Lake ice

Sea ice

macroscopic

microscopic
Lake ice

**Texture**: size, shape, orientation and relative spatial arrangement of component crystals

**Microstructure**: distribution of liquid and solid inclusions within the crystal matrix, morphology and substructure of individual crystals

**Fabric**: spatial orientation of crystal principal axes (occasionally also indicating preferred orientation)

Modern geological literature: texture and microstructure synonymous (Passchier and Trouw, 1996)

Materials science (and other languages): terms may have different meanings.

Sea ice
The wonders of water & ice

Properties of sea ice controlled by

- properties of water molecule
- hydrogen bonding
- crystal lattice structure
- accommodation of interstitial atoms in lattice
Properties of the water molecule

Valence bond theory:

1. O ground state:
   - 6 valence electrons in
   - one 2s orbital and three 2p orbitals

2. bonding with 2 H→ sp³ hybridization:
   - linear combination of
     - s and p wave functions
   - constraint: orthogonal hybrid wave functions

3. O electron distribution:
   - two lone-pair orbitals
   - two valence orbitals involved in covalent bond
Properties of water molecule

- lone-pair orbitals and orbitals bonding H result in characteristic electron charge density distribution for water molecule
- diffuse zone of net negative partial charge at lone-pair orbital and pointed net positive partial charge at proton sites
- net charge distribution distorts bonds to 104.5°, i.e. close to tetrahedron bisector angle of 109.5°
- water molecules arranged tetrahedrally in fours around central molecule

Fig. 1.3. Electron density contours in the water molecule, as calculated by Bader. Densities are given in atomic units (1 a.u. = \( 6.02 \times 10^{-31} \text{ g}^{-1} \text{ A}^{-3} \)).
Atomic and molecular configurations

- relative positions of oxygen atoms in lattice are prescribed
- protons are free to realize a number of mutually coordinated positions (Bernal-Fowler rules, Bjerrum and ion defects)
- as a result of different ensembles of proton-bond configurations, ice Ih is associated with a finite zero-point (or residual) entropy

Fig. 1.15. A simplified point-charge model for ice Ih. O—oxygen atoms. • ○—positions of potential minimum for protons. ◊—centroids of equivalent orbitals. ——— hydrogen bonds. ——— valence bonds. $e_0$ is the charge on a free proton.
Lattice energy & hydrogen bonding

Fig. 2.6. The energy of an O-H...O bond as a function of proton position for a fixed O-O distance of 2.76 Å, as calculated from the semi-empirical model of Lippincott & Schroeder (1955).

Fig. 2.7. The effective interaction potential between two oxygen atoms joined by a hydrogen bond O-H...O as calculated from the model of Lippincott & Schroeder (1955).
Clustering of water molecules

- Tetrahedral arrangement of water molecules fosters development of di- and polymers (clusters) held by hydrogen bonding
- Clusters allow for dense packing in liquid state (in some cases denser than solid!)
The water phase diagram
Atomic and molecular configurations

- Lattice for Ice I h (dihexagonal pyramidal: 6 mm symmetry class of crystal)

{11\overline{2}0} plane of ice (a) Ic and (b) Ih
Crystallographic reference frames

**Bravais-Miller index** (hexagonal lattice)

(hkil) with \(i=-(h+k)\) to indicate similarity, and \(l\) in direction of \(c\)-axis

- Basal plane and basal faces \((0001)\),
- Prismatic faces \((\bar{1}100)\) etc.
- \(c\)-axis \([0001]\), \(a\)-axes \([\bar{2}110], [\bar{1}2\bar{1}0], [\bar{1}\bar{1}20]\)

planes

(1\(\bar{1}20\)) particular plane
{1\(\bar{1}20\)} equivalent planes

directions

[1\(\bar{1}20\)] particular direction
<1\(\bar{1}20\)> equivalent directions

Plane spanned by \(a_1, a_3\) and \(-\frac{1}{2}a_2\)
is \((1\bar{2}10)\) plane normal: \([\bar{2}1\bar{2}0]\)

Plane spanned by \(a_1, -a_2\), and parallel \(a_3\)
is \((\bar{1}\bar{1}00)\)
Atomic and molecular configurations
### Table 2.2. Components of the lattice energy of ice (in kcal mole\(^{-1}\)) as calculated by various authors

The experimental value is 13.4 kcal mole\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrostatic</td>
<td>14.2</td>
<td>9.4</td>
<td>14.9</td>
<td>12</td>
<td>6.5</td>
<td>8.9</td>
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<tr>
<td>Polarization</td>
<td>—</td>
<td>0.3</td>
<td>—</td>
<td>16</td>
<td>2.0</td>
<td>—</td>
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<tr>
<td>Dispersion</td>
<td>4.1</td>
<td>1.8</td>
<td>—</td>
<td>6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Overlap</td>
<td>-6.8</td>
<td>1.8</td>
<td>—</td>
<td>-16.8</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Total</td>
<td>11.5</td>
<td>11.5</td>
<td>—</td>
<td>17.2</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

at 0 K:
- Covalent O—H bond: 5 eV
- Hydrogen bond: 0.29 eV

1 eV = 96 kJ/mol = 23 kcal/mol

\(\text{H}_2\text{O}: 18 \text{ g/mol}\)
how many hydrogen bonds break during melting?
Clustering of water molecules

- Tetrahedral arrangement of water molecules fosters development of di- and polymers (clusters) held by hydrogen bonding
- Clusters allow for dense packing in liquid state (in some cases denser than solid!)
He (0.14 nm radius) pathways (left) and CO$_2$ (0.4 nm dimensions) pathways (right) through ice crystal lattice from Molecular Dynamics simulations (Ikeda-Fukazawa, 2004)
Consequences of impurity rejection by ice

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Seawater at $S = 35^\circ_\text{oo}$ (g kg$^{-1}$)$^a$</th>
<th>(g kg$^{-1}$) - Chlorinity$^b$</th>
<th>(mol kg$^{-1}$) - Chlorinity</th>
<th>Residence Time in Oceans, log $\tau$ (years)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>10.77</td>
<td>0.556</td>
<td>0.0242</td>
<td>7.7</td>
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<tr>
<td>Mg$^{2+}$</td>
<td>1.29</td>
<td>0.068</td>
<td>0.0027</td>
<td>7.0</td>
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<tr>
<td>Ca$^{2+}$</td>
<td>0.4121</td>
<td>0.02125</td>
<td>0.000530</td>
<td>5.9</td>
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<tr>
<td>K$^+$</td>
<td>0.399</td>
<td>0.0206</td>
<td>0.000527</td>
<td>6.7</td>
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<tr>
<td>Sr$^{2+}$</td>
<td>0.0079</td>
<td>0.00041</td>
<td>0.0000047</td>
<td>6.6</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>19.354</td>
<td>0.9989</td>
<td>0.0282</td>
<td>7.9</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>2.712</td>
<td>0.1400</td>
<td>0.0146</td>
<td>6.9</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>0.1424</td>
<td>0.00735</td>
<td>0.00012</td>
<td>4.9</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.0673</td>
<td>0.00348</td>
<td>0.000044</td>
<td>8.0</td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.0013</td>
<td>0.000067</td>
<td>0.0000035</td>
<td>5.7</td>
</tr>
<tr>
<td>B</td>
<td>0.0045</td>
<td>0.000232</td>
<td>0.0000213</td>
<td>7.0</td>
</tr>
</tbody>
</table>

$^a$Seawater at $S = 35^\circ_\text{oo}$ (g kg$^{-1}$) and the corresponding (g kg$^{-1}$) - Chlorinity and (mol kg$^{-1}$) - Chlorinity values.

$^b$Chlorinity is defined as the ratio of seawater concentration to the concentration of saline water.

$^d$Residence Time in Oceans, log $\tau$ (years) is the time it takes for a substance to be completely removed from the ocean.
Consequences of impurity rejection by ice

convective vs. stratified cooling

**Figure 2.2** For water of salinity less than 24.7 psu, the temperature of maximum density ($T_p$) is less than the freezing temperature ($T_f$). For seawater with a salinity greater than 24.7 psu, the water freezes before it reaches its hypothetical maximum density.
Consequences of impurity rejection by ice convective vs. stratified cooling

Figure 2.2 For water of salinity less than 24.7 psu, the temperature of maximum density ($T_p$) is less than the freezing temperature ($T_f$). For seawater with a salinity greater than 24.7 psu, the water freezes before it reaches its hypothetical maximum density.
Large-scale Meridional Overturning Circulation

Kulbrodt et al. (2007)
The 24.7 salinity contour and its relation to ice formation in nature

Lena Delta New Siberian Islands

Rodrigues, 2008

Fig. 2. Changes in the distribution of the length of the ice-free season in the Arctic during the 1979–2006 period (variations measured in days).
The 24.7 salinity contour and its relation to ice formation in nature

Lena Delta
New Siberian Islands
Sept 1
The 24.7 salinity contour and its relation to ice formation in nature
Grease ice (frazil) forming on the ocean
Grease ice (frazil) forming on the ocean
Frazil ice formation

Ice growth in pure water at a supercooling of 2-9°C. The basal plane of the nucleating crystal is directed downwards into the liquid, the photograph being taken from above. Magnification: 4·1 x.

Fig. 1.

5·5°C supercooling. Magnification: 5·0 x.

Macklin & Ryan, 1966
Pancake ice
Supercooling and nucleation

Figure 2. The (a) $^4\text{He}$ and (b) $\delta^{18}\text{O}$ versus potential temperature plots for stations located in the Filchner Depression close to the ice shelf front. The data are from Schloesser et al. [1990]. Stations were occupied during the cruise ANT III-3 of the German Polar Research Vessel Polarstern. The horizontal line indicates the freezing point of seawater at surface pressure.

Figure 5. The $\theta/S$ diagram for various stations along the drift track of Ice Station Weddell. Reprinted with permission from Gordon et al. [1993a]. Copyright 1993 American Association for the Advancement of Science.
Supercooling and nucleation

Fig. 1. Schematic picture comparing different nucleation mechanisms for the freezing of a liquid. $T_m$ is the melting point of the crystalline phase.
Heterogeneous nucleation

- Clay minerals and iron oxides as suitable nucleators
- Role of biogenic particles

Figure 1. Freezing spectra for sea water and plankton.
Ice growth rates from supercooled freshwater

Fig. 9. 10. Growth velocities of ice perpendicular to the c-axis ($V_a$) and parallel to the c-axis ($V_c$). $V_a$ (-----), Hallett (1964). $V_c$ ‘imperfect crystals’ (---------), Hillig (1958). $V_a$ (- - -), Kost (1953). $V_c$ ‘perfect crystals’ (-----), Hillig (1958).
Frazil ice formation

Habits of ice crystals grown in pure water at various degrees of supercooling (Macklin and Ryan, 1966)

<table>
<thead>
<tr>
<th>Supercooling, K</th>
<th>Crystal habit</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 0.9</td>
<td>Disc crystals, plane stellar dendrites, surface needles</td>
</tr>
<tr>
<td>0.9 - 2.7</td>
<td>Plane stellar dendrites, dendrite sheets</td>
</tr>
<tr>
<td>2.7 - 5.5</td>
<td>Simple double pyramids (composite crystals)</td>
</tr>
<tr>
<td>≥5.5</td>
<td>Complex double pyramids w/ secondary/higher-order non-rational growth</td>
</tr>
</tbody>
</table>

Ice growth in pure water at a supercooling of 2.9°C. The basal plane of the nucleating crystal is directed downwards into the liquid, the photograph being taken from above. Magnification: 4.1 x.

Fig. 1

Ice growth in pure water at a supercooling of 5.5°C. Magnification: 5.0 x.

Fig. 2
Dendritic (non-equilibrium) growth morphology

Fig. 9.1. Successive stages in the growth of a disc crystal into a stellar dendrite. Magnification × 3.7. From Arakawa (1955).
Fig. 9.4. Influence of supercooling on (a) the width and (b) separation of dendritic branches and (c) the angle of the periphery of advancing dendritic tips. From Hallett (1964) with changes.