Amorphous Ices
Part 1: Thermodynamics, Preparation

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“Water and Water Systems: 3rd course on “Neutron Science and Instrumentation”


AUSTRIA
International boundary
State boundary
National capital
State capital
Railroad
Road
CZECHOSLOVAKIA
FEDERAL
REPUBLIC
OF
GERMANY
NIEDEROSTERREICH
OBEROSTERREICH
Munich
Salzburg
Innsbruck
SALZBURG
STEIERMARK
BURGENLAND
KARNTEN
TIROL
HUNGARY
SWITZERLAND
Bressanone
Bolzano
ITALY
YUGOSLAVIA
ITALY

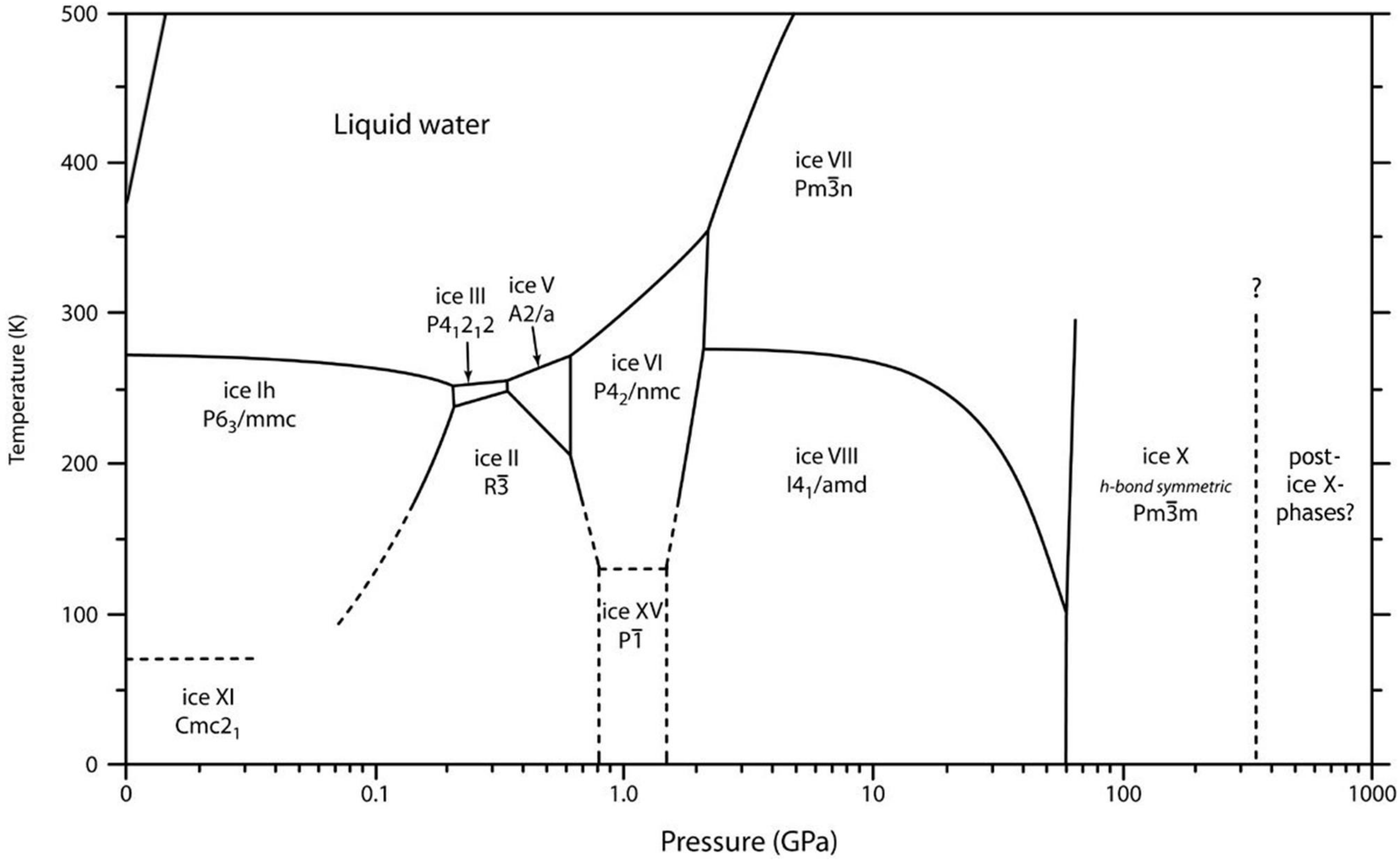
European Research Council erc

ÖAW Österreichische Akademie der Wissenschaften

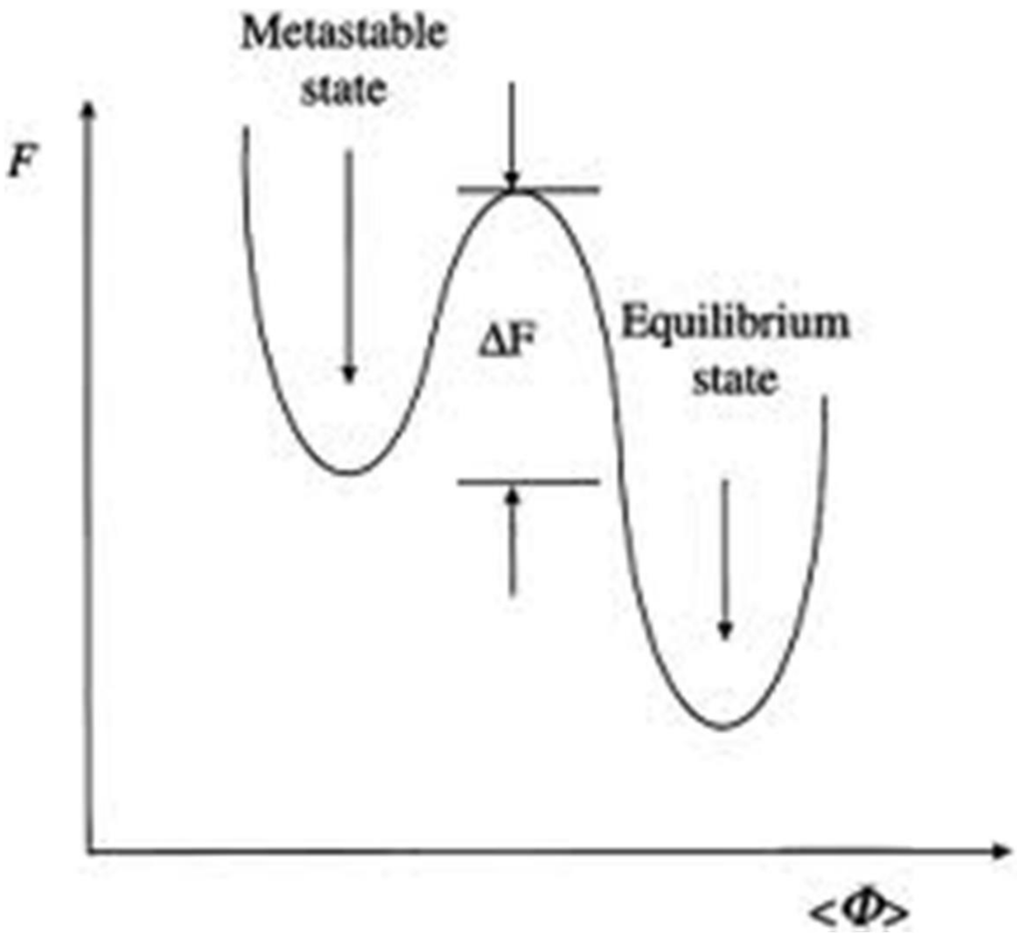
FWF Der Wissenschaftsfonds.

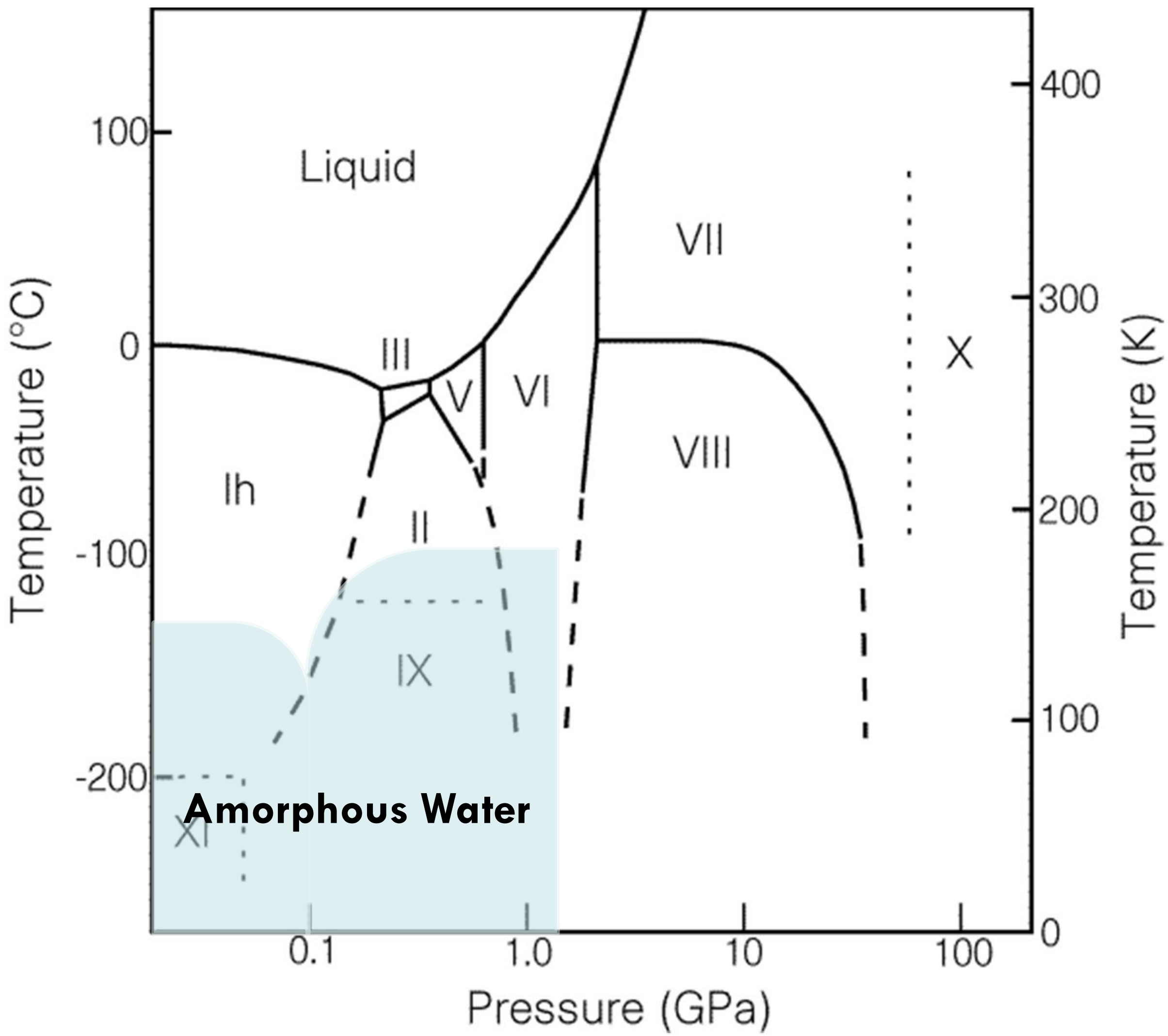
FFG

Phase-Diagram of Water

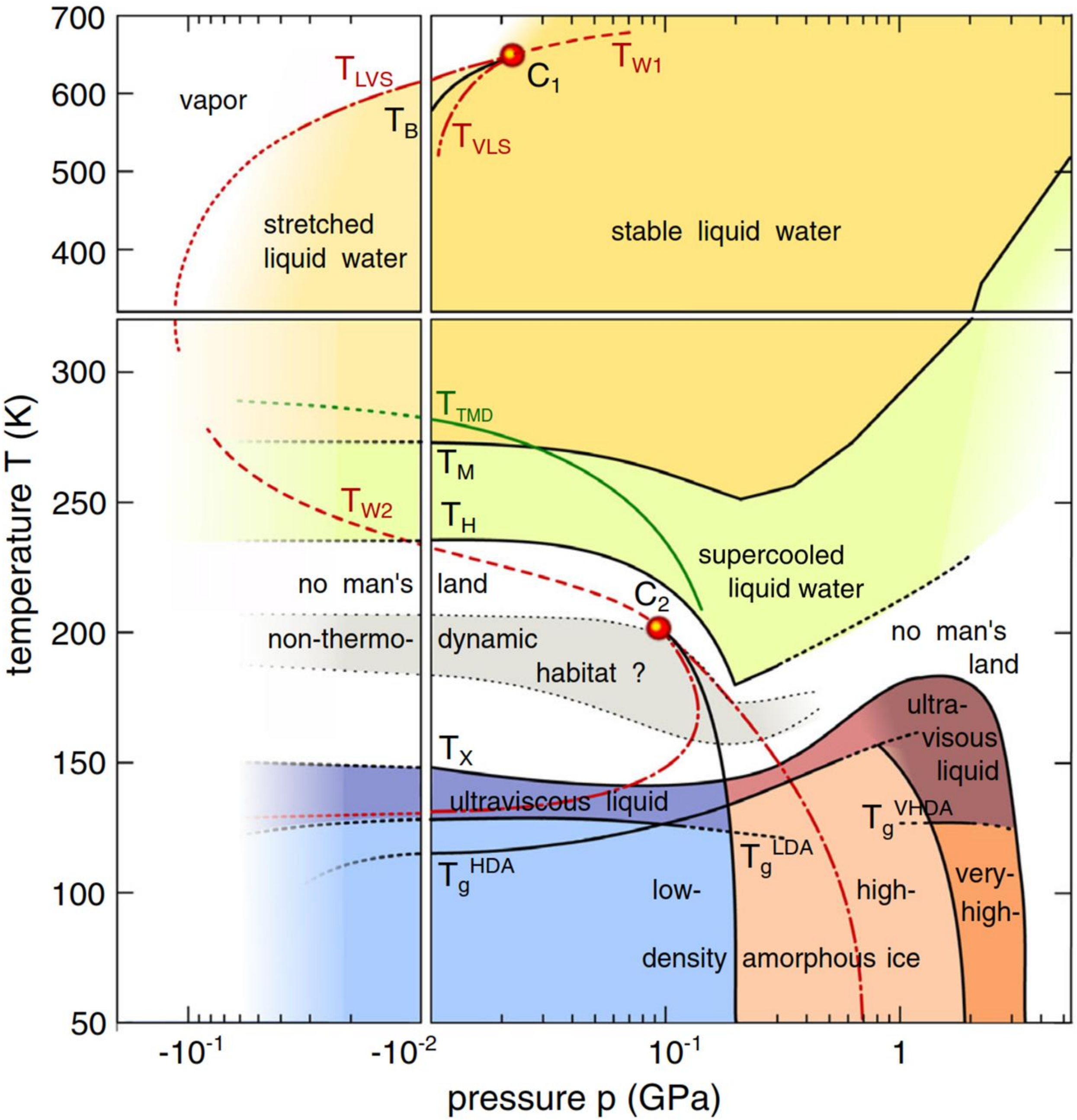


Metastability





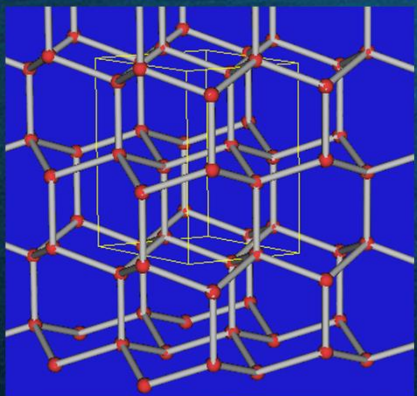
C. Lobban, et al.; Nature **391** (1998), 268

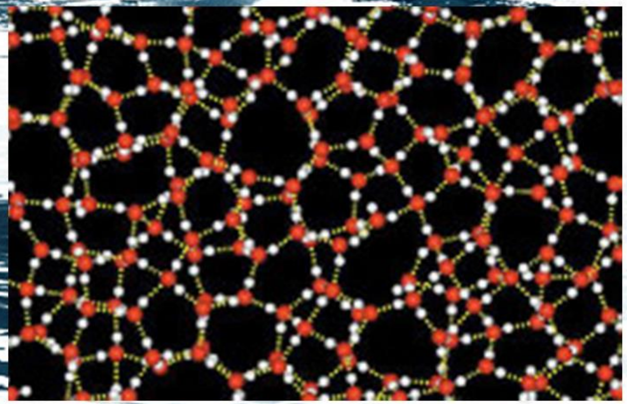


Amann-Winkel et al., **Rev. Mod. Phys.** *88* (2016) 011002.

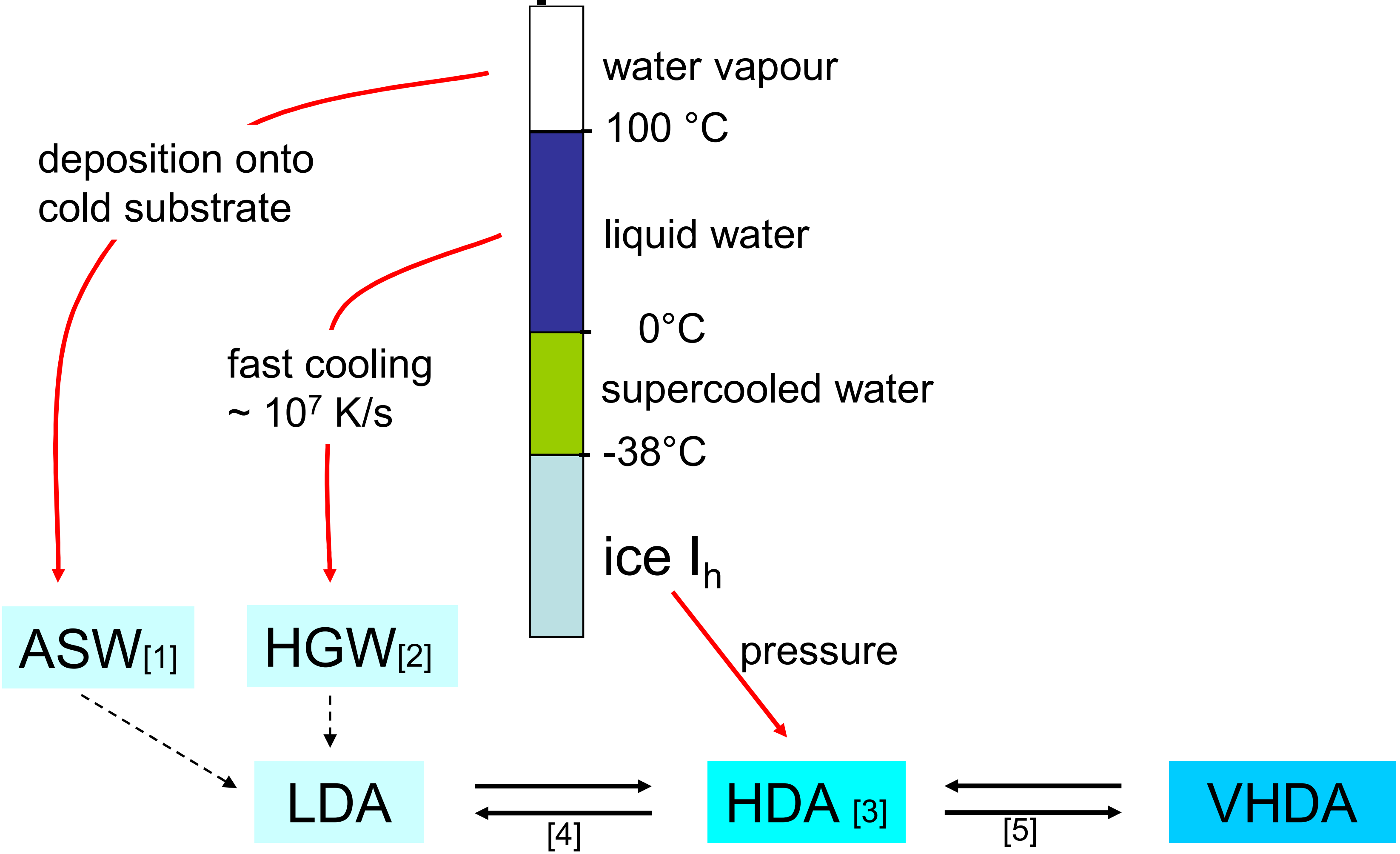
earth:
hexagonal ice

outer space:
amorphous forms of ice





Amorphous ice



[1] E.F. Burton and W.F. Oliver, *Proc. R. Soc. A*, 153, 1935
[2] P. Brüggeller, E. Mayer, *Nature,* 288, 1980; E. Mayer, *J. Appl. Phys.,* 58, 1985
[3] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 310, 1984;
[4] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 314, 1985
[5] T. Loerting, C. Salzmann, I. Kohl, E. Mayer, A. Hallbrucker, *PCCP*, 3, 2001

AMORPHOUS SOLID WATER (ASW)

Amorphous Solid Water (ASW)

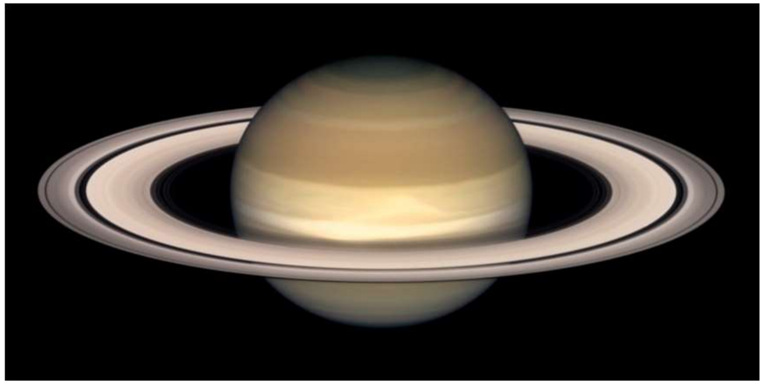
Interstellar Dust

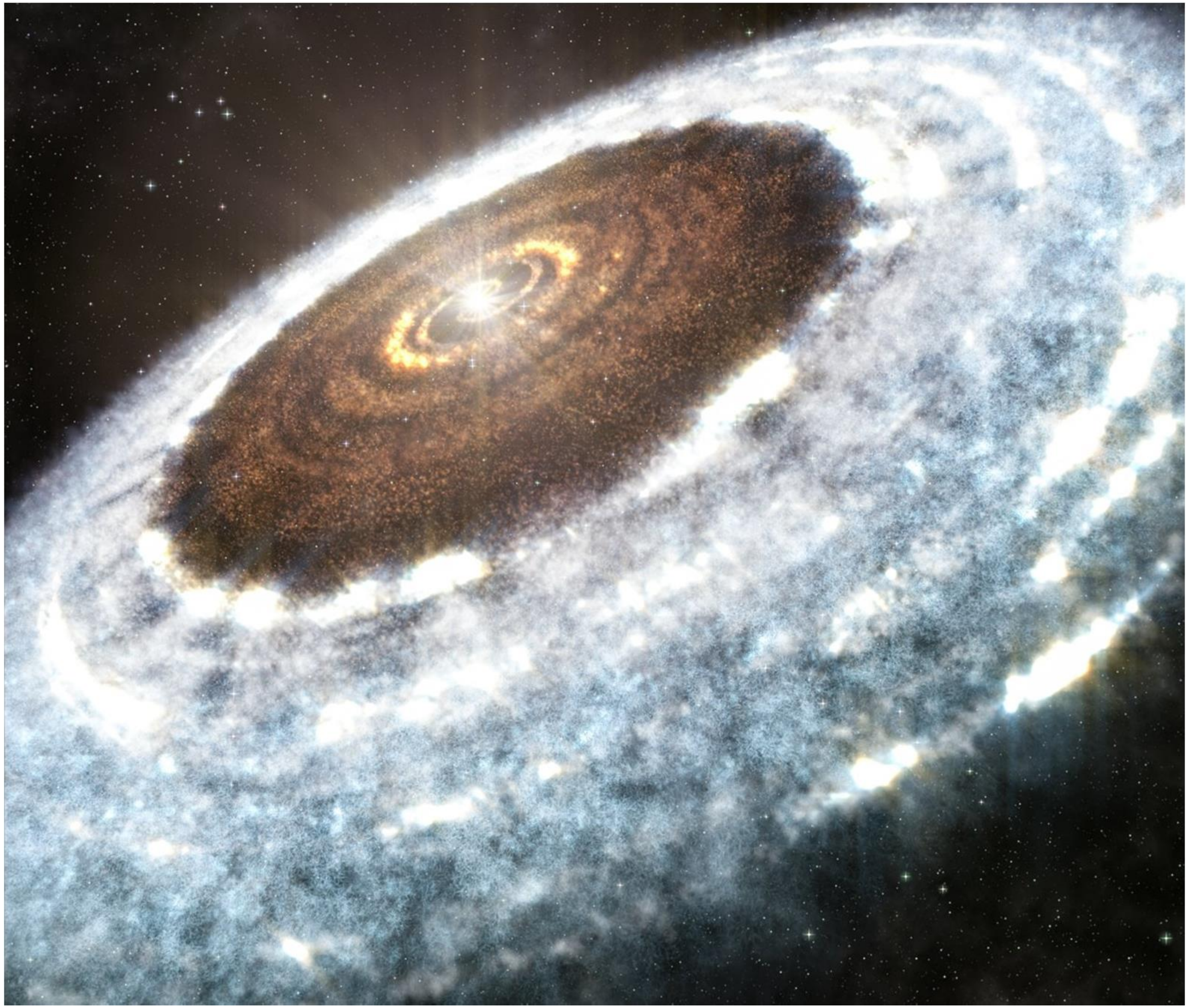
Agglomeration of Interstellar Dust Grains

Courtesy: Leiden Observatory, Netherlands

Comet Hale-Bopp

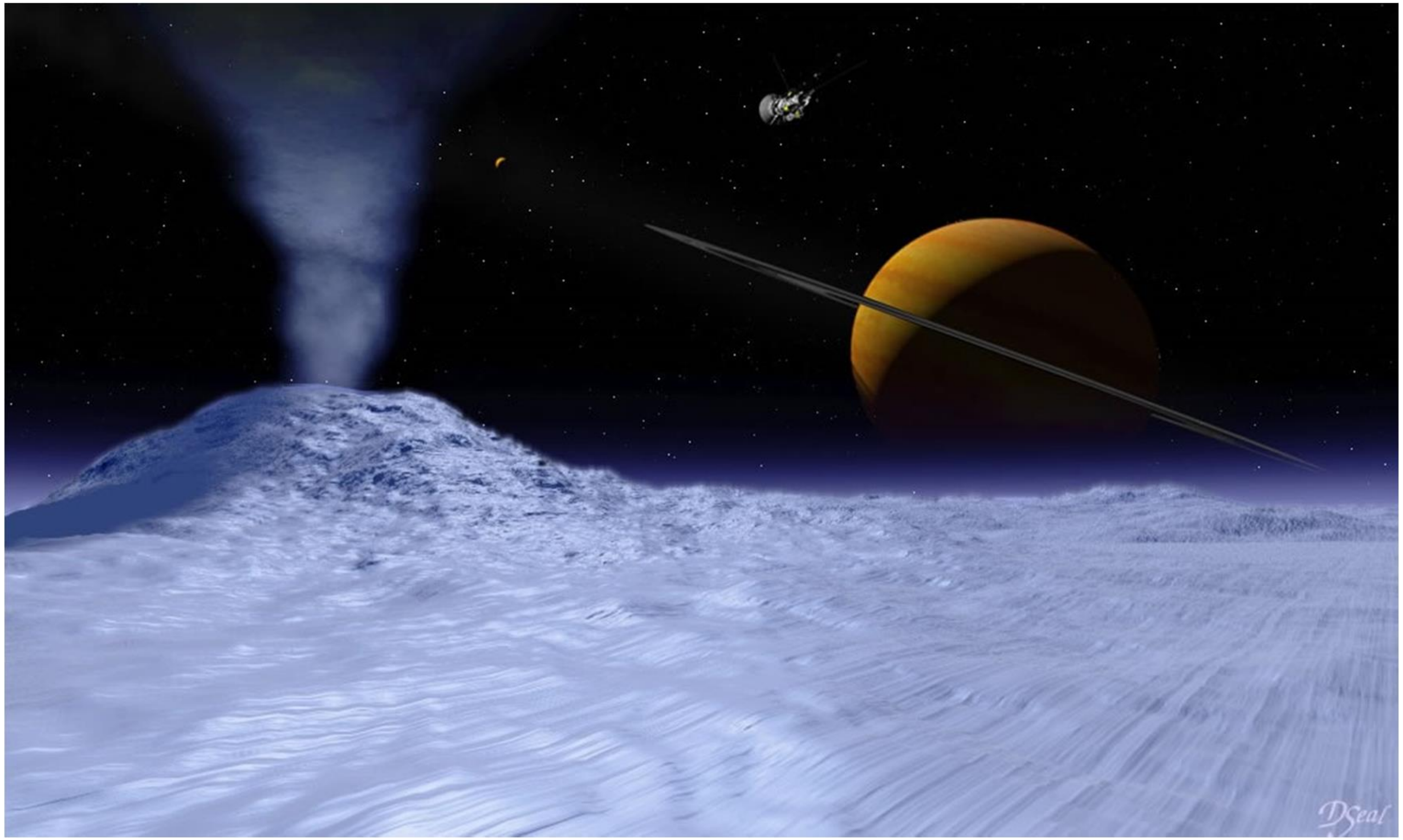
Saturn Rings





Water snow line within protoplanetary disc around young star V883 Orionis
Observed by Atacama Radio Telescope (ALMA)
Cieza et al. Nature (2016) July14 issue

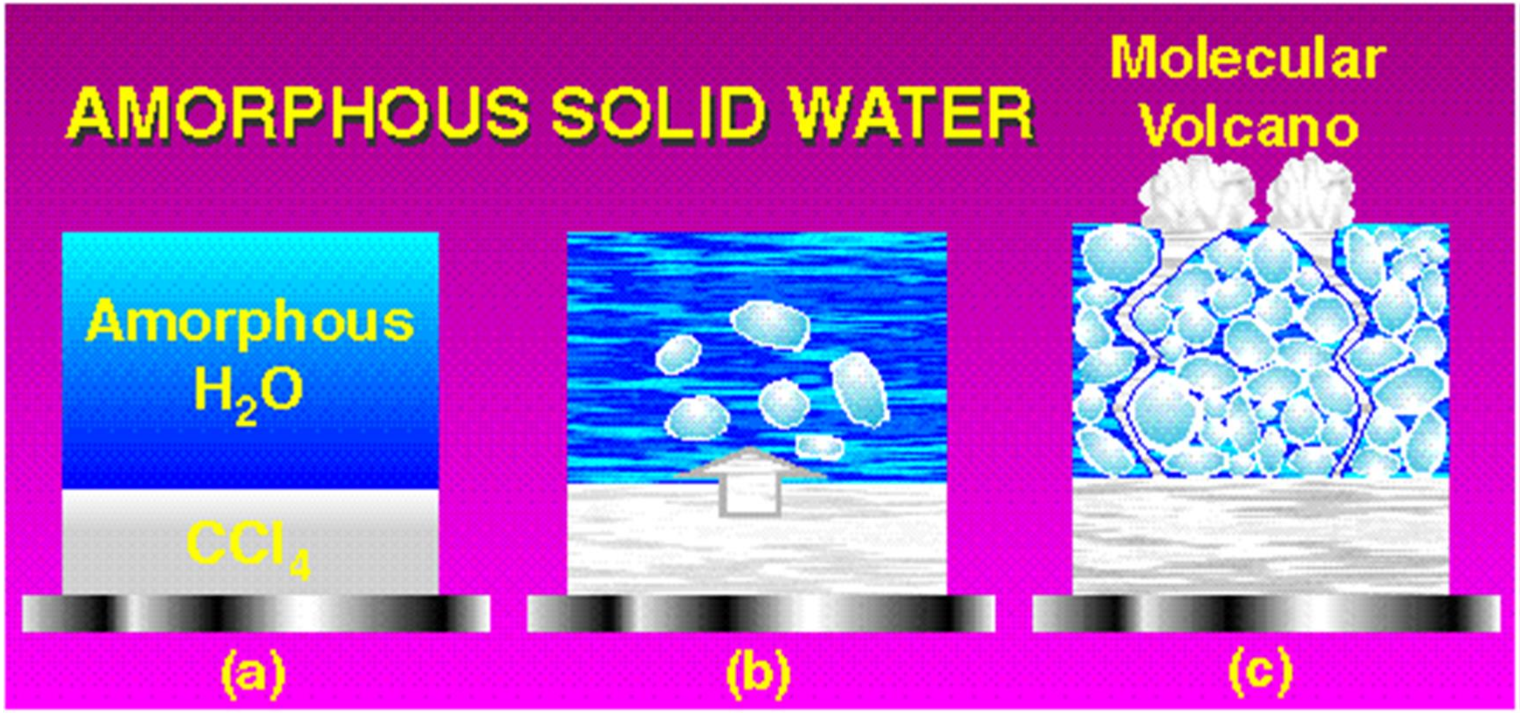
Cryovolcanoes („Ice Volcanoes“)



e.g. Triton (Neptun), Enceladus/Titan (Saturn), Pluto/Charon

Cryovolcanoes („Ice Volcanoes")

Image of Enceladus (Cassini)



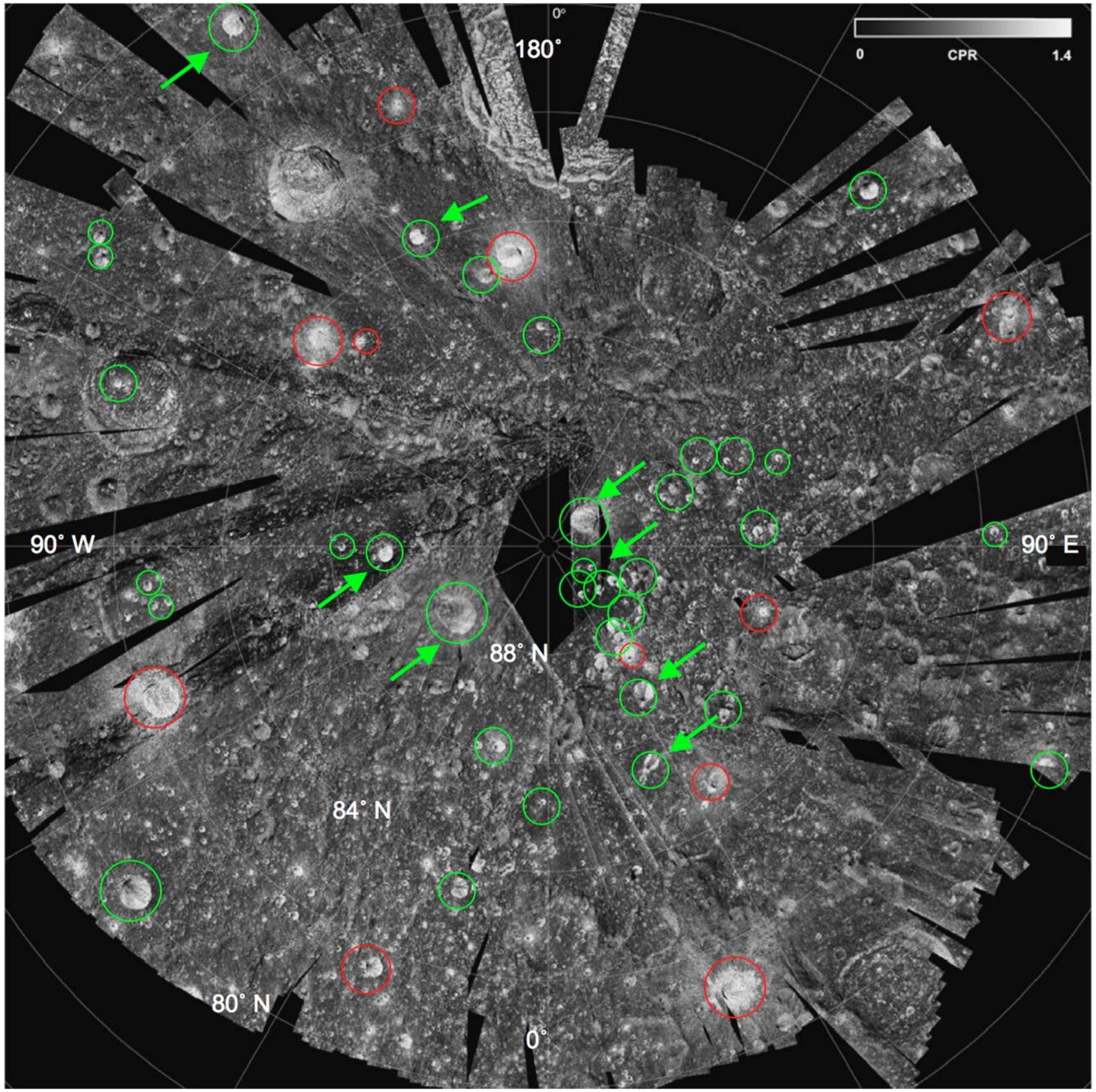
T < 140 K
ASW deposited on CCl_4

T ~ 140-150 K
crystallization

T > 150 K
CCl_4 evaporates

Courtesy: Bruce Kay, PNNL

Ice on the Moon

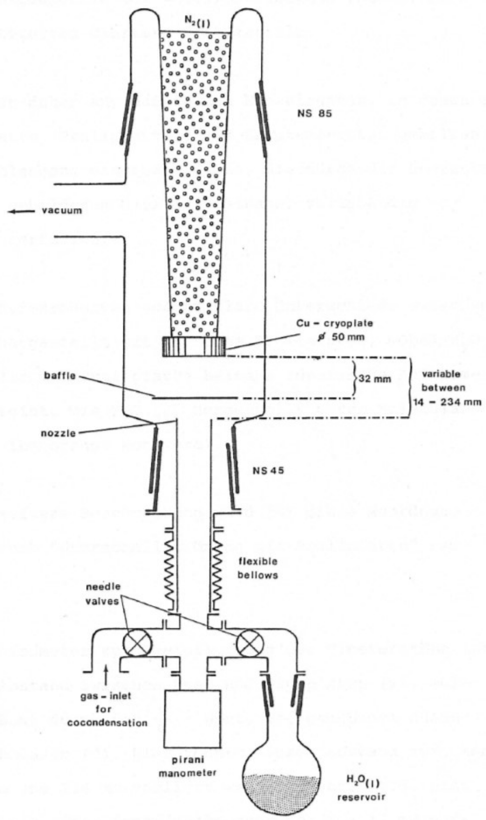


Fresh craters

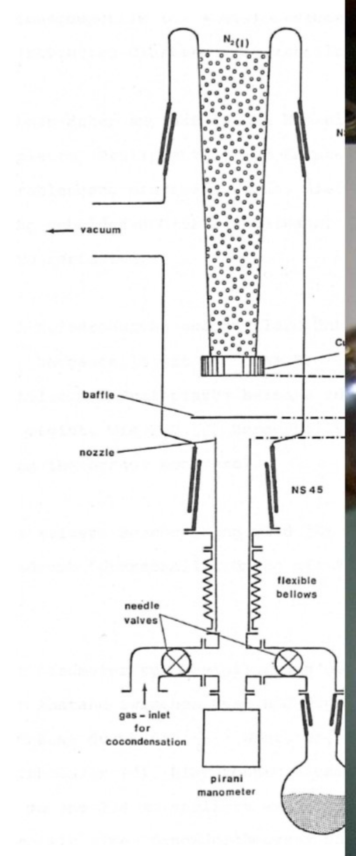
Anomalous craters

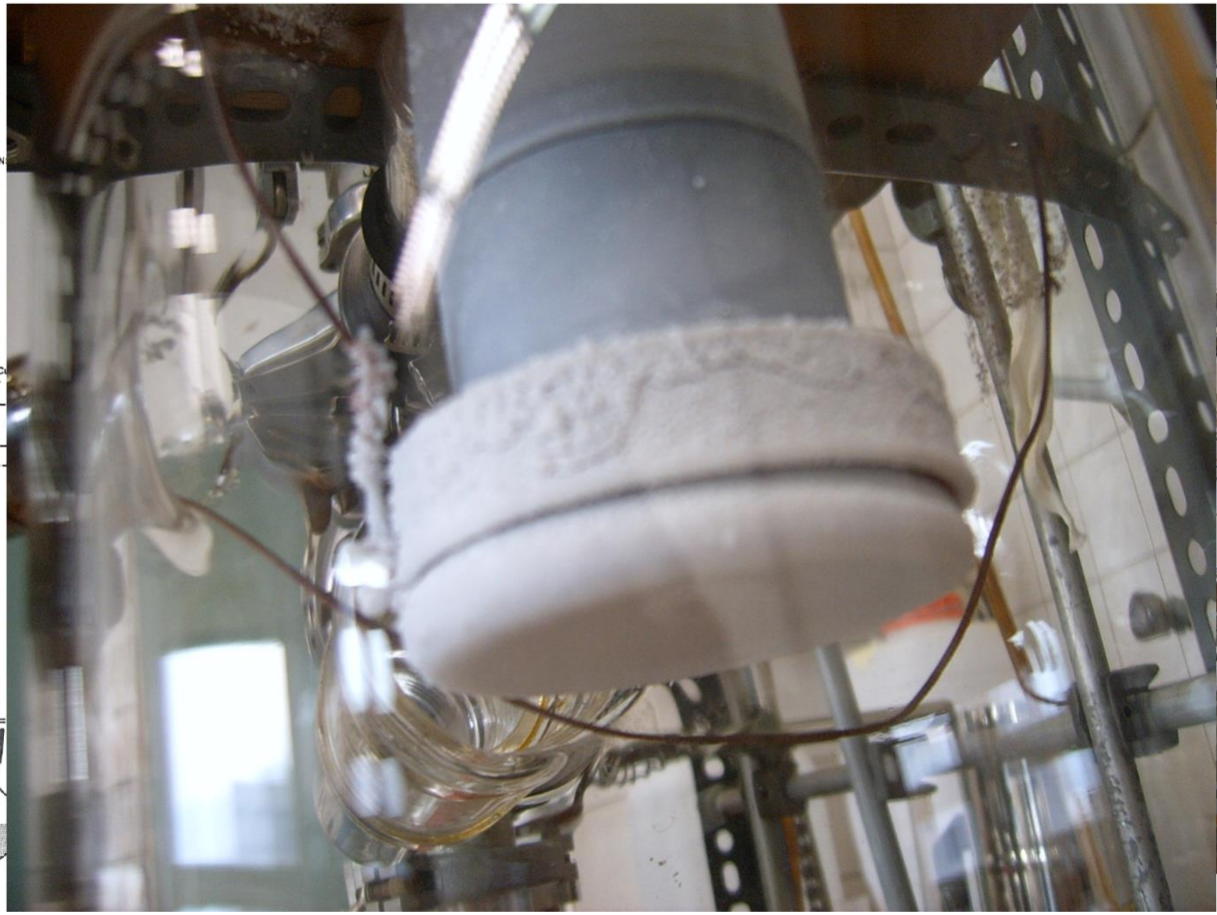
Data from:
Mini-SAR radar aboard
Chandrayaan-1 spacecraft
(2010)

600 million tons of almost pure ice detected, at a temperature of 110 K



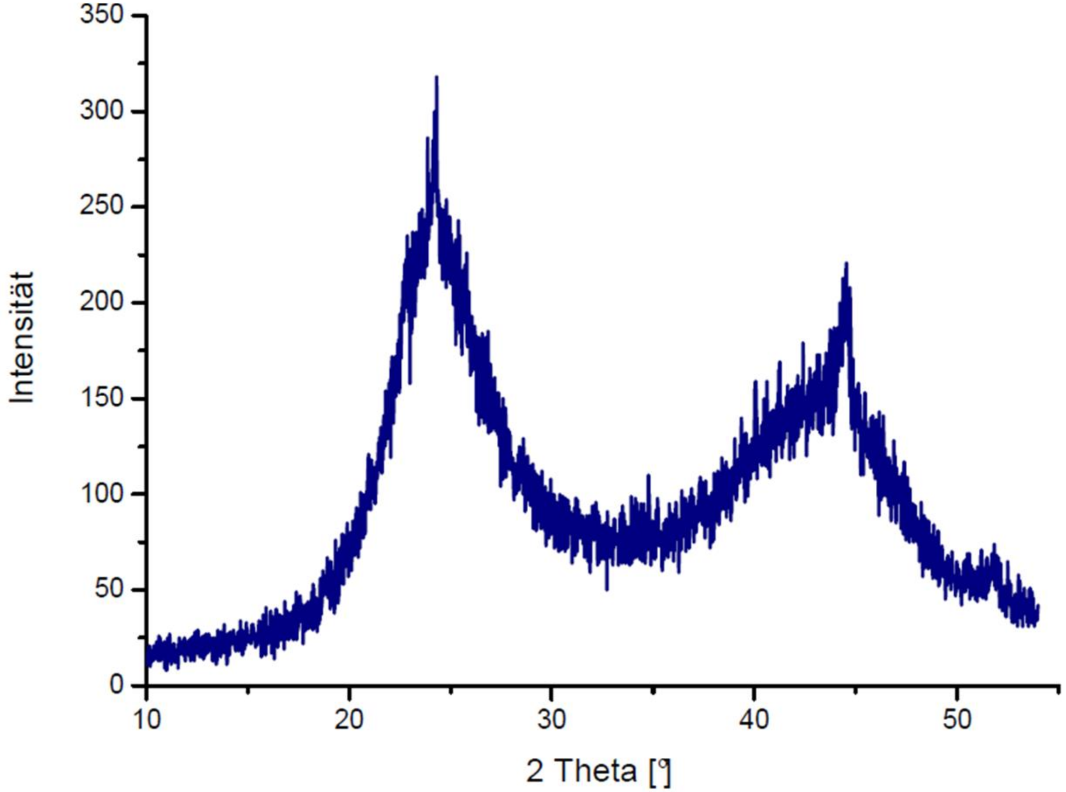
[1]E. Mayer et al.; Journal of Chemical Physics 1984; 80, 2939-2952
[2]A. Hallbrucker; PhD - Thesis 1989; Innsbruck



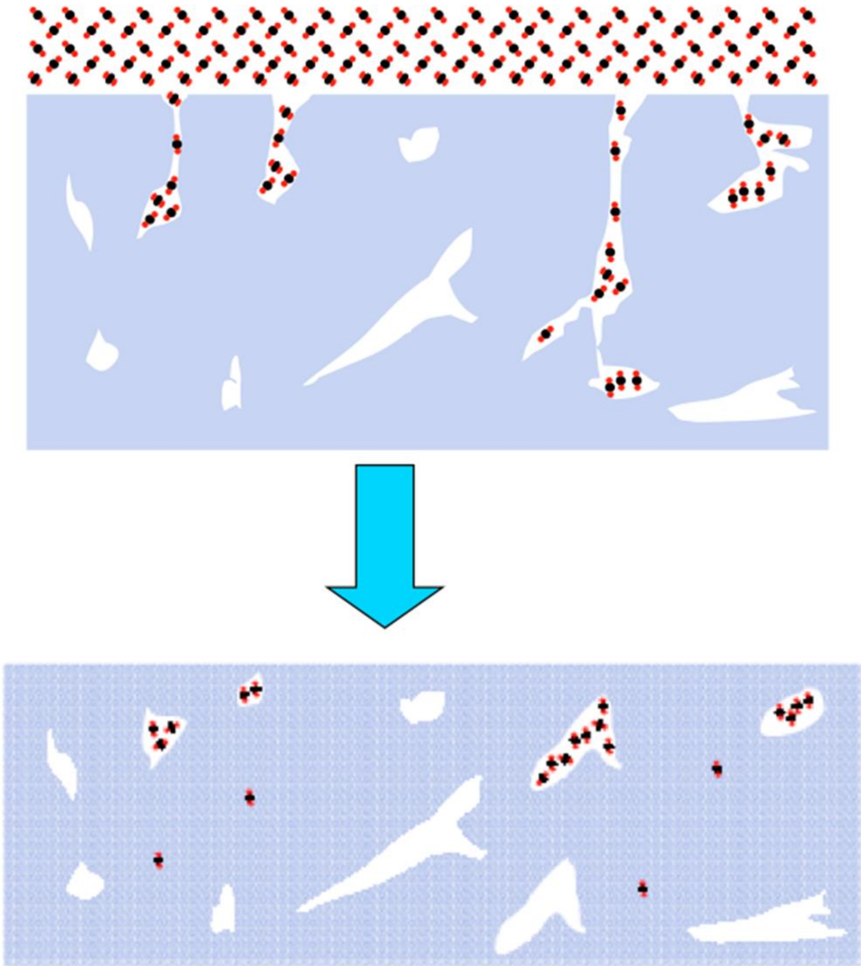


[1]E. Mayer et al.; Journal of Chemical Physics 1984; 80, 2939-2952
[2]A. Hallbrucker; PhD - Thesis 1989; Innsbruck

ASW



ASW: A Highly Microporous Solid



Courtesy: H. Reisler, USC (LA)

PRL 116, 215501 (2016) PHYSICAL REVIEW LETTERS week ending 27 MAY 2016

Neutron Scattering Analysis of Water's Glass Transition and Micropore Collapse in Amorphous Solid Water

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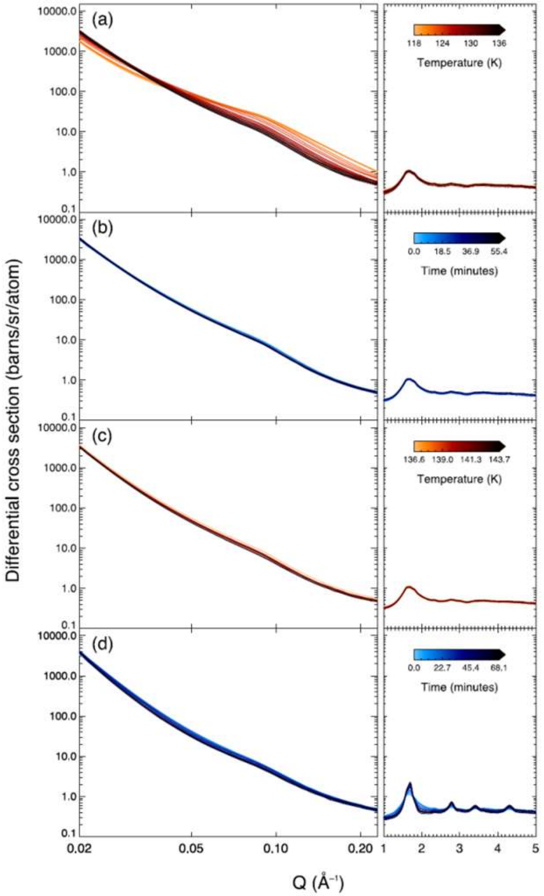
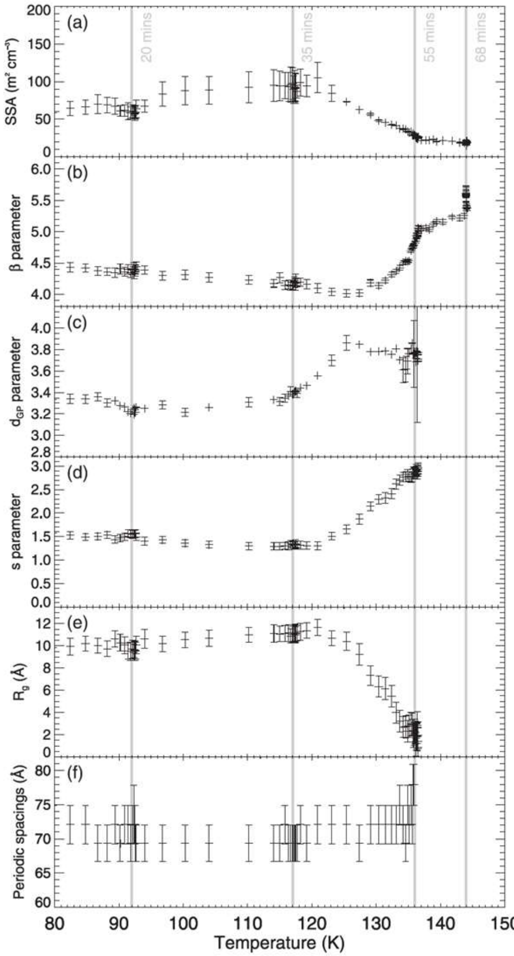
[2]Institute of Physical Chemistry, University of Innsbruck, A-6020 Innsbruck, Austria
[3]ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxon OX11 0QX, United Kingdom
(Received 28 August 2015; published 26 May 2016)



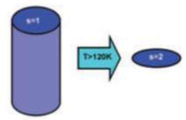


NIMROD instrument (ISIS)

80 – 115 K:
Rough, cylindrical pores

115 – 121 K:
Smoothing of pore surfaces

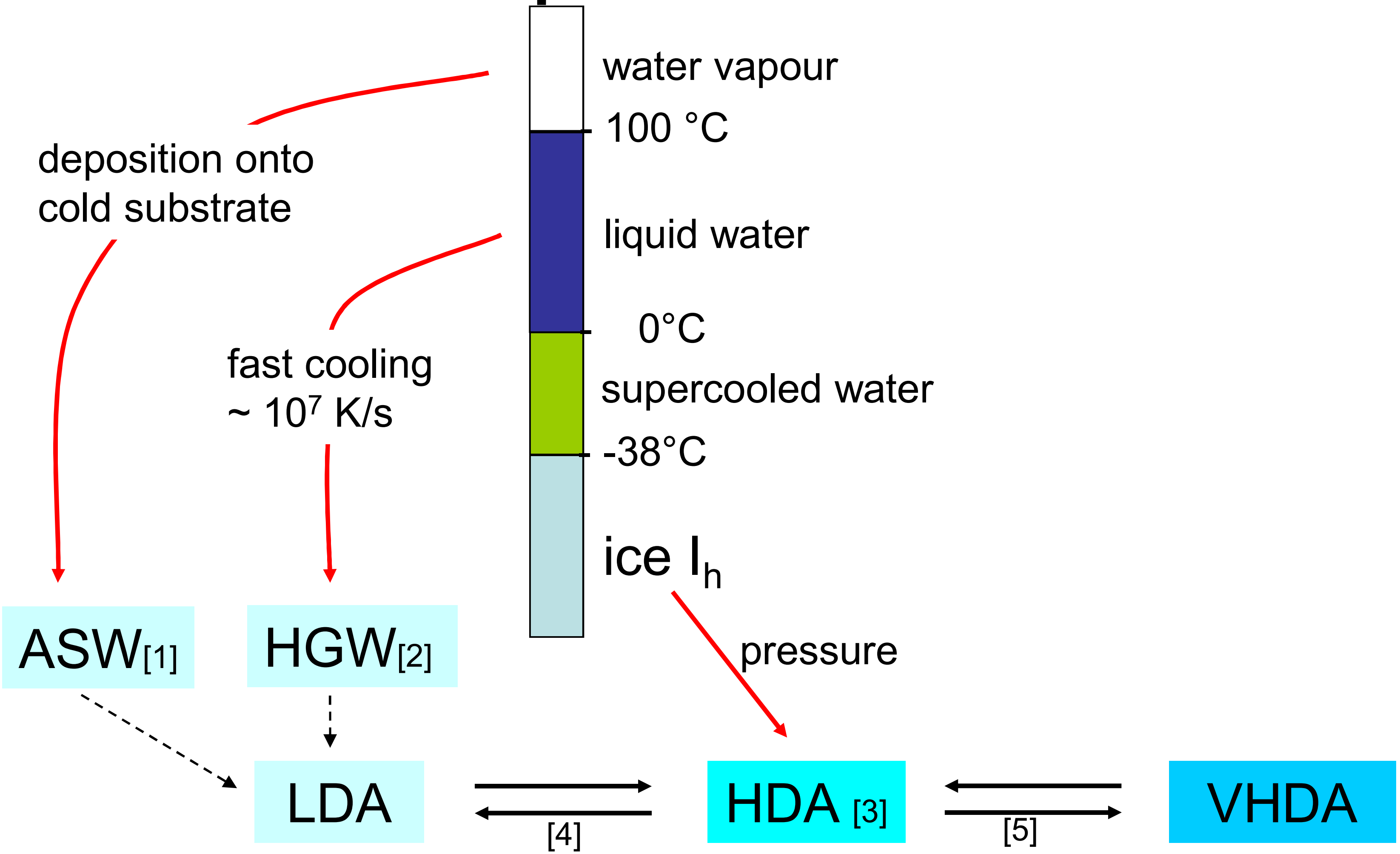
121 – 136 K:
Translational diffusion,
Micropore collapse



136 – 144 K:
Amorphous water (LDL)

144 K:
Crystallization

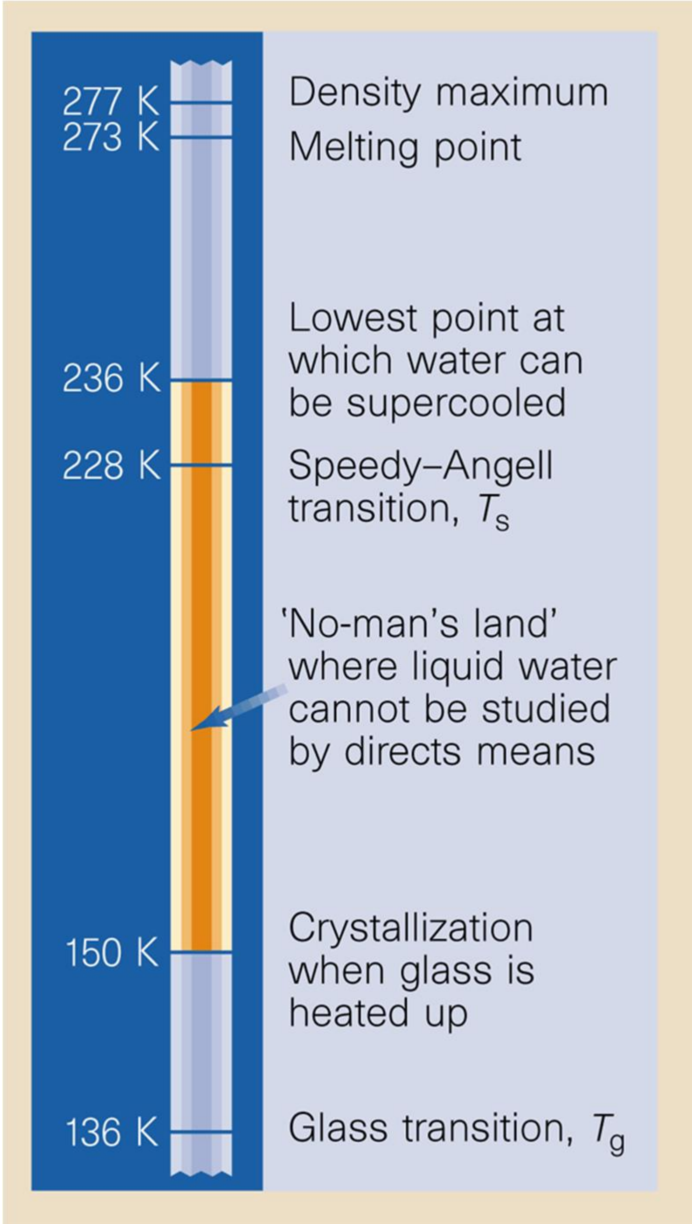
Amorphous ice



[1] E.F. Burton and W.F. Oliver, *Proc. R. Soc. A*, 153, 1935
[2] P. Brüggeller, E. Mayer, *Nature,* 288, 1980; E. Mayer, *J. Appl. Phys.,* 58, 1985
[3] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 310, 1984;
[4] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 314, 1985
[5] T. Loerting, C. Salzmann, I. Kohl, E. Mayer, A. Hallbrucker, *PCCP*, 3, 2001

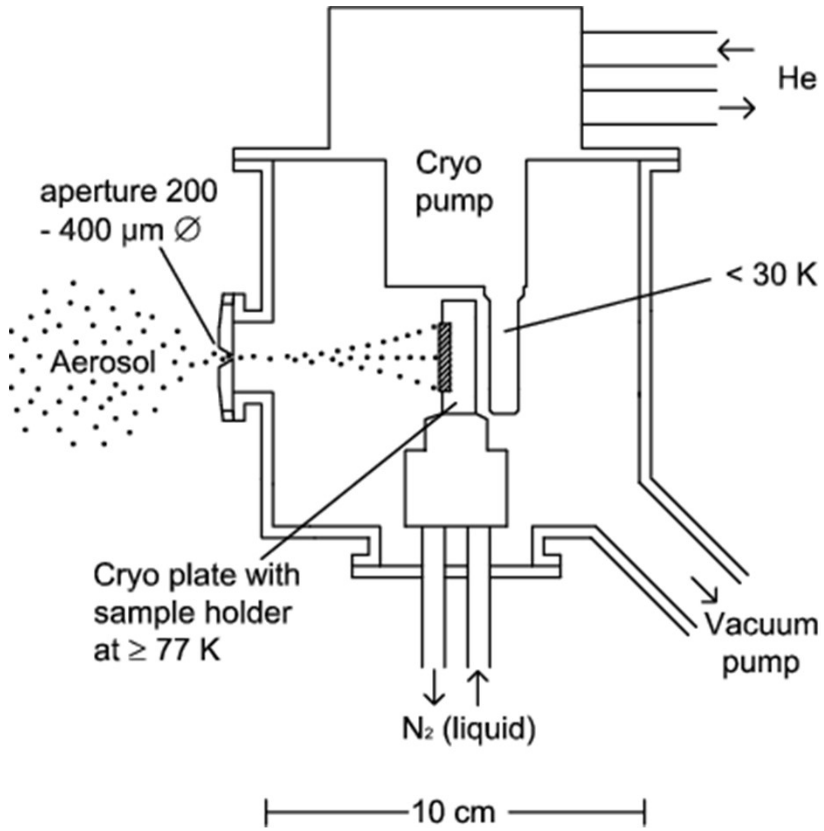
HYPERQUENCHED GLASSY WATER (HGW)

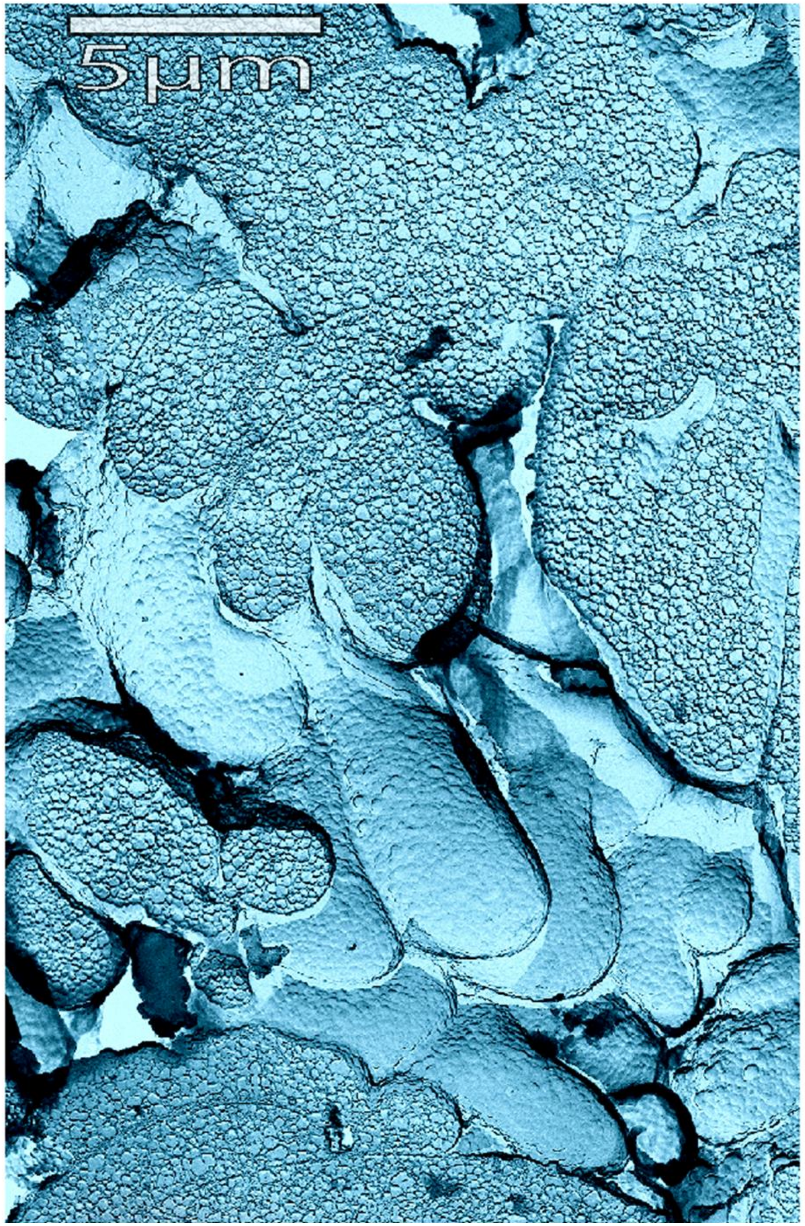
Ambient and Subambient Pressure



S. Sastry, *Nature* 398, *467-470* (1999)

Hyperquenched Glassy Water (HGW)

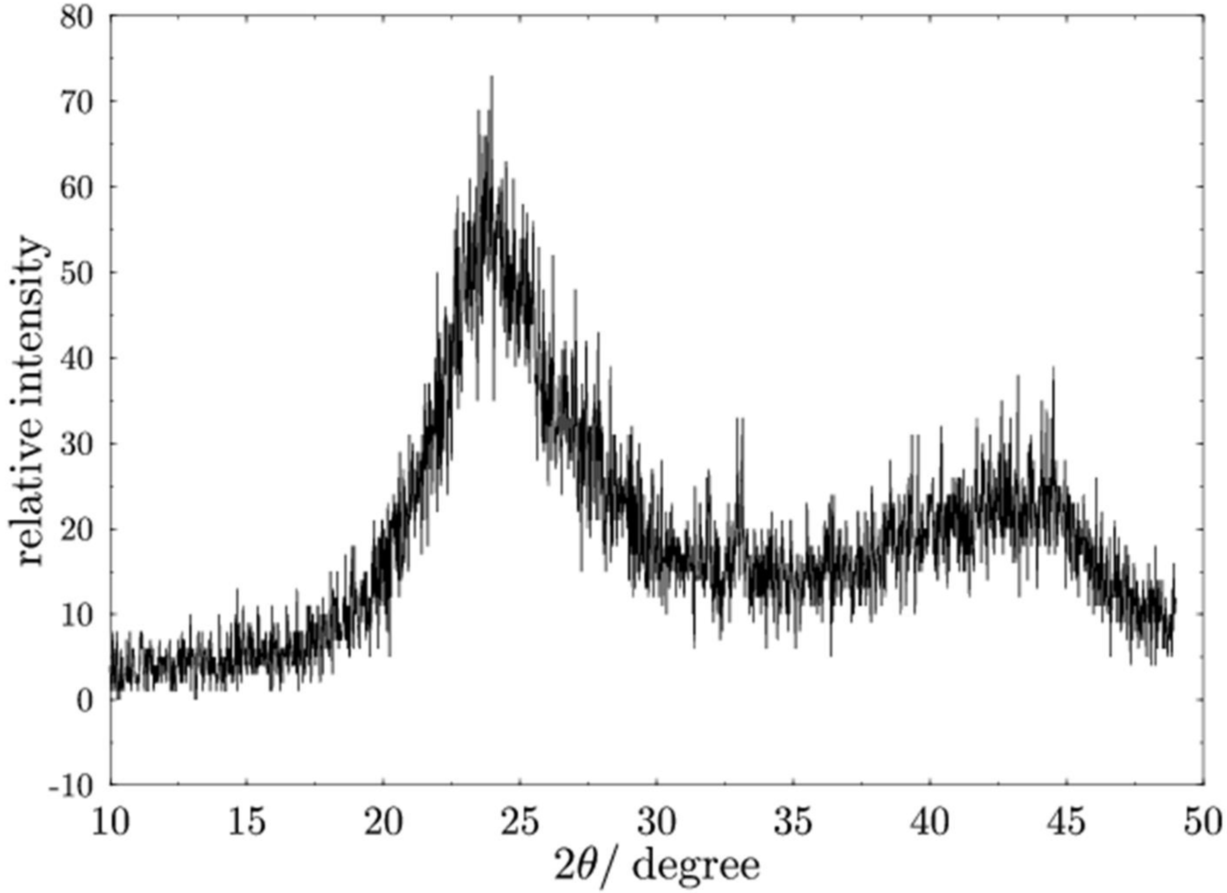


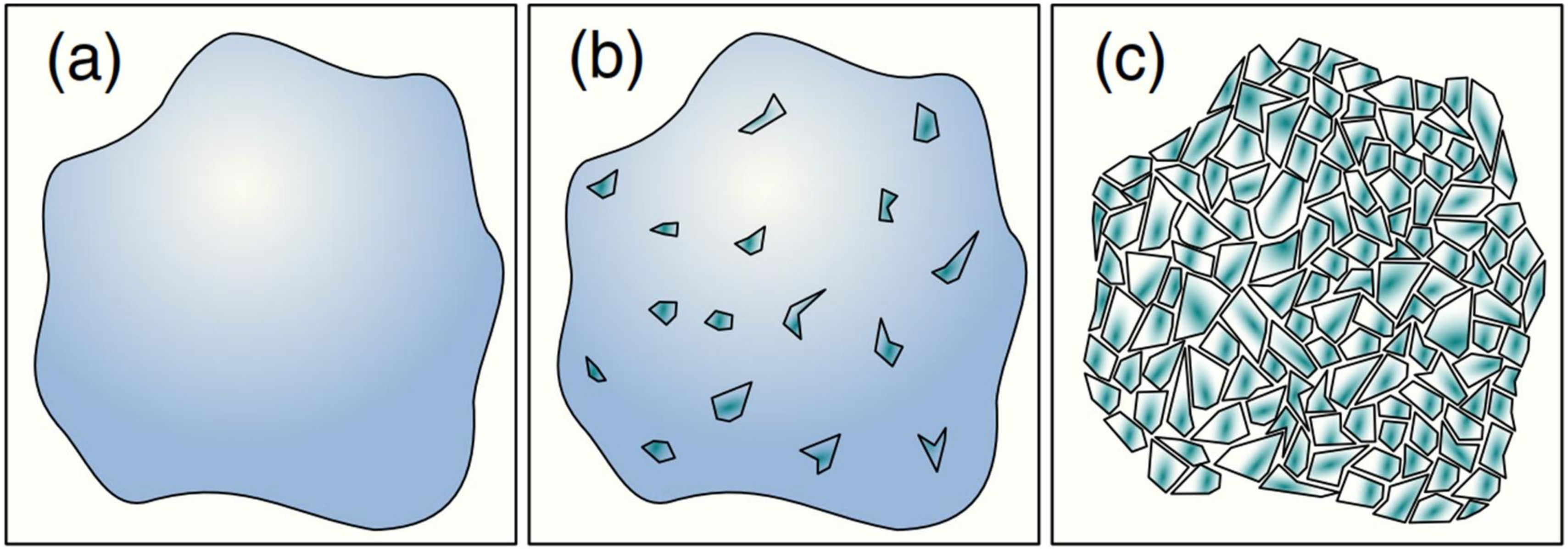


G. P. Johari, A. Hallbrucker & E. Mayer **Nature** 330 (1987), 552.

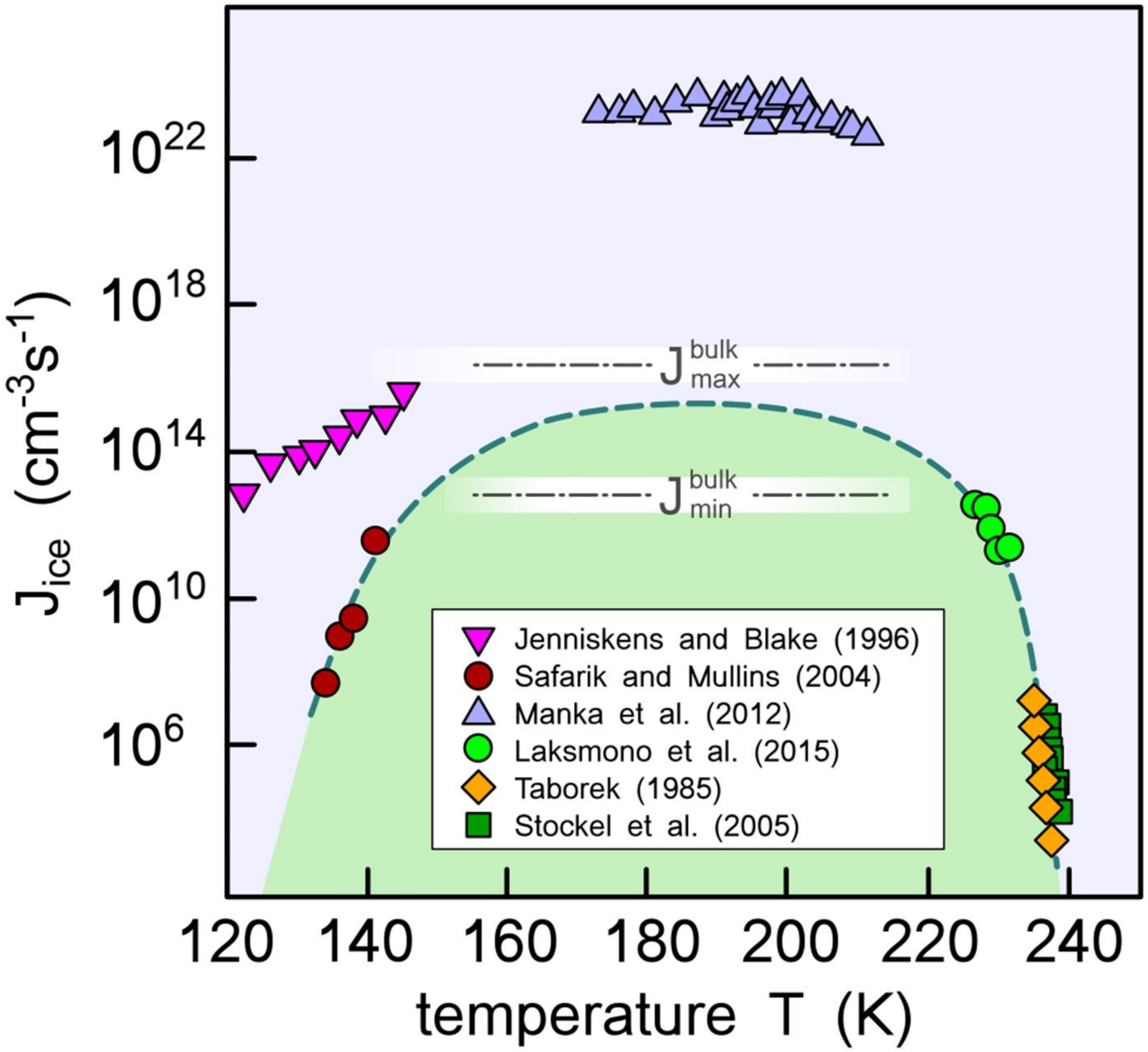
I. Kohl, L. Bachmann, A. Hallbrucker, E. Mayer, T. Loerting, **Phys. Chem. Chem. Phys.** 7 (2005), 3210.

HGW cooled at > 10^6 K/s = ASW

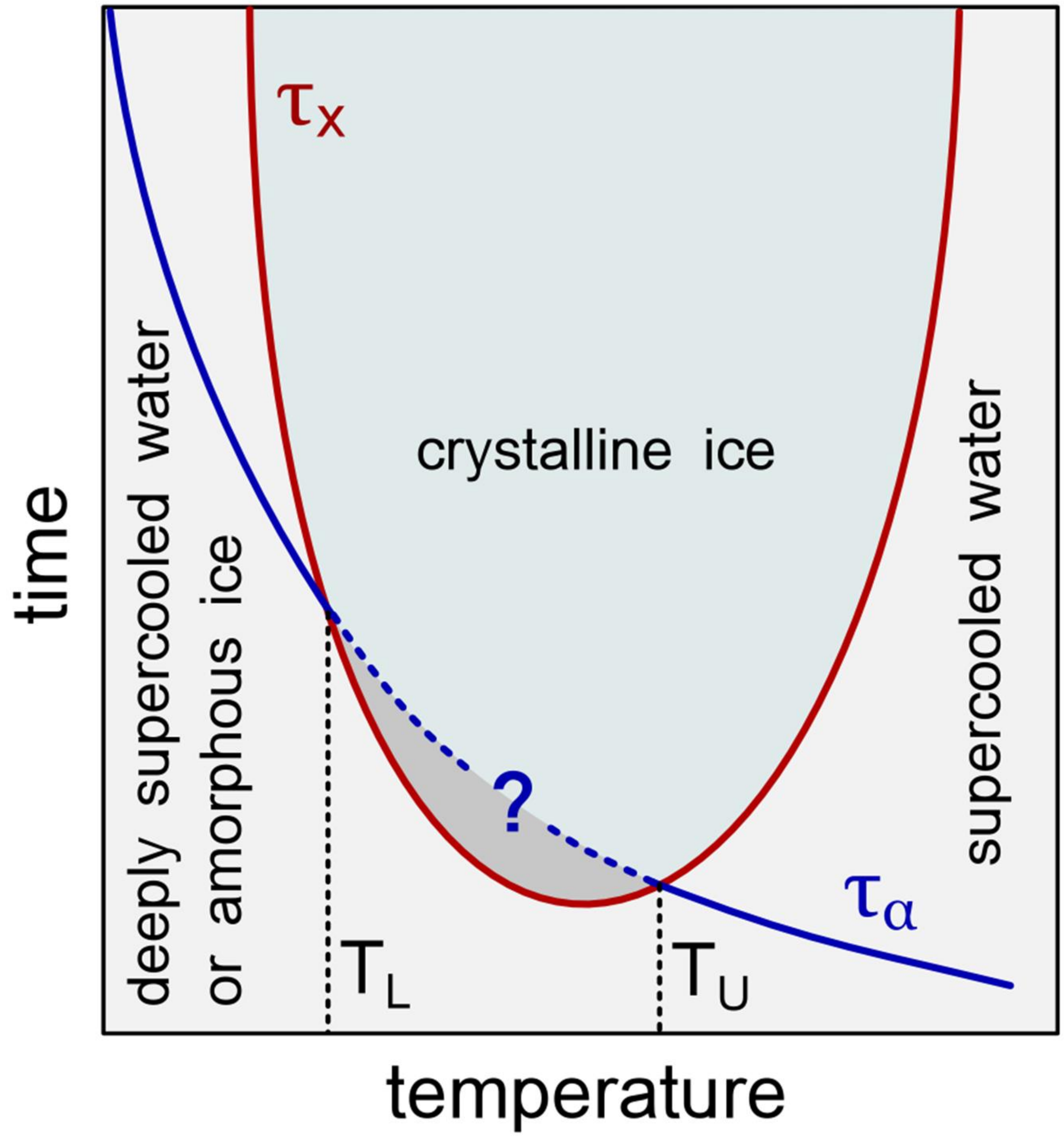




$> 10^6$ K/s $\quad$ 10^4-10^6 K/s $\quad$ $< 10^4$ K/s

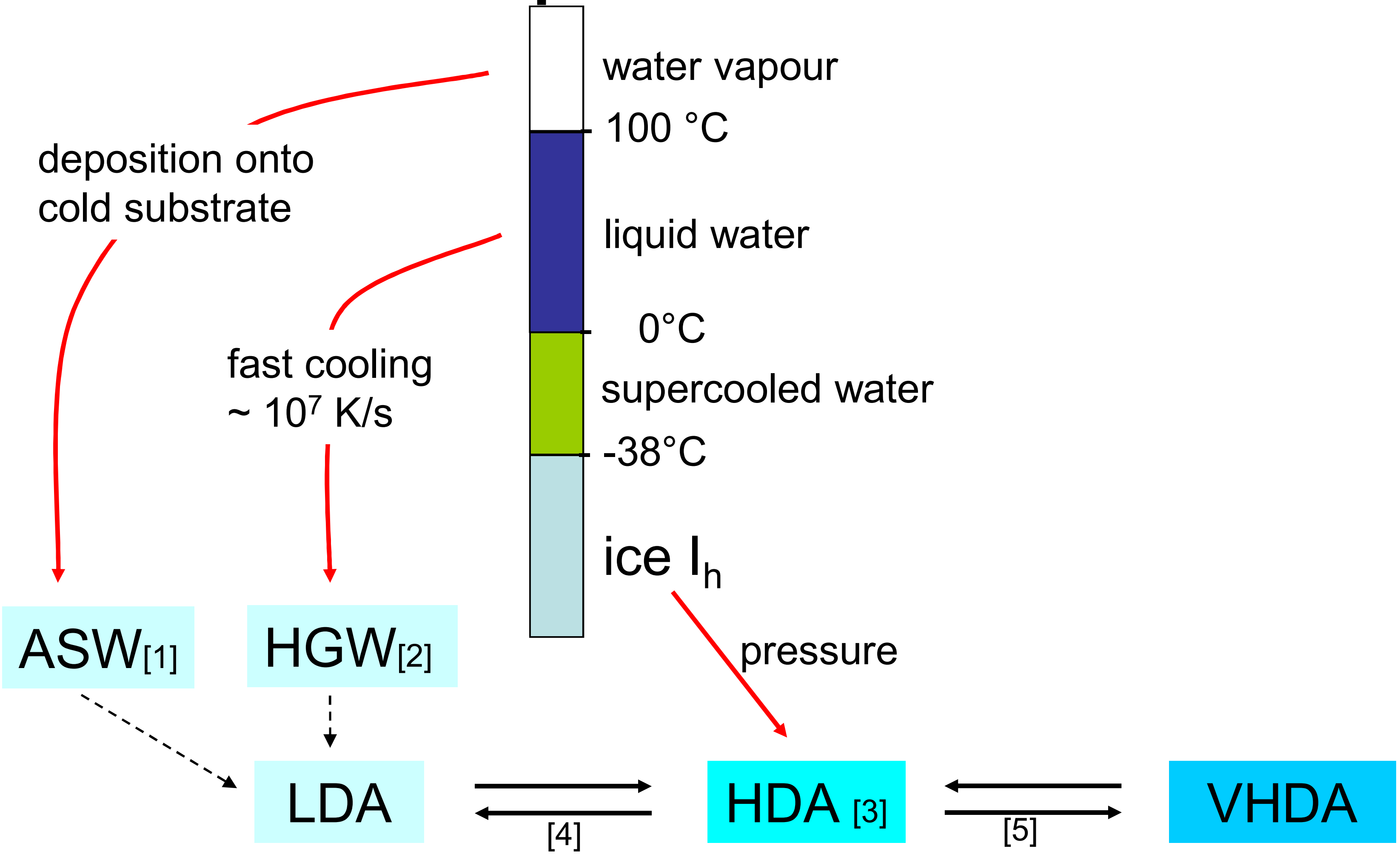


Amann-Winkel et al., **Rev. Mod. Phys.** *88* (2016) 011002.
Laksmono et al., **J. Phys. Chem. Lett.** *6* (2015) 2826–2832.



time
temperature
τ_x
τ_α
crystalline ice
deeply supercooled water
or amorphous ice
supercooled water
?
T_L
T_U

Amorphous ice



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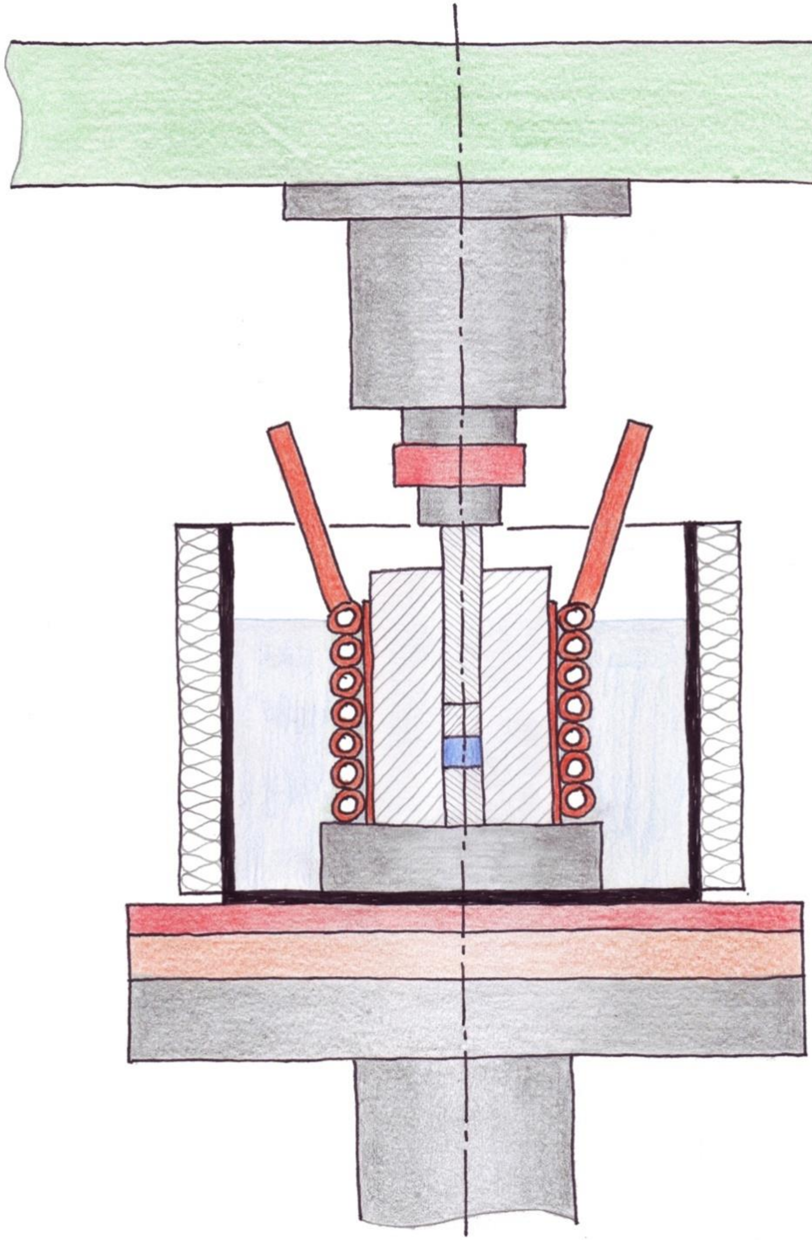
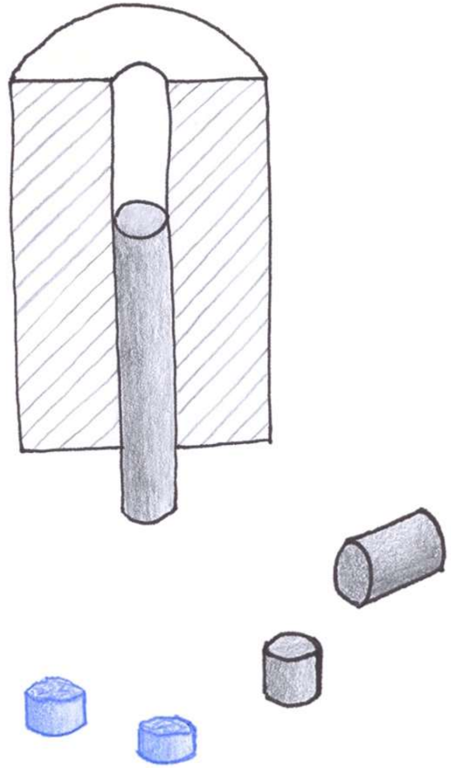
[3] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 310, 1984;

[4] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 314, 1985

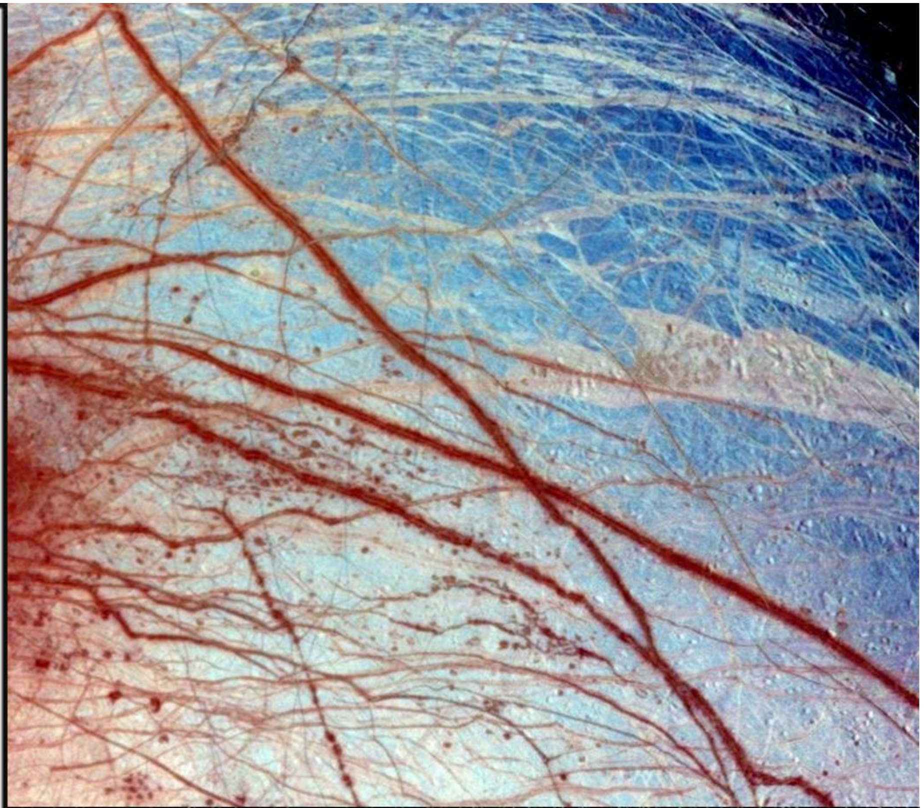
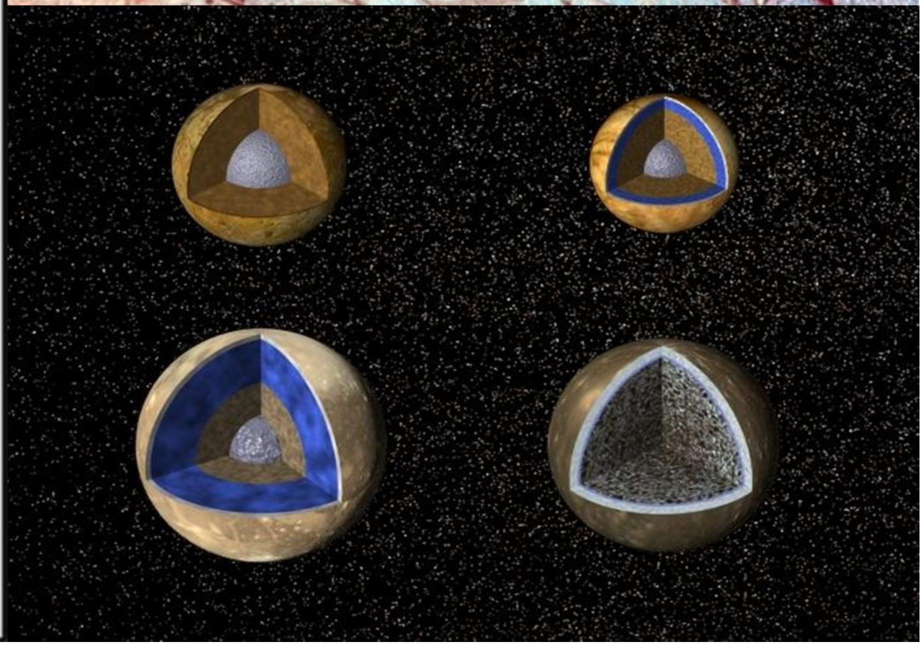
[5] T. Loerting, C. Salzmann, I. Kohl, E. Mayer, A. Hallbrucker, *PCCP*, 3, 2001

HIGH-DENSITY AMORPHOUS ICE (HDA)

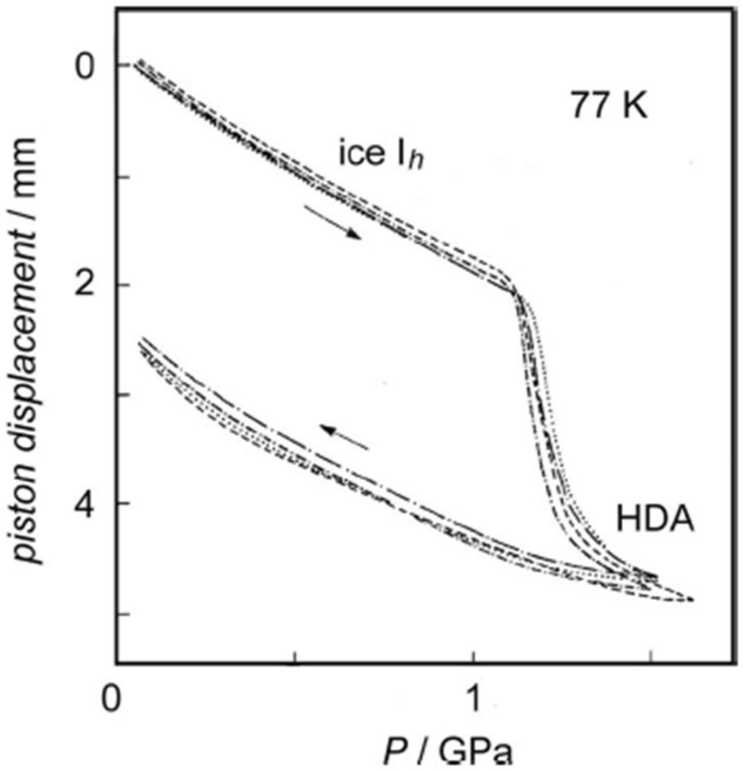




Phase Transformation to High Pressure Phases:
requires at least 100 MPa (10 km of ice column)

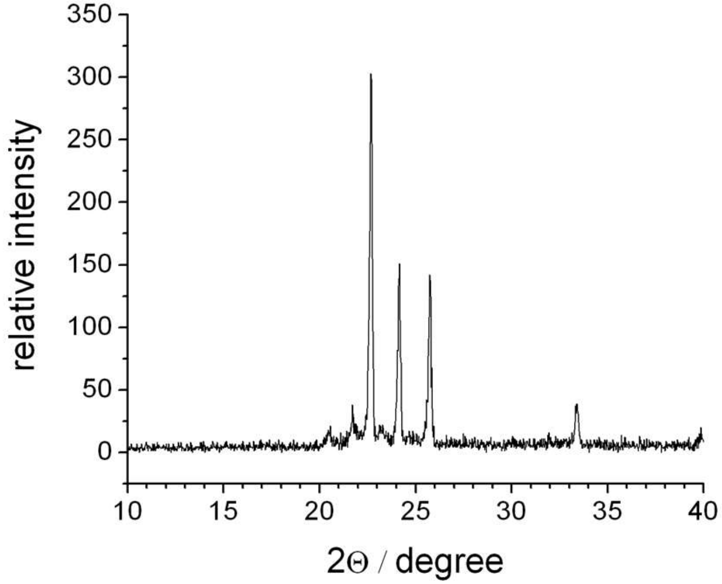




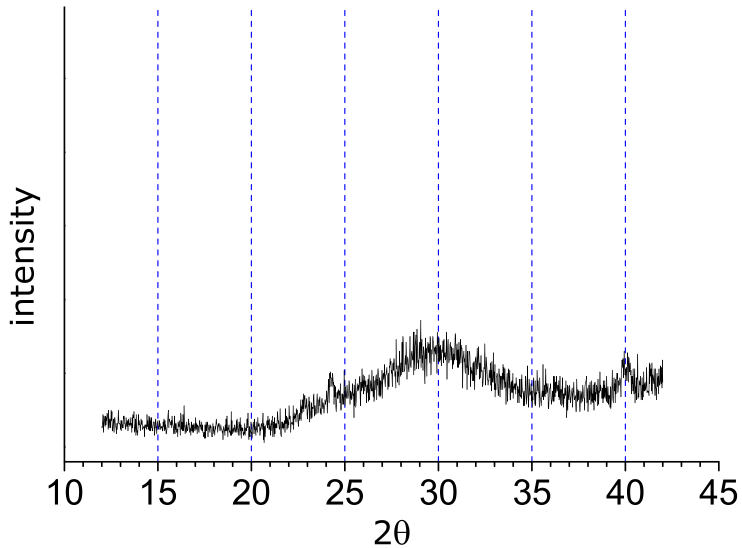
High-Density Amorphous Ice (HDA)



$\rho \approx 1.15\ g\ cm^{-3}$

O. Mishima et al.; Nature **1984**; 310, 393-395

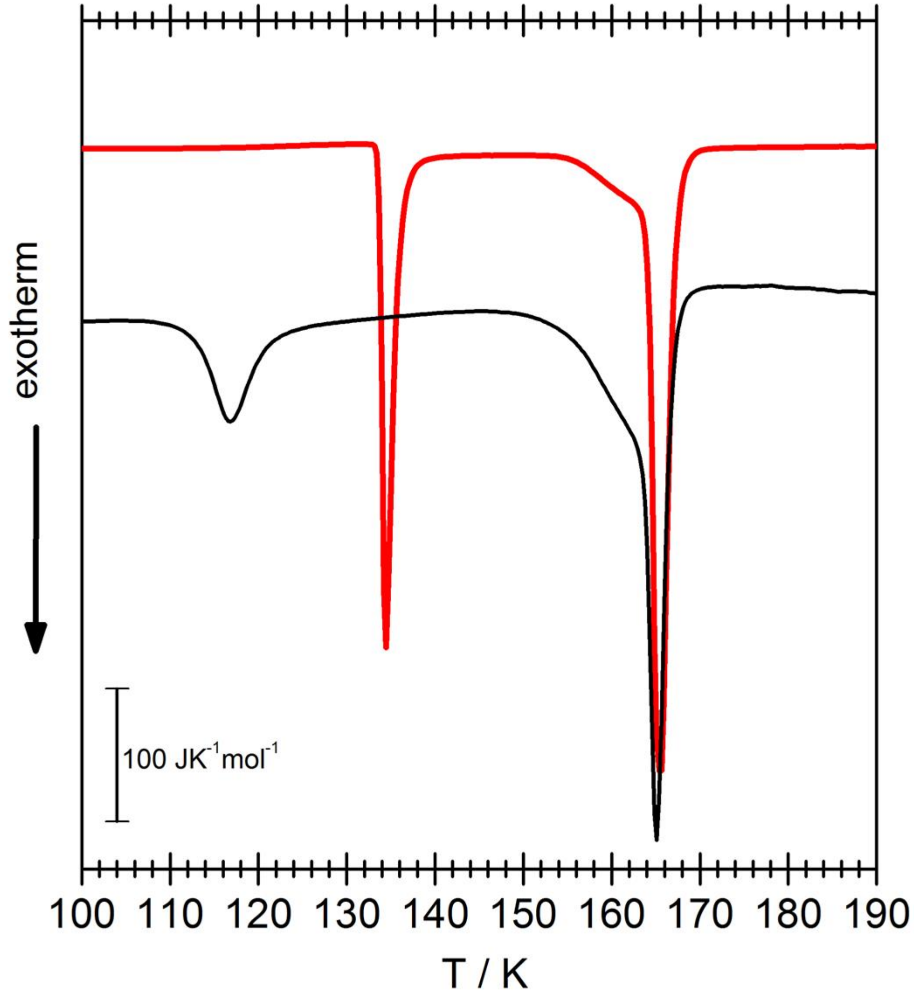




Pressure induced amorphization!

Unrelaxed (uHDA) vs. Relaxed HDA (eHDA)

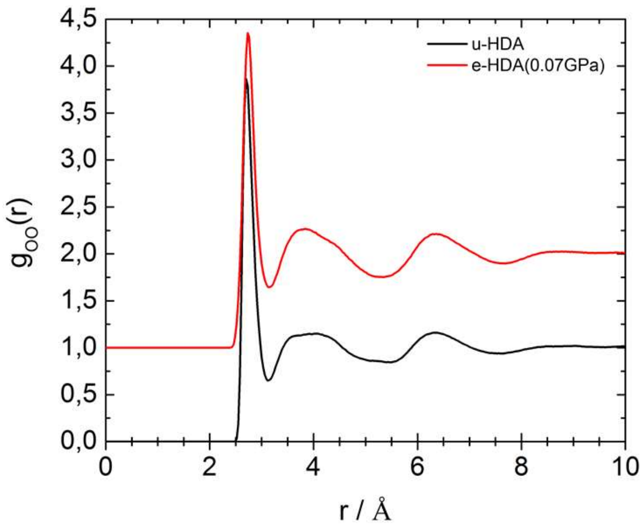
HDA → LDA → ice I



Heating rate: 10 K/min
Transition temperatures:

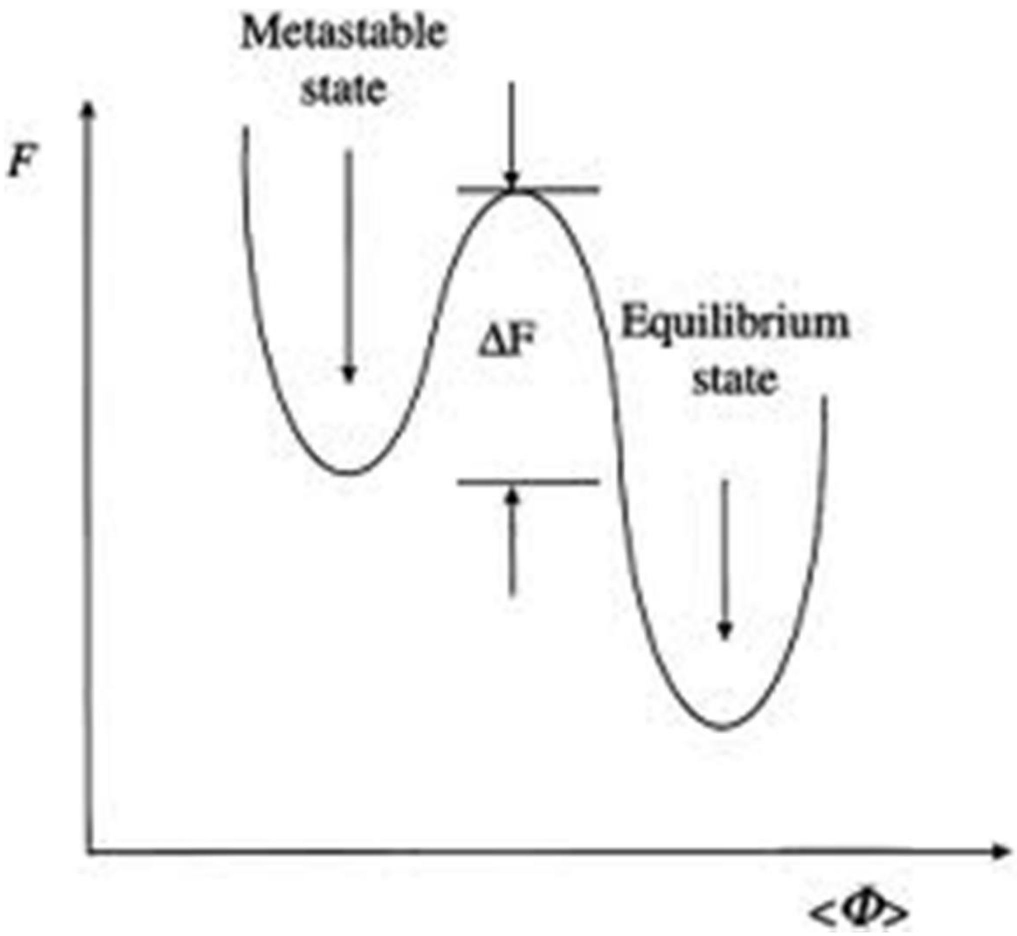
e-HDA: 133 K

u-HDA: 112 K

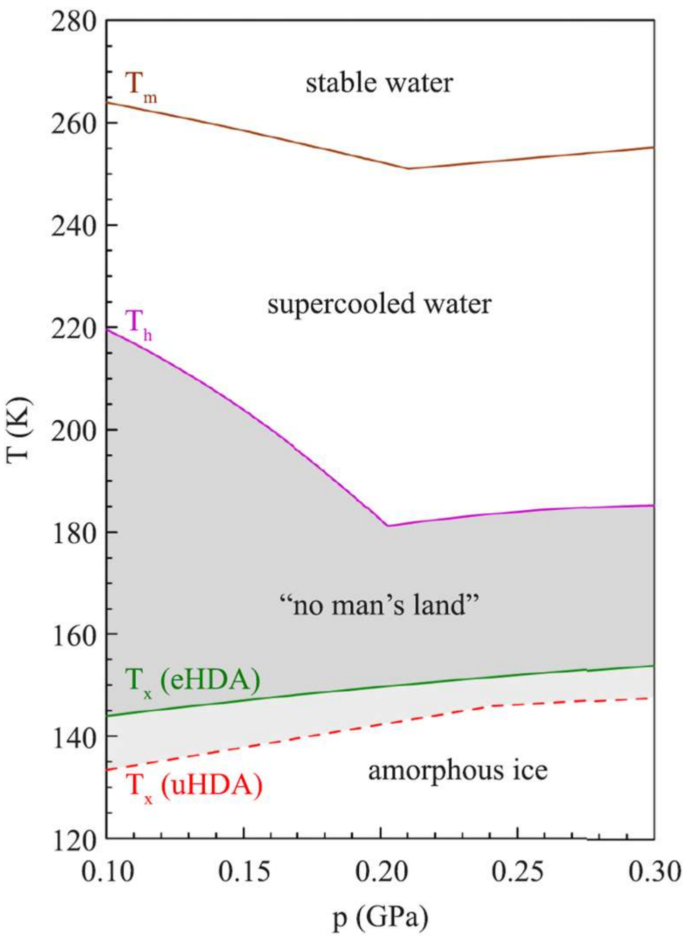


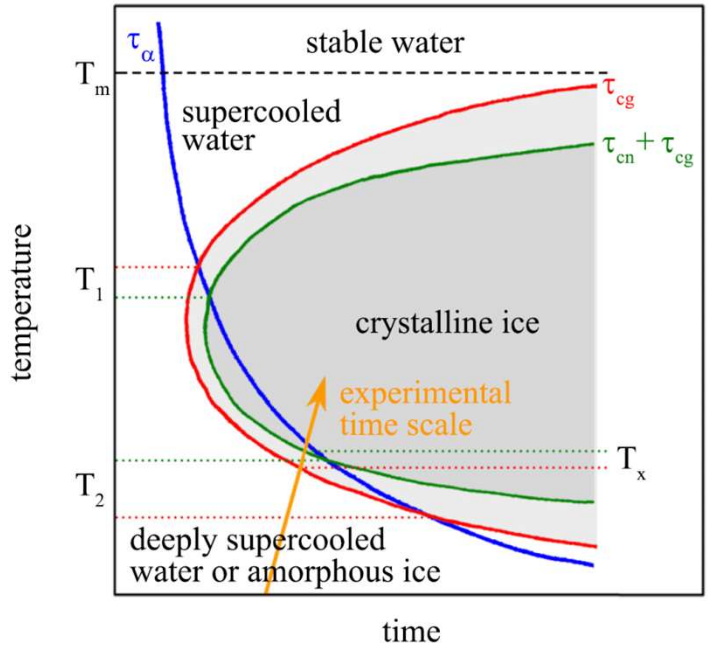
Loerting et al., PCCP, **13**, 2011

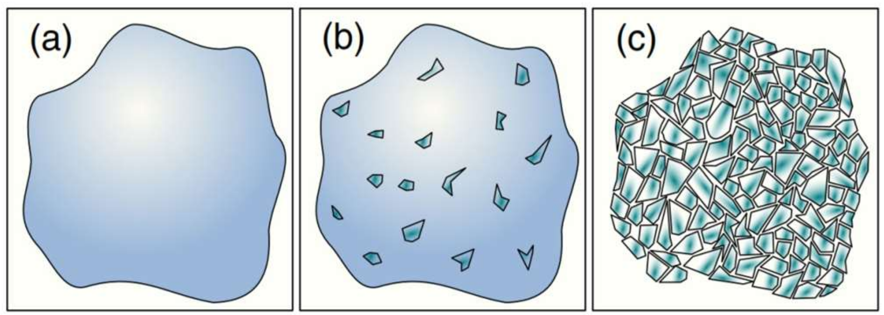
Metastability



Shrinking no man's land



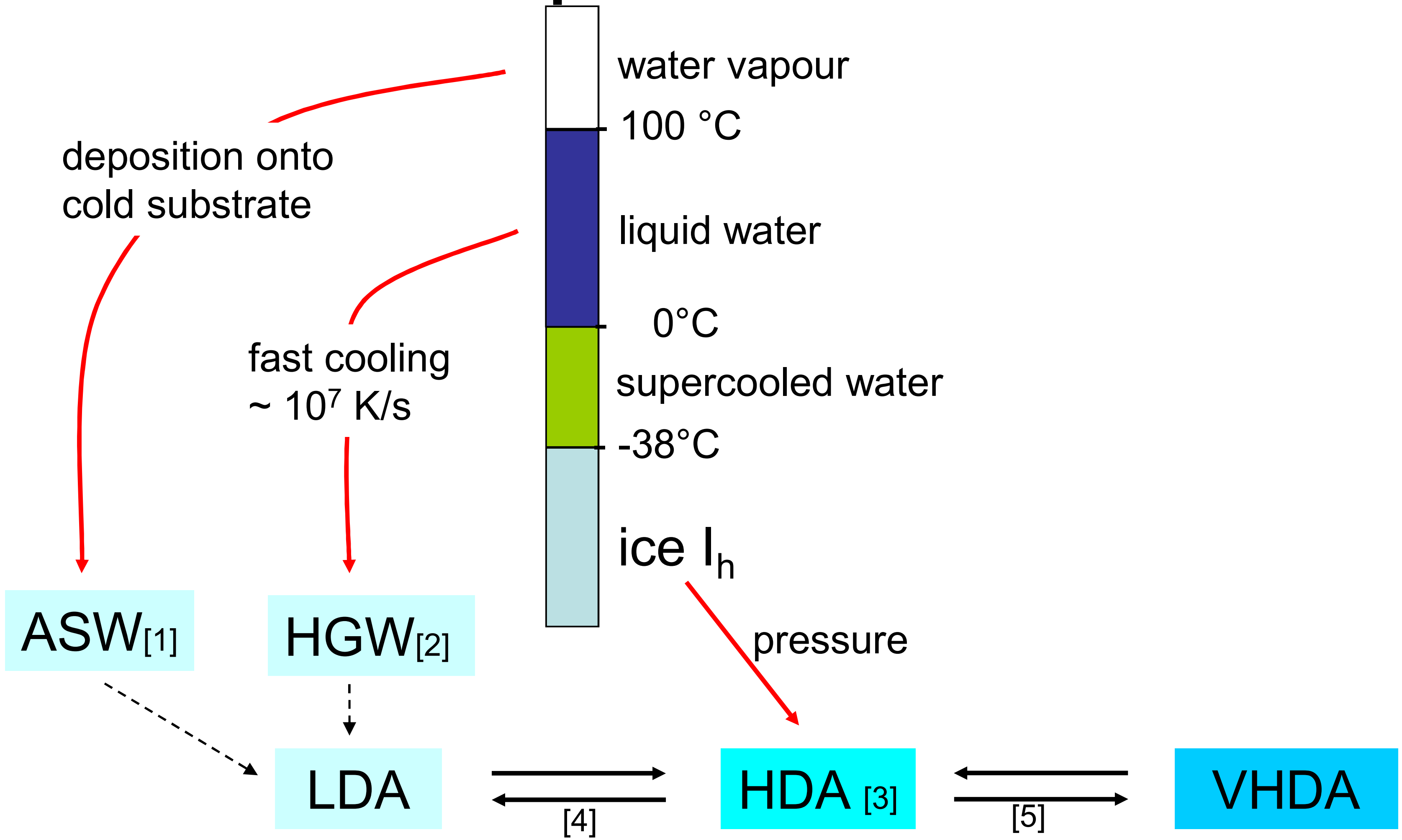




eHDA uHDA

SEIDL, FAYTER, STERN, ZIFFERER, AND LOERTING PHYSICAL REVIEW B **91**, 144201 (2015)

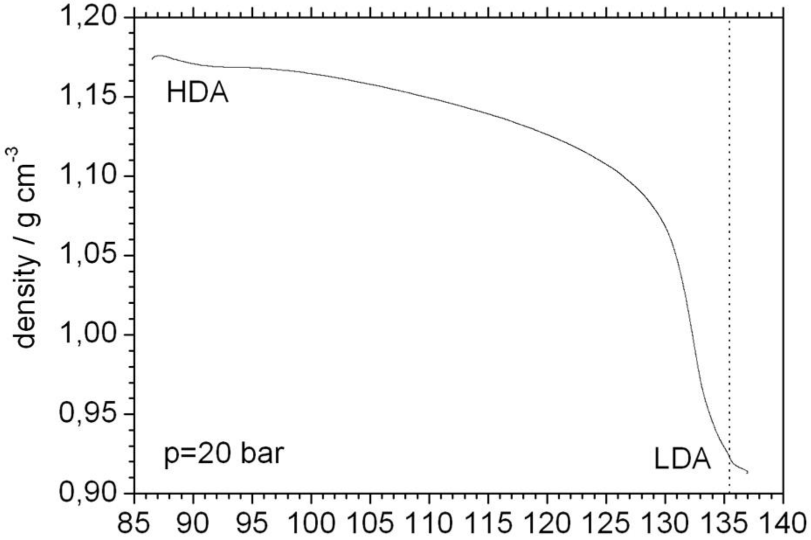
Amorphous ice



[1] E.F. Burton and W.F. Oliver, *Proc. R. Soc. A*, 153, 1935
[2] P. Brüggeller, E. Mayer, *Nature,* 288, 1980; E. Mayer, *J. Appl. Phys.,* 58, 1985
[3] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 310, 1984;
[4] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 314, 1985
[5] T. Loerting, C. Salzmann, I. Kohl, E. Mayer, A. Hallbrucker, *PCCP*, 3, 2001

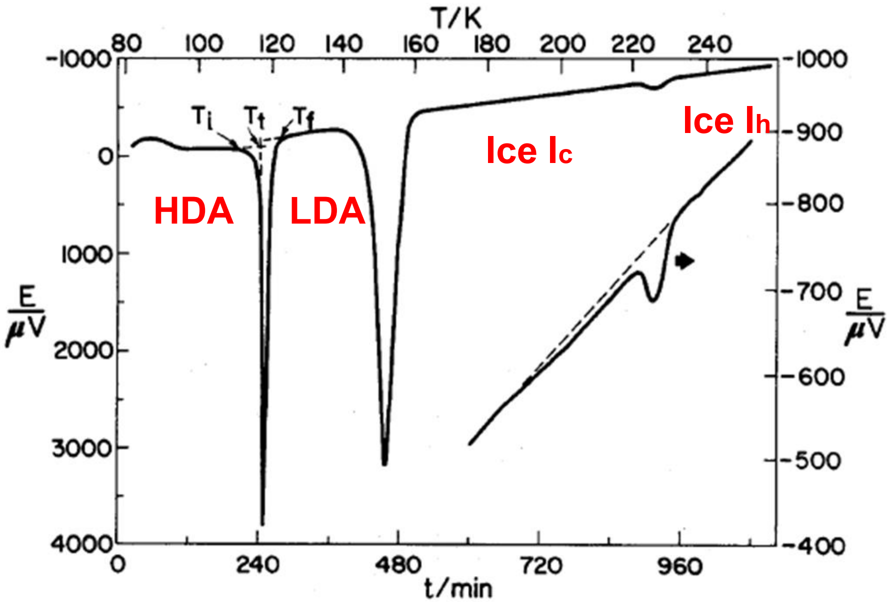
LOW-DENSITY AMORPHOUS ICE
(LDA)

Low-Density Amorphous Ice (LDA): amorphous-amorphous transition

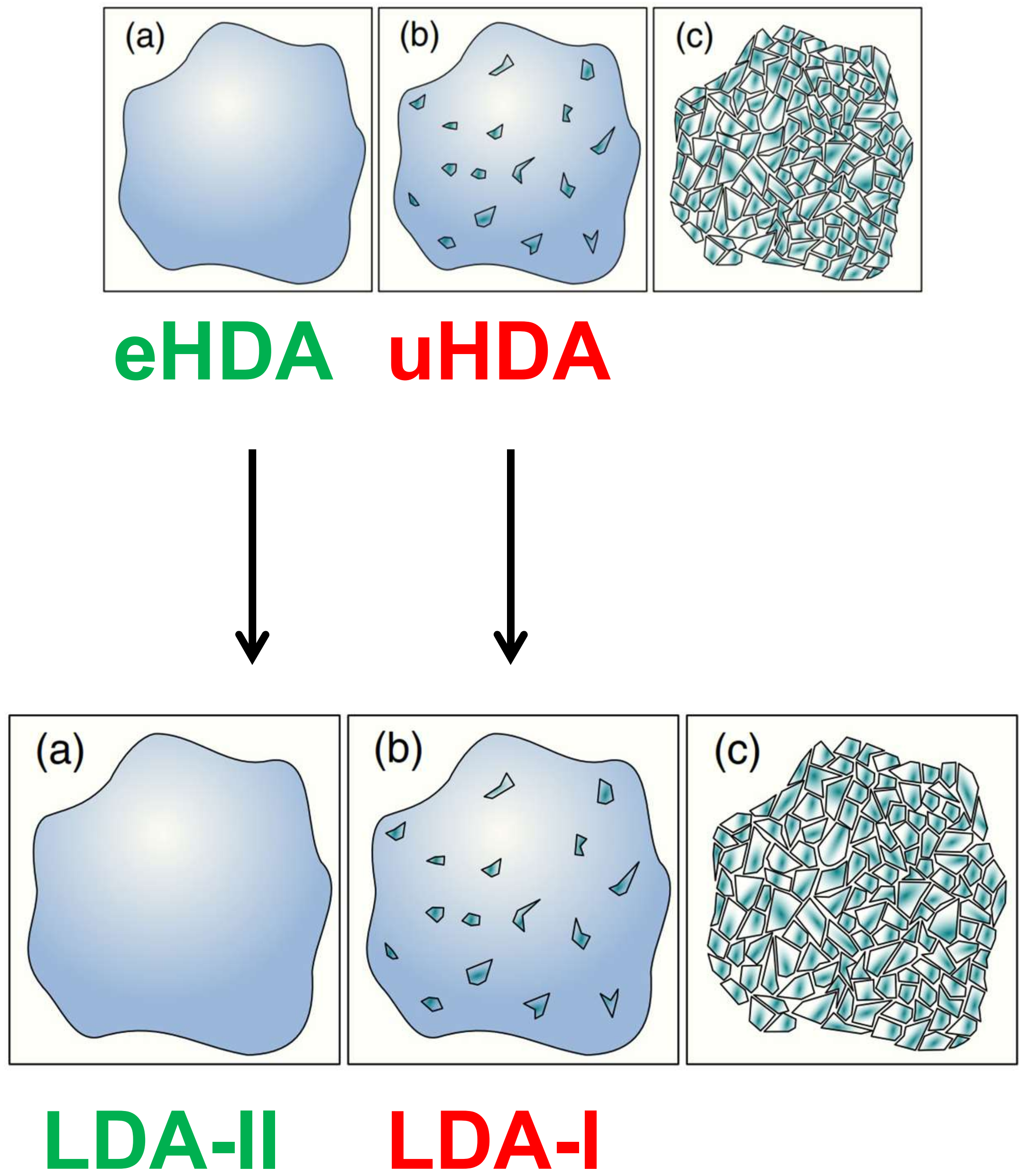


T. Loerting, N. Giovambattista, **J. Phys. Cond. Mat.** 18 (2006) 919.

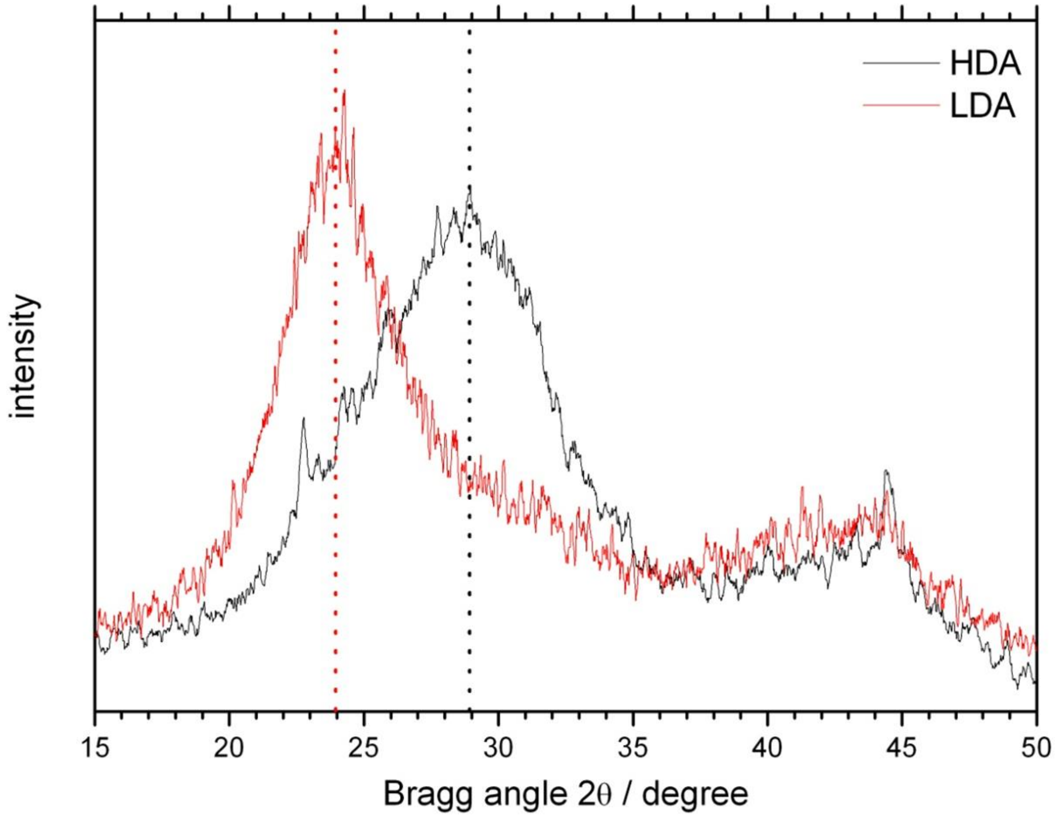
$\rho \approx 0.92$ g cm^{-3}



J. P. Handa, O. Mishima, E. Whalley, **J. Chem. Phys. 84** (1986) 2766.


(a)
(b)
(c)
eHDA
uHDA
(a)
(b)
(c)
LDA-II
LDA-I

Poly-amorphism



Poly-amorphism: Low Density Amorphous Ice (LDA)

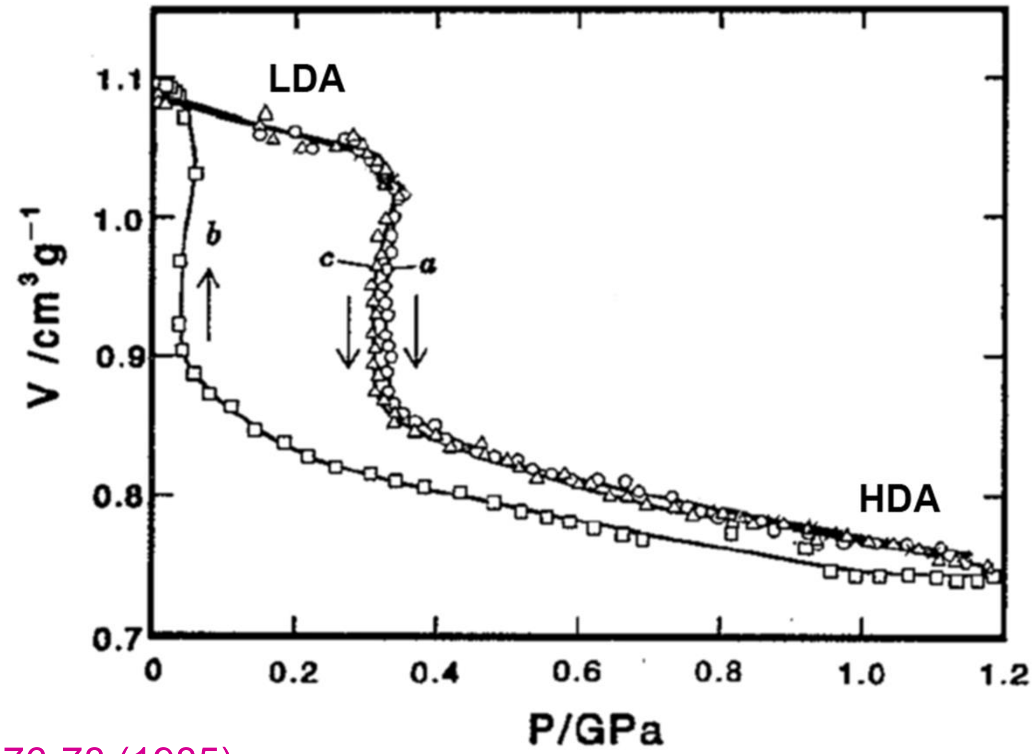
LDA ⇄ HDA

"apparently first-order"*)

$\rho \approx 0.93\ g\ cm^{-3}$

compression and decompression

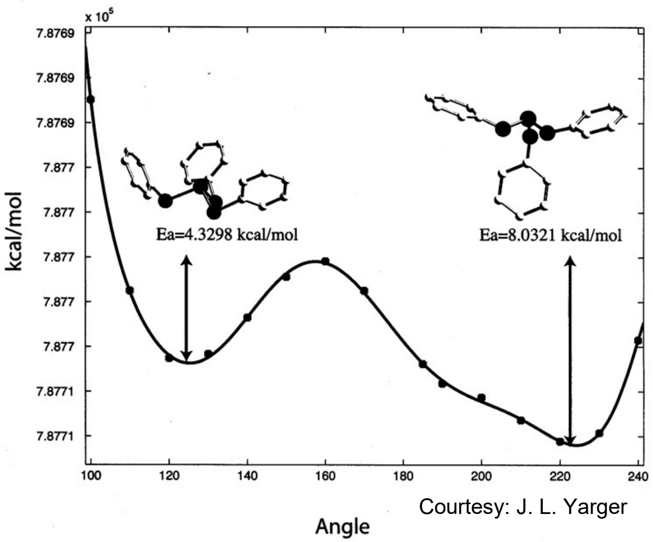
T = 130 – 140 K



*) O. Mishima et al. *Nature* **314**, 76-78 (1985)
O. Mishima *J.Chem.Phys* **100,** 5910 (1994)

Correlation: Poly-amorphism ↔ Anomalous Liquids

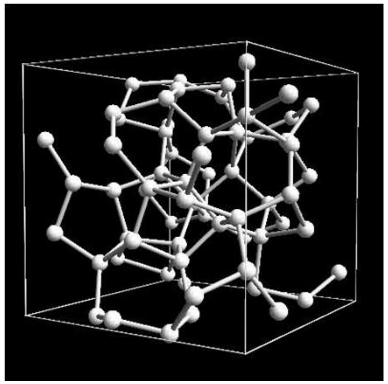
Organic: Triphenylphosphite (TPP)



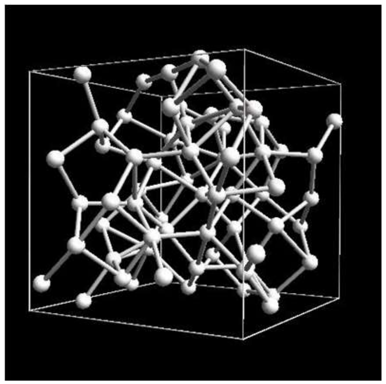
Courtesy: J. L. Yarger

Triphenyl phosphite calculations using RHF/6-31G
SCRF=dipole was used to simulate solvation where
ε=3.05 and the radius of TPP was 2.92

Atomic: P, Si, C



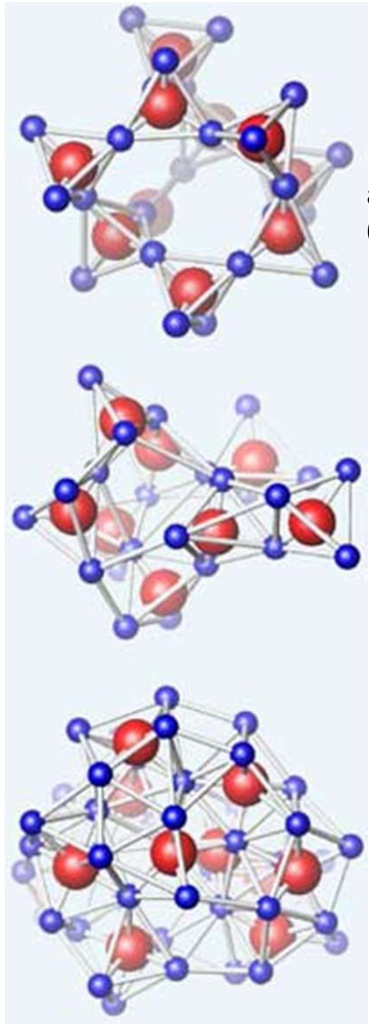
LDA-Si



HDA-Si

Courtesy: T. Morishita

Open Tetrahedral Networks: SiO_2, GeO_2, H_2O

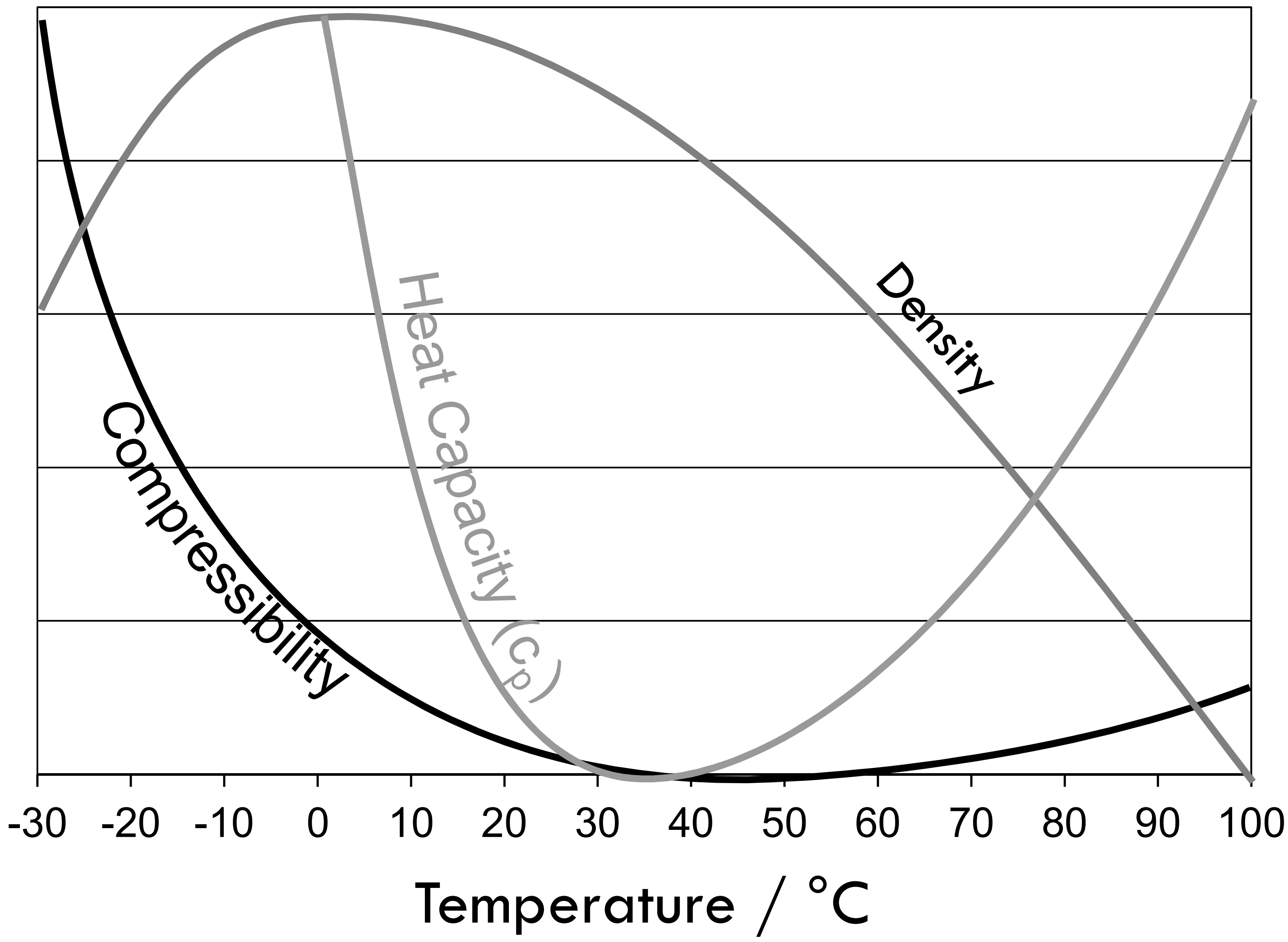


a-GeO_2
0.1 MPa (1bar)

a-GeO_2
5 GPa (50 kbar)

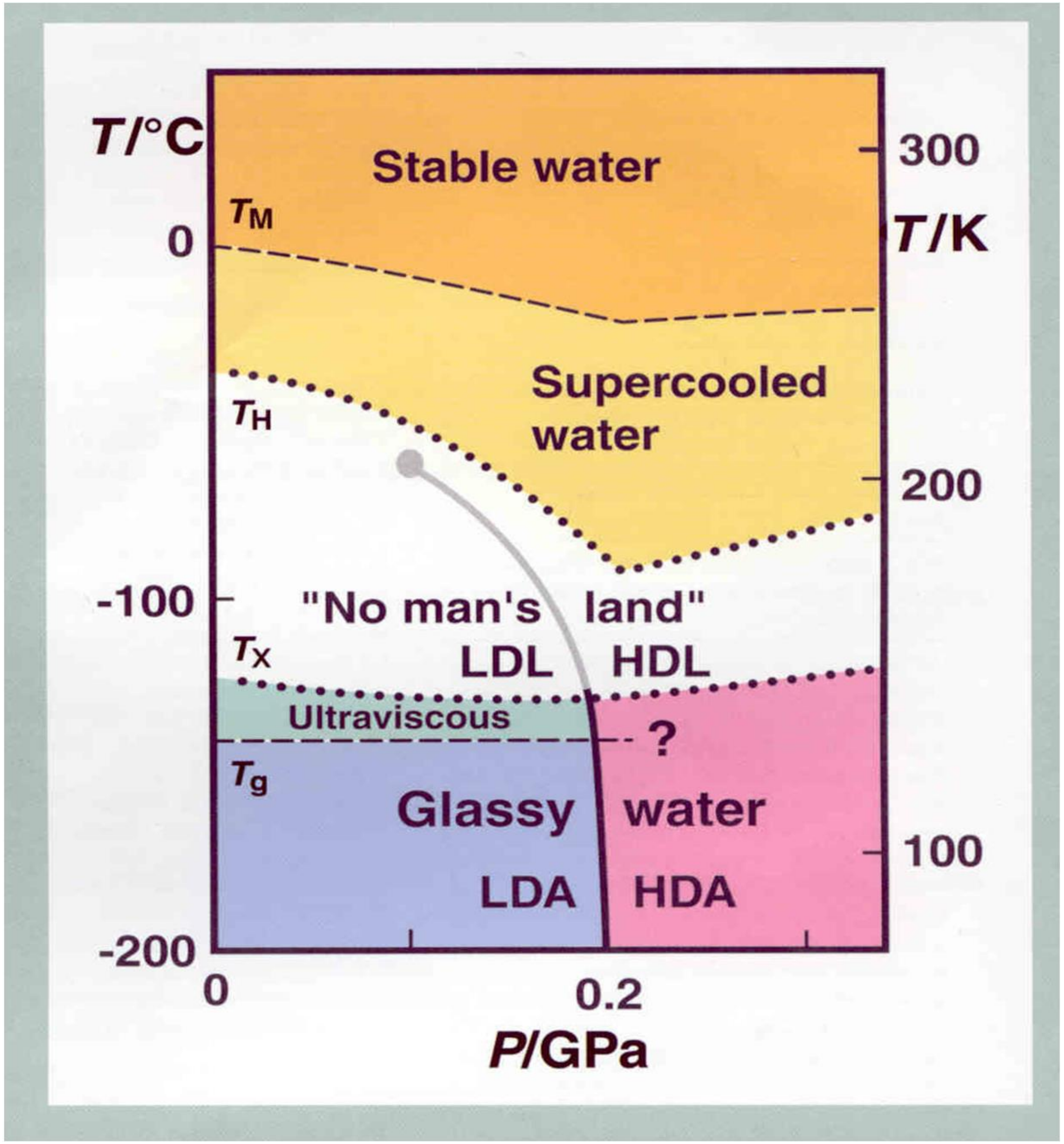
a-GeO_2
10 GPa (100 kbar)

Courtesy: C. Benmore



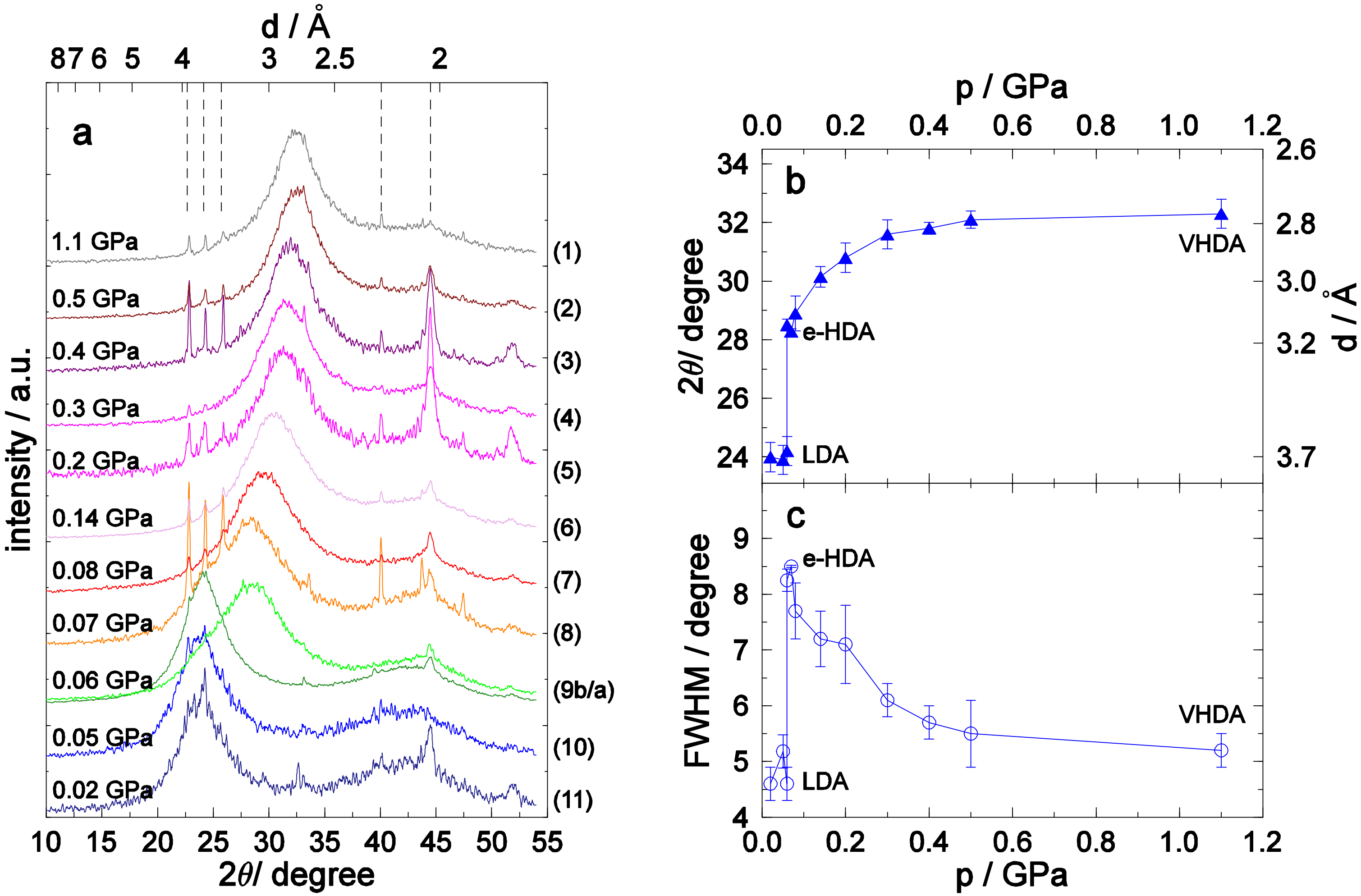
Adapted from http://www.lsbu.ac.uk/water/

Phasediagram of Non-Crystalline Water

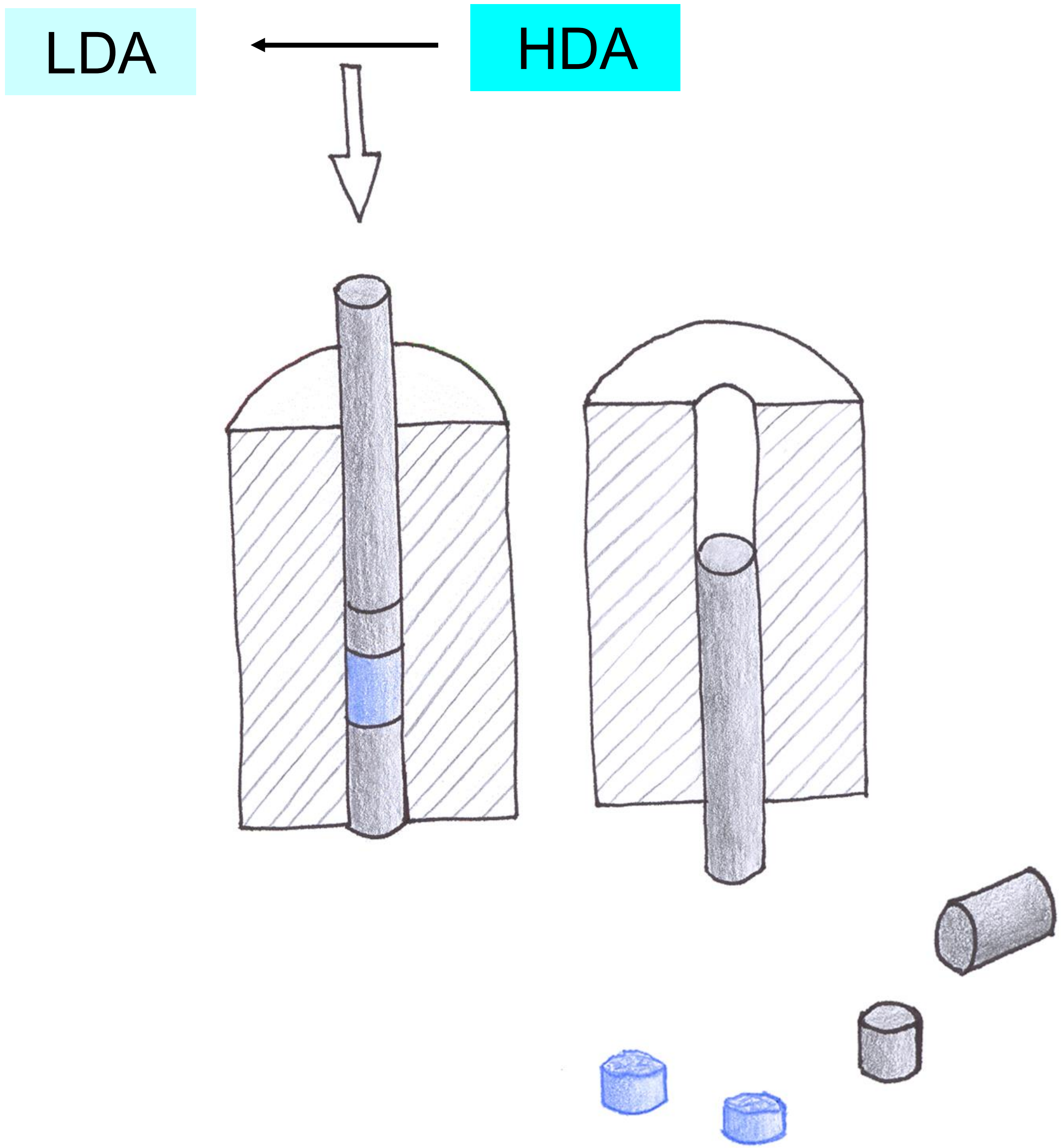


H. E. Stanley et al., PCCP 2, 1551-1558 (2000)

Courtesy: O. Mishima



K. Winkel, M. S. Elsaesser, E. Mayer, T. Loerting, **J. Chem. Phys.** *128(4)* (2008) 044510


LDA
HDA


MIN MAX
°C°F K
HOLD
T1 T2 T1-T2
LOGGING
RECALL
SETUP
ENTER
Bottom
Top

Condensed matter

One substance, two liquids?

Pablo G. Debenedetti

Water, like any other liquid, can be supercooled — cooled below its freezing point without crystallizing. The physical properties of supercooled water are unusual: the lower its temperature, the easier it is to compress, and the more pronounced its anomalous tendency to expand when cooled. Most other liquids contract when cooled, and are more difficult to compress the lower their temperature. As if these characteristics were not peculiar enough, on page 164 of this issue[1], Mishima and Stanley offer new evidence for the notion that two different forms of supercooled water may coexist. Although coexistence of liquid mixtures with different compositions is common, a phase transition between two liquid forms of a pure substance, both lacking long-range order, has never been observed.

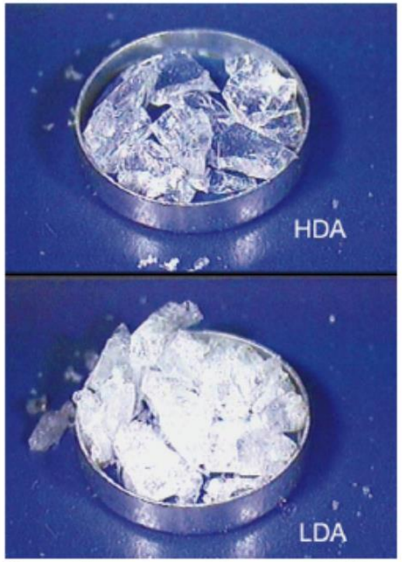


Figure 1 **The two forms of glassy water. LDA is formed by rapidly cooling water at atmospheric pressure; HDA is formed by compressing either LDA or ordinary ice at low temperature. These amorphous solids might be able to coexist, as might two structurally similar liquid waters, LDL and HDL.**

When liquid water is cooled fast enough to avoid crystallization, it forms a glass[2]. Such vitreous water is found as frost on interstellar dust in dense molecular clouds, and comets are made of it[3]. In 1985, Mishima and co-workers[4] proposed the existence of a transition between two forms of glassy water: low-density and high-density amorphous ice (LDA and HDA; Fig. 1). They observed

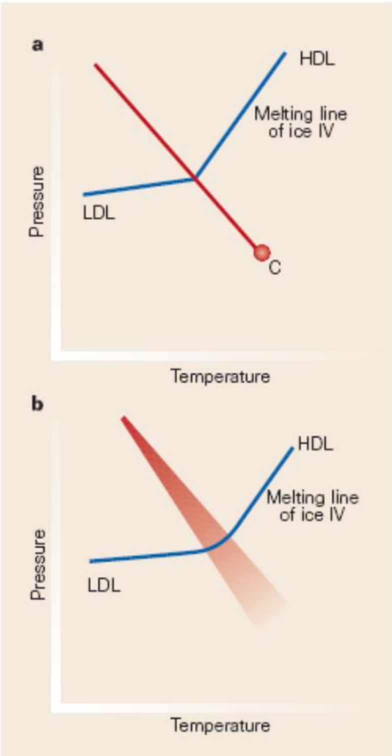
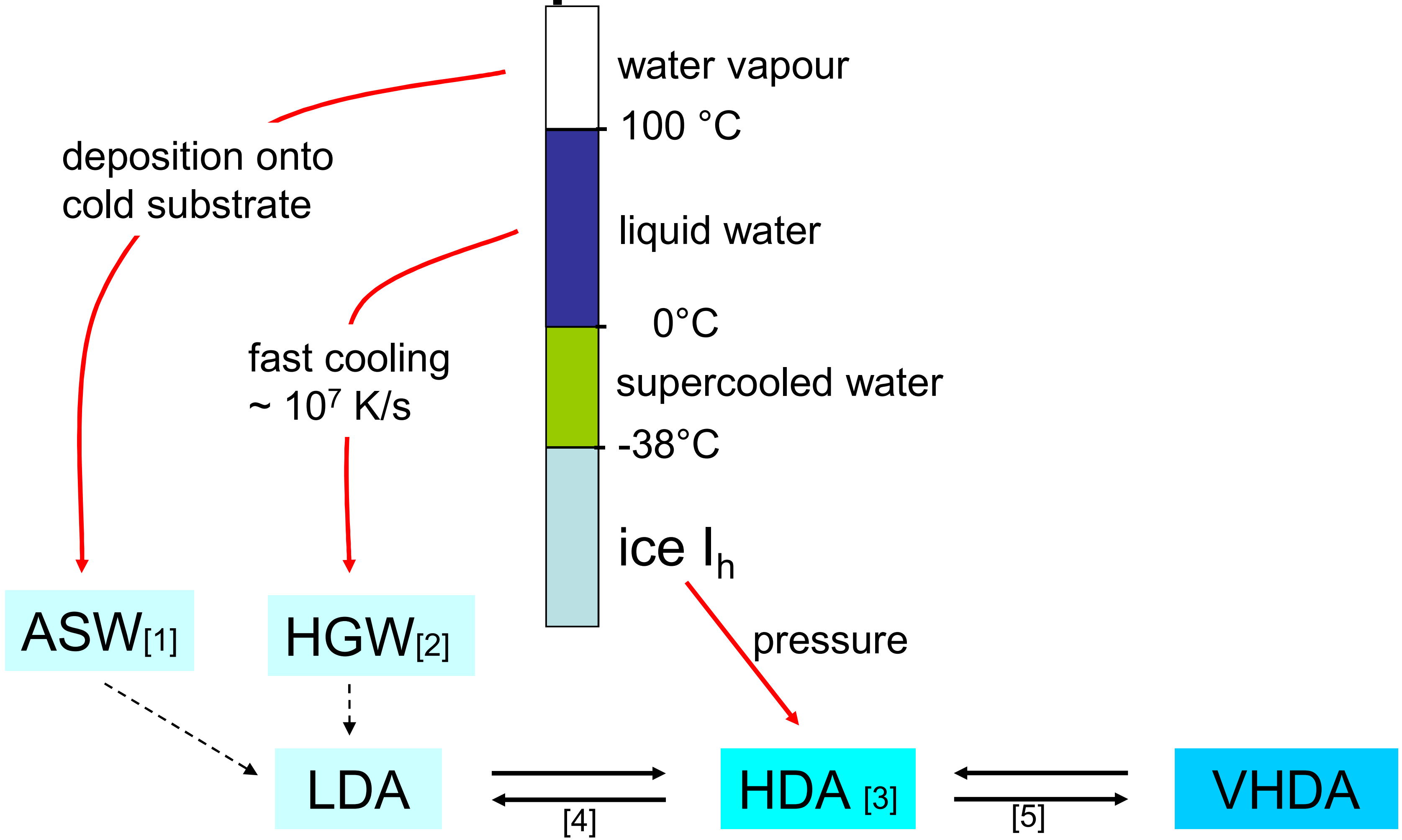


Figure 2 **The melting line of ice IV. The sharp change in its slope implies a sudden change in the density and entropy of liquid water[1]. This could occur, (a) along a line of coexistence between a low-density and a high-density liquid (LDL, HDL), terminating at a critical point[5], C; or (b) over a limited range of temperatures and pressures that becomes progressively narrower at low temperatures and high pressures[7].**

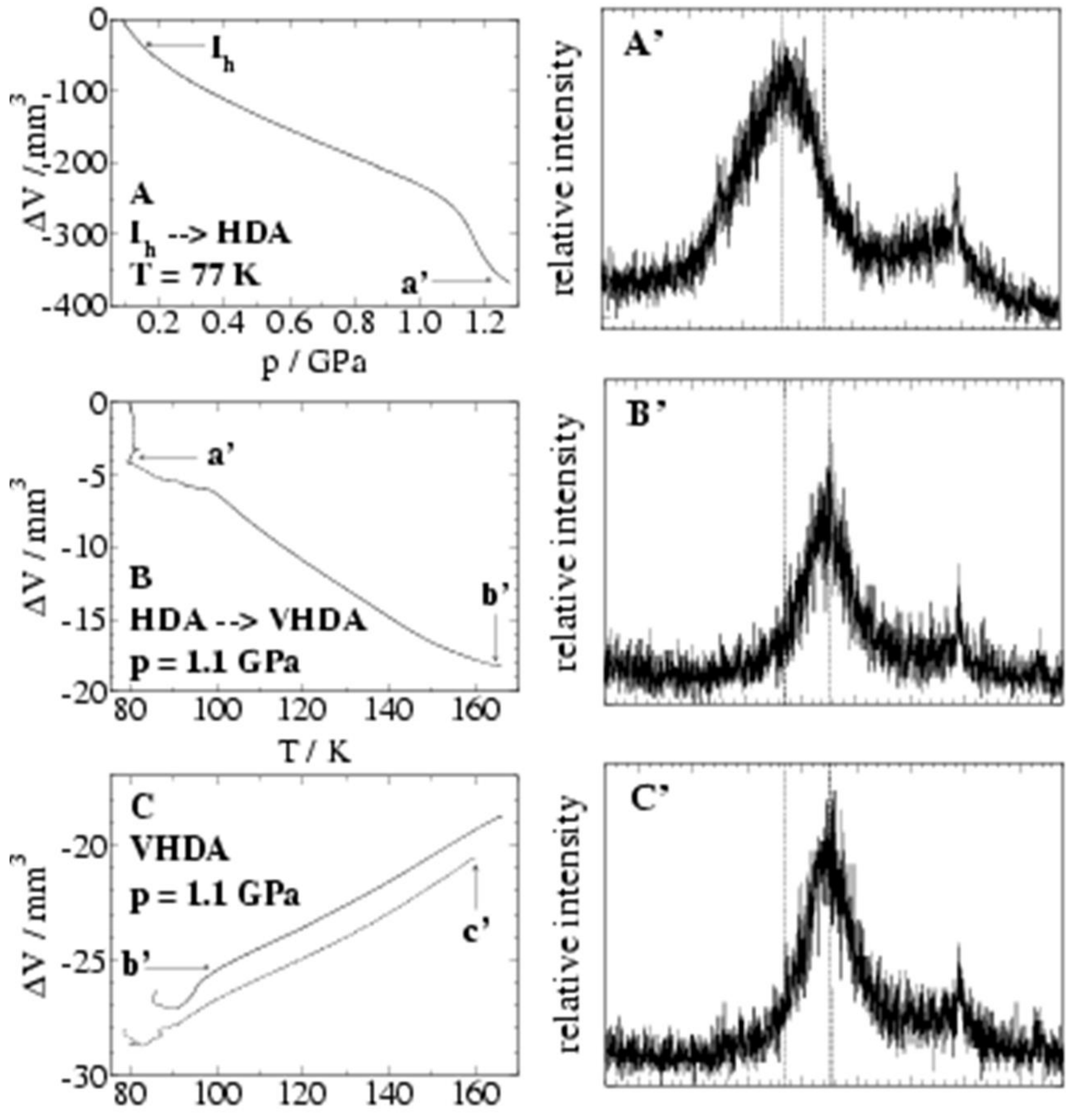
P. Debenedetti, *Nature* **392**, 1998

Amorphous ice



[1] E.F. Burton and W.F. Oliver, *Proc. R. Soc. A*, 153, 1935
[2] P. Brüggeller, E. Mayer, *Nature,* 288, 1980; E. Mayer, *J. Appl. Phys.,* 58, 1985
[3] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 310, 1984;
[4] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 314, 1985
[5] T. Loerting, C. Salzmann, I. Kohl, E. Mayer, A. Hallbrucker, *PCCP*, 3, 2001

VERY HIGH-DENSITY AMORPHOUS ICE (VHDA)



T. Loerting, C. G. Salzmann, I. Kohl, E. Mayer, A. Hallbrucker,

Phys. Chem. Chem. Phys. 3 (2001) 5355-5357

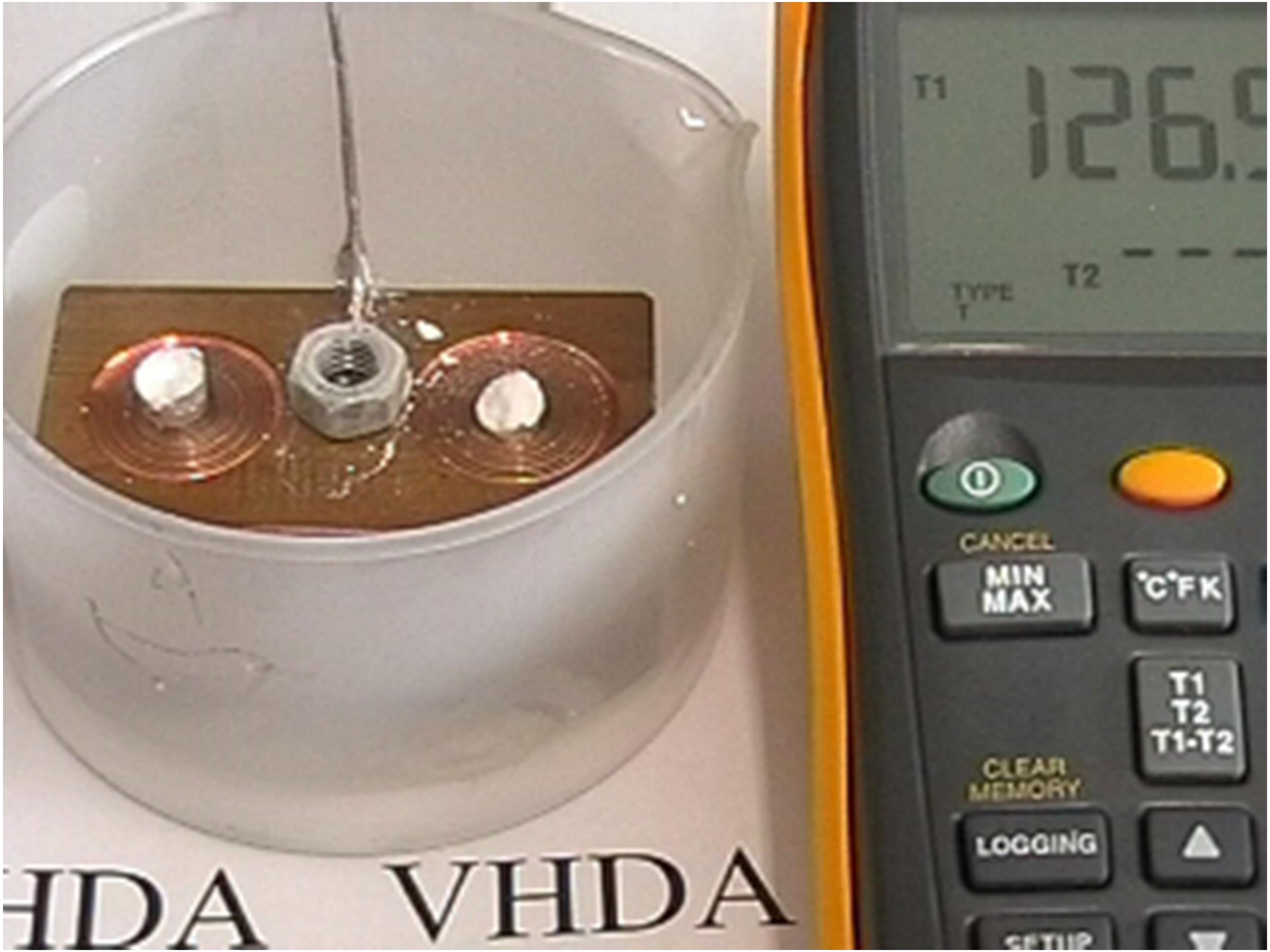
J. L. Finney, Daniel T. Bowron, A. K. Soper, E. Mayer, A. Hallbrucker, T. Loerting

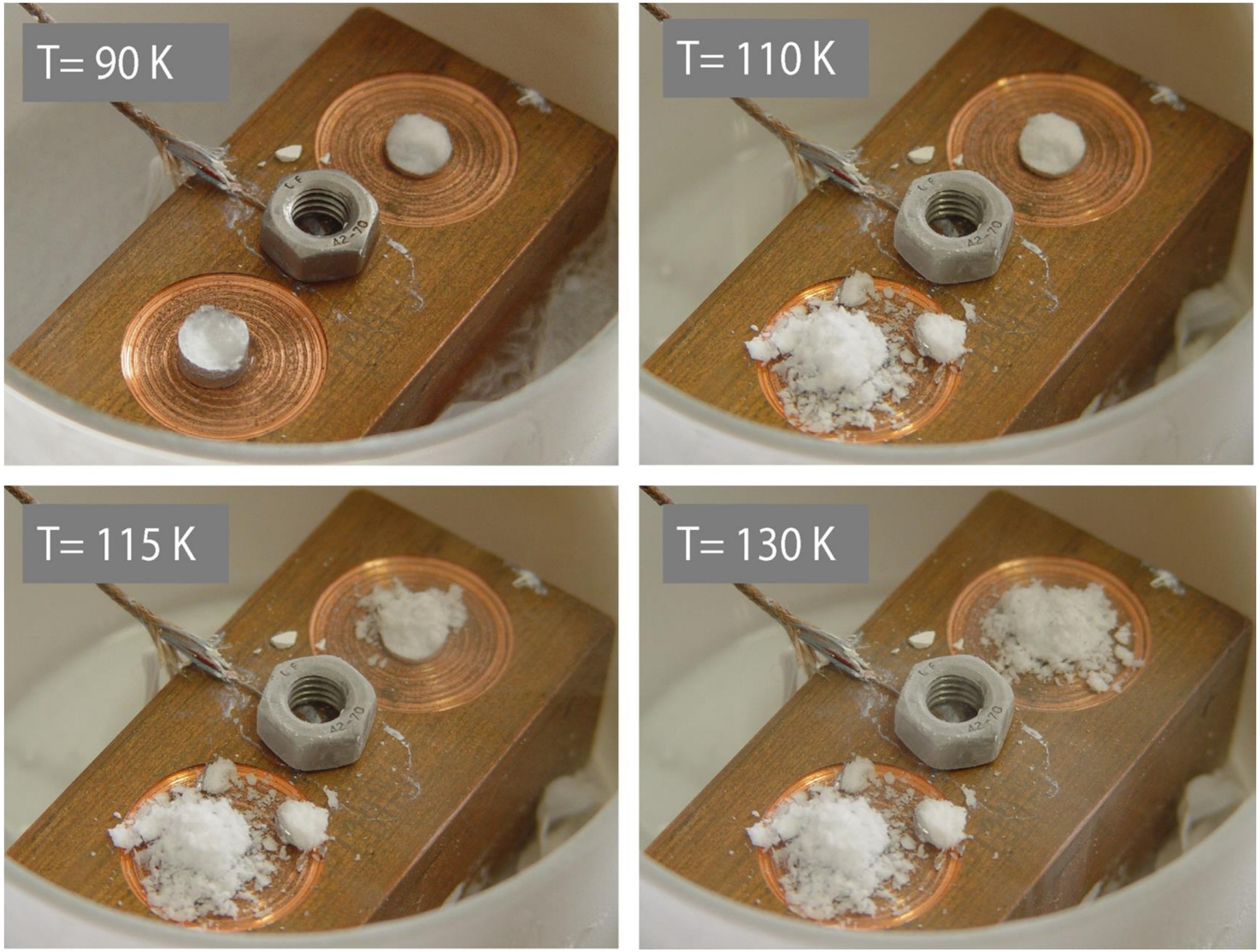
Phys. Rev. Lett. 89 (2002) 205503

D. D. Klug,

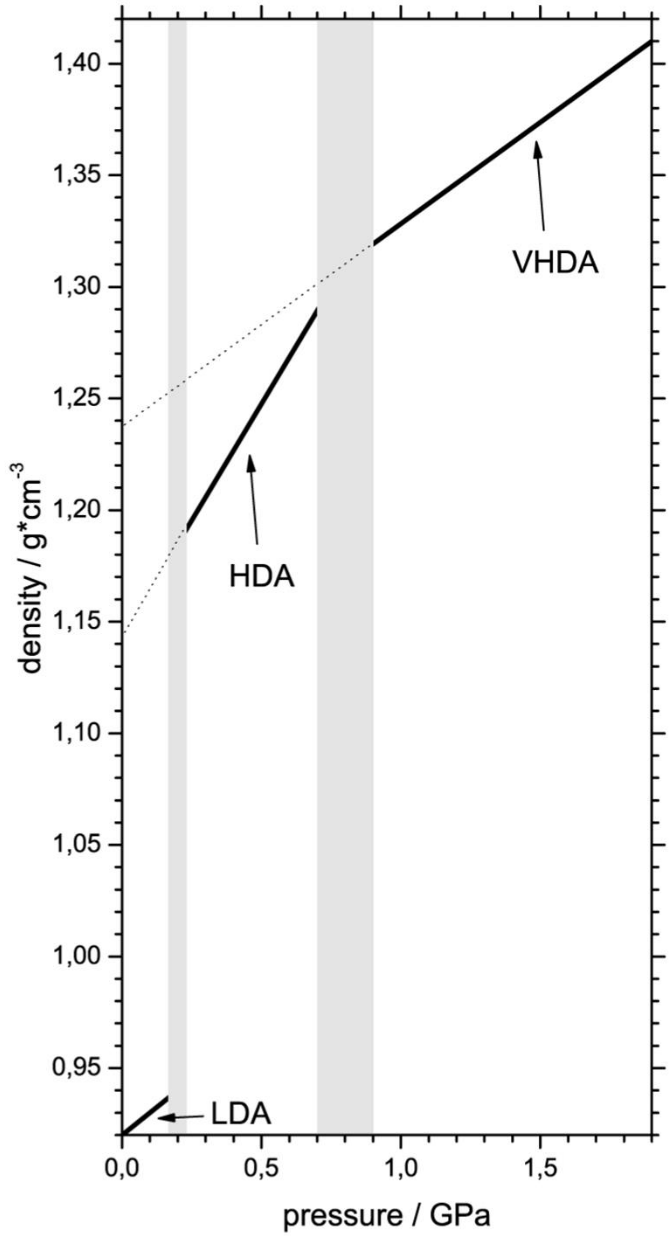
Nature 420 (2002), 749-751.

$\rho \approx 1.26\ g\ cm^{-3}$


T1
T2
TYPE
CANCEL
MIN MAX
°C °F K
T1 T2 T1-T2
CLEAR MEMORY
LOGGING
HDA VHDA

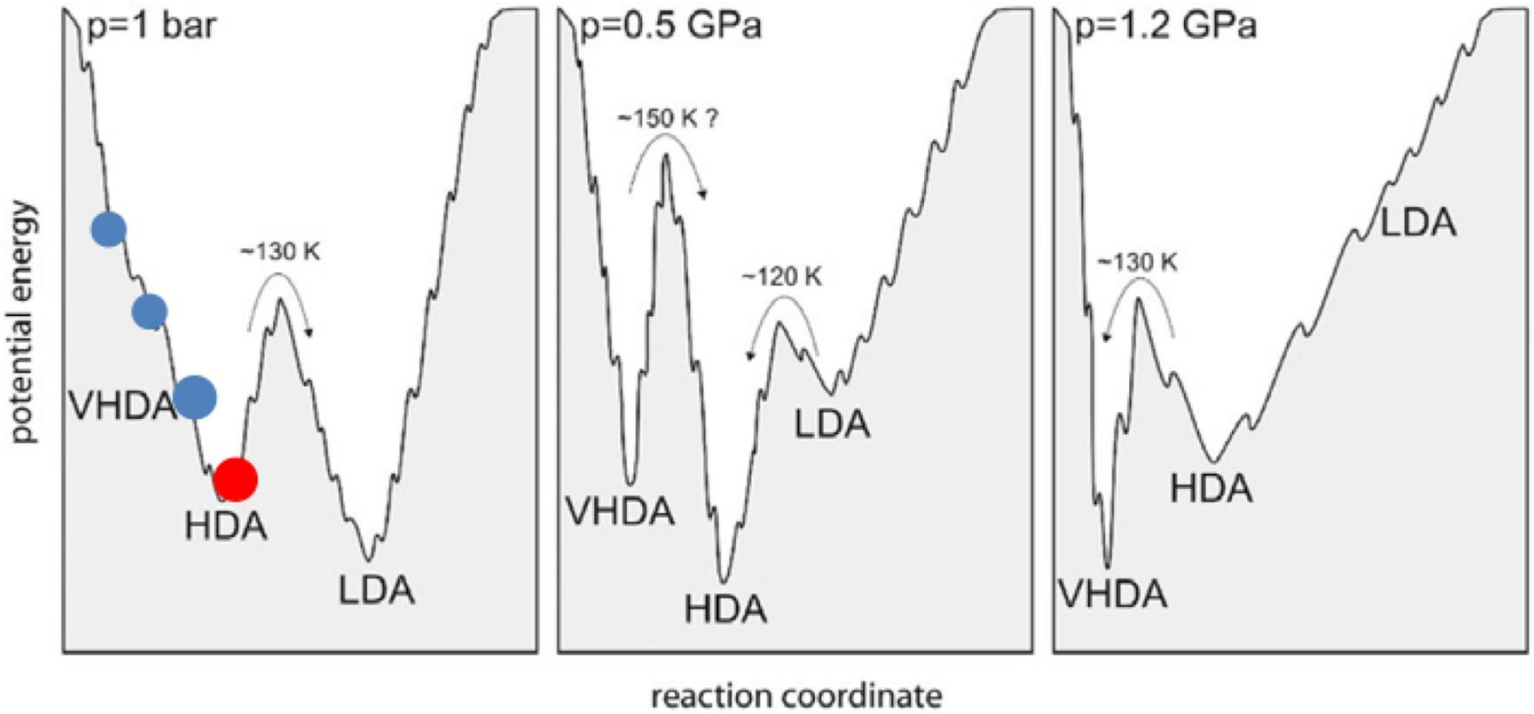


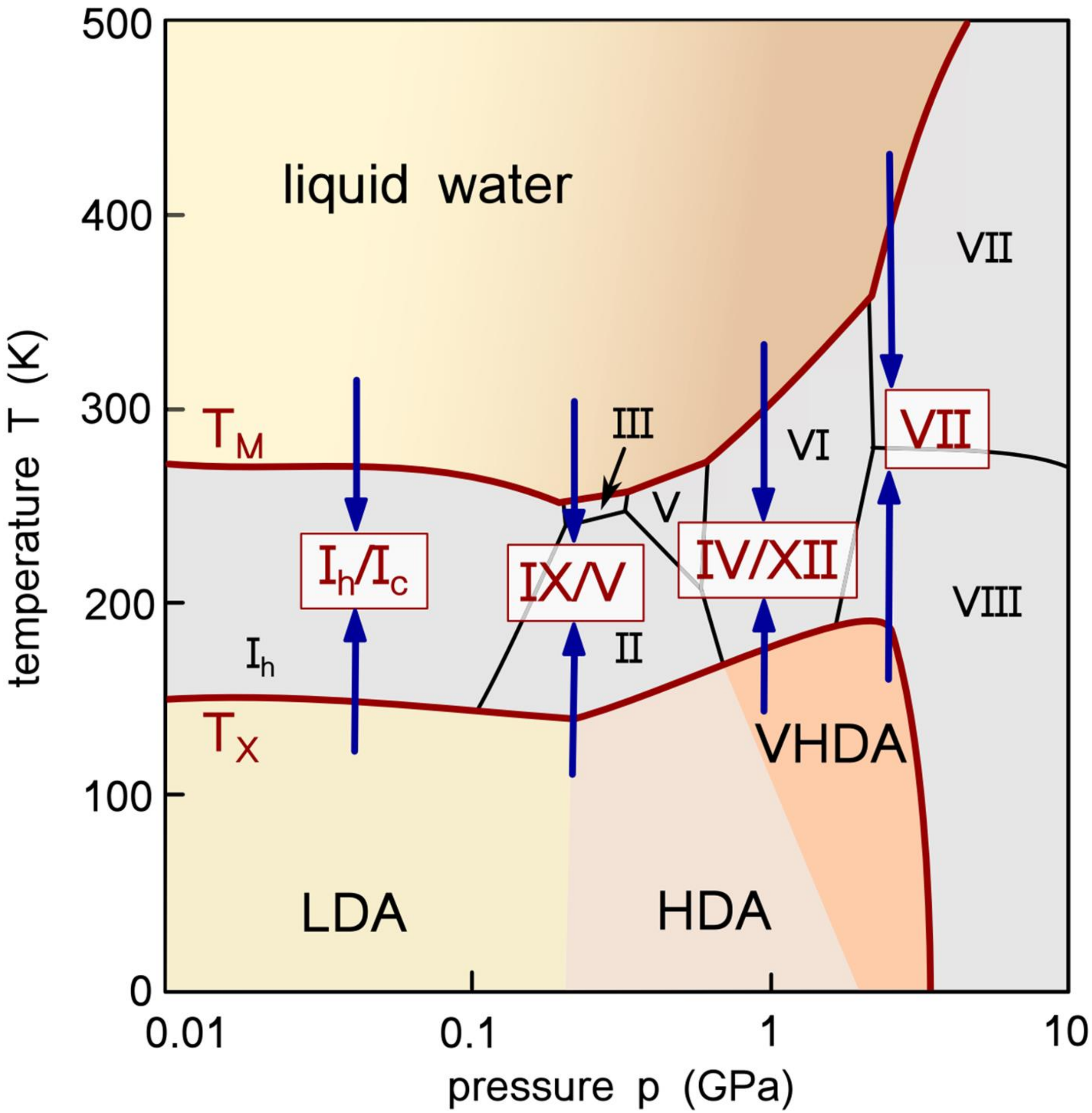
T= 90 K
T= 110 K
T= 115 K
T= 130 K



Salzmann et al., **Phys. Chem. Chem. Phys.** *8* (2006) 386–397.
Loerting et al., **Phys. Chem. Chem. Phys.** *13* (2011) 8783–8794.

Relaxing amorphous ices at different pressures





500
400
300
200
100
0
temperature T (K)
0.01
0.1
1
10
pressure p (GPa)
liquid water
T_M
T_X
I_h/I_c
IX/V
IV/XII
VII
III
V
VI
VII
VIII
II
I_h
VHDA
LDA
HDA