Calcium carbonate as ikaite crystals in Antarctic sea ice

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[1] We report on the discovery of the mineral ikaite ($CaCO_3 \cdot 6H_2O$) in sea-ice from the Southern Ocean. The precipitation of $CaCO_3$ during the freezing of seawater has previously been predicted from thermodynamic modelling, indirect measurements, and has been documented in artificial sea ice during laboratory experiments but has not been reported for natural sea-ice. It is assumed that $CaCO_3$ formation in sea ice may be important for a sea ice-driven carbon pump in ice-covered oceanic waters. Without direct evidence of $CaCO_3$ precipitation in sea ice, its role in this and other processes has remained speculative. The discovery of $CaCO_3 \cdot 6H_2O$ crystals in natural sea ice provides the necessary evidence for the evaluation of previous assumptions and lays the foundation for further studies to help elucidate the role of ikaite in the carbon cycle of the seasonally sea ice-covered regions. **Citation:** Dieckmann, G. S., G. Nehrke, S. Papadimitriou, J. Göttlicher, R. Steininger, H. Kennedy, D. Wolf-Gladrow, and D. N. Thomas (2008), Calcium carbonate as ikaite crystals in Antarctic sea ice, *Geophys. Res. Lett.*, *35*, L08501, doi:10.1029/2008GL033540.

1. Introduction

[2] When sea ice forms, the hyper-saline brine generated within the ice matrix at sub-zero temperatures undergoes substantial changes with respect to mineral-liquid thermodynamic equilibria in the large spatial and temporal salinity and temperature spectra of the sea ice system. These physicochemical changes are conducive to sequential mineral precipitation [*Marion*, 2001]. Ikaite has been identified in a number of low temperature marine and saline terrestrial environments [e.g., *Buchardt et al.*, 1997] and is thermodynamically viable in sea ice brine at equilibrium with current atmospheric CO_2 at $-4.5°C$, in the absence of the formation of the anhydrous $CaCO_3$ minerals. However, although precipitation of calcium carbonate ($CaCO_3$) in sea ice has been proposed for more than 50 years [*Assur*, 1958], actual evidence of its formation in sea ice has so far only been indirect [*Killawee et al.*, 1998; *Papadimitriou et al.*, 2004; *Tison et al.*, 2002]. Not only has the question as to whether $CaCO_3$ precipitates in natural sea ice remained unresolved, but also the polymorph of $CaCO_3$ that would precipitate has

been controversially discussed, e.g., thermodynamic calculations have been used that predict calcite to be the most likely precipitate in natural sea ice [*Marion*, 2001]. We first observed $CaCO_3$ crystals in sea ice off Adelie Land, Antarctica in 2001 [see *Delille et al.*, 2007]. Some of the crystals had the typical hexagonal and idiomorphic shape of the mineral ikaite ($CaCO_2 \cdot 6H_2O$). However, the crystals could not be investigated further because of incorrect handling. Ikaite is not stable at temperatures above $4°C$ and mineralogical phase identification requires that the crystals are processed, transported, and measured in a cryogenic environment. Thus, in order to correctly identify and quantify crystals from Antarctic sea ice, we again analysed ice cores collected from sea ice in the Weddell Sea, Antarctica during an expedition with the German research icebreaker *Polarstern* in austral spring (September–October) 2006.

2. Methods

[3] Sea ice cores where taken on different locations in the Weddell Sea, Antarctica between 60° and 66° south and 50° and 58° west. The cores represent different sea ice types, from 25 cm thick Nilas ice to 225 cm thick multi-year ice. Collection and processing of ice cores in the field proceeded with standard techniques [*Horner et al.*, 1992]. Crystals were extracted from the ice cores as described below for (1) mineralogical phase identification and (2) quantitative determination of the crystals in the ice. In order to avoid decomposition of the crystals, the temperature throughout the sample preparation was maintained below $4°C$.

[4] Ice cores were cut into 10 cm segments, which were transferred into clean plastic containers, sealed and melted on board ship in a cold room at $4°C$ for two days. The melting was monitored several times a day and as soon as the sections had melted, processed within 2 minutes. Temperature of the melt water thus never rose much above $0°C$. After swirling the melt water and allowing particles to settle in the vortex, crystals were pipetted into a plastic vial containing 75% Ethanol and frozen at $-18°C$ for later mineralogical phase identification, or onto pre-weighed GF/F filters for quantitative measurements. Filters were, rinsed with 75% ethanol, and kept frozen at $-18°C$. Before crystals were transferred they were briefly inspected under the binocular microscope to check for differences in morphology. Crystals for mineralogical phase identification were obtained from pooled triplicate sea ice cores of the top 30 cm of sea ice, from 13 stations. For comparison, 10 cm sections were cut from of an archive core (companion ice cores taken at each station and returned to the home laboratory in plastic tubes, at $-18°C$) and processed in a temperature controlled room (T $\sim 2°C$) as described for ship board samples. Analyses were done by means of X-ray diffraction using synchrotron radiation (X-ray beamline of

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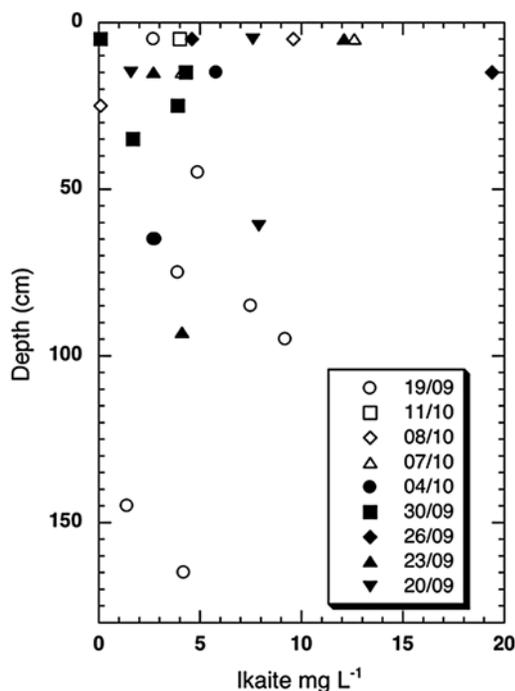
Figure 1. Distribution of the concentration of ikaite mass with depth in sea ice. Numbers in legend denote day/month of collection in 2006 (the ice-snow interface is assigned to x = 0).

the Synchrotron Laboratory for Environmental Studies SUL-X at the synchrotron radiation source ANKA, Forschungszentrum Karlsruhe). Ikaite crystals were precipitated as reference material according to *Marland* [1975], 24 h before analysis. During transport to the synchrotron, samples were kept at a temperature below 2°C. Diffracted intensities were collected from crystals that were either crushed and filled into glass capillaries or mounted on glass fibres in a cryogenic N_2 gas stream with a focussed (150 μm x 150 μm) monochromatic X-ray beam (14 keV), using a CCD detector with a fibre-optic taper in the unbinned mode
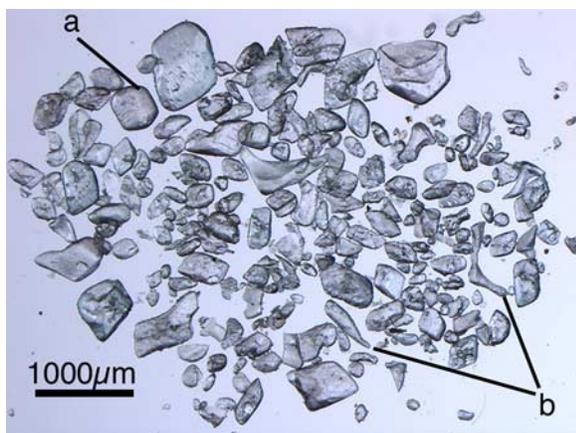

Figure 2. Photograph of ikaite crystals taken from a single bulk sea ice sample showing various crystal shapes and sizes: a, idiomorphic; and b, shape of brine pockets or channels.

(31.2 μm optical pixel size; type XDI-VHR, Photonic Science). Diffraction angles were calibrated with silicon and integrated to one dimensional background corrected powder diffractograms [Diffrac Plus Evaluation Package (1996–2001) Socabim; FIT2D, Hammerslay A. (1987–2005) ESRF].

[5] Quantification of crystals within sea ice was done using cores taken on 9 of the 13 stations. Filters prepared on board ship where dried in an oven at 60°C for 10 hours and weighed in the home laboratory. Because of the thermal instability of ikaite, the mineral mass thus quantified was
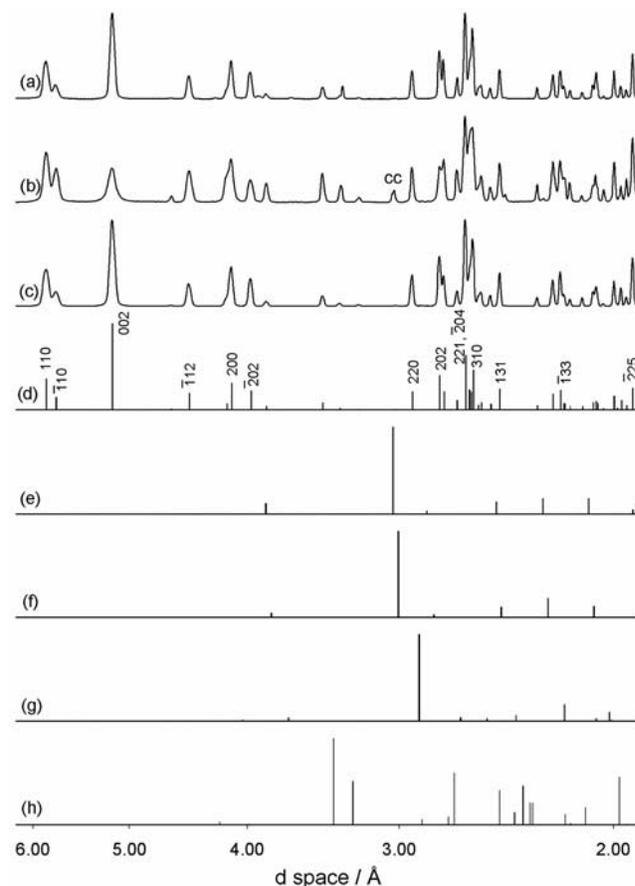

Figure 3. Synchrotron X-ray diffraction patterns (lattice spacing d vs. diffracted intensity, strongest peak normalized to 1000, intensity scales shifted for clarity) of (a) crystals isolated from an archived sea ice core in the home laboratory, (b) crystals isolated in the onboard laboratory and stored in 75% ethanol, (c) synthetic ikaite, and (d) line pattern with hkl reflections (JCPDS data base 75-1733, JCPD-International Centre for Diffraction Data (1999) PCPDFWIN v. 2.02.) from structure refinement data of ikaite from sea sediments in Bransfield Strait, Antarctica [*Suess et al.*,1982; *Hesse et al.*, 1983]. Small amounts of calcite (cc) were detected in Figure 3b, probably from decomposition of ikaite. Line patterns for (e) calcite ($CaCO_3$), (f) calcite magnesium, (g) dolomite (($Ca,Mg)CO_3$), and (h) aragonite ($CaCO_3$) from the JCPDS database are added for comparison. The database numbers from Figures 3e–3h are 00-005-0586, 00-043-0697, 00-036-0426, and 00-041-1475.

attributed to anhydrous $CaCO_3$ and was converted to ikaite mass per liter of melted sea ice by multiplying with a factor of 2.08 (mineral molecular weight ratio). The area-weighted mineral mass was calculated from the sum of mineral mass isolated per core (corer ID = 9 cm).

3. Results and Discussion

[6] Since all crystals extracted from the ice cores had the same morphology, it is most likely that the XRD identification as ikaite is representative for all crystals used in this study. Ikaite crystals were found throughout the sea ice and in all ice types but were not distributed uniformly with depth in the ice cores and up to 19.4 mg of ikaite were found per liter of melted sea ice (Figure 1). The size of the ikaite crystals ranged from <5 μm to 600 μm, and their shape varied from almost idiomorphic (well developed crystal faces) to xenomorphic (no distinguishable crystal faces) (Figure 2). In some, the crystal shape was apparently constrained by the dimensions of the brine pockets in the ice. The discovery of ikaite crystals clearly indicates that the brine of the sampled sea ice was supersaturated with respect to ikaite, and that the formation of less soluble phases, e.g., calcite, aragonite or vaterite, appears to be kinetically inhibited. The total area-weighted mass of ikaite recovered from the cores ranged from 0.3 to 3.0 g m^{-2}.

[7] Synchrotron X-ray diffraction patterns confirmed that the crystals were ikaite (Figure 3). The sequence of the X-ray reflections of the field samples matches that of the synthetic ikaite prepared in the laboratory and the calculated line pattern of ikaite.

[8] The significance of ikaite authigenesis in sea ice on processes of global relevance can as yet not be fully assessed. At this point, little is known on the spatial and temporal occurrence of ikaite precipitates in polar sea-ice, but our subsequent discovery of crystals throughout fast ice off Adelie Land, Antarctica, in November 2007, morphologically identical to those from the north-western Weddell Sea, indicates that ikaite formation in sea ice is not a localized phenomenon. In sea ice, calcite or vaterite appear to be kinetically inhibited. A comparable environmental setting must be present in Antarctic sediments where ikaite is also found [*Suess et al.*, 1982; *Domack et al.*, 2007], although an exact understanding of the physio-chemical properties conducive to ikaite precipitation remains elusive. For sea ice, this knowledge is crucial since the precipitation of $CaCO_3$ is implicated in many processes of global significance, such as the sea ice-driven carbon pump and the global carbon cycle [*Delille et al.*, 2007; *Rysgaard et al.*, 2007] with possible implications even for tropospheric ozone concentrations since calcium carbonate ($CaCO_3$) precipitation is thought to reduce the buffering capacity of sea ice brine, thus facilitating its acidification and triggering the bromine explosion considered responsible for the catalytic destruction of ozone [*Sander et al.*, 2006].

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