23Na NMR spectroscopy and Diffusion weighted MRI studies on sea-ice at different temperatures. The influence of environmental effects on ice growth

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Abstract

Knowledge of the physico-chemical properties of sea-ice with its inclusions of liquid brine is essential for our understanding of the role of polar ice covers in climate change. Spin-Echo, Diffusion-weighted MRI and ^{23}Na-NMR were conducted on sea-ice sampled in Arctic Alaska to study the thermal evolution of brine inclusions over a temperature range from –30 to –3°C. An in-plane resolution of 100 micrometers allowed us to investigate the increase in pore size, changes of diffusion constants as well as the different precipitation points of hydrohalite and mirabilite with temperature. The results are in good agreement with theoretical predictions.

Introduction

Sea-ice covers almost 6% of the earth's surface area. Its unique properties with its sub-millimetre to decimetre-sized liquid brine inclusions require in-depth studies of its physico-chemical and microstructural evolution in order to understand and predict its role in ocean-atmosphere energy exchange and in the wider context of the climate system. Recently, it could be shown that magnetic resonance imaging (MRI) provides an elegant method for non-destructive microstructural analysis and studies of the thermal evolution of liquid brine channels in natural sea ice (1). Furthermore, Menzel et al. (2) applied q-space imaging to determine self-diffusion propagators of artificial sea-ice. In this work, we combined morphological Spin-echo MRI with Diffusion-weighted imaging and ^{23}Na-NMR spectroscopy for the study of two types of naturally grown sea-ice at different temperatures.

Materials and methods

Samples of young sea ice (total thickness 0.28 m) were obtained in Elson Lagoon near Barrow in northern Alaska in November of 2000, stored at in-situ temperatures and transported in insulated ice-core transport containers to the AWI. For NMR studies sea-ice samples were placed in 6x4x3 cm^3 Perspex chambers, equipped with a fiber-optic probe for determination of in-situ ice temperatures inside the MR. In order to maintain constant temperatures the sample containers were kept in a cooling unit, providing a temperature stability of ± 1°C from the setpoint (1). Experiments were carried out on a Bruker Biospec 4.7T scanner equipped with a mini-imaging unit (max. gradient strengths of 200 mT m^{-1}). Cylindrical probes adapted to high-conductivity samples were used for signal transmission and detection (9 cm diameter). For morphological studies a multi slice spin echo sequence was used (matrix size: 512x256, axial FOV 3.6x3 cm^2, slice thickness 0.4 mm, 9 slices, slice separation 4.6 mm, RF pulses: sinc3 of 3000 μs, TR= 540 ms,

TE= 40 ms, 24 averages, acquisition time 2 h). Diffusion-weighted imaging (DWI) was conducted using a 4 point Stejskal-Tanner pulsed gradient Spin echo sequence (parameters: 128x128, FOV 3.6x3 cm^2, 9 slices, slice thickness 0.4 mm, slice separation 4.6 mm, sinc3 of 3000 μs, 8 averages, acq time 20 min, big delta= 18.93 ms, b-values: 11, 316, 623, 930 s/mm^2). ^{23}Na NMR spectra were acquired using 50 μs bp32 pulses, sweep width of 4000 Hz, acquisition size of 1K, repetition time 0.5 s, ns= 1200 scans resulting in an acq time of 10 min. MSME, DWI and ^{23}Na NMR spectroscopy (from the overall sea-ice volume) were executed consecutively at four different temperatures (average temperatures: -27.6 °C, -15.6°C, -6.1 °C, -3.2°C) on two sea-ice samples from a different origin. One sample contained very small brine channels (A), whereas the other sample was formed from very porous ice and implied therefore regions with bigger brine channels (B). Figure 1 shows axial morphological MRIs of the two samples at –3.2°C.

Results and discussion

MR experiments could be performed on sea-ice samples over a time scale of several days under controlled in-situ temperatures without microstructural or physico-chemical changes detectable. Morphological spin echo images obtained from sea ice at different temperatures revealed a thermal evolution of brine inclusions similar to those reported previously (1). The thermal evolution of calculated diffusion constants (D) determined from different sets of brine channels from the two samples is presented in Table 1. At low temperatures the diffusion constant from sample 1 (columnar sea ice, 0.20-0.23 m depth, salinity 5.0 ppt, 1), is one order of magnitude lower in comparison to sample 2 (granular sea ice 0.02-0.05 m depth, salinity 10.7 ppt) with its higher volume fraction of more connected inclusions. At higher temperatures with increasing brine channels and channel diameters the diffusion constants of both samples converged to the diffusion constant obtained for a saturated NaCl solution (D_{NaCl}= 7.0 x 10^{-10} m^2/s, 2). This indicates that changes of diffusion constants are dependent on the brine channel diameter, as controlled by the thermal evolution of brine channels.

This finding is of interest also in the context of the in-situ NMR studies of Callaghan et al. (3) who observed substantial increases in the self-diffusion coefficients of water molecules as a result of brine convection in a temperature gradient. Since we can largely rule out the effects of convection as samples were maintained under isothermal conditions (1), the data in Table 1 are only affected by the impact of changes in pore microstructure (including surface-melt interaction at sub-micrometer scales) which can help separate out these two competing effects for a variable temperature regime.

T (°C)	$D_{sample1}$ (m^2/s)	$D_{sample2}$ (m^2/s)
-27.6	1.63 x 10^{-12}	1.95 x 10^{-11}
-15.6	1.57 x 10^{-10}	3.96 x 10^{-10}
-6.1	5.31 x 10^{-10}	5.67 x 10^{-10}
-3.2	6.26 x 10^{-10}	7.43 x 10^{-10}

Figure 2 presents the changes in the concentration of sodium ions (in solution), Na$^+$(l), within both samples derived from peak integrals of ^{23}Na-NMR spectroscopy. The observed changes in concentration are in good agreement with predictions based on equilibrium concentrations in natural seawater (4). The latter indicate onset of precipitation of mirabilite (Na$_2$SO$_4$ · 10 H$_2$O) at –8.2°C, with 91 % of sodium present as Na$^+$(l) at –15.6°C. Hydrohalite (NaCl · 2H$_2$O) is predicted to precipitate at –22.8 °C, with 22 % of sodium present as Na$^+$(l) at –27.6 °C. The percentage changes of the ^{23}Na signal integral are in good correspondence with the predicted changes of NaCl concentrations with temperature based on (4).
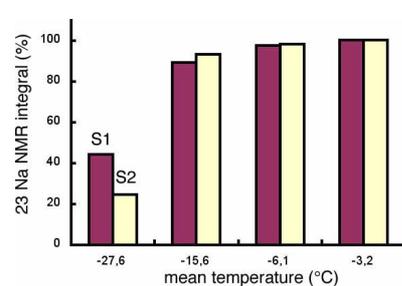
Conclusions

The combination of morphological-, Diffusion-weighted MRI and ^{23}Na-NMR spectroscopy allowed the characterisation of the connection between brine channel geometry, water diffusion and Na$^+$(l) content, as well as the differentiation between sea ice with different growth history and microstructure. Thus, MRI can be of great help in furthering our understanding of how the physico-chemical properties of sea ice affect its role in the polar regions and the global climate system.

References

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