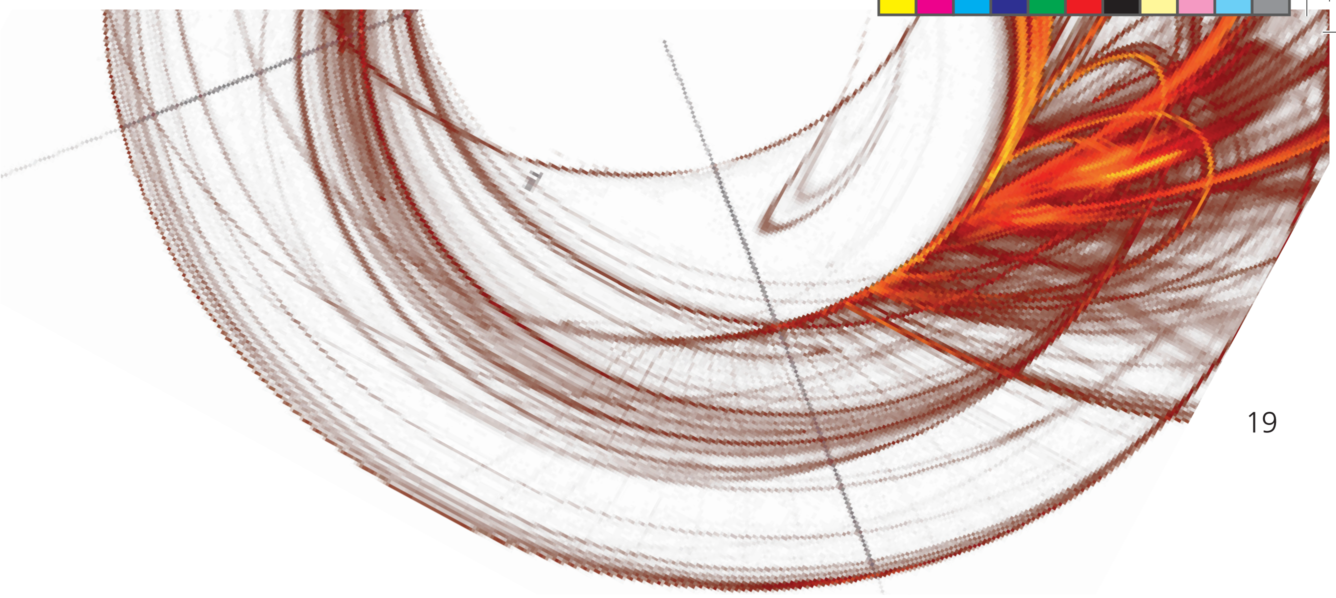

Climate-relevant Carbonate Mineral Discovered in Antarctic Sea-Ice

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Thoroughly temperature controlled sample processing and analysis using synchrotron based micro X-ray diffraction enabled us to solve a 50 year old question on the type of calcium carbonate precipitation in sea ice, and hence provide the basis for quantitative considerations of climate relevant processes between ice covered ocean waters and atmosphere [1].

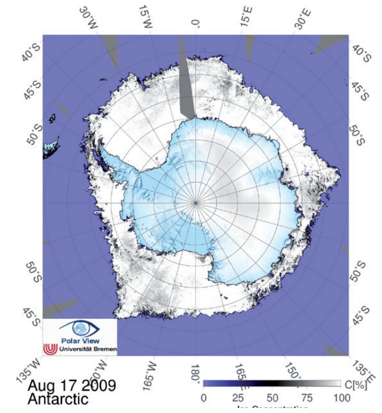

Fig. 1: Maximum extent of the winter sea ice in the Antarctic 2008 (grey-white area); source: http://www.iup.uni-bremen.de:8084/amsr/amsre.html

Fig. 2: Dr. Gerhard Dieckmann and his scientific assistant (Michael Fischer) are taking a sea ice sample in front of the French station of Dumont D'Urville in the Antarctic

Sea-ice which forms in the Earth's polar oceans covers vast areas (Fig. 1). Since the ocean water has a salinity of about 3.5 % and ice crystallizes as pure H2O the salinity of water between the crystals (brines) increases as temperatures drop. Such physicochemical conditions cause supersaturation and lead to mineral precipitation. One of the precipitants that have been predicted from thermodynamic modelling is either calcite (CaCO3) or ikaite (CaCO3 x 6 H2O). Ikaite has been identified in low temperature marine and saline terrestrial environments but it has up to now not been possible to prove its precipitation in natural sea-ice because it decomposes rapidly above about 4 °C. It is assumed that calcium carbonate formation in sea ice may affect atmospheric processes. However, although precipitation of calcium carbonate in sea ice has been proposed for more than 50 years, without direct evidence, its role in this and other processes has remained speculative. Thus, in order to correctly identify and quantify mineral precipitations from Antarctic sea ice, we analysed ice cores collected from sea ice in the Weddell Sea, Antarctica during an expedition with the German research icebreaker Polarstern in austral spring 2006 (Fig. 2).

Crystals were extracted from the ice cores for mineralogical phase identification in a temperature controlled room (T ~ 2 °C) on board ship and in the home laboratory (Fig. 3). Additionally, ikaite crystals were synthesized as reference material. X-ray diffracted intensities were collected from crystals that were either crushed and filled into glass capillaries or mounted on glass fibres in a cryogenic N2 gas stream with a focussed monochromatic X-ray beam, using a CCD detector at the SUL-X beamline (Figs. 4a-c). Diffraction angles were integrated to one dimensional background corrected powder diffractograms (Fig. 5). Quantification of crystals within sea ice was done by drying and weighing the filters. The area-weighted mineral mass was calculated from the sum of mineral mass isolated per core.

Synchrotron X-ray diffraction (XRD) patterns confirmed that the crystals were ikaite. (Fig. 5). Ikaite crystals were found throughout the sea ice and in all ice types but were not distributed uniformly with depth in the ice cores. Up to 19.4 mg of ikaite per liter of melted sea ice were recorded (Fig. 6). The crystal shape of ikaite varied from almost idiomorphic (well developed crystal faces) to xenomorphic (no distinguishable crystal faces). In some cases their shape was apparently constrained by the dimensions of the brine pockets in the ice (Fig. 4). The discovery of ikaite crystals clearly indicates that the brines were supersaturated with respect to ikaite, and that the formation of less soluble calcium carbonate phases, e.g., calcite, aragonite or vaterite (all chemically CaCO3, but with different crystal structures), appears to be kinetically inhibited. The total area-weighted mass of ikaite ranged from 0.3 to 3.0 g m-2. The significance of ikaite authigenesis in sea ice on processes of global relevance can as yet not be fully assessed. However, our subsequent discovery of crystals throughout fast ice off Adelie Land, Antarctica indicates that ikaite formation in sea-ice is not a localized phenomenon. This is crucial since the precipitation of calcium carbonate is implicated in many processes of global significance, such as the sea ice-driven carbon pump and the global carbon cycle [2,3] with possible implications even for tropospheric ozone depletion events, since calcium carbonate 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 [4].

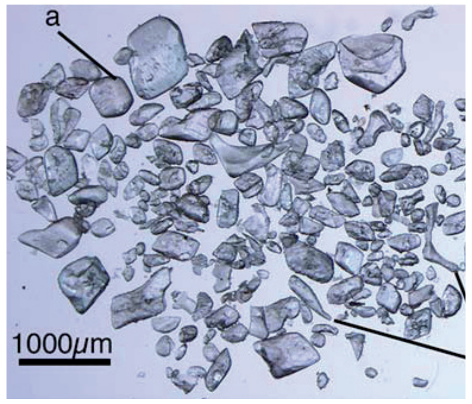

Figure 3: Microscopic photograph of ikaite crystals taken from a sea ice sample showing various crystal shapes and sizes: a, idiomorphic; and b, shape of brine pockets or channels

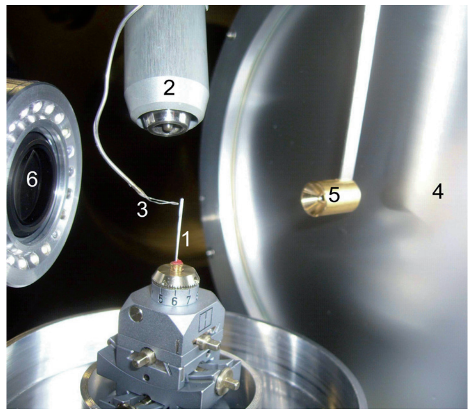

Figure 4a: Setup for X-ray diffraction in cryogenic N_2 gas stream. sample (1), cryogenic gas outlet (2), thermocouple (3), CCD-detector (4), beam stop (5), light microscope (6)

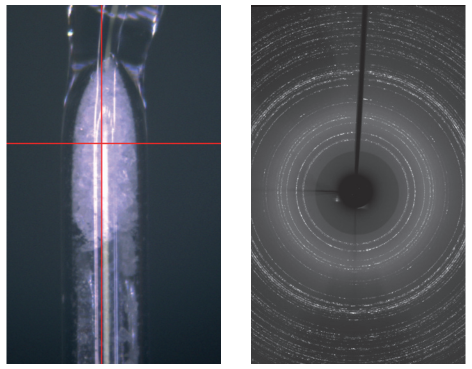

Figure 4b: Crushed crystals in a glass capillary , and corresponding CCD frame

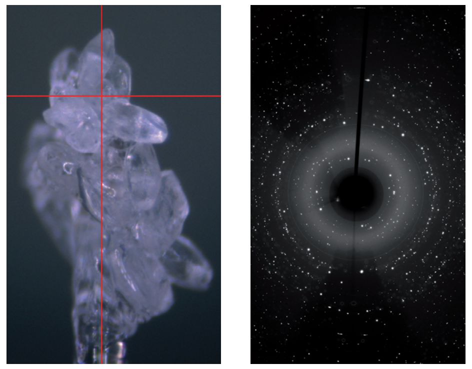

Figure 4c: A few crystals mounted on a glass fibre, and corresponding CCD frame

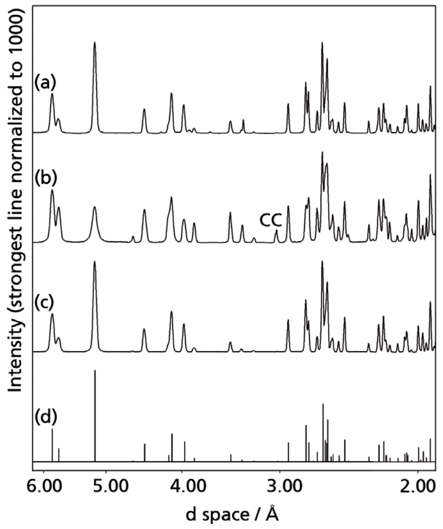

Figure 5: Synchrotron X-ray diffraction patterns (lattice spacing d vs. diffracted intensity) of (a) crystals isolated from a sea ice core in the home laboratory, (b) crystals isolated in the onboard laboratory, (c) synthetic ikaite, and (d) line pattern with hkl reflections (ICDD-JCPDS data base no. 75-1733). Small amounts of calcite (cc) in (b) are probably due to decomposition of ikaite.

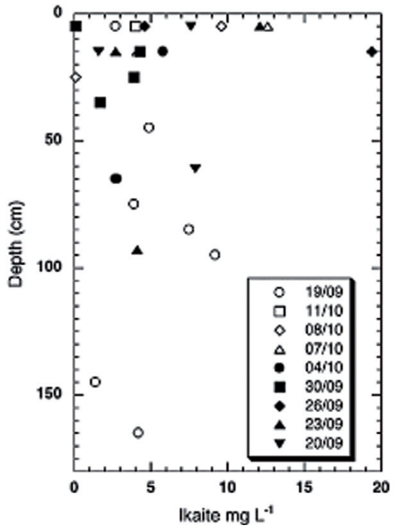

Figure 6: Distribution of the concentration of ikaite mass with depth in sea ice. Numbers in legend denote day/month of collection in 2006 (the ice-snow interface is assigned to x = 0).

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