7 days). Sea ice thickness shows an exponential, but slower sea ice growing rate than in experiment 1. Sea ice increased to 16 cm thickness up to the end of the experiment. Salinity increases along the time, showing salt rejection into the sea water. The methane concentration shows the same trend like in freezing experiment 1, i.e.

fast freeze. The concentration is decreasing during the first time and increasing again at the end of the experiment. The methane isotopic signature shows a variation about 8‰ in sea water throughout the experiment.

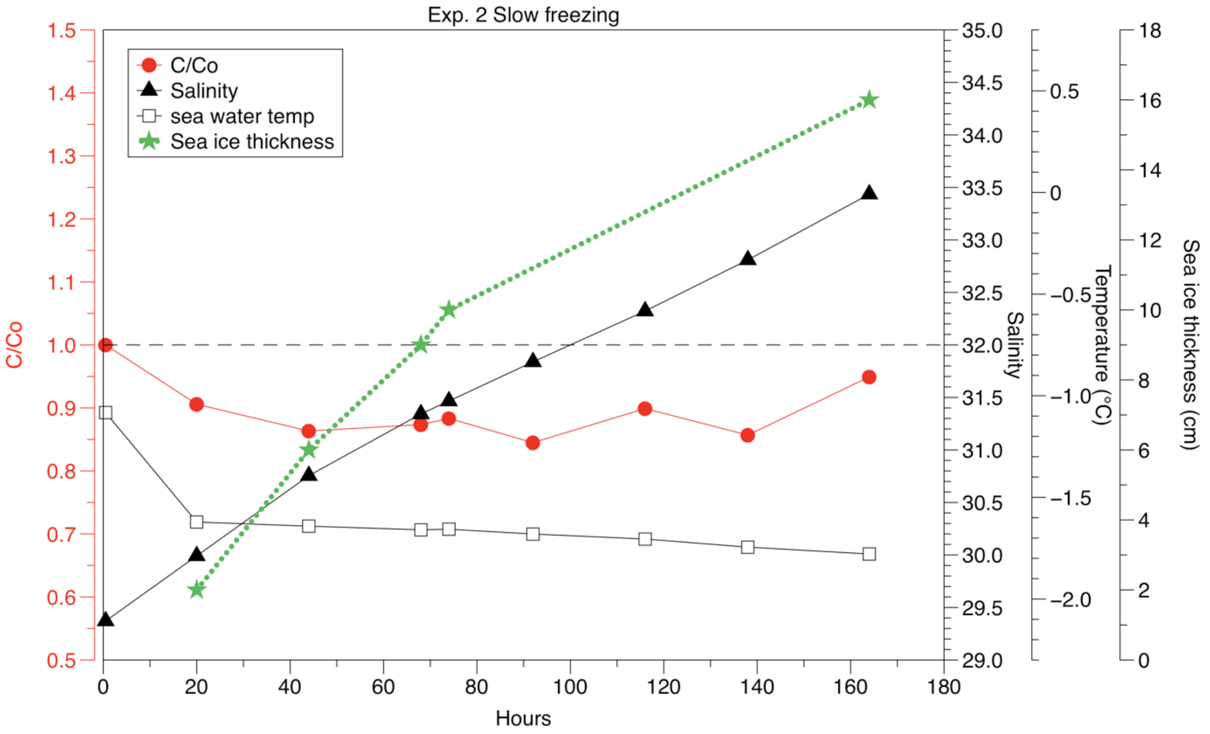

Figure 2: Methane concentration (red dots) (normalized to the initial concentration (Co)), salinity, sea water temperature and the sea ice thickness (preliminary results). The decrease/increase in methane concentrations in sea water refer to an uptake/release in/from sea ice during the experiment.

3. *Experiment 3: Fast freezing followed by slow melting*

Sea water temperature sharply decreases from 0.45 to -1.72°C (first stage of the experiment) reaching 16 cm of sea ice at the end of the third day. It was followed by a slightly temperature increase up to -1.43°C when the room temperature was set up to -2°C. Temperature arises up to -0.95°C, when the room temperature was set up again to 5°C. Salinity increased from 29.06 to 32.27 during the first 80 hours of experiment followed by a decrease up to 29.6 when the room temperature was set up to 5°C (sea ice melting). These features were also observed on methane concentration in sea water which slightly increases over the time until the ice starts melting, when its concentration quickly response decreasing until it reaches the same concentration when the experiment started. Concerning the methane isotopic signature, a variation of 5‰ was observed in sea water.

4. *Experiment 4: Fast freezing followed by fast melting*

Sea water temperature decreased sharply from -0.29 to -1.7°C and salinity increased from 28.94 to 32.51 on the first stage of the experiment. After reaching 16 cm of ice thickness, the room temperature was set up to 10°C reflected on the sea water temperature increase (up to -0.87°C) and a salinity decrease (up to 31.03). Methane concentration shows the same trend like salinity, where it increased until the maximum of sea ice thickness (16 cm) and then it sharply decreases together with sea ice melting. The change in δ^{13}C of methane during the experiments was about 5.5‰.

Outcome and future studies

The results from these experiments will be published in a scientific journal.

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