

Brief Communication: Ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) discovered in Arctic sea ice

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Abstract. We report for the first time on the discovery of calcium carbonate crystals as ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) in sea ice from the Arctic (Kongsfjorden, Svalbard) as confirmed by morphology and indirectly by X-ray diffraction as well as XANES spectroscopy of its amorphous decomposition product. This finding demonstrates that the precipitation of calcium carbonate during the freezing of sea ice is not restricted to the Antarctic, where it was observed for the first time in 2008. This observation is an important step in the quest to quantify its impact on the sea ice driven carbon cycle.

1 Introduction

Precipitation of calcium carbonate, during the formation of sea ice is considered fundamental in catalyzing chemical processes such as the boundary layer ozone depletion events (ODEs) (Sander et al., 2006; Piot and von Glasow, 2008; Morin et al., 2008; Sander and Morin, 2009), as well as the formation and subsequent draw down of CO_2 via brine drainage (Rysgaard, 2007, 2009). Furthermore, calcium carbonate found in firn off Talos Dome, Antarctica is thought to originate from sea ice and therefore could act as a proxy for sea ice cover (Sala et al., 2008). It has to be noted that until recently all these considerations were based on theoretical calculations and data from laboratory experiments.

Obviously, due to the lack of direct confirmation of calcium carbonate precipitation in sea ice, estimates on its significance in the sea ice carbon cycle and consequently for polar or even global carbon budgets (Jones and Coote, 1981; Rysgaard et al., 2007, 2009) have been constrained. However, direct evidence of calcium carbonate precipitation based on field observations was obtained for the first time in 2008 (Dieckmann et al., 2008), after decades of controversial discussion on its possible existence. They isolated crystals from sea-ice collected at different locations in Antarctica and unambiguously identified them as ikaite, a hydrated calcium carbonate polymorph, by means of synchrotron based X-ray diffraction. Even though it is now known that measureable calcium carbonate precipitation occurs during the formation of sea ice, more data on the spatial and temporal occurrence is needed to estimate the impact of this phenomenon on the polar and global carbon cycle. Currently it is not clear whether ikaite is the only calcium carbonate polymorph forming in natural sea ice and we are not aware if this occurs in Arctic sea ice. From the rare observations in which ikaite has been found in the natural environment (e.g. Buchardt et al., 1997; Dahl and Buchardt, 2006; Omelon et al., 2001; Pauly, 1963), it appears that elevated phosphate concentrations play a crucial role in its formation. Therefore it had been speculated that the occurrence of ikaite in the Arctic is unlikely, since the phosphate concentrations in Arctic seawater are in general lower than in Antarctic seawater. Here we report for the first time on the occurrence of calcium carbonate, again in the form of ikaite, in sea ice from the Arctic (Kongsfjorden, Svalbard).



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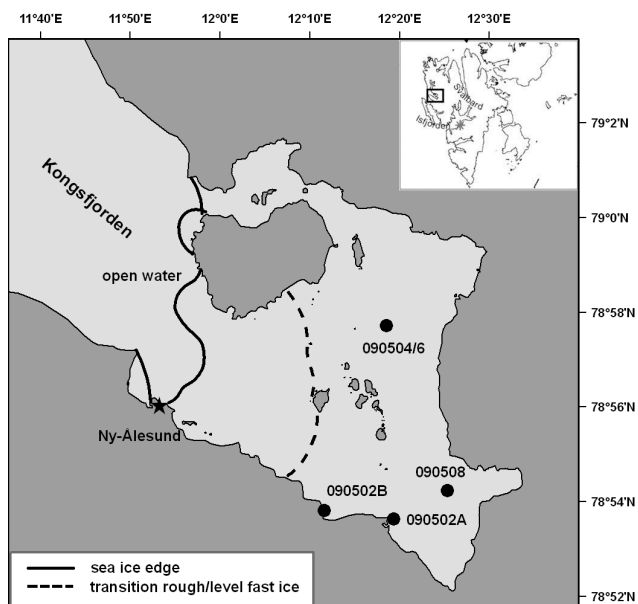


Fig. 1. Map showing sea ice stations in Kongsfjorden, Svalbard, in the vicinity of Ny-Ålesund. Solid line denotes the outer ice edge, and the dashed line indicates the outer edge of level first-year sea ice in the inner part of the fjord. Numbers denote day of sampling (yy/mm/dd).

2 Methods

Sea ice samples were collected at four stations in Kongsfjorden, a fjord on Spitsbergen in the Svalbard archipelago, between 2 and 8 May 2009 (Fig. 1). Inner Kongsfjorden is annually covered with first-year sea ice for several months (Gerland and Renner, 2007).

Seven cores were collected with a Mark III corer (Kovacs) and cut into sections of 4 cm beginning at the top. Alternatively, two samples were scraped off the sea ice surface. In both cases loose snow was first removed. Samples were stored in 1 L plastic cans and allowed to melt in a refrigerator (+4 °C). During melting, samples were monitored and as soon as the remaining ice had melted, samples were filtered through 2.0 µm polycarbonate filters (Millipore). Filters were preserved in absolute alcohol and stored frozen (−20 °C) in small vials. They were subsequently transported on ice to the home laboratory where they were stored in a refrigerator until further processing a few weeks later. Parallel ice cores were taken to determine temperature and salinity. Temperature was recorded immediately after core removal at 5 cm intervals along the length of the core. Precipitates collected on the filters were used for qualitative investigations only. Subsamples were used for visualization under a binocular microscope while additional subsamples were investigated by X-ray diffraction and Ca K-edge X-ray absorption near edge structure (XANES) spectroscopy at the SUL-X beamline of the synchrotron radiation source ANKA of the Karlsruhe Institute of Technology.

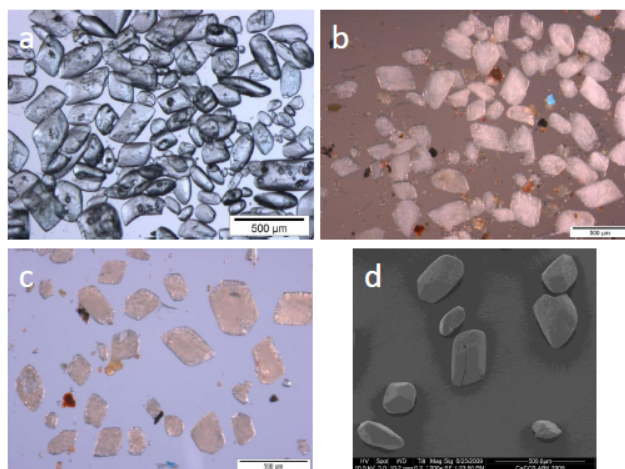


Fig. 2. Light microscopy image (a) of Ikaite crystals from Antarctic sea ice (Dieckmann et al., 2008). Light microscopy image – (b) and (c) – and scanning electron micrograph (d) of ikaite crystals from Kongsfjorden sea ice after transformation into amorphous calcium carbonate.

3 Results and discussion

All cores contained CaCO_3 crystals, but these could not be quantified and no clear stratification within the core was determined due to minute amounts found in most sections. Maximum visual concentrations were, however, observed in the upper core sections below the snow cover, a similar observation as was made in Antarctic sea ice cores (Dieckmann et al., 2008). Also the crystals had the same morphology as the Antarctic crystals, although they were less transparent (Fig. 2). This milky appearance was not observed directly after the samples were taken, but was visible after the samples had been transported to the home laboratory. Surprisingly no clear X-ray diffraction pattern could be obtained on these crystals (Fig. 3), even though they had perfect crystal faces. However, the obtained XRD pattern matches the one reported for amorphous calcium carbonate shown by Raz et al. (2002) (Fig. 3). Ca K-edge XANES spectra obtained on the crystals match the ones for amorphous calcium carbonate as published in Michel et al. (2008) (Fig. 4). In contrast to the sample treatment applied to the crystals discovered in Antarctic sea ice in 2007 (Dieckmann et al., 2008), the crystals collected on Svalbard were mistakenly stored in absolute ethanol (>99.9%), rather than in 50% ethanol. The apparent decomposition of the crystals into amorphous calcium carbonate in absolute ethanol is indicative of a water-containing compound, thus confirming the identification as ikaite on morphological grounds. As can be seen from Fig. 2c, some crystals show the six-sided appearance of the monoclinic morphology well known from inorganically precipitated ikaite crystals. This morphology was also observed in some of the crystals from Antarctic sea-ice (Dieckmann et al., 2008).

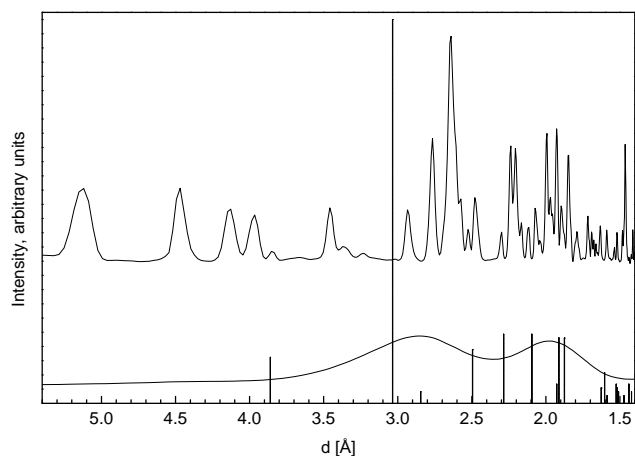


Fig. 3. Synchrotron X-ray diffraction (XRD) pattern of synthetic ikaite (upper panel) and of ikaite from Antarctic sea ice, decomposed to amorphous calcium carbonate (lower panel). Additionally, the line pattern of calcite is shown to demonstrate the similarity of the diffractogram of decomposed ikaite to the one of amorphous calcium carbonate (ACC) in *Crustacean Orchestia cavimana* (Raz et al., 2002).

During the period of sampling, the sea ice temperature ranged from -1.8°C to -3.0°C and the air temperature from -3.7°C to 3.6°C . These temperatures lie well within the stability range for ikaite. However, due to the lack of quantitative data as well as supplementary details on the physical and chemical conditions prior to the time of sampling it is not possible to determine the exact conditions that led to the formation of ikaite at this location. The air temperature until the end of April was below 0°C , with average air temperatures in Ny-Ålesund being about -16°C in March and April. Based on this, the ice had only recently warmed up to the observed temperatures. The sea ice thickness in the sampled area ranged from 43 to 64 cm, and the age of the ice can be estimated to about 2 to 2.5 months, being slightly older in the northern part and younger in the southern part of the inner fjord.

As mentioned earlier, elevated phosphate concentrations are considered to represent an important precondition in the formation of ikaite (besides low temperatures, $<4^\circ\text{C}$). The phosphate levels in the seawater in Kongsfjord range between almost zero ($0.2\ \mu\text{mol l}^{-1}$) in summer and over $1.1\ \mu\text{mol l}^{-1}$ in late winter when the fjord is still ice covered (Aguilera et al., 2002; Woelfel et al., 2009). During onset of sea ice formation, however, concentrations are at their lowest. Whether these concentrations, particularly the apparently low levels at the onset of sea ice formation are conducive to ikaite precipitation, needs to be investigated. The formation of ikaite is thus shown to occur not only in the Antarctic, but also in the Arctic. However, the results do not provide the temporal and spatial dimension of calcium carbonate formation in polar sea ice, yet they confirm the

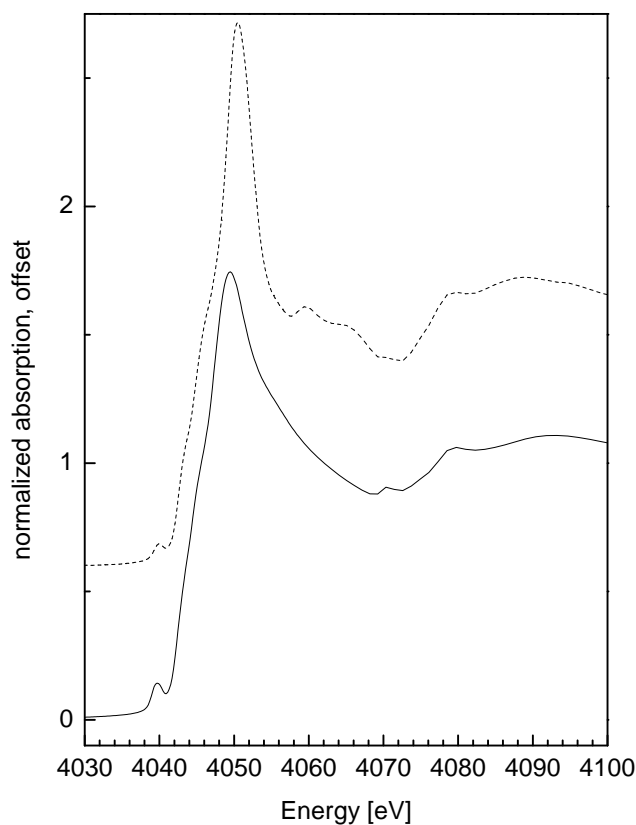


Fig. 4. Ca K-edge X-ray near edge structure (XANES) spectrum of precipitates from arctic sea ice stored in pure ethanol (solid line) compared to a spectrum of synthetic ikaite (dashed line). The spectrum of ikaite stored in pure ethanol matches with the ones of amorphous calcium carbonate (ACC) in Michel et al. (2008).

potential of this process also in the Arctic, which is a crucial prerequisite on the way of further investigations regarding its role in the polar and global carbon cycles (Thomas and Dieckmann, 2010).

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