

Quantification of ikaite in Antarctic sea ice

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Abstract. CaCO₃ precipitation in sea ice is thought to potentially drive significant CO₂ uptake by the ocean, however, little is known about the quantitative spatial and temporal distribution of CaCO₃ within sea ice. This is a quantitative study providing a systematic investigation of hydrous calcium carbonate, as ikaite, in sea ice. Ice cores and brine samples were collected from pack and land

5 fast sea ice between September and December 2007 during an expedition in the East Antarctic and another off Terre Adélie, Antarctica. Samples were analysed for CaCO₃, salinity, dissolved organic carbon/nitrogen (DOC, DON), inorganic phosphate, and total alkalinity. A relationship between these parameters and CaCO₃ precipitation could not be determined. We found calcium carbonate, as ikaite, mostly in the top layer of sea ice with values up to 126 mg ikaite per liter melted sea ice.

10 This potentially represents an important contribution to the annual carbon flux in polar oceans. The horizontal distribution of ikaite in sea ice was heterogeneous. We also found the precipitate in the snow on top of the sea ice in some of the sampling locations.

1 Introduction

Sea ice covers up to 7% of the total surface area of the oceans at its maximum extent (Comiso, 2010).

15 The physical barrier itself has a major impact on the gas exchange between atmosphere and ocean, and recently the discussion has extended to considering how physical and biogeochemical processes within the ice itself can affect diffusion and flux of gases to both atmosphere and ocean (Tison et al., 2002; Delille, 2006; Rysgaard et al., 2007, 2009, 2011; Miller et al., 2011; Loose et al., 2011).

On the basis of thermodynamic equilibrium calculations, the precipitation of CaCO_3 was predicted to occur during natural sea ice formation (Gitterman, 1937; Jones and Coote, 1981; Anderson and Jones, 1985) and it was proposed to precipitate as calcite (Marion, 2001). However, actual evidence was, for a long time, only indirect (Killawee et al., 1998; Papadimitriou et al., 2004; Tison et al., 2002) until Dieckmann et al. (2008) found calcium carbonate as ikaite $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ in Antarctic sea ice, and more recently in Arctic sea ice (Dieckmann et al., 2010). Rysgaard et al. (2007, 2009, 2012) showed that with brine, dissolved organic carbon (DIC) is rejected from growing sea ice to the underlying waters. They ascribe the high pCO_2 (partial pressure of CO_2) levels found below sea ice to calcium carbonate precipitation. Delille et al. (2007) proposed that CaCO_3 precipitation in sea ice could drive significant CO_2 uptake by the ocean and therefore contribute significantly to a polar carbon pump.

Besides its function as a component in the carbon cycle, the mineral is also thought to have a key role in tropospheric ozone depletion events (ODEs) at high latitudes (Sander et al., 2006; Sander and Morin, 2010). Simulations of the chemistry occurring in polar regions over recently formed sea ice relate the ODE to the transformation of inert sea-salt bromide to reactive bromine monoxide (BrO) when precipitation of calcium carbonate from freezing sea water is taken into account. The discovery of ikaite in firn ice of the Antarctic continent, which appears to be derived from sea ice 300 km away, may also have implications for its use as a sea ice proxy (Sala et al., 2008). However, to date most studies of calcium carbonate in sea ice have been mainly qualitative and little is known about the spatial and temporal distribution of CaCO_3 within sea ice.

There is also a lack of knowledge on the exact conditions leading to ikaite precipitation as well as on the amount and fate of ikaite: e.g. one assumption is that phosphate and dissolved organic matter (DOM) may reduce the precipitation of calcium carbonate (Bischoff et al., 1993; Zullig and Morse, 1988). Both dissolved inorganic phosphate and DOM can be present in sea ice in very high concentrations (Thomas et al., 1998, 2001), and it can be hypothesized that where these parameters are present in high concentrations that precipitation of some polymorphs of calcium carbonate will be inhibited.

The objective of this study therefore was to: (1) Provide the first systematic observation and quantification of CaCO_3 precipitation in Antarctic sea ice on a spatial and temporal scale and (2) to investigate relationships between calcium carbonate and alkalinity, phosphate, and dissolved organic matter.

2 Methods

Two campaigns were performed between September and December 2007. During the first campaign (Sea Ice Physics and Ecosystem eXperiment (SIPEX) onboard RSV Aurora Australis from September to October 2007) fourteen ice cores (S1 to S14) were taken at different locations between 64°

and 66° south and 116° and 128° east (Fig. 1). The cores were cut into 10 cm sections within a few minutes after sampling and stored in plastic containers. Ice cores from station S1 to S4 and S6 to S14 represent pack ice with different degrees of deformation (Table 1). The ice core from station S5 was taken from fast ice between grounded icebergs. Further details on ice types, bulk salinity, ice temperature, and brine volume, see table 1, Meiners et al. (2011), figure 8, and figure 9. A general description of the ice conditions during the expedition can be found in Worby et al. (2011). Brine from sackholes from 10 out of 14 stations (see table 2) was collected for nutrient and DOM analyses (see Norman et al. (2011)).

On the second campaign (from November to December 2007) sea ice samples were collected close to the French base Dumont d'Urville, S66° 39' 13" E140° 00' 5" near station C described in Delille et al. (2007). Six complete ice cores (D1 to D6) were taken from young fast ice (age: \approx 3 months, Anne Jacquet, pers. comm.) which had formed in August. This area was predominantly free of snow with only isolated patches of snow being present. The cores were also cut into 10 cm sections and stored as described above. In order to determine small-scale vertical distribution of ikaite, we also collected four surface cores (D7 to D10) between 10 and 15 cm length (Table 1). Cores D7 and D9 were taken from the main sampling site without any snow on top, while D8 was taken next to it and included snow. Ice sample D10 was taken from older fast ice approximately 200 m away from the main sampling site. Ice core D10 was taken from sea ice which had formed in autumn and had remained intact since its formation, in contrast to cores D1-D9 which were from younger sea ice. Ice cores D7 to D10 were cut into 2 cm sections. In addition, to determine horizontal spatial variability of calcium carbonate, we chose an area 50 m away from the first sampling site. On this site the first top 10 cm of fast ice were sampled every 5 m (x and y direction) in a grid of 20 m by 20 m (D-SP1 to D-SP25, Table 1). The partial ice cores obtained were stored in clean plastic containers. At the main sampling site, sackholes (D-SH1 to D-SH7) of 30 cm were cored every two or three days for a temporal analysis of brine and ice. All samples were collected within an area of 10 m x 10 m to minimize bias due to spatial heterogeneity. The partial ice core obtained from these sackholes was also stored in clean plastic containers. Brine was allowed to accumulate in the sackholes and sampled with a vacuum pump and transferred into different vials for total alkalinity (TA), dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and phosphate analyses. Samples for DOM and nutrients were collected as described by Norman et al. (2011) and kept frozen until analyses within 6 months. The TA samples were measured directly in the base laboratory.

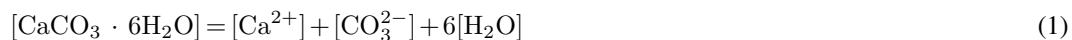
Two sediment traps MST6 (HYDRO-BIOS, 0.005 m² surface) and a current-meter RCM7 (ANDERRA) were deployed under the sea ice at Dumont d'Urville from 13/11/07 to 04/12/07 immediately adjacent to the temporal study site. The first sediment trap at 5 m under the ice and the second one at 25 m. Water depth at the site was 53 m. Mercuric chloride was used for fixation of the samples. Sediment trap samples were immediately analysed under the binocular microscope after the traps were retrieved.

We also sampled glacial firn ice 6 kilometer away from the ice shelf at Prud'homme to test if calcium carbonates are found on the ice shelf in this region. One surface core (1m) was collected and cut into 3 equal sections. The sections were stored in plastic containers and brought to the base laboratory.

All sea ice samples were slowly melted in a climate controlled room where the temperatures never exceeded 4°C to avoid decomposition of the mineral ikaite. Regular monitoring (several times a day) guaranteed a processing of the samples as soon as the cores, or sections were melted. This ensured that the temperature of the melt water never rose above 0°C. The melt water was filtered through 0.2 µm polycarbonate filters using a vacuum pump and the volume determined. The filters with crystals were then placed in a plastic vial (Safe-Lock Tubes 2ml, Eppendorf, Germany) and subsequently filled with 75% v/v ethanol and frozen at –18°C for later mineralogical phase identification and quantitative measurements. In several instances crystals were collected after swirling the melted samples and allowing crystals to settle in the resulting vortex. The crystals were transferred from the vortex to a petri dish using a glass pipette (see Dieckmann et al. (2008) for methods). These were briefly inspected under the binocular microscope and photographed to check the morphology and subsequently also filtered as described above.

Mineral phase identification was conducted by micro X-ray diffraction (µ-XRD) under cryogenic conditions on selected samples at the Synchrotron Laboratory for Environmental Studies SUL-X at the synchrotron radiation source ANKA, Forschungszentrum Karlsruhe (now Karlsruhe Institute of Technology) as described by Dieckmann et al. (2008).

To quantify the amount of ikaite within the sample, the quantity of calcium ions were determined using Inductively-Coupled Plasma Optical Emission Spectrometry (ICP OES). The Safe-Lock tubes containing the filters were rinsed with concentrated ethanol and the content was transferred to larger vials. The transferred samples were dried at 60°C until all the ethanol had evaporated, leaving only the calcium carbonate crystals. 5 ml concentrated HNO₃ was added to dissociate all molecules according to equation 1 before the samples were analysed in the ICP OES. The amount of ikaite was calculated using a molar calcium/ikaite ratio of 1.



Brines from sackholes (D-SH1 to D-SH7 and from 10 stations during the SIPEX campaign) were analyzed for in situ concentrations of phosphate, DON, DOC and alkalinity (table 2). Analysis for the major dissolved inorganic nutrients, nitrate (NO₃⁻), nitrite (NO₂⁻) and of dissolved inorganic phosphorus (DIP) was done using standard colorimetric methodology (Hanson and Koroleff, 1983) as adapted for flow injection analysis (FIA) on a LACHAT Instruments Quick-Chem 8000 autoanalyzer (Hales et al., 2004). Dissolved organic carbon was analysed by high temperature combustion on an MQ1000 TOC analyzer according to Qian and Mopper (1996). Dissolved organic nitrogen was determined by subtraction of NO₃⁻, and NH₄⁺ from the total dissolved nitrogen (TDN) analyzed using on-line peroxodisulfate oxidation coupled with ultraviolet radiation at pH 9.0 and 100°C (Kroon,

1993). Total alkalinity (D-SH1 to D-SH7) was measured at the station laboratory within one day after sampling as described by Nomura et al. (2010).

For the spatial analyses of the horizontal distribution of $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ a conventional geostatistical spatial interpolation was applied by using the simple kriging method (Sarma, 2009).

3 Results

Calcium carbonate crystals were found in all samples analyzed, including snow, sea ice and glacial ice. Mineral phase identification of selected samples confirmed that ikaite was the precipitate present. Since all crystals extracted from the ice cores showed the same morphological features, it is most likely that the XRD identification as ikaite is representative for all crystals found in this study (Fig. 2). Ikaite concentrations (in melted sea ice) ranged from 0.01 to 126 mg l^{-1} . The maximum amount of ikaite was found in older fast ice (D10). Data from 14 ice cores of the SIPEX campaign show the distribution of the ikaite crystals with highest concentrations in the top layers of ice (Fig. 3). Though the highest concentration of ikaite in melted sea ice in the pack ice samples was 9.5 mg ikaite l^{-1} melted sea ice, most of the values in the first ten centimeters did not exceed 2 mg ikaite l^{-1} . Below a depth of 20 cm (with the exception of two ice cores (S3 and S6)) in the pack ice, ikaite concentrations ranged between 0.02 and 0.3 mg l^{-1} . Ice texture analyses of cores S3 and S6 showed it to be rafted sea ice.

The ikaite concentrations in land fast ice off Terre Adélie were of a similar magnitude but generally higher than the pack ice cores (Fig. 4): Most were between 2 and 5 mg l^{-1} in the top layer. A higher resolution sampling (2 cm) over the first 10 to 15 cm showed that the highest concentrations of the mineral were in the top 2 to 4 cm of the cores (Fig. 5). Ice core D10 (Fig. 6) was taken at a location of older fast ice 133 cm thick, 200 m away from the initial sampling site. This core had higher mineral concentrations than those from the younger sea ice. Ice core D8 from snow covered ice (Fig. 7) had ikaite crystals throughout the core and even in the snow itself. The highest concentration (38.77 mg l^{-1} melted sea ice) was observed at the snow/ice interface. Salinity profiles were similar to those of the amount of ikaite in core D8 (Fig 7).

A temporal change in ikaite concentration during the period of sampling between 14 to 27 November 2007 was not observed. Values of the temporal and spatial experiment are in the same range (0.06 and 3.93 mg l^{-1} , Fig. 10, Table 2). Hence, we could not differ temporal from spatial heterogeneity. Values from the spatial experiment showed that the distribution of $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ in sea ice is already heterogenous.

The sediment trap samples did not have any CaCO_3 crystals in the sample bottles.

When brine concentrations are normalized to a salinity of 35 (see Papadimitriou et al. (2007)), DON_{35} and DOC_{35} concentrations increase non-linearly over a period of time. In our study during the DDU campaign, phosphate (normalized to $S=35$) shows the same trend as DON_{35} and DOC_{35} at

the beginning, it did not increase over time and remained low. Only NO_3 shows a trend which might indicate biological activity. Alkalinity fell from almost 2600 to approximately 2200 $\mu\text{mol l}^{-1}$. TA did not show a linear trend, similar to the other measured chemical parameters. Neither DIC, DON, DOC concentrations (from SIPEX and DDU campaign) nor TA (DDU campaign) correlated significantly with the amount of hydrous calcium carbonate present in the ice horizons from where the brines were collected from. Comparison of theoretical values of brine salinity (calculated according Petrich and Eicken (2010)) versus measured values (table 2) showed that brine was not influenced by seawater (Fig. 8 and Fig 9.)

4 Discussion

Our results together with previous observations (Dieckmann et al., 2008) indicate, that calcium carbonate precipitation is widespread in Antarctic sea ice, albeit that its concentration is heterogenous, as is the case for most other biogeochemical parameters in sea ice (Thomas and Dieckmann, 2010). Although we were not able to verify the CaCO_3 polymorph for each sample collected, the visual characterisation by light microscopy confirmed that the morphology of all crystals was identical to those analyzed by X-ray diffraction. We are therefore convinced that ikaite was always the precipitate. Higher brine salinities, and correspondingly high Ω_{ikaite} (ikaite saturation state of seawater) values, resulted in a more likely precipitation of ikaite near the ice surface than in lower parts in sea ice where temperatures are higher and brine salinity can drop to seawater values. However, it is still not clear at what point in time ikaite precipitation occurs, and our interpretation is confounded because the various biogeochemical parameters measured during sample collection do not reflect conditions at the time of precipitation. For example the question arises why a TA decrease by 400 μmol did not result in a correlation with the precipitation of calcium carbonate. As discussed above, the measurements reflect only a small time frame in the seasonal carbon cycle within sea ice and not necessarily the conditions at time of precipitation. Observations of higher values of hydrous calcium carbonate precipitation in older land fast ice (Fig. 6) also raise the question if precipitation also takes place during subsequent sea ice growth or if ikaite, after it has formed in young sea ice, remains stable under various conditions until the sea ice melts and therefore does not alter TA or the carbonate system itself.

Based on a thermo-molecular pressure gradient as described by Wettlaufer and Worster (1995), brine, as unfrozen liquid, can be transported from the ice interior toward the relatively colder surface (Rankin and Wolff, 2002). The accumulated brine at the surface has a salinity of about 100 (Perovich and Richter-Menge, 1994) and favors the precipitation of salts. Under those conditions frost flowers may start to grow (Perovich and Richter-Menge, 1994; Rankin and Wolff, 2002; Obbard et al., 2009) and in turn can initiate CaCO_3 precipitation. However, conditions not necessarily leading to frost

flower formation, may also lead to CaCO_3 precipitation if the temperature is low and salinity is high. The occurrence of calcium carbonate in the snow cover can most likely also be explained by the thermomolecular pressure gradient and capillary transport, which is supported by the maximum
200 occurrence of ikaite at the snow ice interface (Fig. 8).

Higher values of calcium carbonate in some middle layers of sea ice were attributable to rafting of floes subsequent to sea ice formation (see Meiners et al. (2011)). Floes which slide over each other where the surface layer of one of the floes is transformed into a middle layer of the resulting one. Although CaCO_3 concentrations were on the same order of magnitude in pack ice and land fast ice
205 there appear to be differences in the amount of precipitated calcium carbonate. The highest values were recorded in approximately 1 year old land fast sea ice, followed by high amounts in land fast ice and the lowest concentration in pack ice. The reason why we found different values in different types of sea ice is not clear yet. One explanation could be, that CaCO_3 also precipitated during subsequent sea ice growth. Another reason could be, that sea ice is experiencing different growth
210 conditions i.e. such as higher temperatures resulting in lower salinities and saturation states and thus lower values of ikaite.

It is not possible to determine the temporal development of CaCO_3 in the sea ice investigated during the DDU campaign. This is due to the extreme variability in CaCO_3 concentrations even on small spatial scales. The reason for this heterogeneity might be due to the inherent variability in many sea
215 ice properties ranging from temperature, salinity, texture, chemistry and lastly biological activity. The spatial and temporal heterogeneity are already apparent on small scales as shown by the spatial and temporal studies during the DDU campaign. Thus, it is difficult to draw conclusions on the temporal evolution of the precipitation of ikaite.

The high concentrations of DOC and DON found in sea ice during the campaign off Terre Adélie
220 were expected to inhibit CaCO_3 precipitation (Bischoff et al., 1993). Zullig and Morse (1988) and Berner et al. (1978) have shown that DOM influences the precipitation of some polymorphs of calcium carbonate. However, these studies refer only to the inhibition for anhydrous polymorphs of CaCO_3 . Besides the repression by polyphosphate and magnesium ions on the precipitation of anhydrous calcium carbonate in favour of hydrated forms, Dickens and Brown (1970) postulate that
225 hydrated salts may play an important part in biological mineralization. Taking this into account, additionally to the elevated Ω_{ikaite} , microbial biomass, such as cell surfaces and/or extracellular polymeric substances, could catalyze the precipitation of calcium carbonate (Kandianis et al., 2008). This also coincides with findings of elevated abundance of bacteria and exopolymers in frost flowers (Bowman and Deming, 2010) and the top layer of experimentally formed sea ice (Aslam et al.,
230 2012) which supports the hypothesis of CaCO_3 precipitation during frost flower and initial sea ice formation as discussed above.

The reasons why we did not find CaCO_3 in the sediment trap are not clear and the absence can at this stage only be attributed to several factors which cannot be verified: These include the dissolution

of crystals during ice melt, which means crystals do not leave the sea ice as temperatures increase.

235 The dissolution in the sediment trap itself before the trap was retrieved, but this would mean that crystals, which dropped out of the ice a day before retrieval would also have dissolved.

Previous studies have pointed out the importance of sea ice for the carbon uptake in polar oceans due to i.e. CaCO_3 precipitation (Tison et al., 2002; Delille, 2006; Nedashkovsky et al., 2009; Rysgaard et al., 2009, 2011). An estimation of the contribution of calcium carbonate precipitation to the polar

240 carbon cycle would be useful. However, the large heterogeneity observed in the distribution of ikaite will make such an estimate highly uncertain. In addition the large amount of ikaite in the snow has to be taken into account. Considering the vast areal extent of sea ice in the polar regions the high concentrations of ikaite found in sea ice and in the snow would be a significant addition to the polar carbon flux. Considering polynyas with new sea ice forming during the winter and taking into ac-

245 count, that CaCO_3 precipitation mainly occurs during young sea ice and frost flower formation, this phenomenon might then contribute even to a larger extent to the air-sea flux. However, this would be only the case if CO_2 , which is released during CaCO_3 precipitation, is rejected to the underlying water column. While sea ice is still permeable during sea ice formation, high pCO_2 in brine (due to salinity effect), and CaCO_3 precipitation in the top layer of sea ice, a large amount of CO_2 would
250 be released to the atmosphere and would thus not contribute to the sea ice carbon pump as proposed by Rysgaard et al. (2007, 2011) and Loose et al. (2011). It is essential to determine and quantify the CO_2 pathways during sea ice formation to fully quantify the contribution of calcium carbonate precipitation to the air-sea CO_2 flux.

With ikaite mainly in the top layer of sea ice our findings support the work of Sander et al. (2006)
255 and Sander and Morin (2010) which describes the contribution of CaCO_3 precipitation to ozone depletion events. It also supports the work of Sala et al. (2008), since ikaite crystals at the snow-ice interface and in the snow are more likely exposed to aeolian transport and may therefore serve as sea ice proxy.

5 Conclusions

260 This is the first study providing a systematic investigation of the spatial and temporal distribution of CaCO_3 in sea ice. We showed the heterogeneous occurrence of CaCO_3 in sea ice. Large scale quantification of CaCO_3 precipitation in different types of sea ice and during the entire season in both the Arctic and Antarctic is necessary to validate these findings and to provide a quality data set to estimate its contribution to the polar carbon cycle. Since parameters measured during sample
265 collection do not reflect conditions at the time of precipitation, much work is needed to evaluate the conditions of calcium carbonate precipitation within sea ice and its fate during sea ice melt.

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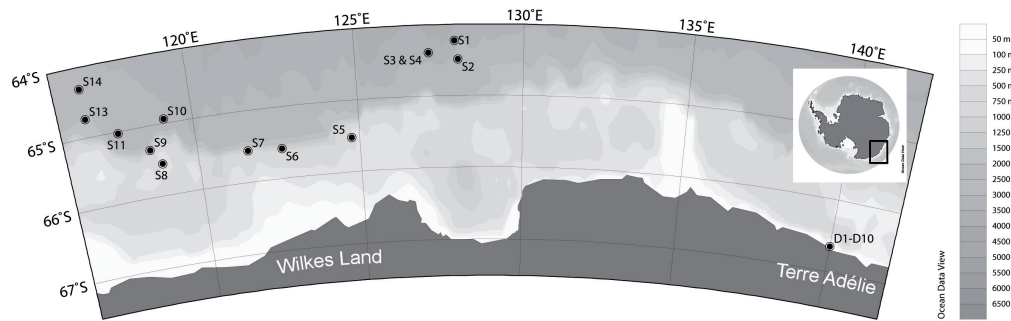


Fig. 1. Locations of ice stations sampled during SIPEX and DDU campaign

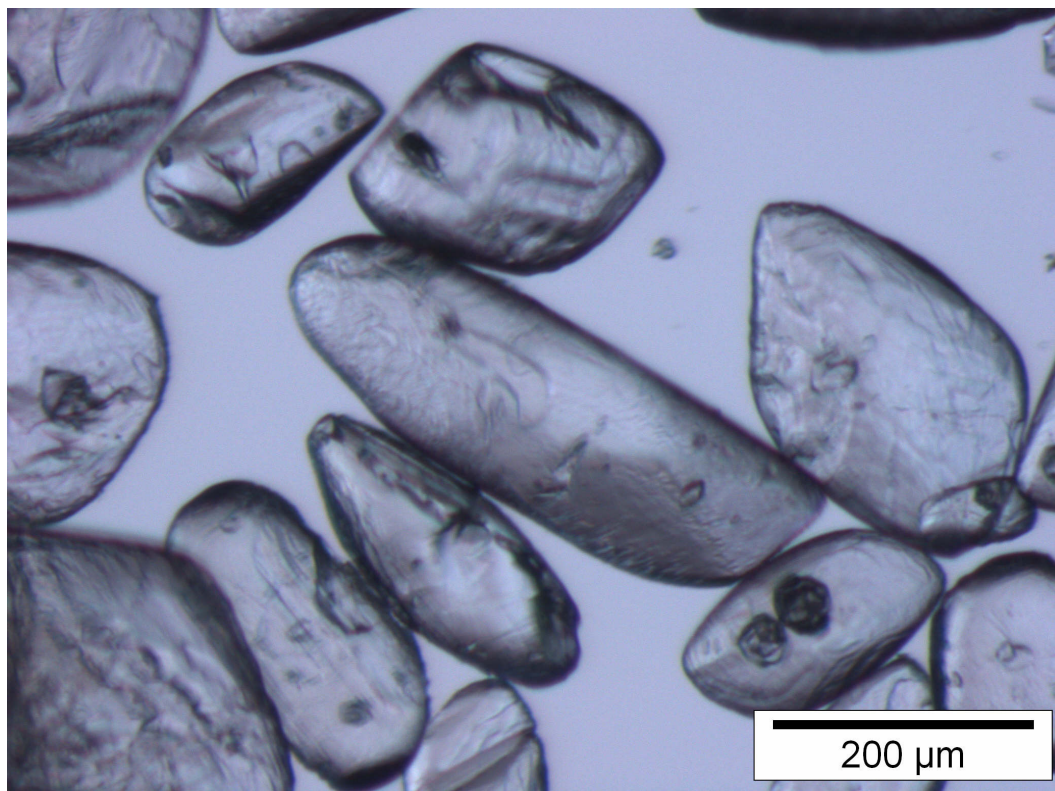


Fig. 2. Light microscopy image of ikaite crystals taken from a single bulk sea ice sample from land fast ice off Terre Adélie

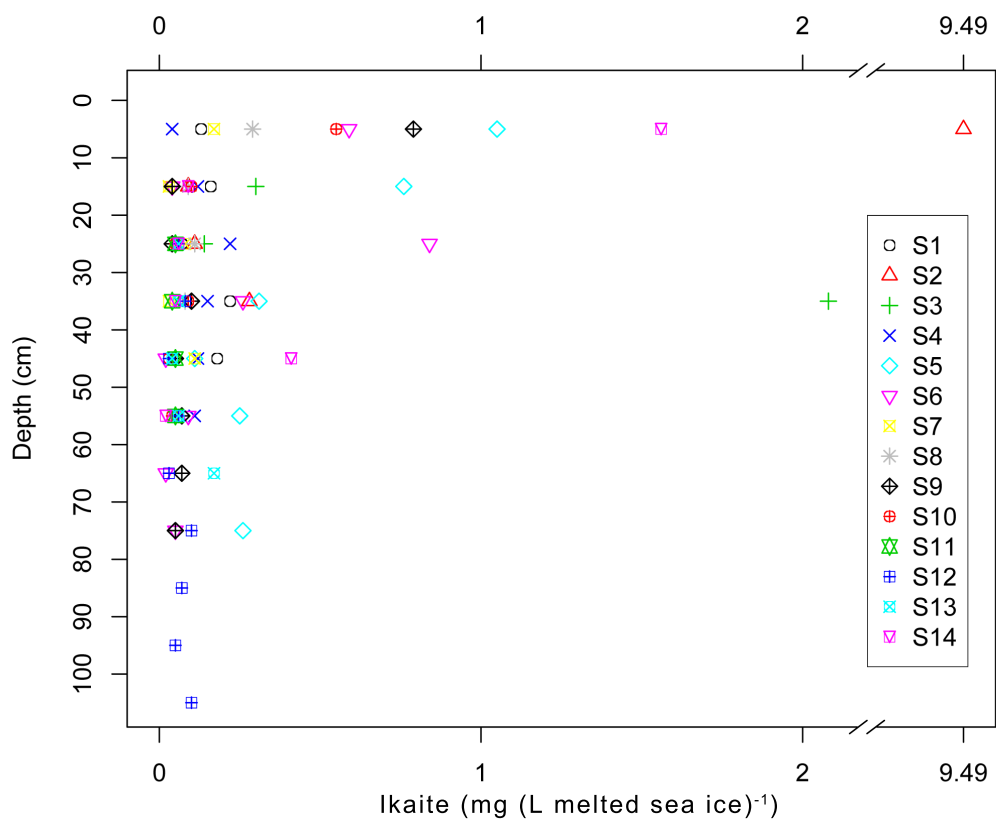


Fig. 3. Distribution of ikaite in sea ice during SIPEX cruise in different ice cores taken between September and October 2007 in East Antarctic

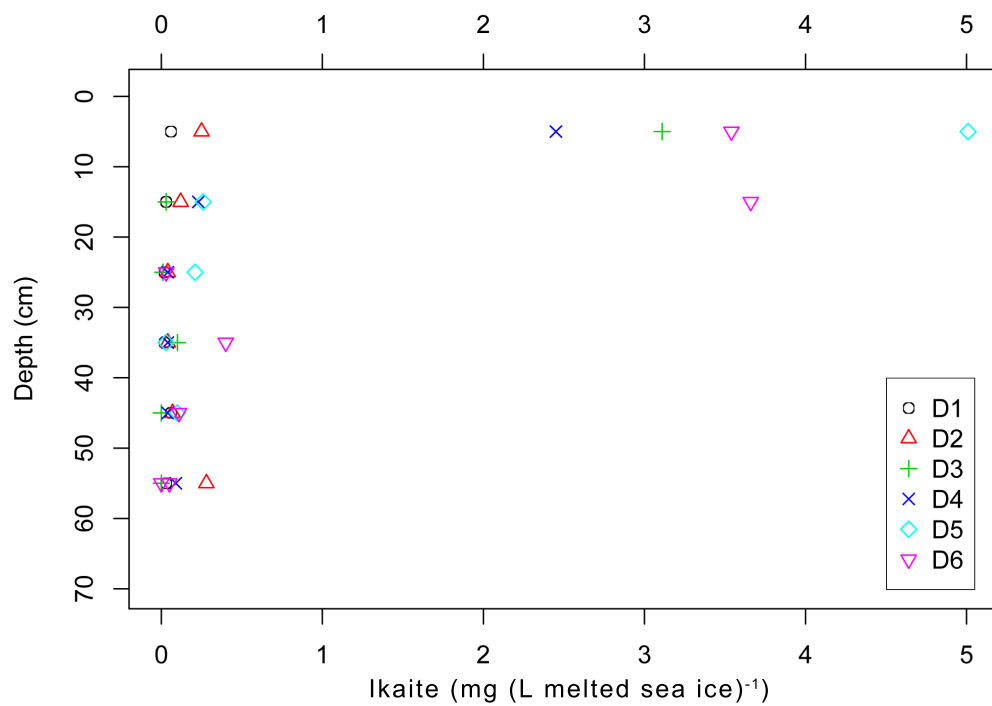


Fig. 4. Distribution of ikaite in sea ice during DDU campaign in land fast sea ice off Terre Adélie sampled in November 2007

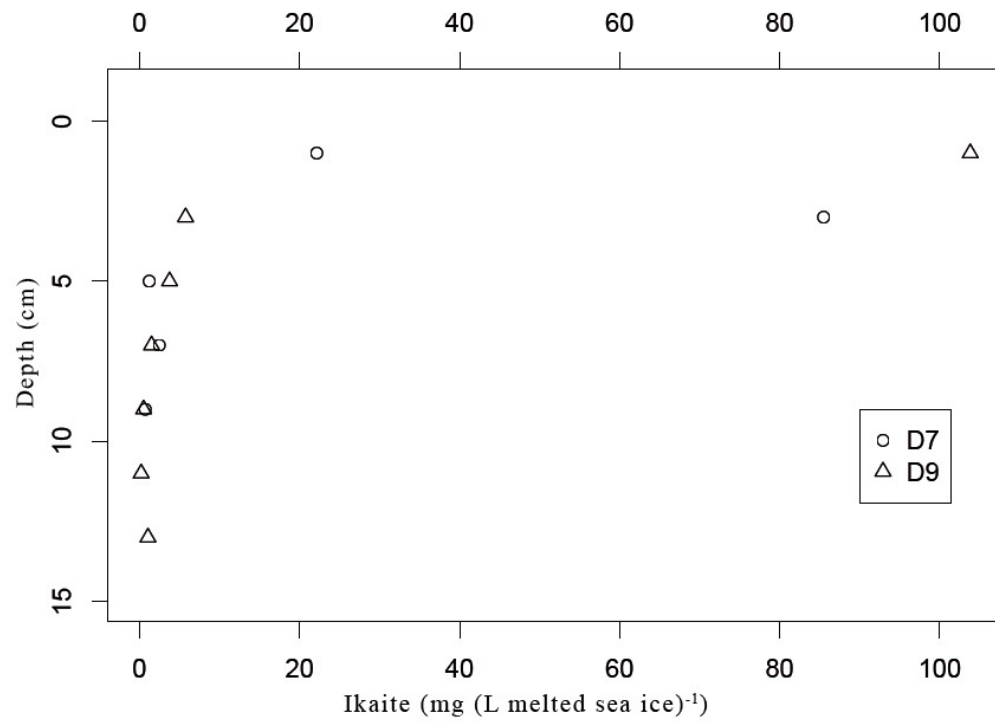


Fig. 5. Distribution of ikaite in the top layer of young (≈ 3 month) land fast sea ice off Terre Adélie (DDU)

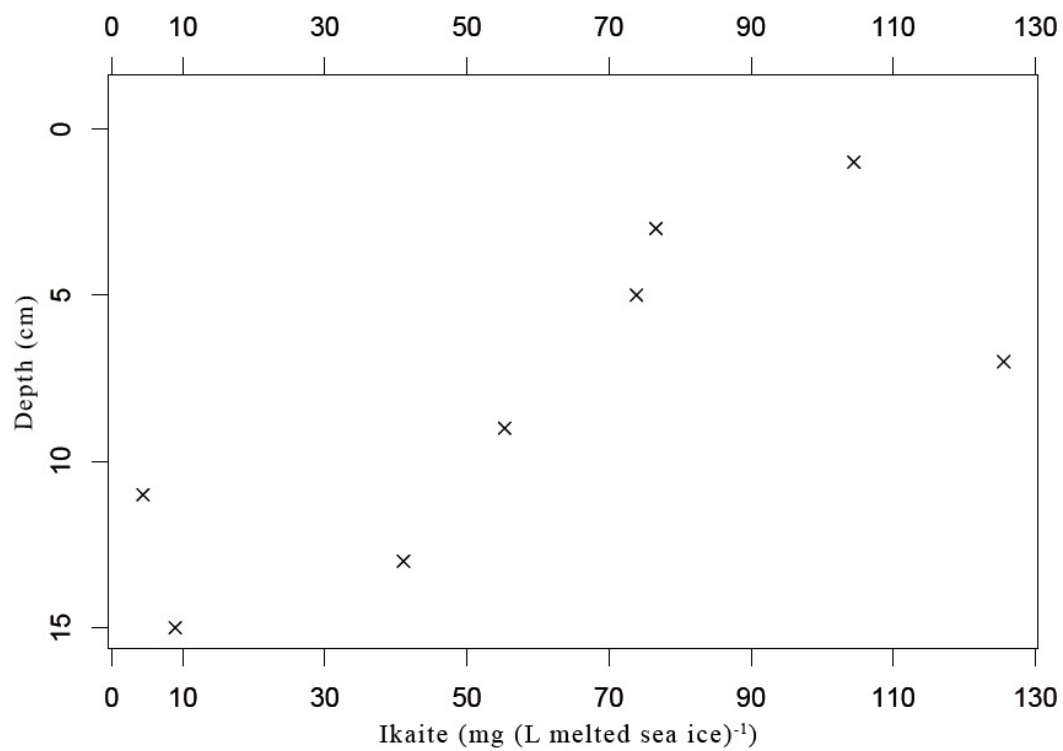


Fig. 6. Distribution of ikaite in the top layer of older (≈ 1 year) land fast sea ice, off Terre Adélie (DDU) in November 2007 core D10

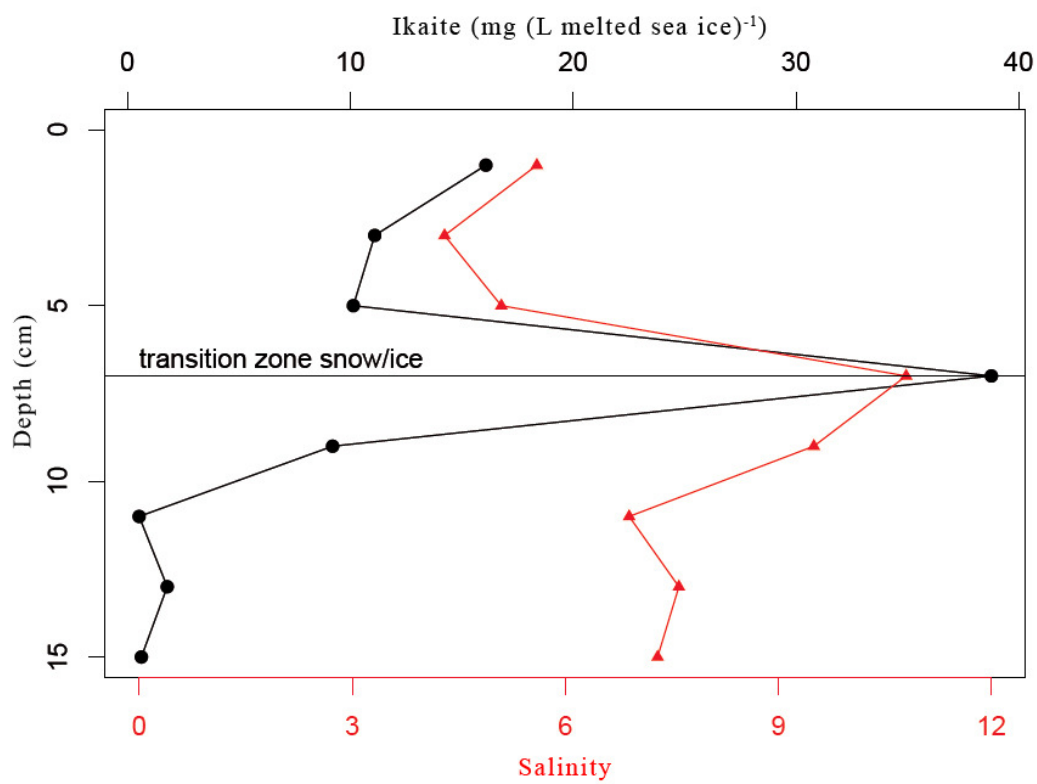


Fig. 7. Distribution of ikaite across the snow-ice interface from top layer of land fast sea ice off Terre Adélie (DDU) in November 2007, core D8, Black line = amount of ikaite, red line = bulk salinity

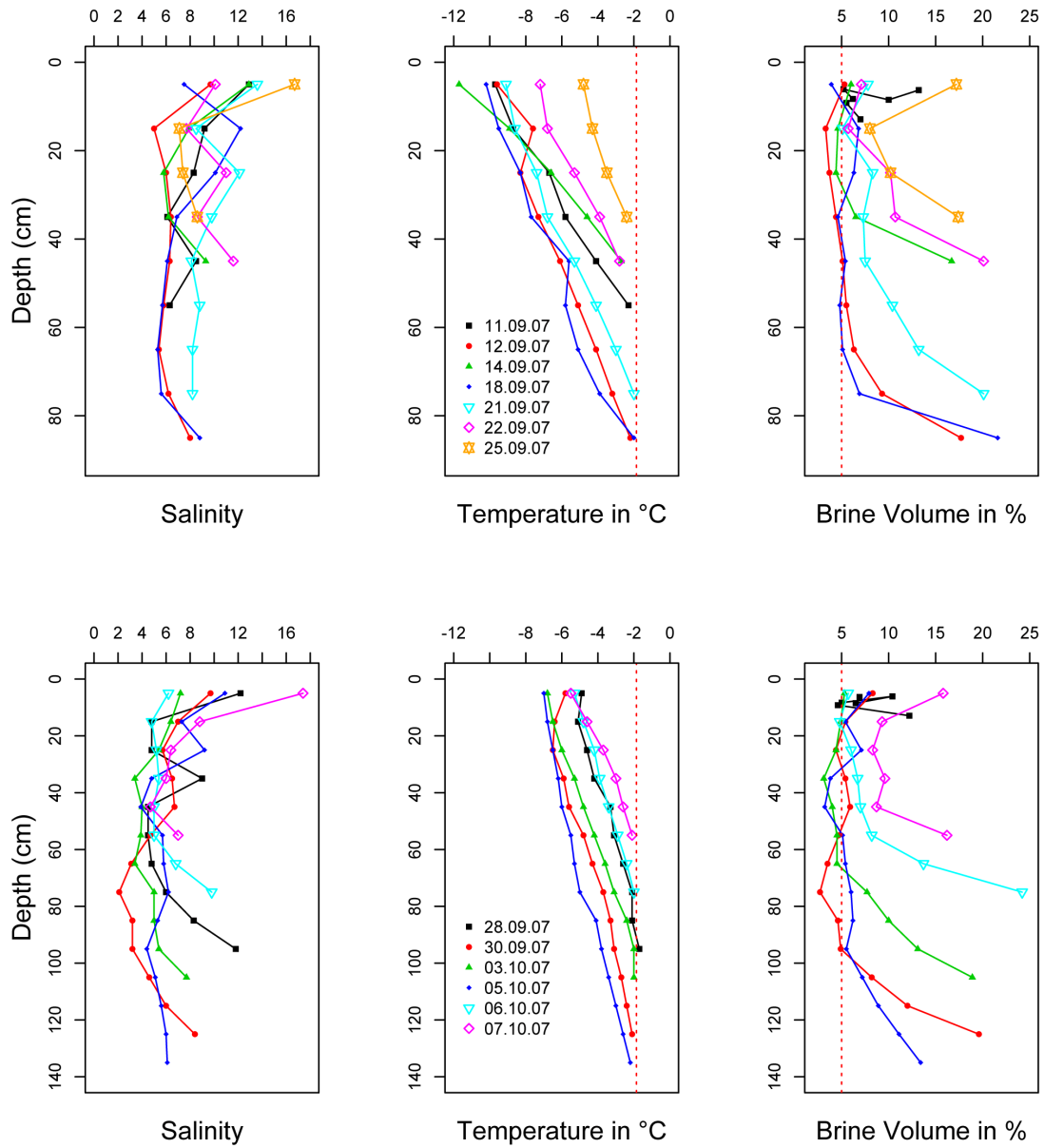


Fig. 8. Bulk (melt) salinity (S), sea ice temperature, and calculated (Cox and Weeks, 1986) brine volume in different ice cores taken between September and October 2007 in East Antarctic during SIPEX campaign

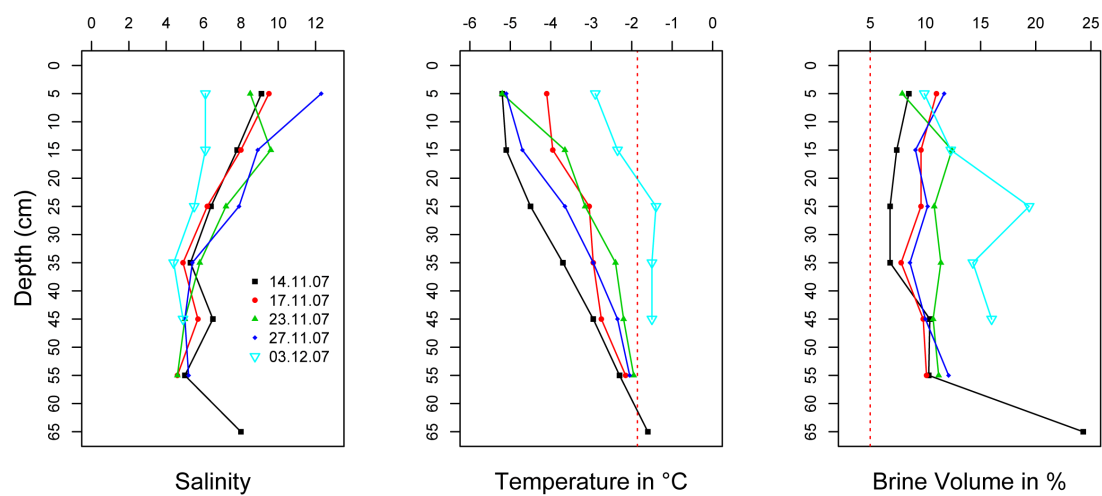


Fig. 9. Bulk (melt) salinity (S), sea ice temperature, and calculated (Cox and Weeks, 1986) brine volume in land fast sea ice cores taken between November and December 2007 in East Antarctic during DDU campaign

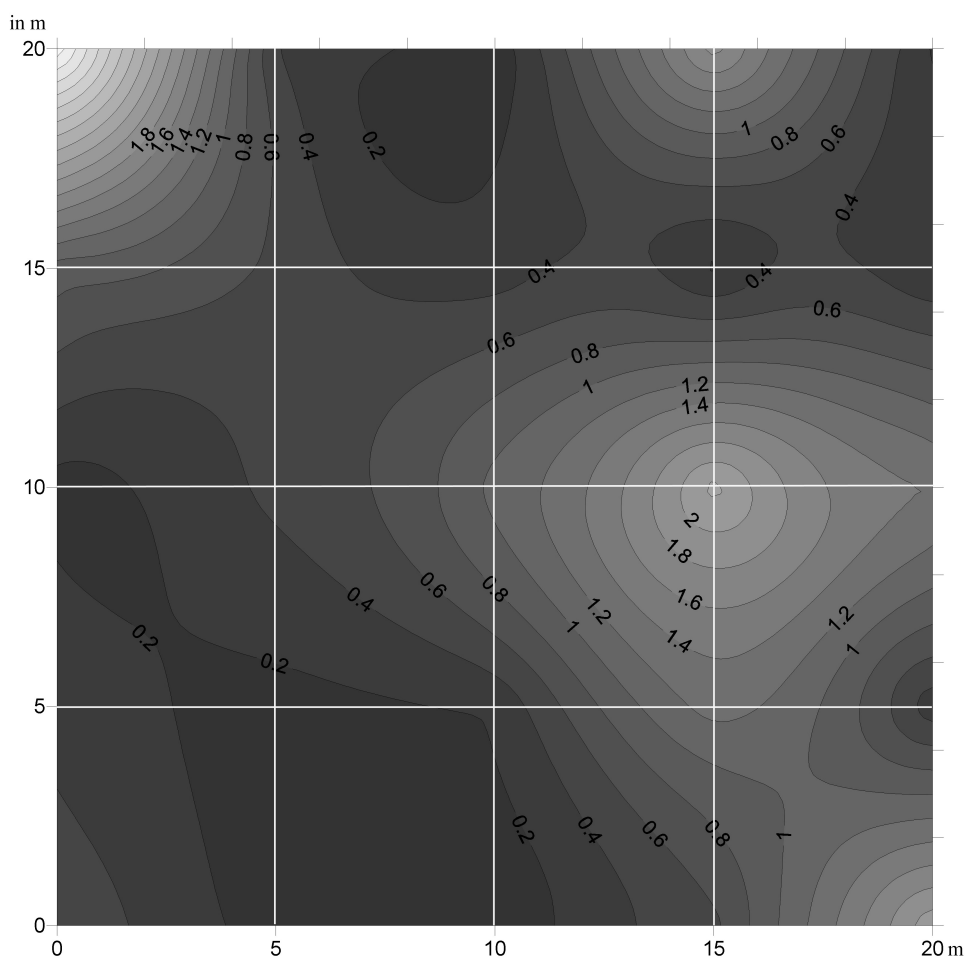


Fig. 10. Contour plot of the spatial distribution of ikaite in the first 10 cm of land fast sea ice off Terre Adélie (DDU) in November 2007 on a 20 m x 20 m grid with sample points every 5 m by 5 m (shown by intersections of the white lines and at the edges). Values are in mg ikaite l^{-1} melted sea ice.

Table 1. Sample types and thickness of sea ice during SIPEX and DDU campaign

Sample	Cruise	Date of Sampling	Time (UTC)	T _{Air}	T at 5 cm below surface	Sample type	Sample thickness in cm
S1	SIPEX	11.09.2007	04:00	-15,9	-8,7	Pack ice, Brine from sackhole	51
S2	SIPEX	12.09.2007	06:00	-18,6	-9,6	Pack ice, Brine from sackhole	98
S3	SIPEX	14.09.2007	06:00	-20,1	-11,7	Pack ice, Brine from sackhole	49
S4	SIPEX	17.09.2007	08:00	-19	N/A	Pack ice, Brine from sackhole	55
S5	SIPEX	18.09.2007	08:00	-18	-10,2	fast ice between grounded icebergs, brine from sackhole	85
S6	SIPEX	21.09.2007	03:00	-11,7	-9,1	heavily rafted ice floes, brine from sackhole	81
S7	SIPEX	22.09.2007	02:30	-12,3	-7,2	Pack ice, brine from sackhole	53
S8	SIPEX	25.09.2007	10:00	-7	-4,9	large level floe, brine from sackhole	37
S9	SIPEX	28.09.2007	03:00	-11,1	-4,9	heavily rafted and deformed ice, brine from sackhole	98
S10	SIPEX	30.09.2007	04:00	-14,8	-4	large level floe, coring site on an adjacent rafted area, probably an old chunk caught by new ice, brine from sackhole	133
S11	SIPEX	03.10.2007	02:00	-7,3	-6,8	rafted floe, ice surface very rough probably crushed together pancakes at an earlier stage, brine from sackhole	101
S12	SIPEX	05.10.2007	07:00	-6,9	-6,5	rafted ice floes, brine from sackhole	109
S13	SIPEX	06.10.2007	02:00	-7,8	-5,3	rafted floes, ice surface very rough probably consisting of thin rafted ice chunks, brine from sackhole	78
S14	SIPEX	07.10.2007	01:00	-10	-5,5	Pack ice, brine from sackhole	64
D1	DDU	14.11.2007	N/A	-6,6	-5,2	young (approx. 3 month) fast ice, 10 cm sections	65
D2	DDU	17.11.2007	N/A	-3,2	-4,1	young (approx. 3 month) fast ice, 10 cm sections	65

Sample	Cruise	Date of Sampling	Time (UTC)	T _{Air}	T at 5 cm below surface	Sample type	Sample thickness in cm
D3	DDU	23.11.2007	N/A	-5,9	-5,2	young (approx. 3 month) fast ice, 10 cm sections	60
D4	DDU	24.11.2007	N/A	-2,6	N/A	young (approx. 3 month) fast ice, 10 cm sections	60
D5	DDU	27.11.2007	N/A	-2,9	-5,1	young (approx. 3 month) fast ice, 10 cm sections	60
D6	DDU	03.12.2007	N/A	-4,6	-2,9	young (approx. 3 month) fast ice, 10 cm sections	60
D7	DDU	23.11.2007	N/A	-5,9	-5,2	young (approx. 3 month) fast ice, 2 cm sections	10
D8	DDU	24.11.2007	N/A	-2,6	N/A	young (approx. 3 month) fast ice, 2 cm sections, snow on top	16
D9	DDU	24.11.2007	N/A	-2,6	N/A	young (approx. 3 month) fast ice, 2 cm sections	14
D10	DDU	05.12.2007	N/A	-2	-5,4	fast ice (age = 1 year), 2 cm sections	16
D-SH1	DDU	14.11.2007	N/A	-6,6	-5,2	ice and brine samples from sackholes in fast ice	30
D-SH2	DDU	17.11.2007	N/A	-3,2	-4,1	ice and brine samples from sackholes in fast ice	30
D-SH3	DDU	18.11.2007	N/A	-3,5	-4,2	ice and brine samples from sackholes in fast ice	30
D-SH4	DDU	23.11.2007	N/A	-5,9	-5,2	ice and brine samples from sackholes in fast ice	30
D-SH5	DDU	25.11.2007	N/A	-0,2	-2,65	ice and brine samples from sackholes in fast ice	30
D-SH6	DDU	27.11.2007	N/A	-2,9	-5,1	ice and brine samples from sackholes in fast ice	30
D-SP1 - D-SP25	DDU	02.12.2007	N/A	-2	N/A	top layer of fast ice	10

Table 2. Physico-chemical properties of brine collected from sackholes from land fast ice off Terre Adélie (DDU) in November 2007 (D-SH1 to D-SH7) and from sea ice in East Antarctic (see map) between September and October 2007 (S1 to S14). TA, DON, DOC, and nutrients are normalized to S=35. Ikaite values are from ice cores (30cm) obtained from the sackholes (D-SH1 to D-SH7, DDU campaign) and ice cores adjacent to the sackholes (S1 to S14, SIPEX cruise, sum of the first three 10 cm sections) and presented in mg l^{-1} melted sea ice.

Sample	Date	T_{brine}	S_{brine}	$[PO_4^{2-}]_{35}$	$[Si]_{35}$	$[NO_2]_{35}$	$[NO_2] + [NO_3^-]_{35}$	$[SNH_4]_{35}$	DON_{35}	DOC_{35}	Ikaite	TA_{35}
D-SH 1	14.11.07	-4.8	86	0.50	50.30	0.12	16.17	0.37	4.91	85.99	1.03	2573.79
D-SH 2	17.11.07	-4	76	1.53	41.39	0.14	10.63	2.04	17.50	146.17	0.68	2236.36
D-SH 3	18.11.07	-3.9	76	0.30	62.18	0.05	3.06	0.45	8.45	78.80	0.22	2370.92
D-SH 4	23.11.07	-4	74	1.33	53.12	0.07	3.11	0.91	33.41	180.04	1.23	2311.20
D-SH 5	25.11.07	-2.5	45	1.77	68.80	0.11	4.71	1.47	27.75	183.44	1.58	2171.08
D-SH 6	27.11.07	-3.6	65	0.45	49.83	0.08	0.98	0.32	12.51	130.84	0.53	2394.29
D-SH 7	03.12.07	-2.6	46	0.47	55.53	0.03	0.20	0.77	27.59	195.34	N/A	2215.04
S1	11.09.07	-5.1	88	1.75	36.37	0.14	28.48	N/A	2.40	41.52	0.34	N/A
S2	12.09.07	-12.4	179	0.92	52.21	0.36	32.07	N/A	2.35	68.24	9.69	N/A
S3	14.09.11	-8.3	138	1.17	40.07	0.25	28.15	N/A	4.06	49.46	N/A	N/A
S4	17.09.07	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
S5	18.09.11	-9.3	153	0.64	45.91	0.18	28.18	N/A	1.59	55.68	5.89	N/A
S6	21.09.07	-7.8	132	1.57	45.52	0.25	28.64	N/A	0.98	67.31	1.47	N/A
S7	22.09.07	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.28	N/A
S8	25.09.07	-3.9	73	1.93	52.25	0.13	29.93	N/A	3.55	61.38	0.49	N/A
S9	28.09.07	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.87	N/A
S10	30.09.07	-5.0	97	2.78	55.56	0.16	33.89	N/A	3.89	43.33	0.7	N/A
S11	03.10.07	-5.1	98	0.07	54.95	0.04	3.15	N/A	4.90	73.15	N/A	N/A
S12	05.10.07	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
S13	06.10.07	-3.7	78	1.44	42.63	0.10	23.78	N/A	4.94	73.14	N/A	N/A
S14	07.10.07	-5.2	78	0.27	46.92	0.13	10.00	N/A	5.00	67.31	1.71	N/A