Lake ice

Sea ice

macroscopic

microscopic
Sea-ice thermodynamics

- system fully described by set of state variables $G$, $T$, $P$ and $\Sigma n_i$ (with thermodynamic equilibrium requiring $dG = 0$)

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} dn_i$$

with the chemical potential

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

- the state of a system is thus fully prescribed by 3 state variables $G$, $T$, $P$ minus the number of phases present $p$ and the number of compounds $c - 1$, yielding the Gibbs phase rule that describes the number of parameters that can be varied without altering the phase composition of the system (degrees of freedom):

$$f = c - p + 2$$

- for a simplified sea-ice case represented by the 2-component system of NaCl and $H_2O$ pressure can usually be held constant ($P_{atm}$)

the phase fractions $f_A$, $f_B$ and their composition can be derived from the phase diagram according to the lever rule

bulk composition $c(\text{NaCl}) = f_A(s) \times c(s) + f_B(l) \times c(l)$:
- Phase diagram in steady-state $dQ/dt = 0$

- Cooling path in natural system with $dQ/dt = \text{const}$
Constructing phase diagrams for sea ice

(1) **empirical/experimental approach**: this approach is presently underlying all studies of sea ice as a porous medium

(2) **thermodynamic-geochemical modelling** of freezing-point depression: except for lack of activity data at extreme compositions/temperatures, theoretically possible and likely to be pursued to a higher degree in future
The semi-empirical approach after Assur (1960)

- "standard sea ice": seawater is a multi-component system with a complex thermal phase evolution; Assur (1960) chose to represent seawater by water and 6 ionic species, Cl\(^{-}\), Na\(^{+}\), SO\(_4^{2-}\), Mg\(^{2+}\), Ca\(^{2+}\), K\(^{+}\), based on Sverdrup et al. (1942) (note that due to charge-balance constraints this does not correspond to a system of 7 independent components).

- bi-linear approximation to \(-23^\circ\)C (see Fig. 1.2.1.3) for a brine salinity \(S_b\) (in g per kg of H\(_2\)O):

\[
T(\degree C) = -54.11 \frac{S_b}{1-S_b} \iff \frac{S_b}{1-S_b} < 0.142
\]

\[
T(\degree C) = 42.8973 \left( \frac{S_b}{1-S_b} - 0.14244 \right) \iff \frac{S_b}{1-S_b} \geq 0.142
\]

NB, here: \(0 \leq S_b \leq 1\)
The semi-empirical approach after Assur (1960)
### Table 1.2.1.1: Salts precipitating in sea ice and their main properties (after Weeks and Ackley, 1986)

<table>
<thead>
<tr>
<th>Salt composition</th>
<th>Mineral name</th>
<th>Crystallogr. system</th>
<th>Density (Mg m(^{-3}))</th>
<th>Eutectic (aq) (°C)</th>
<th>Precip. T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO(_3)•6H(_2)O</td>
<td>monocl</td>
<td>1.771</td>
<td>?</td>
<td>-2.2</td>
<td></td>
</tr>
<tr>
<td>Na(_2)SO(_4)•10H(_2)O</td>
<td>Mirabilite</td>
<td>1.464</td>
<td>-3.6</td>
<td>-8.2</td>
<td></td>
</tr>
<tr>
<td>MgCl(_2)•8H(_2)O</td>
<td></td>
<td>1.24</td>
<td>33.6</td>
<td>-18.0</td>
<td>&lt;</td>
</tr>
<tr>
<td>NaCl•2H(_2)O</td>
<td>Hydrohalite</td>
<td>1.630 (0°C)</td>
<td>-21.1</td>
<td>-22.9</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>Sylvite</td>
<td>1.984</td>
<td>-11.1</td>
<td>-36.8</td>
<td></td>
</tr>
<tr>
<td>MgCl(_2)•12H(_2)O</td>
<td></td>
<td>(1.24)</td>
<td>-33.6</td>
<td>-43.2 (erratic)</td>
<td></td>
</tr>
<tr>
<td>CaCl(_2)•6H(_2)O</td>
<td>Antarcticite</td>
<td>hexagonal</td>
<td>1.718 (4°C)</td>
<td>-55.0</td>
<td>&lt;55.0</td>
</tr>
</tbody>
</table>
Validation of the Assur model

- Liquid water fraction in artificial sea ice as determined by NMR (dots) and from Assur's phase relations (Richardson and Keller, 1966)
Validation of the Assur model

- NMR studies (Richardson, 1976) provide indication of fraction of precipitated salts (nucleation, kinetics)

- Photo from salt precipitation experiments and NMR studies of precipitation
Microscopic Observations

- Light et al. (2003): precipitation of salts and distribution within brine pockets

Figure 12. (a) Photomicrograph of thin section showing individual mirabilite crystals at $-15^\circ$C. (b) Enlargement of box in Figure 12a.
Thermal evolution and precipitation of salts: Mirabilite (T < −8.2 °C)
Hydrohalite ($\text{NaCl} \cdot 2 \text{H}_2\text{O}$) precipitation

0 hrs: $-15 \degree \text{C}$

3 hrs: $-29 \degree \text{C}$, Hydrohalite prep.

6.5 hrs: $-15 \degree \text{C}$, diss.
Geochemical modeling of brine composition and fraction

- the freezing-point depression (liquidus curve) can be derived from the Clausius-Clapeyron equation as:

  \[
  \ln \left( \frac{a_{x,l}}{a_{x,s}} \right) = \frac{\Delta H_f}{R} \left( \frac{1}{T^*_f} - \frac{1}{T_f} \right)
  \]

  with \( \Delta H_f \) enthalpy of formation, \( R \) universal gas constant, \( T_f \) freezing temperature of solution and pure compound (●) and a activity of liquid and solid phase; activity corresponds to product of activity coefficient and the molar fraction of the relevant component \( \gamma_i x_i \)
Geochemical modeling: Example

- Concentrations of different seasalt ions as a function of temperature for freezing of seawater. Dots represent measurements from Nelson and Thompson (1954), curves are from geochemical thermodynamic model of Spencer et al. (1990)
Validation of the Assur model

- Liquid water fraction in artificial sea ice as determined by NMR (dots) and from Assur's phase relations (Richardson and Keller, 1966)
Geochemical modeling: What is the eutectic of seawater?

- Marion & Farren (1999):
  Eutectic depends on freezing pathway

"traditional picture"

[Diagram of salt precipitation with eutectic temperature at -53.8°C]
Geochemical modeling: What is the eutectic of seawater?

- Marion & Farren (1999):
  Eutectic depends on freezing pathway

  can be observed if equilibration period is hours & fractional crystallization

  can be observed if equilibration period is weeks

Fig. 17. Experimental and model simulations of chloride, sodium, sulfate, and calcium molalities during seawater freezing along (a) the Gitterman pathway, and (b) the Ringer-Nelson-Thompson pathway.
Sea water/ice thermal evolution

Seawater, FREZCHEM2 model, Mironenko et al. (1997)

Eutectic ($V_l/V = 0$) at about $-55 \, ^\circ C$

$V_l/V$, %

activity $a(H_2O)$

osmotic coefficient $\phi$

Temperature, K

MgCl$_2$•12H$_2$O
KCl
NaCl•2H$_2$O
NaSO$_4$•10H$_2$O
H$_2$O(s)
T and S as state variables

- Temperature and salinity jointly control the liquid volume fraction in sea ice (brine porosity), which in turn controls key ice properties (see Petrich & Eicken, 2010, pp. 45-46)

\[
\frac{V_b}{V} = \left(1 - \frac{V_a}{V}\right) \frac{\rho_i S_{si}}{F_1(T) - \rho_i S_{si} F_2(T)}
\]

\[
F_i(T) = a_i + b_i T + c_i T^2 + d_i T^3
\]

\[
\rho_i = 0.917 - 1.403 \times 10^{-4} T
\]

\[
S_b = \left(1 - \frac{54.11}{T}\right)^{-1} \times 1000
\]

<table>
<thead>
<tr>
<th>Table 2.1</th>
<th>Coefficients for functions (F_1(T)) and (F_2(T)) for different temperature intervals. From Cox &amp; Weeks (1983) and Leppäranta &amp; Manninen (1988).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T, , ^\circ C)</td>
<td>(a_1)</td>
</tr>
<tr>
<td>0 (\geq T &gt; -2)</td>
<td>-0.041221</td>
</tr>
<tr>
<td>-2 (\geq T \geq -22.9)</td>
<td>-4.732</td>
</tr>
<tr>
<td>-22.9 &gt; T (\geq -30)</td>
<td>9899</td>
</tr>
</tbody>
</table>

| \(T, \, ^\circ C\) | \(a_2\) | \(b_2\) | \(c_2\) | \(d_2\) |
| 0 \(\geq T > -2\) | 0.090312 | 0.016111 | 1.2291 \(\times 10^{-4}\) | 1.3603 \(\times 10^{-4}\) |
| -2 \(\geq T \geq -22.9\) | 0.08903 | -0.01763 | -5.330 \(\times 10^{-4}\) | -8.801 \(\times 10^{-6}\) |
| -22.9 > T \(\geq -30\) | 8.547 | 1.089 | 0.04518 | 5.819 \(\times 10^{-4}\) |
Profile properties of cold first-year sea ice

- Profiles of temperature, salinity, brine volume fraction and permeability (from Φ-k model) for May 3, 1999 slab and cores
Pore microstructural evolution & methods of study

- Thin-section analysis: Perovich and Gow, 1996, Light et al., 2003
- Problems with thin-section analysis: destructive, sample processing, 2-dimensional
- X-ray tomography: Kawamura (1988) - low contrast in mass-absorption coefficient between ice and brine; new work by Miner, Pringle, Eicken w/ Cs-doped sea-ice single crystals
- Magnetic resonance: Callaghan et al. (1999), Menzel (2002) - diffusivity measurements

\[
\begin{align*}
-30 ^\circ C, p=0.03 & \quad A=0.015 \text{ mm}^2 & \quad P_A= 0.80 \text{ mm}^{-1} \\
-2.7 ^\circ C, p=0.08 & \quad A=0.041 \text{ mm}^2 & \quad P_A= 1.50 \text{ mm}^{-1} \\
-1.3 ^\circ C, p=0.11 & \quad A=0.108 \text{ mm}^2 & \quad P_A= 1.83 \text{ mm}^{-1}
\end{align*}
\]
Pore microstructural evolution: Assur’s model

- Constriction and segregation of pores during ice thickening and cooling
- Brine layers — brine tubes — brine pockets
- Segregation depends on temperature, salinity (i.e. porosity), pore morphology

(Assur, 1960)
Grain and pore microstructure: Frazil & congelation ice

- Granular ice, 2-5 cm depth
- A: hor, crossed pol; B, C hor & vert MRI (−3 °C)
- Scale bar 10 mm

- Columnar ice, 20-23 cm depth
- A: hor, crossed pol; B, C hor & vert MRI (−3 °C)
- Scale bar 10 mm

Changes in pore microstructure upon warming

- Columnar ice at $-6.0 \, ^\circ C$ (A, C) and $-2.9 \, ^\circ C$ (B, D)
- Granular ice at $-6.2 \, ^\circ C$ (E) and $-3.0 \, ^\circ C$ (F)
- Scale bar 2 mm
Microstructural evolution as a function of temperature: Magnetic resonance imaging

Eicken et al. (CRST, 2000)
Pringle et al. (2009)

### Table 1: Porosity and Segmentation Thresholds

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Porosity ((\rho^*))</th>
<th>Segmentation Threshold ((\rho_{\text{seg}}))</th>
<th>Porosity ((\rho))</th>
<th>Segmentation Threshold ((\rho_{\text{seg}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3</td>
<td>11.67 ± 0.62</td>
<td>10.60</td>
<td>12.52</td>
<td></td>
</tr>
<tr>
<td>-4</td>
<td>8.81 ± 0.48</td>
<td>8.17</td>
<td>9.60</td>
<td></td>
</tr>
<tr>
<td>-5</td>
<td>7.12 ± 0.38</td>
<td>6.53</td>
<td>7.68</td>
<td></td>
</tr>
<tr>
<td>-6</td>
<td>6.00 ± 0.32</td>
<td>5.68</td>
<td>6.65</td>
<td></td>
</tr>
<tr>
<td>-7</td>
<td>5.22 ± 0.28</td>
<td>4.01</td>
<td>5.57</td>
<td></td>
</tr>
<tr>
<td>-8</td>
<td>4.84 ± 0.25</td>
<td>4.02</td>
<td>4.84</td>
<td></td>
</tr>
<tr>
<td>-12</td>
<td>3.08 ± 0.18</td>
<td>2.71</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td>-15</td>
<td>2.54 ± 0.14</td>
<td>2.38</td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>-18</td>
<td>2.24 ± 0.12</td>
<td>1.85</td>
<td>2.25</td>
<td></td>
</tr>
</tbody>
</table>
Brine sheets and tubes at grain boundaries

<table>
<thead>
<tr>
<th></th>
<th>n/V (mm(^{-3}))</th>
<th>width (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chukchi (columnar)</td>
<td>121±98</td>
<td>50.3±71.0</td>
</tr>
<tr>
<td>Elson (granular)</td>
<td>173±132</td>
<td>19.4±24.3</td>
</tr>
</tbody>
</table>

Brine sheets and layers within grains

<table>
<thead>
<tr>
<th></th>
<th>n/V (mm(^{-3}))</th>
<th>width (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
<td>4.0±1.1</td>
</tr>
<tr>
<td></td>
<td>86±96</td>
<td>5.8±3.4</td>
</tr>
</tbody>
</table>

Chukchi Sea fast ice, Mar 14, 1999, 0.03 m above ice bottom
Ice formation and evolution

I. Ice growth

Agitated conditions

Ice growth in a wave-field

Grease ice: aggregations of frazil (spicules and platelets of ice) into surface layer

Calm conditions

Ice growth through quiescent bottom freezing

Nilas:
- dark nilas (<5 cm thick)
- light nilas (5-10 cm thick)

First-year white ice

Young ice:
- grey ice (0.1-0.15 m)
- grey-white ice (0.15-0.3 m)

Old ice (second- and multi-year)

Pancake ice: consolidation of frazil into larger units
Sea-ice microstructure

- Frazil ice (turbulent, open ocean regime)
- Congelation ice (quiet freezing of ice sheet)
Fabric of ice grown in quiet conditions:

1. Brine rejection from ice crystal
   $\rightarrow$ increased brine salinity at growth front

2. Heat diffuses faster than solute
   $\rightarrow$ supercooling

3. Ice growth into supercooled water fastest and
   ice growth faster in the basal plane ((0001))
   than perpendicular ([0001])
   $\rightarrow$ geometric selection $\rightarrow$ horizontal c-axes
Constitutional supercooling

- for ice grown from a melt with low solute concentrations (such as lake water), the (microscopic) equilibrium segregation coefficient \( k_0 \) describing the distribution of impurities between solid and liquid

\[
k = \frac{C_s}{C_l}
\]

has been found to take on a maximum value of approximately \( 2.8 \times 10^{-3} \) (Gross et al., 1977)

- according to Fick's law, the time- and depth-dependent solute concentration is a function of the diffusive flux out of the boundary layer with solute buildup due to the advection of the ice-water interface

\[
\frac{\partial C(z)}{\partial t} = D \frac{\partial^2 C}{\partial z^2} + v_i \frac{\partial C}{\partial z}
\]

for the one-dimensional case, with growth proceeding at a velocity of \( v_i \) in z-direction and \( C \) the concentration of the chemical species with a molecular diffusivity of \( D \) (Garandet et al., 1994)

- the boundary condition at the interface \((z = 0)\) is given by

\[
-D \left( \frac{\partial C}{\partial z} \right)_0 = v_i (1 - k) C_0
\]

and in the far-field \((z \to \infty)\)

\[
C = C_\infty
\]

where \( k \) represents a macroscopic segregation or partition coefficient

- under steady-state conditions \((\partial C/\partial t = 0)\), the solution to the equation system is given by

\[
C(z) = C_\infty \left[ 1 + \frac{1 - k}{k} \exp \left( -\frac{z v_i}{D} \right) \right]
\]

(cf. Weeks, 2010)
Constitutional supercooling

- changes in liquid composition correspond to differences in the freezing point as dictated by the slope of the liquidus curve in the phase diagram:

\[ T_s(C) = T_{0,f} + mC(z) \]

for sea ice, \( m = -0.055 \text{ K \%/}^{-1} \)

- the in-situ temperature profile in the liquid is given as

\[ T(z) = T(0) + \frac{mC(0)}{k} + G_l z \]

where \( G_l \) is the temperature gradient in the liquid

- constitutional supercooling requires that the actual temperature gradient in the liquid is smaller than that of the liquidus curve, i.e.:

\[ \frac{G_l}{v} < \frac{mC(0)}{D} \left( 1 - \frac{k}{D} \right) \]
Fig. 3: Temporal development of interface perturbations occurring on ice front advancing in 2 wt % NaMnO₄ solution. Sequence of photomicrographs taken from video recording, time interval $\Delta t = 1 \text{ s}$. 

Koerber & Rau, 1992
Constitutional supercooling

- as the magnitude of the temperature gradient in the liquid may not be well defined and is not (at least for present practical purposes) the rate-limiting factor in the case of sea-ice growth which is controlled by heat conduction to the ice surface exposed to the cold atmosphere, an alternate approach based on the temperature gradient $G_s$ in the solid can be pursued (Weeks and Ackley, 1986, Tiller, 1991), where the corresponding sets of equations are:

$$
\frac{G_s}{v} < \frac{-mC(0)}{D} \left( \frac{1-k}{k} \right)
$$

$$
G_s = \frac{T_{surf} - T_f}{H}
$$

$$
v = \frac{dH}{dt} = \frac{\kappa}{\rho L} \frac{T_{surf} - T_f}{H}
$$

such that the criterion becomes

$$
\frac{\rho L}{\kappa} < \frac{-mC(0)}{D} \left( \frac{1-k}{k(0)} \right)
$$

- based on typical, conservative values for sea ice, we arrive at:

$$
10^{-4} < \left( \frac{1-k}{k(0)} \right) C(0)
$$

which indicates that only for very small solute concentrations can we expect a stable planar interface.
Constitutional supercooling

platelet spacing from linear stability theory

Wettlaufer, 1992

Zotikov et al., 1980

Wettlaufer, 1992

Zotikov et al., 1980
Planar, cellular, lamellar interfaces
Geometric selection

example: freshwater ice
vertical thin section

crystals with vertical $c$-axes are quickly outgrown

Thin sections: Mueller-Staffel et al. (2009)
c-axes alignment parallel to direction of current

Schmidt equal area net of crystal orientations (c-axes).
"C" indicates the direction of the current

Langhorne & Robinson (1986)

Stander & Michel (1989)
Pore microstructural evolution: Assur’s model

- Entrapment of brine at base of sea ice cover
- Constriction and segregation of pores during ice thickening and cooling

\[ a \leq b < c \]
\[ a \sim 0.1 \text{ to } 0.3 \text{ mm}; \quad b \sim 1 \text{ to } 5 \times a; \quad c > 5 \times a \]
\[ d \sim 0.25 \text{ to } 1.25 \text{ mm (avg 0.7)} \]

(Kovacs, 1996)
Diagram of the four stages in the formation of a brine pocket.

1. Few mm of brine grooves
2. 2-3 cm of brine tubes
3. (Lake and Lewis, 1970)
4. Horizontal cuts through skeletal layer.

Brine grooves

"necking"

Brine tubes

Brine pockets

\[ a = 0.07 \text{mm} (\text{Anderson and Weeks, 1958}) \]

\[ a = 0.05 \text{mm} (\text{Doronin and Kheysin, 1975}) \]
Distribution of microbial biomass in Arctic sea ice

- microalgae concentrated into bottommost centimeters of ice cover
- biomass build-up requires >2-10 times nutrient loading present in seawater congealed into sea ice
- bacteria distributed more evenly through ice

![Graph showing bacterial abundance](image)

- Bacterial abundance: $1.5 \pm 0.5 \times 10^5$ cells ml$^{-1}$ (ice)
- Bacterial abundance: $1.2 \pm 0.6 \times 10^5$ cells ml$^{-1}$ (ice)
Microbial life in sea ice: Exopolymeric substances

• potential freezing point reduction (polysaccharides)
• enhanced salt retention within ice matrix (macroscopically)
• micro-segregation of salts within pore system and retention of supercooled water within polymer network
• Promotion of vitrification at sub-eutectic temperatures?

Krembs et al.
Microbial strategies in mitigating the adverse effects of extreme conditions in frozen environments

![Diagram showing various compounds and their limits](image-url)
Release of exopolymers (EPS) to cope with osmotic stress

Sw = 20 psu
release of osmo-regulators into environment

Sw = 32 psu
build-up of osmo-regulators within cells

Sw = 50 psu
release of EPS
EPS in natural sea ice samples (Chukchi Sea, June 2001)