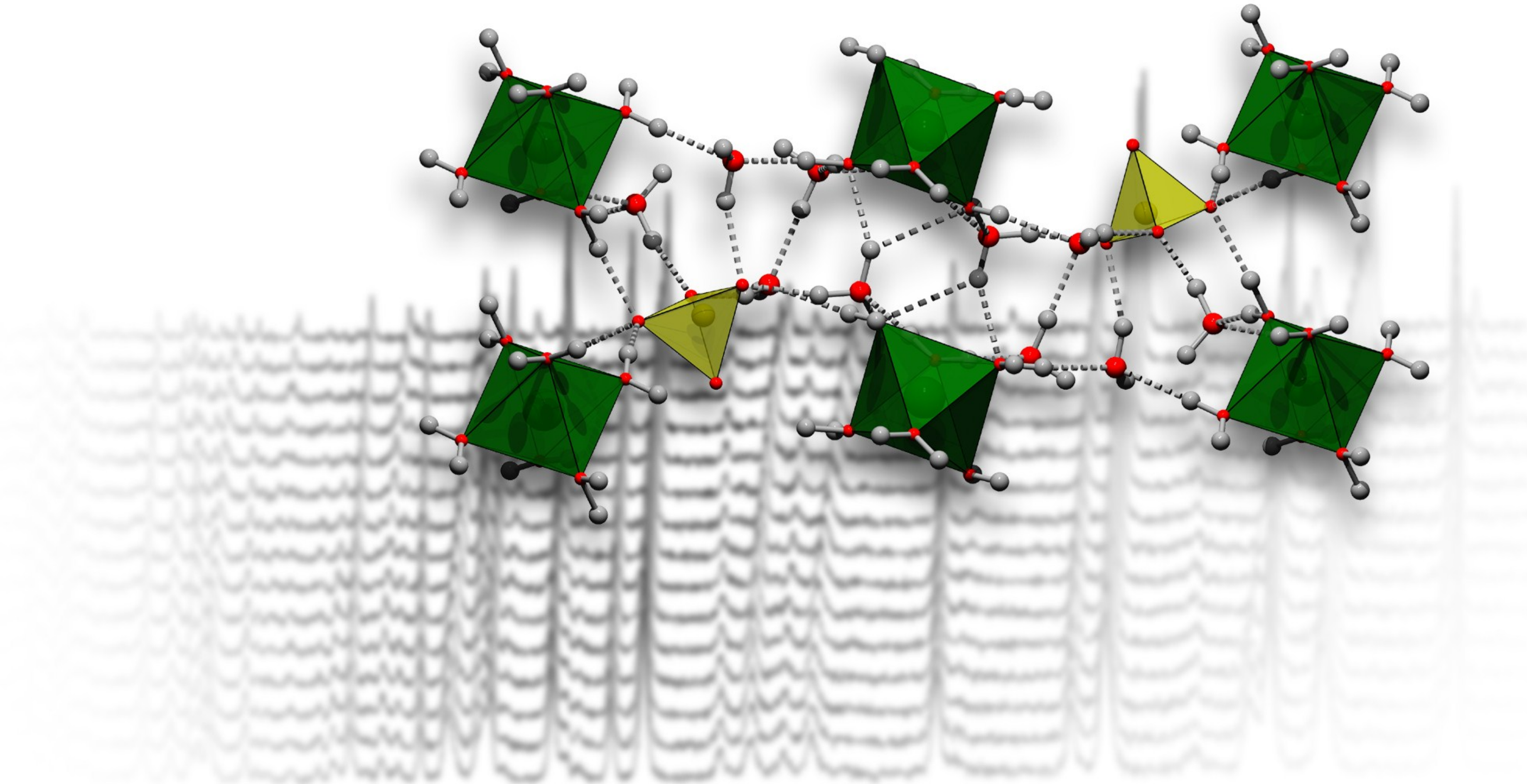
Application of neutron diffraction to planetary ices & hydrates

Dominic Fortes

Department of Earth Sciences, University College London



Oxford Summer School on Neutron Scattering, September 11th 2013

Lecture Outline

1. Introduction – icy bodies of the outer Solar System
   What problems do we need to solve, and how can neutrons help us?

2. Materials and methods

3. Some case studies

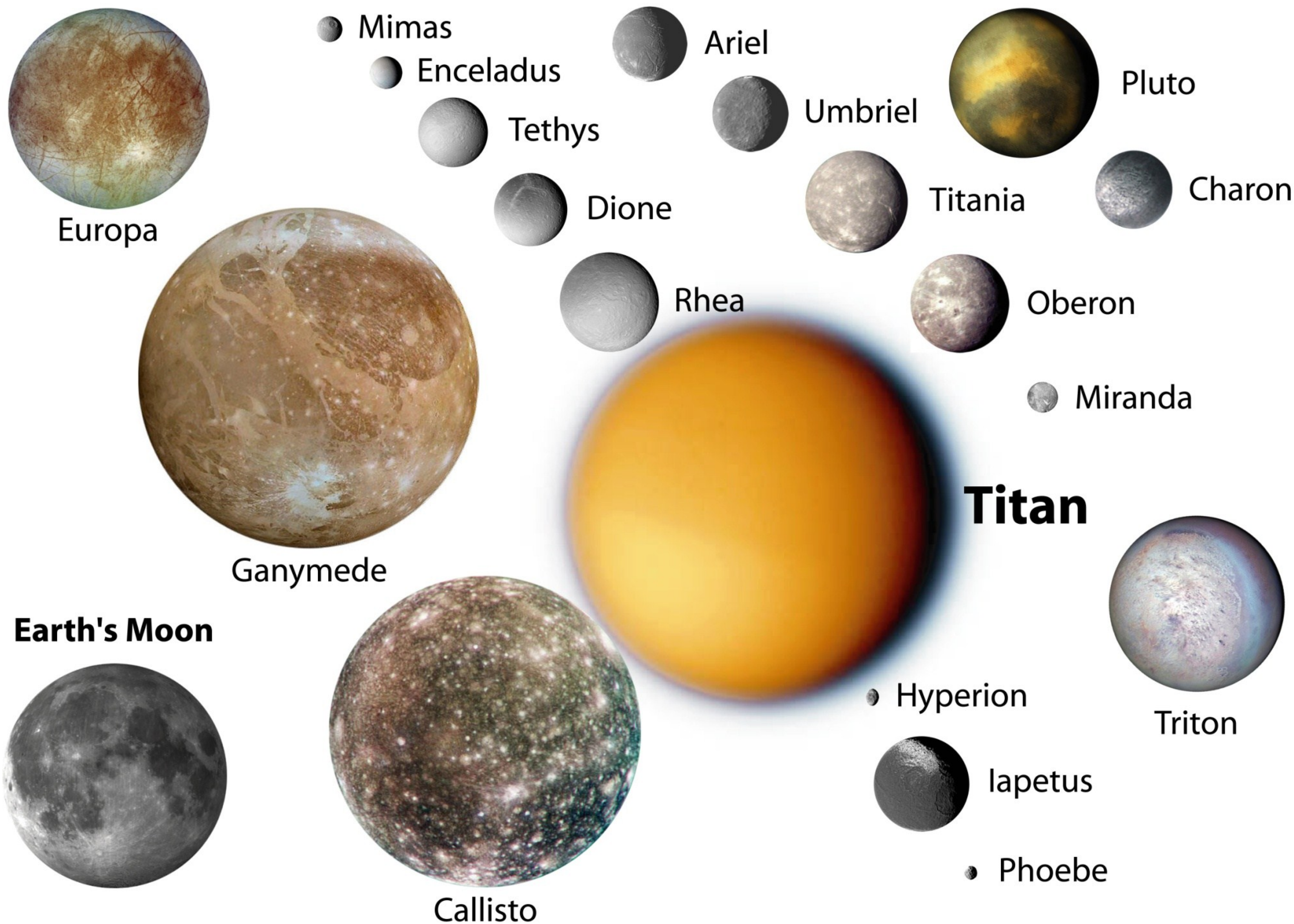
   a) High-pressure behaviour of ammonia dihydrate

   b) High-pressure behaviour of meridianiite ($MgSO_4 \cdot 11H_2O$)

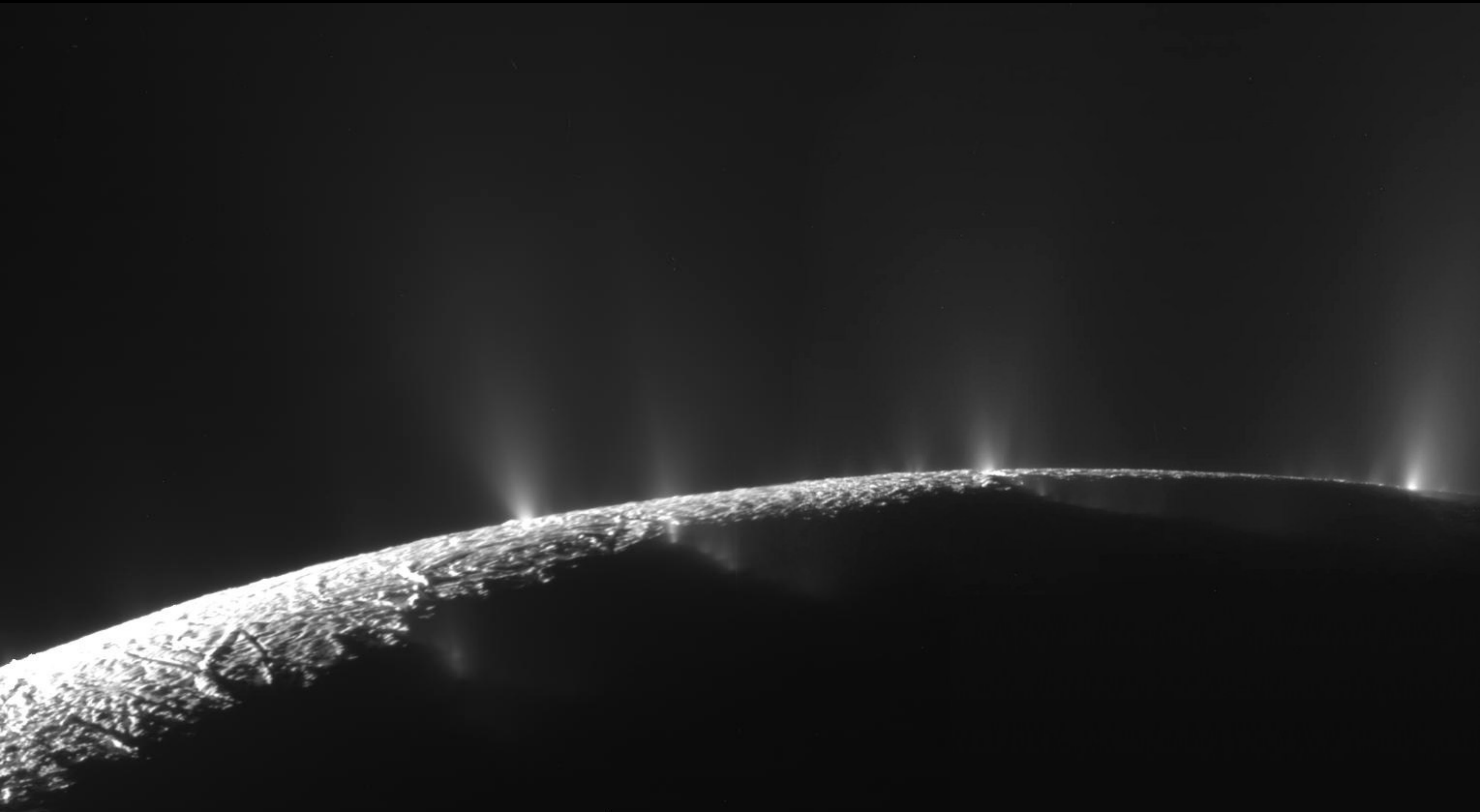
   c) PVT equation of state of ice VI

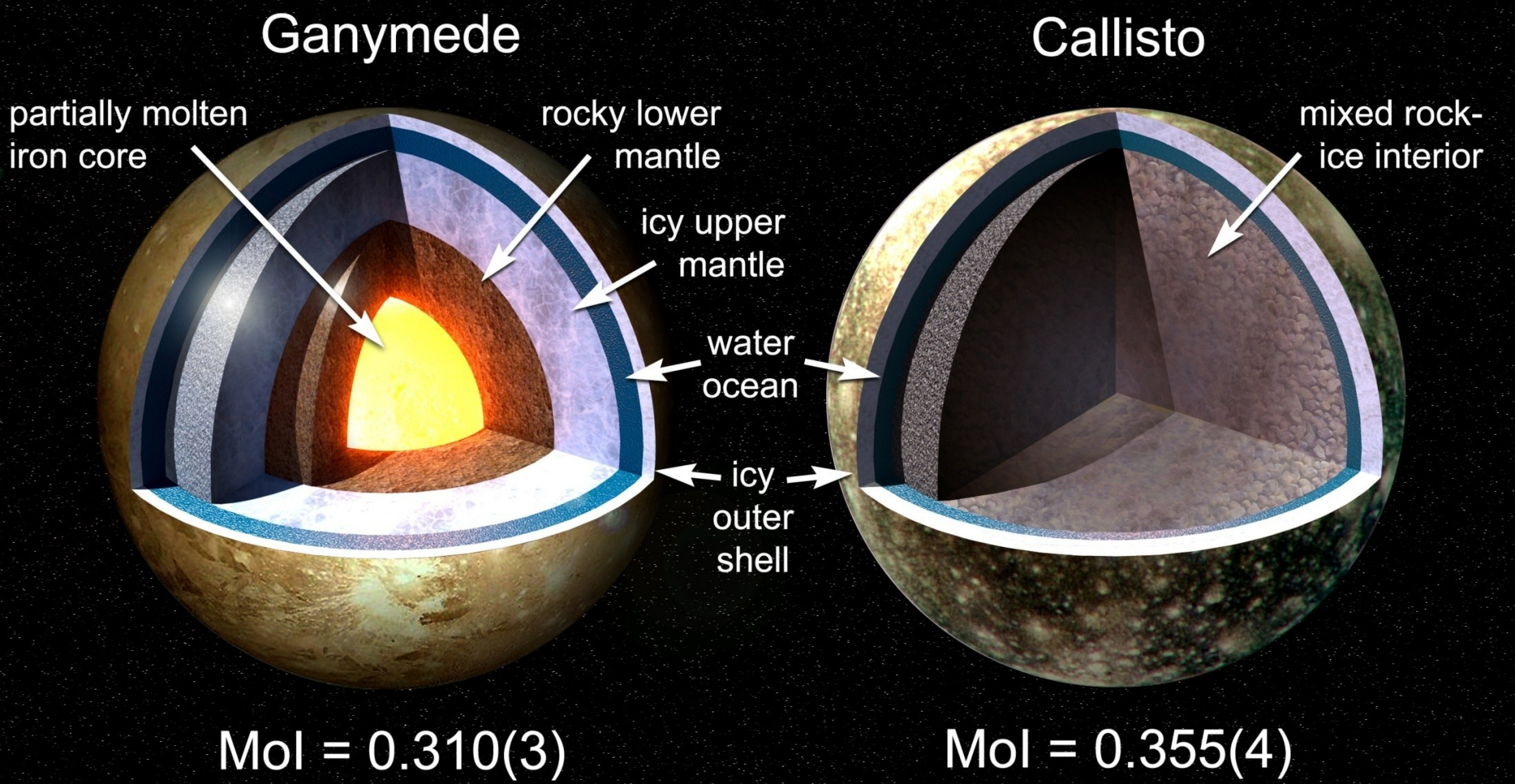
   d) Understanding the thermal expansion of mirabilite ($Na_2SO_4 \cdot 10H_2O$)

A few icy satellites and planetary bodies



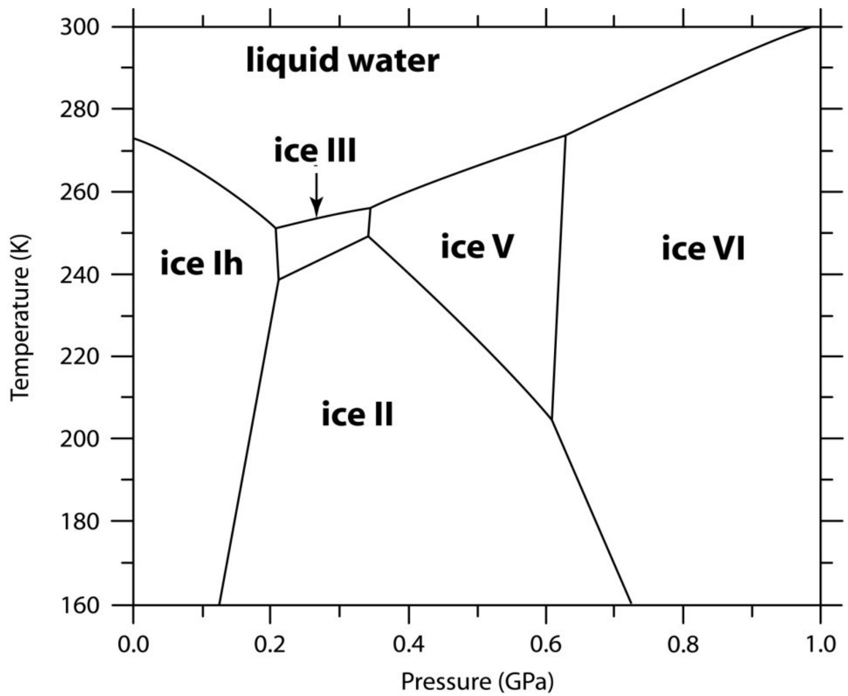
Many icy worlds have been active in the past and some are active even today: Saturn’s tiny moon Enceladus erupts ice and water vapour into space at 100s of m/s.

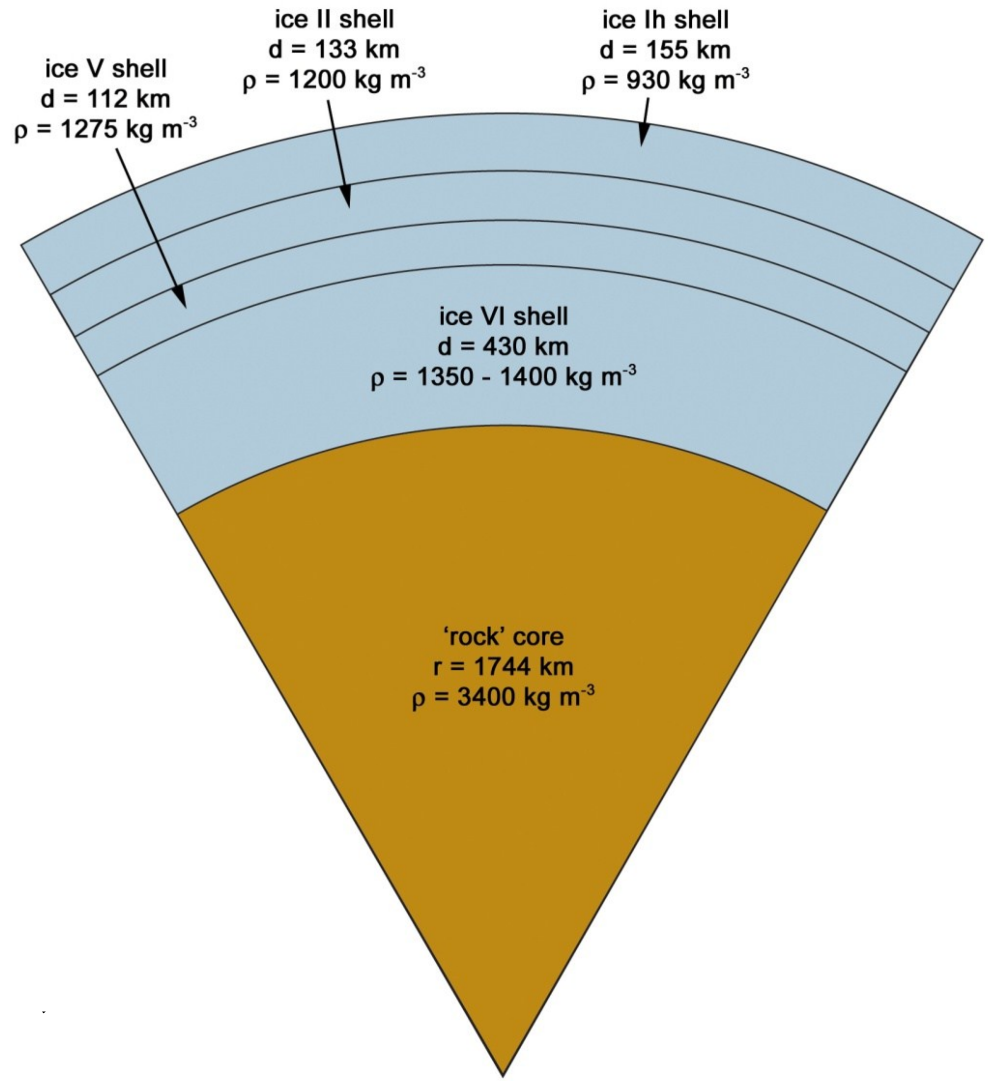




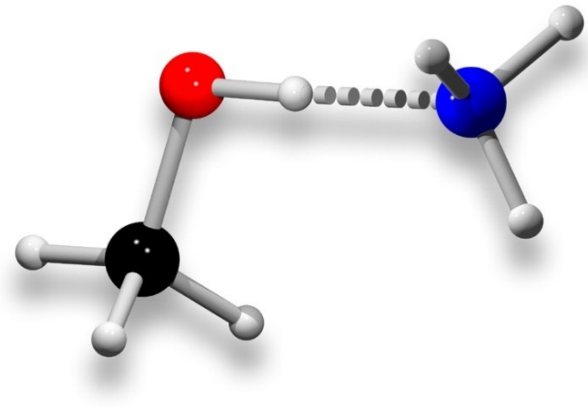
Subsurface oceans are known to exist inside most of the large icy satellites, **Europa**, **Ganymede**, **Callisto** and **Titan**

Modelling structure and thermal evolution





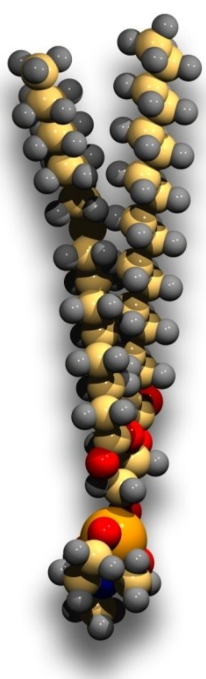
Huaux, A. (1951): Sur un modele de satellite en glace. *Bulletin de l'Académie Royale des Sciences de Belgique* **37**, 534-539.



phase behaviour

crystal structures

Some applications of neutron diffraction



elastic properties

astrobiology

rheology

Candidate materials

Primitive volatiles

NH_3, CH_4, CO, CO_2, N_2

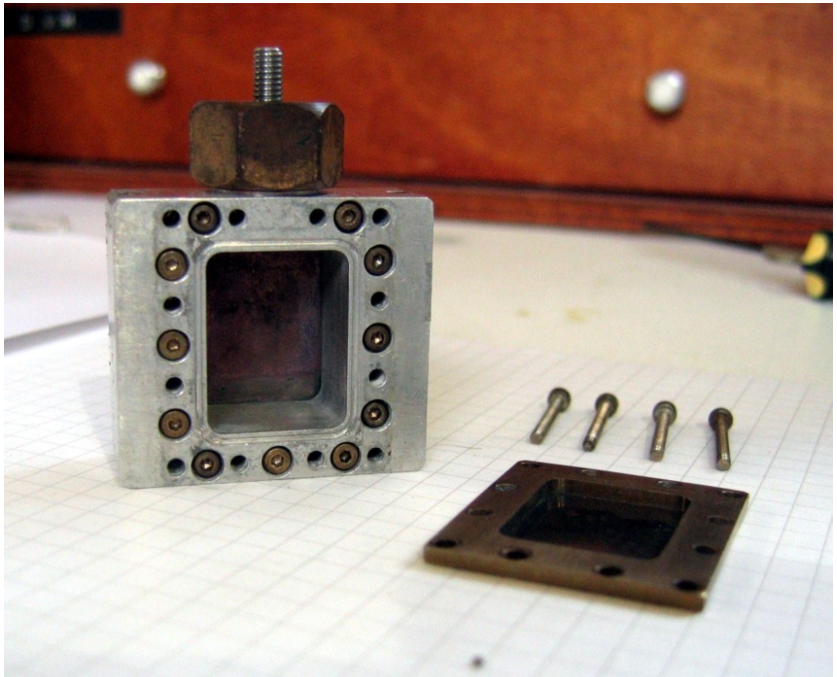
Chondritic salts and acids

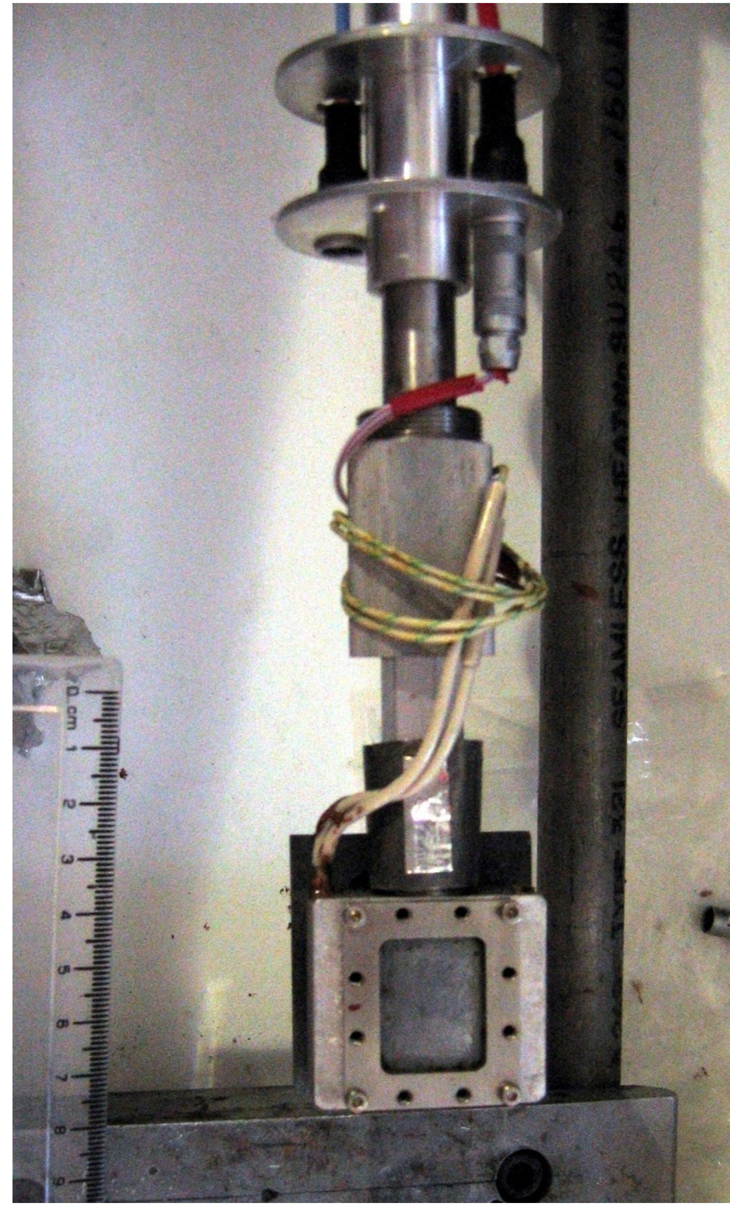
$MgSO_4$, Na_2SO_4, $(NH_4)_2SO_4$, H_2SO_4

Hydrothermal organics

CH_3OH, $(CH_2O)_n$

Fortes & Choukroun (2010) Space Science Reviews 185,





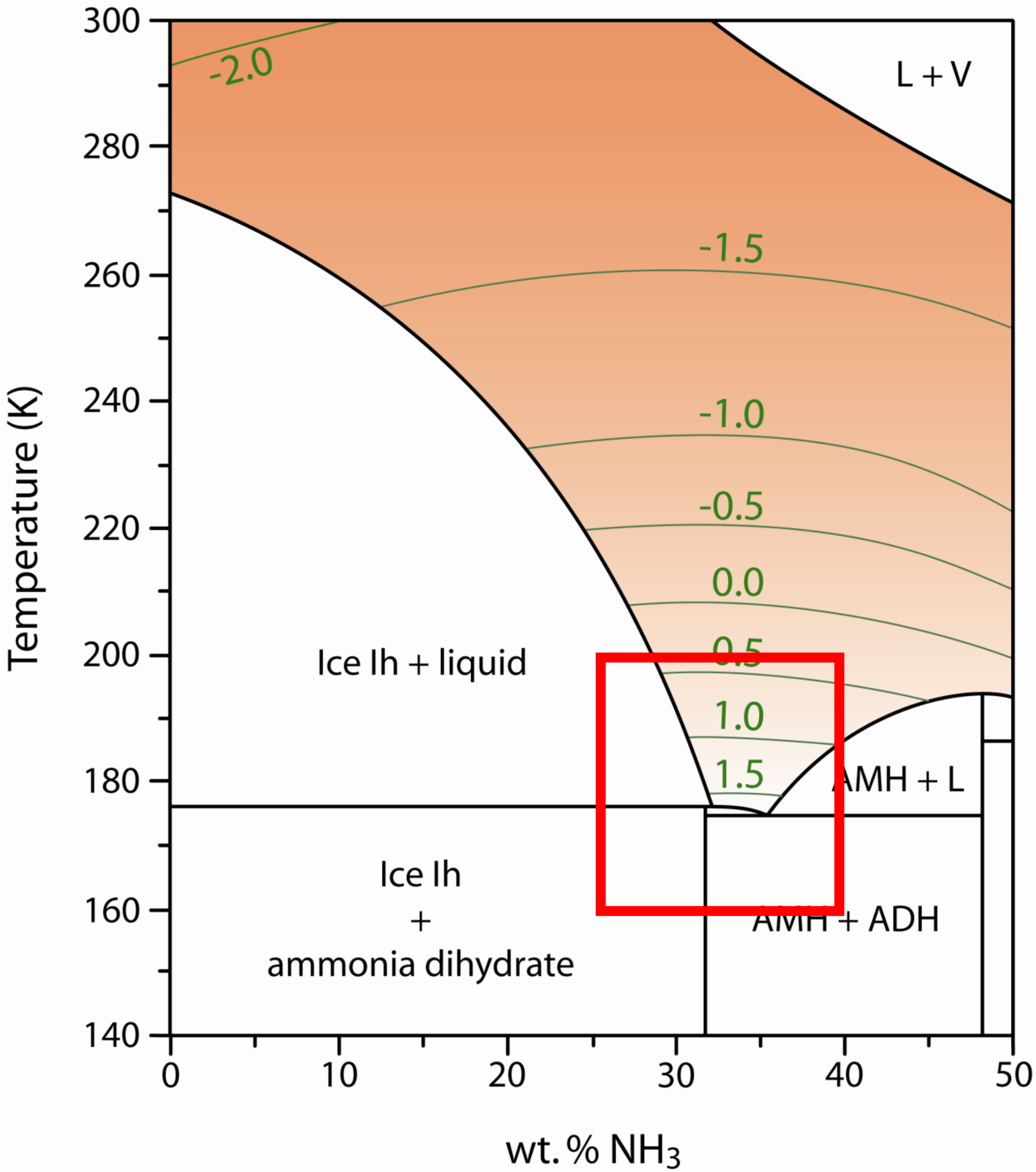
Low temperature studies are made using an aluminium slab can with vanadium windows.

Sample mass ~ 6 grams

(a bucket-load by X-ray standards)

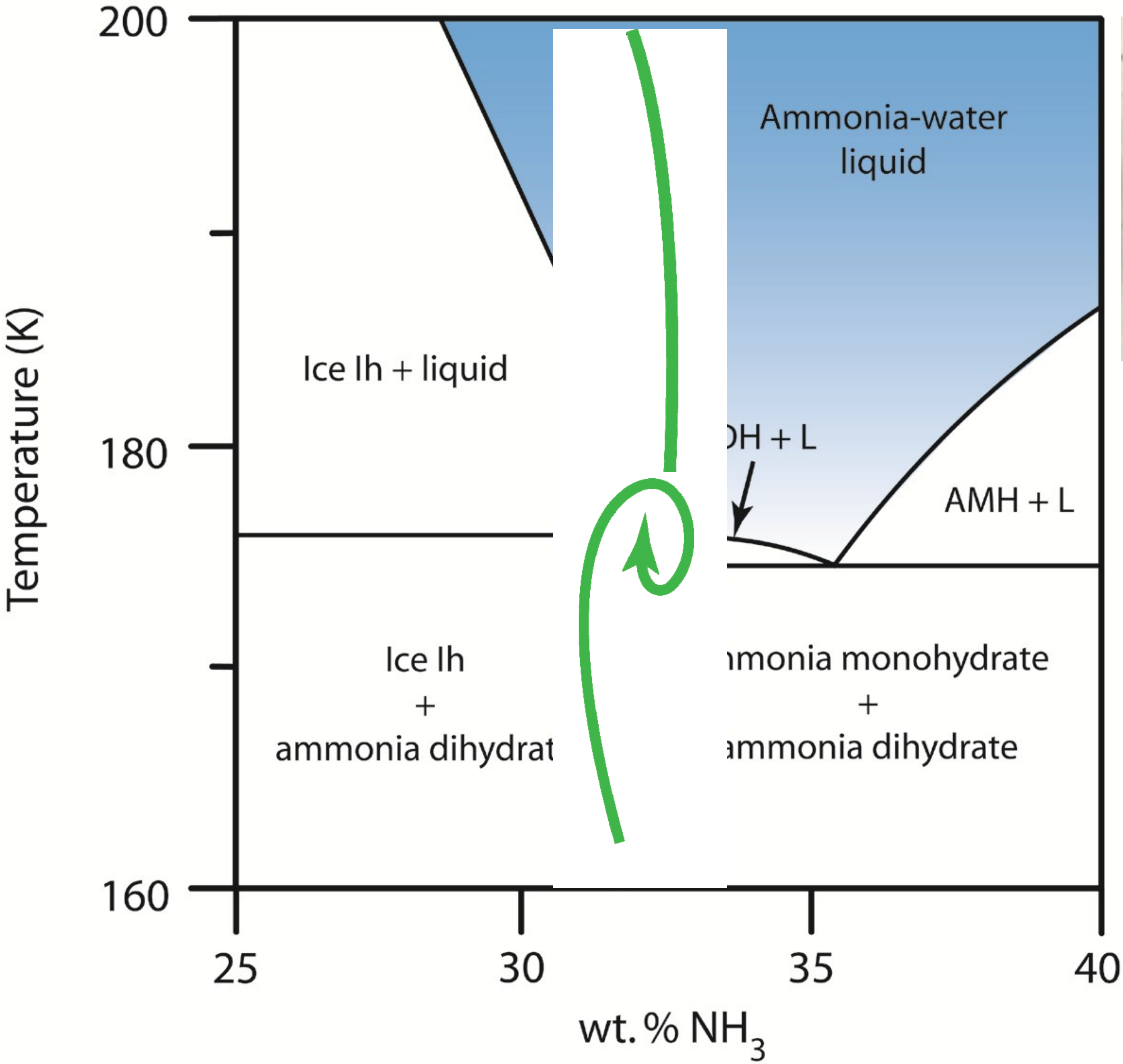

Kevin
Knight

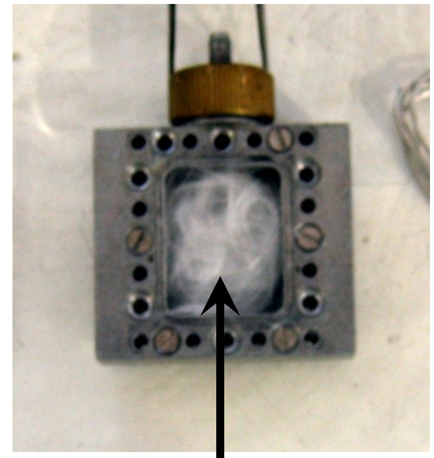
Contours of viscosity (log_{10} poise) for ammonia-water mixtures



The viscosity of the eutectic solution increases by a factor of more than 6000 on cooling from 295 K to 175 K

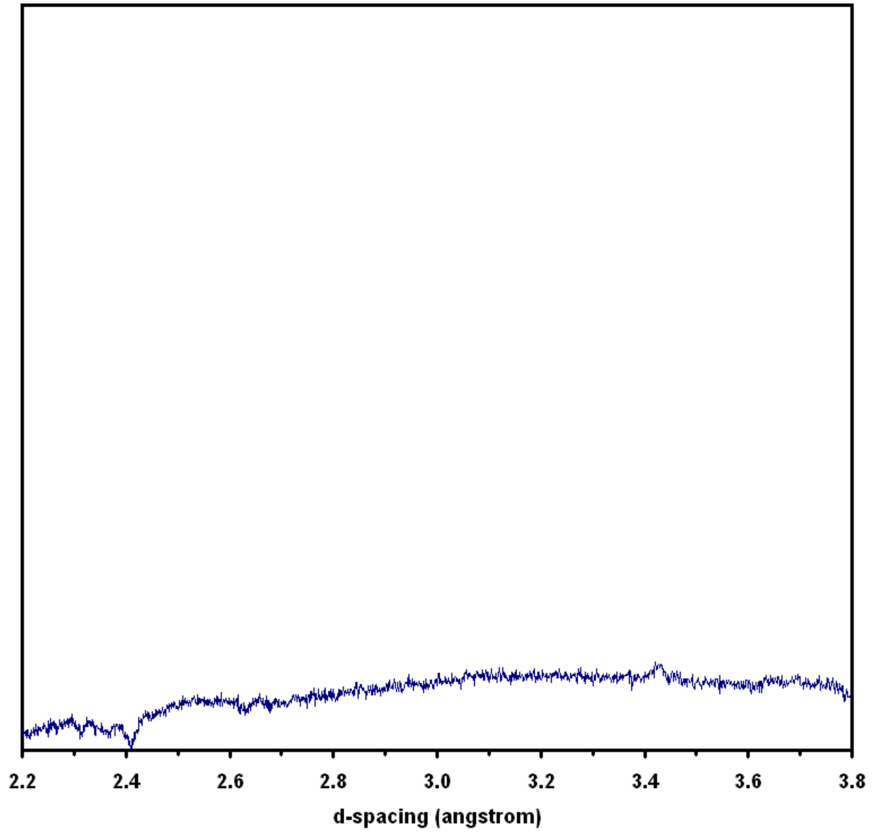
Redrawn after Kargel *et al.* (1991), Icarus **89**, 93-112.


200
180
160
Temperature (K)
25
30
35
40
wt. % NH3
Ammonia-water
liquid
Ice Ih + liquid
AMH + L
Ice Ih
+
ammonia dihydrat
ammonia monohydrate
+
ammonia dihydrate

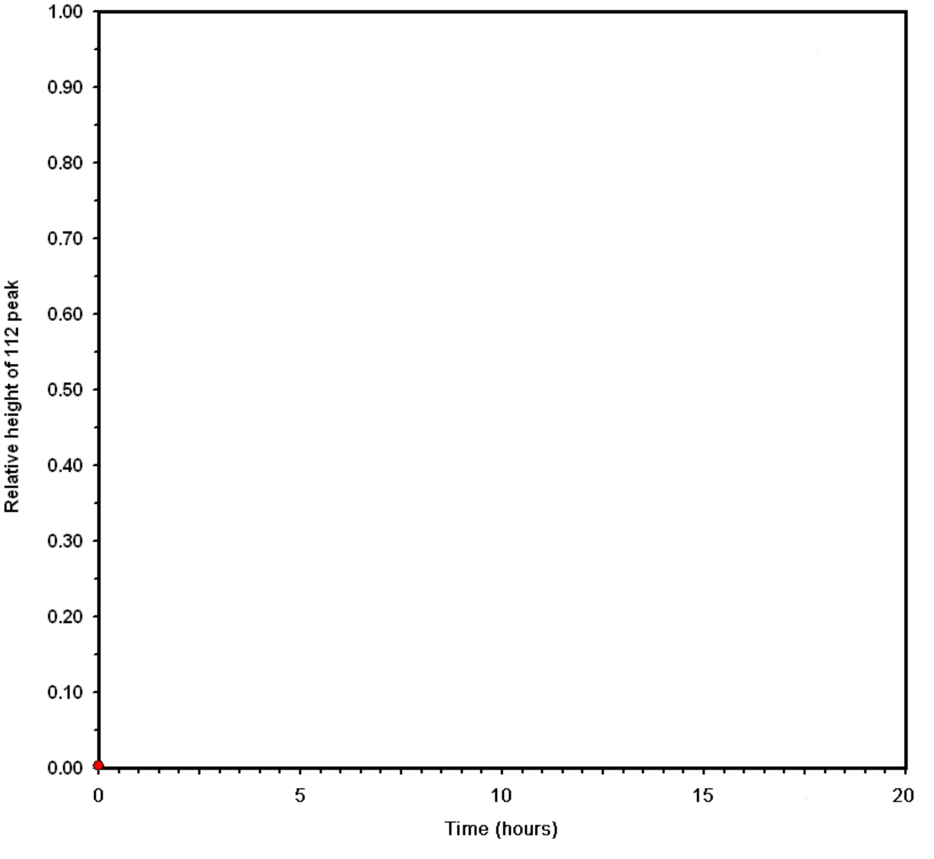

silica wool (~0.1g)

Crystallisation of ammonia dihydrate from glass

~150 bar; temperature cycled from 173 – 179 K

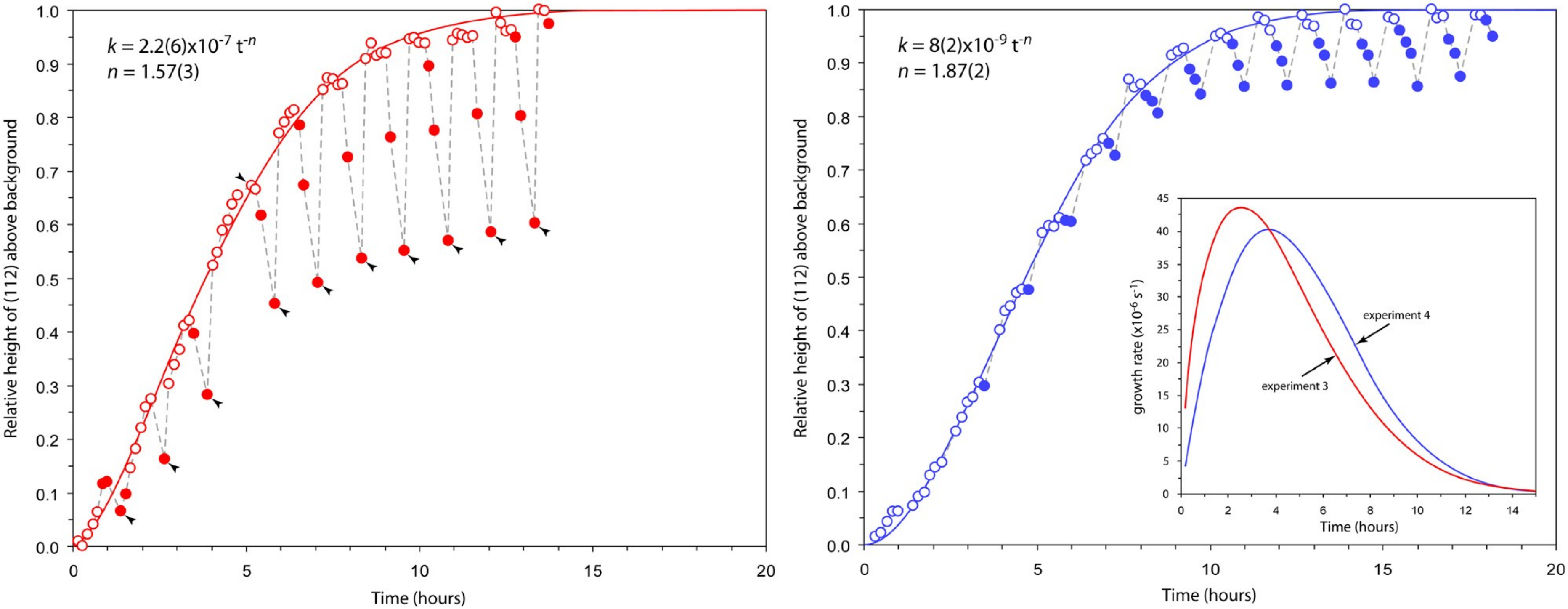


Time dependence of {112} peak height

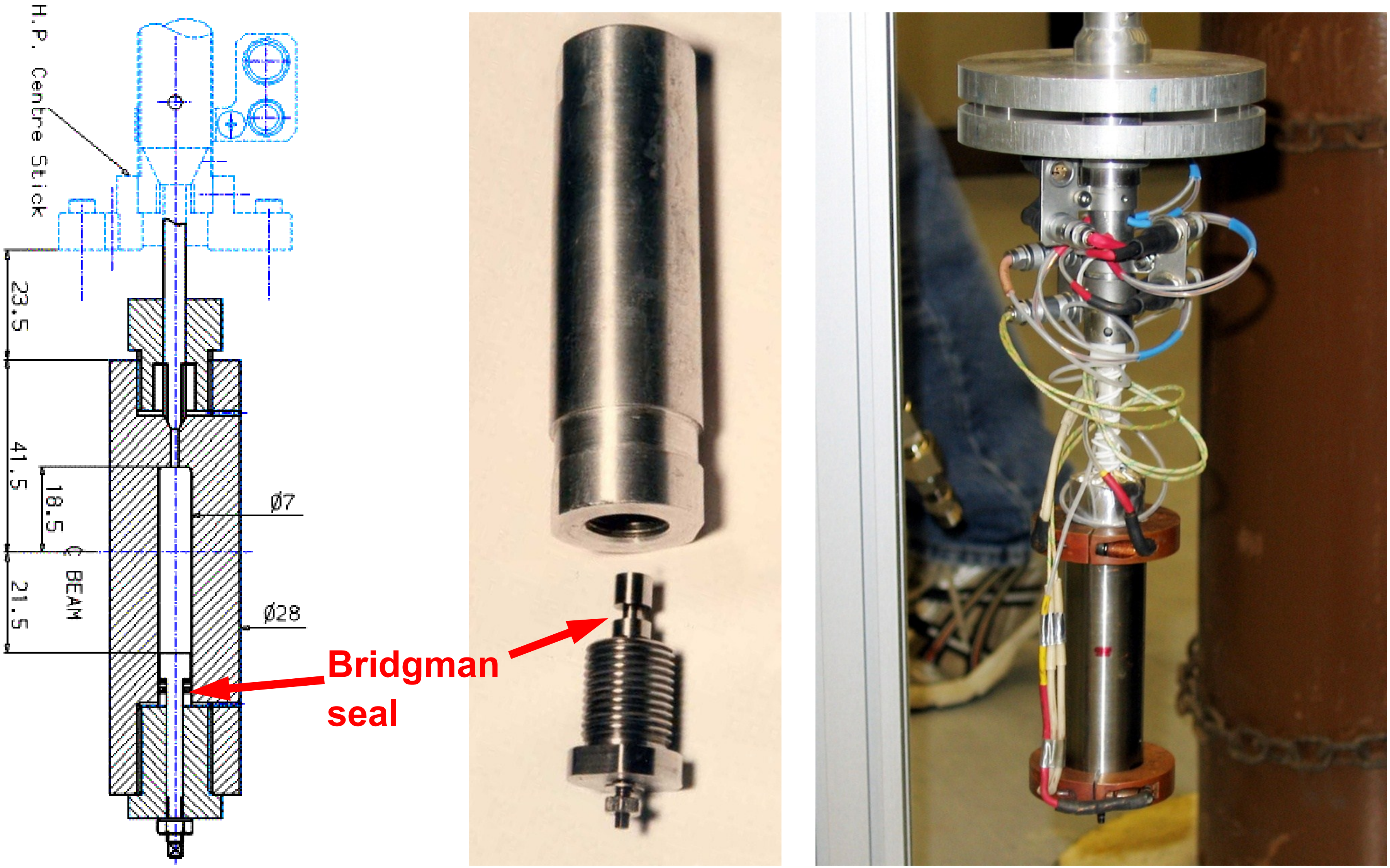


Crystallisation of ADH as a function of time, fitted with Avrami equation

$$X = 1 - \exp(-kt^{n})$$



Fortes *et al.,* (2009) *J. Appl. Cryst.* **42**, 846-866.

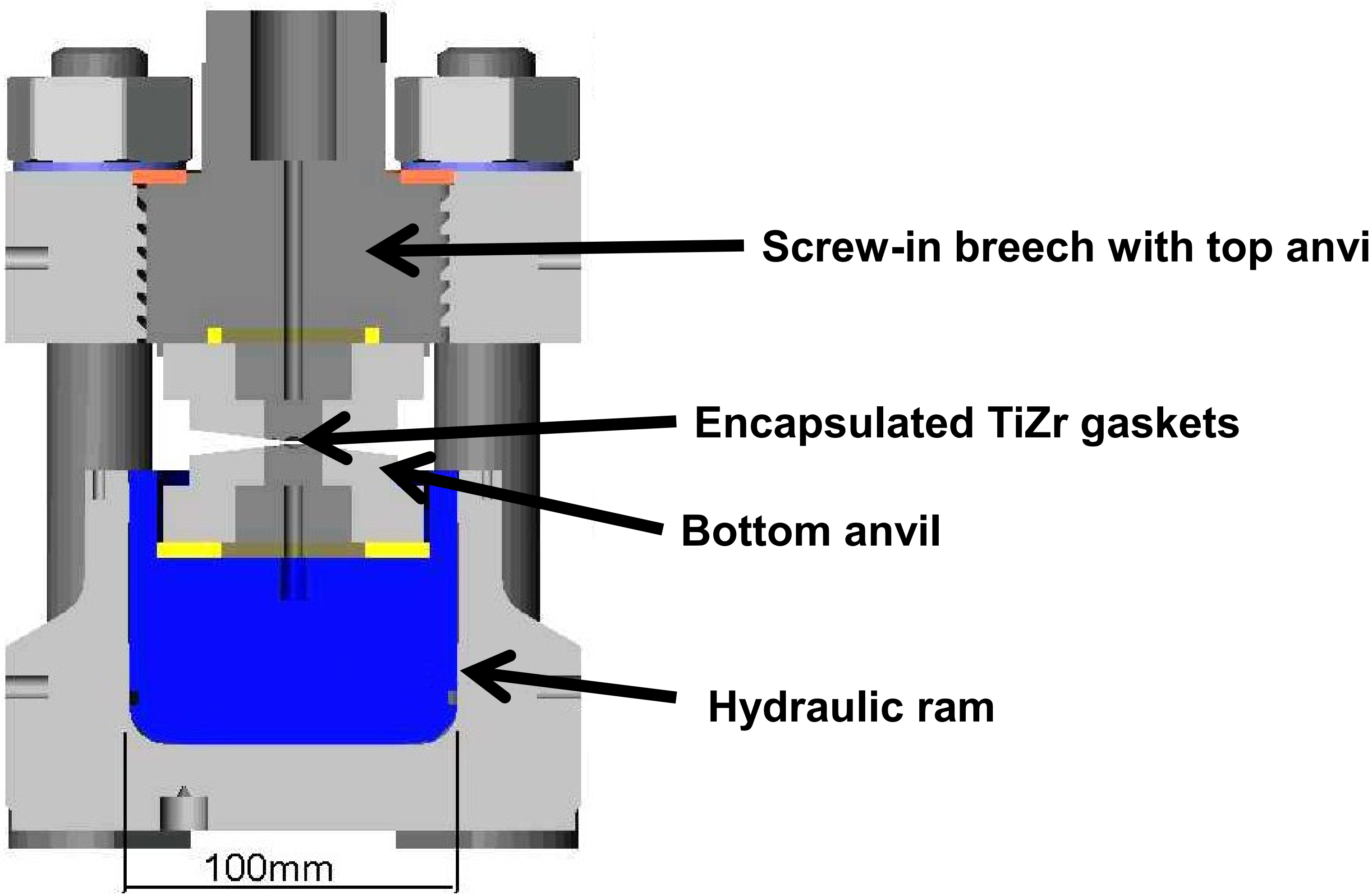


The gas cell design makes a liquid loading unavoidable due to embrittlement of the Bridgman seal at low-T

Al and TiZr gas cell sample volume ~ 1.5 cm^3

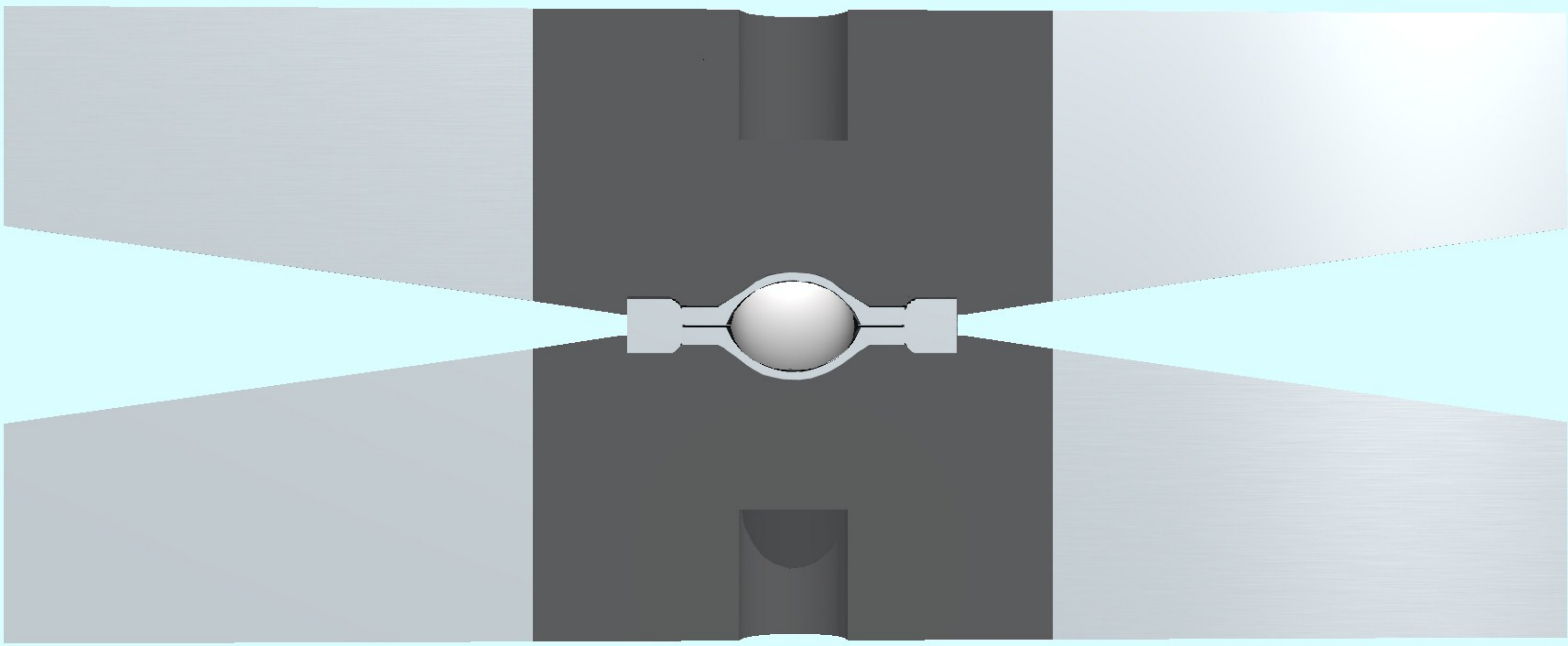
Higher-P sample environment

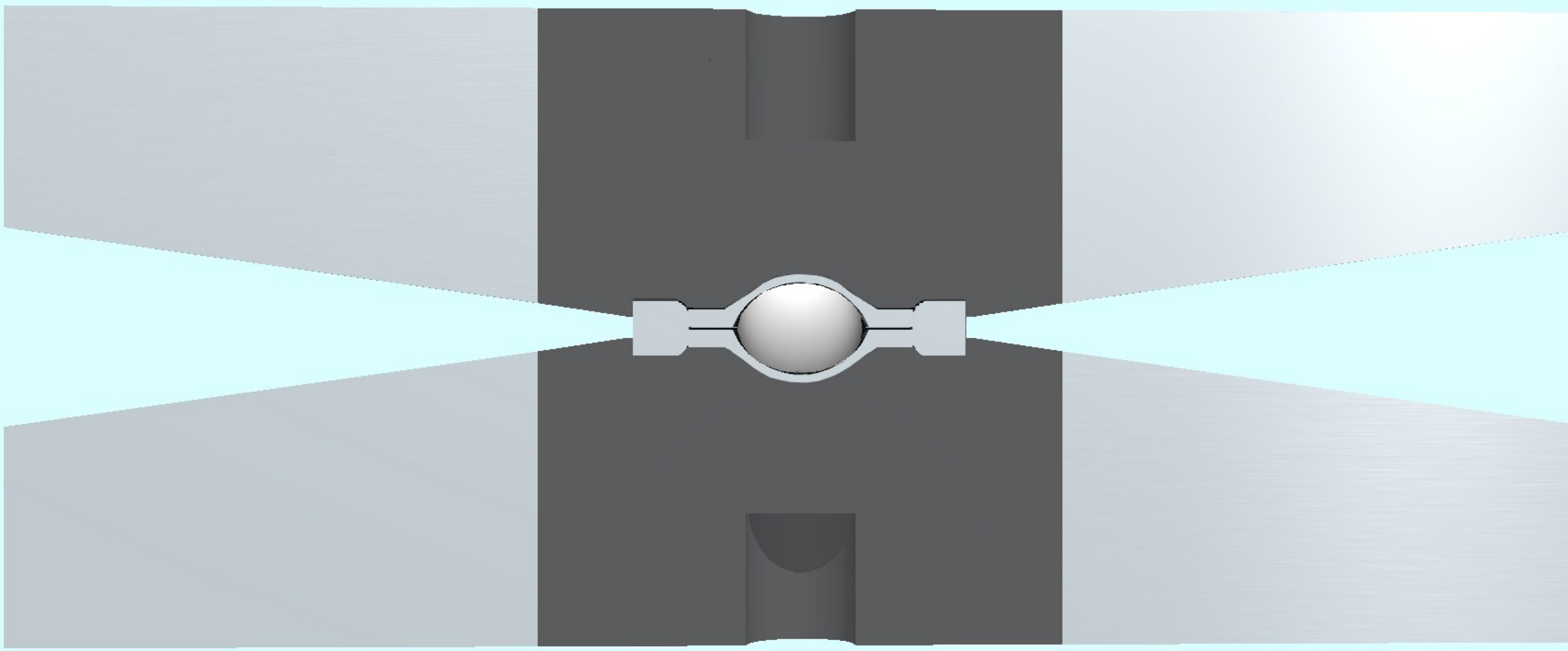
Paris-Edinburgh large-volume press (0 – 10 GPa)



Sample mass ~ 100 mg

For cold loading of solids, need to keep ~ 100 kg of metal cold.



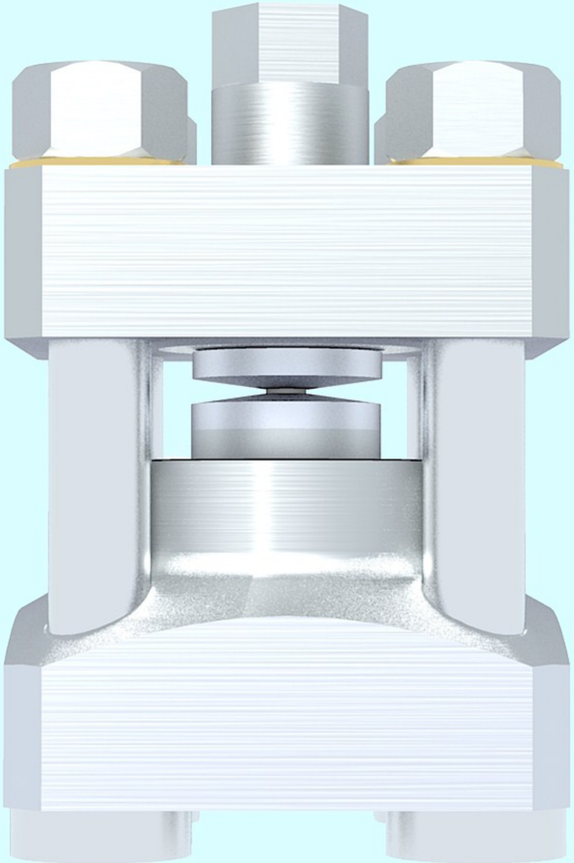


a

PARIS-EDINBURGH HYDRAULIC PRESS

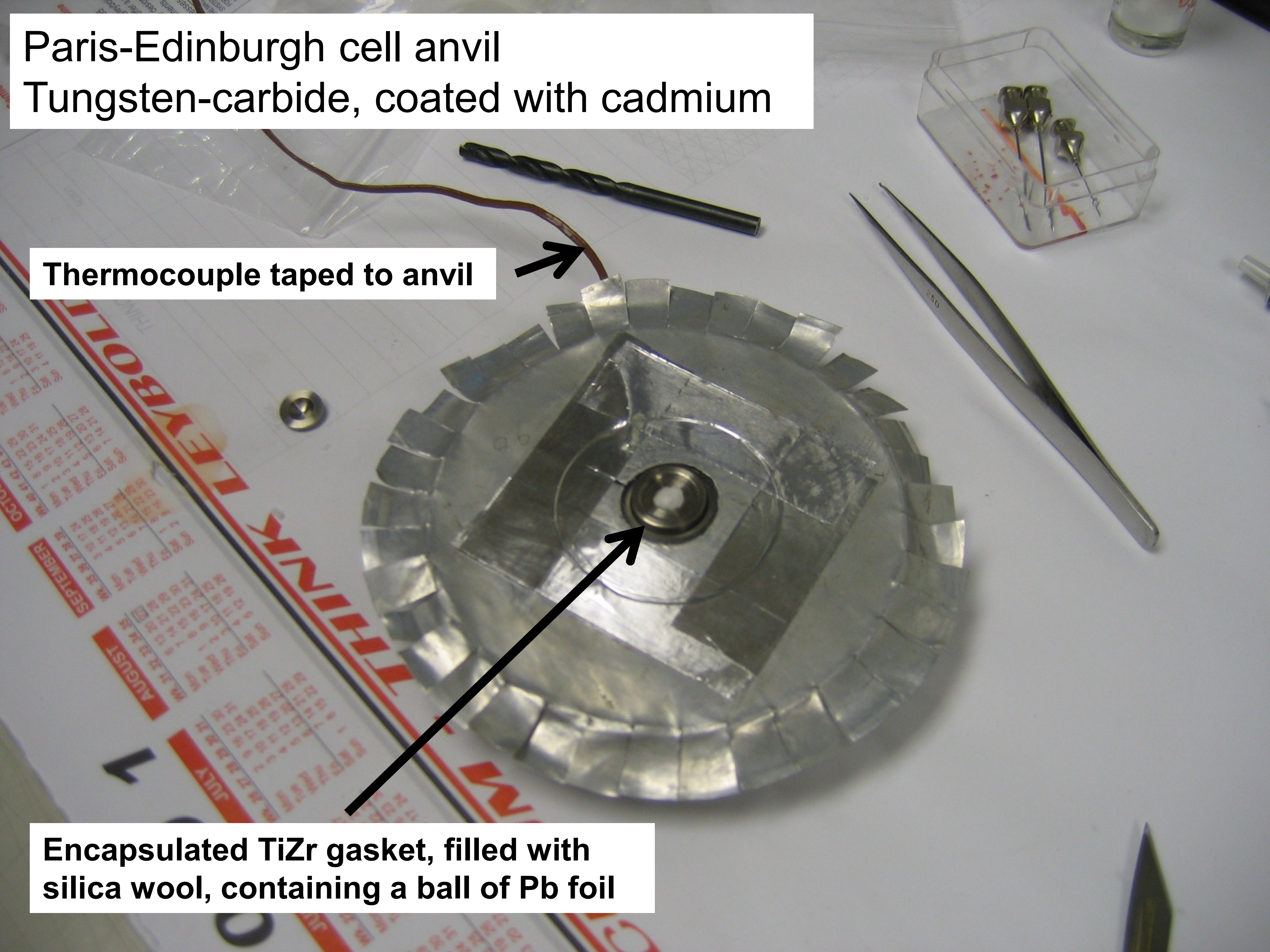
reech

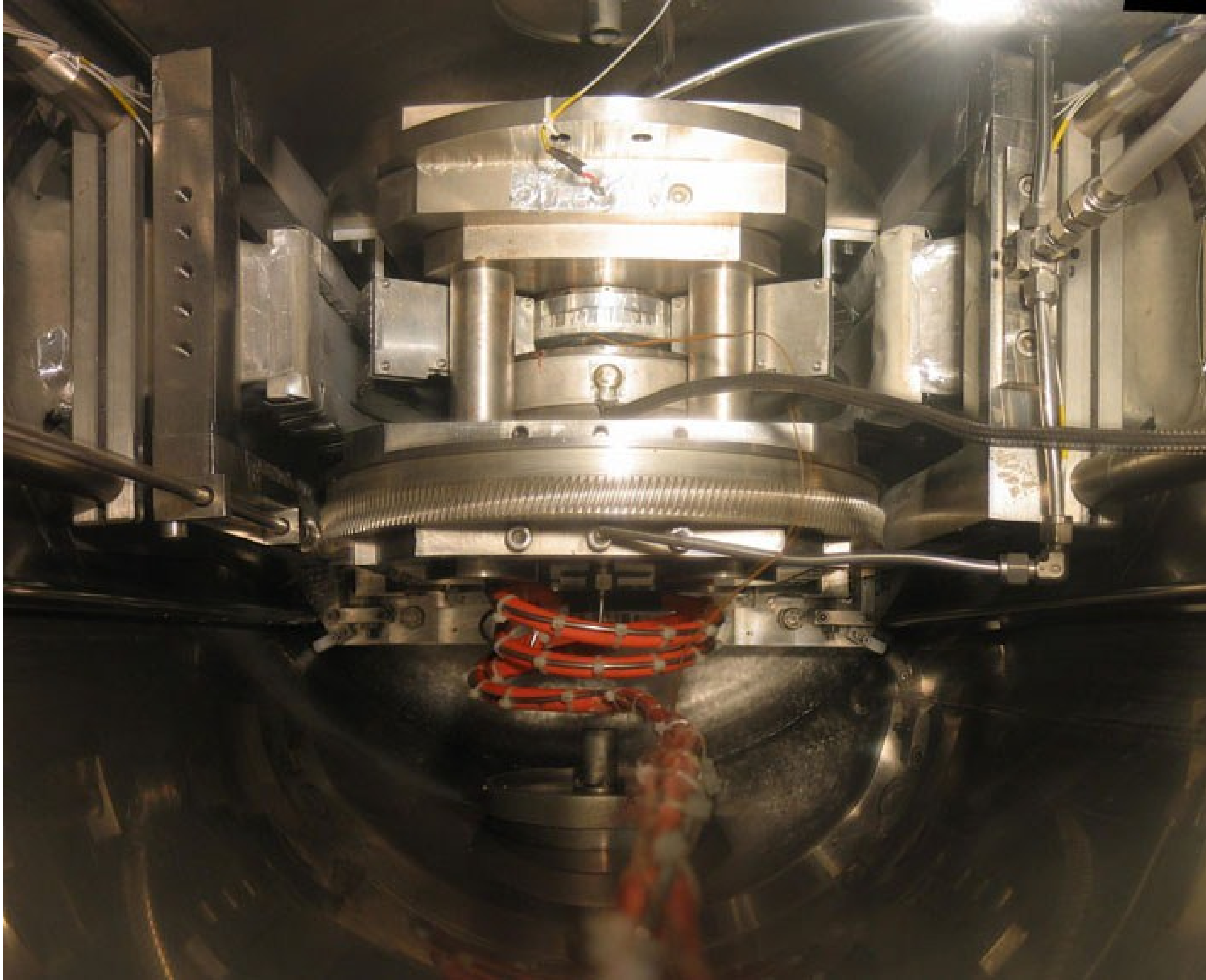
anvil set



illars

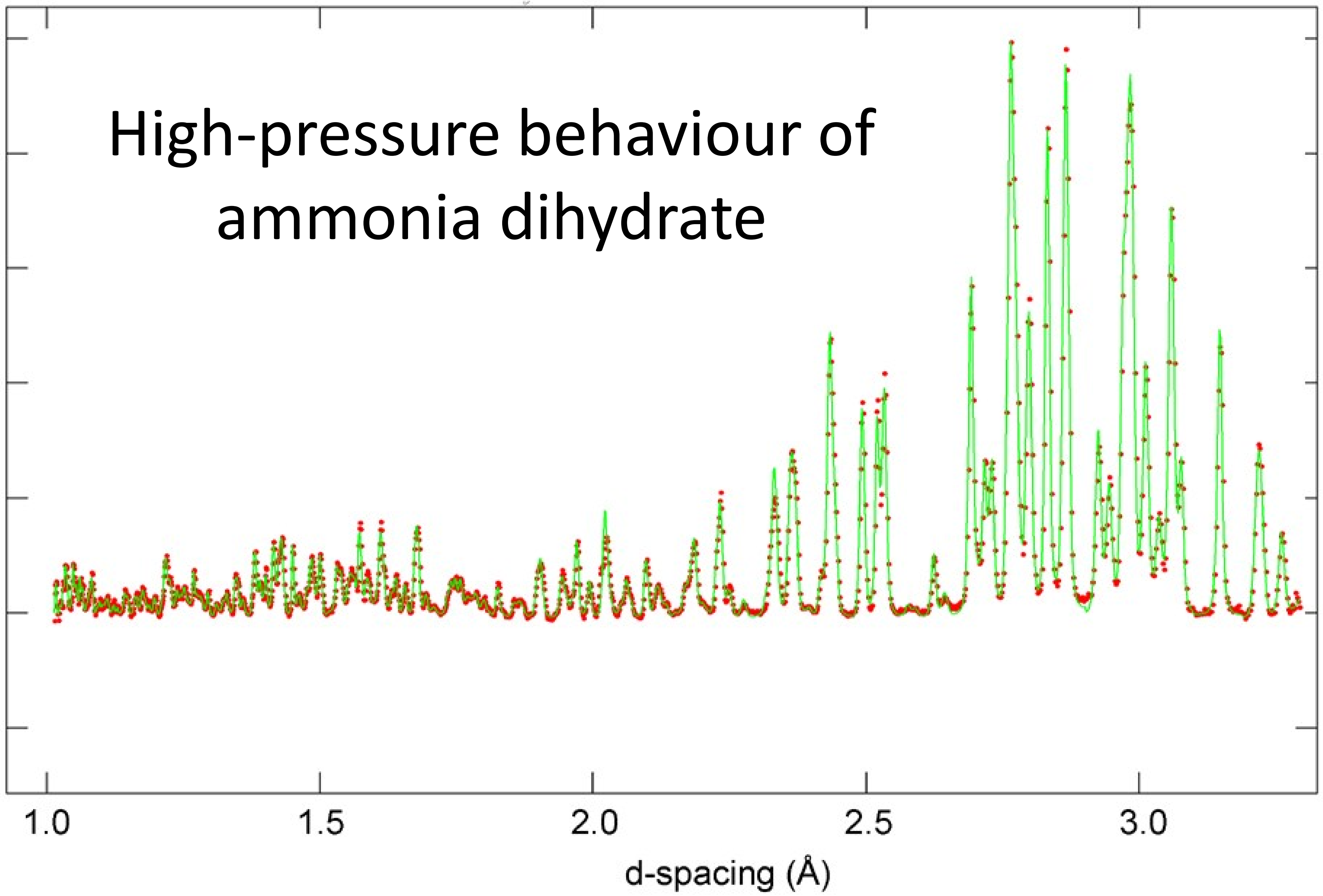
h


Paris-Edinburgh cell anvil
Tungsten-carbide, coated with cadmium
Thermocouple taped to anvil
Encapsulated TiZr gasket, filled with silica wool, containing a ball of Pb foil

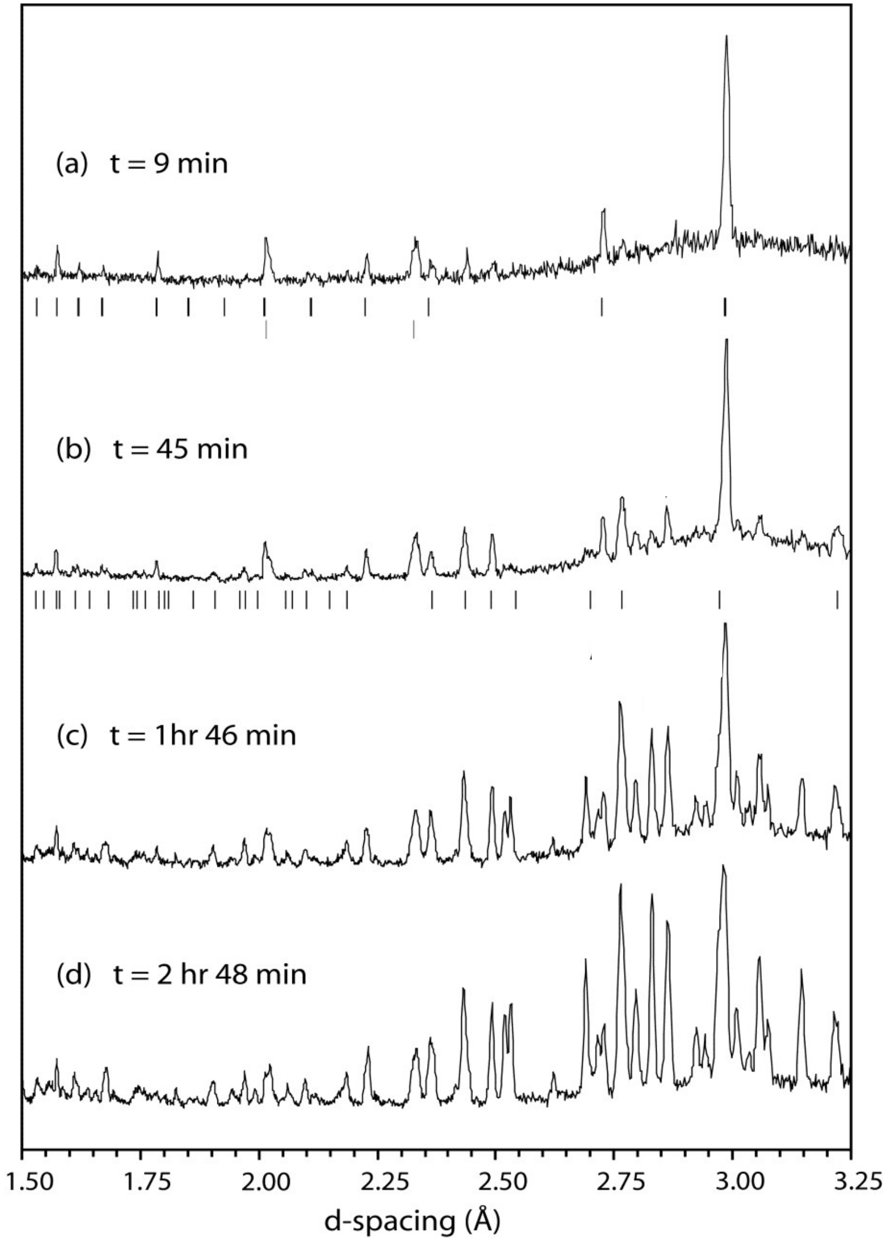


Case study 1:

High-pressure behaviour of ammonia dihydrate



Growth of a phase mixture at high pressure



Re-crystallisation sequence at 174 K at ~ 450 MPa

ice IX + liquid

↓

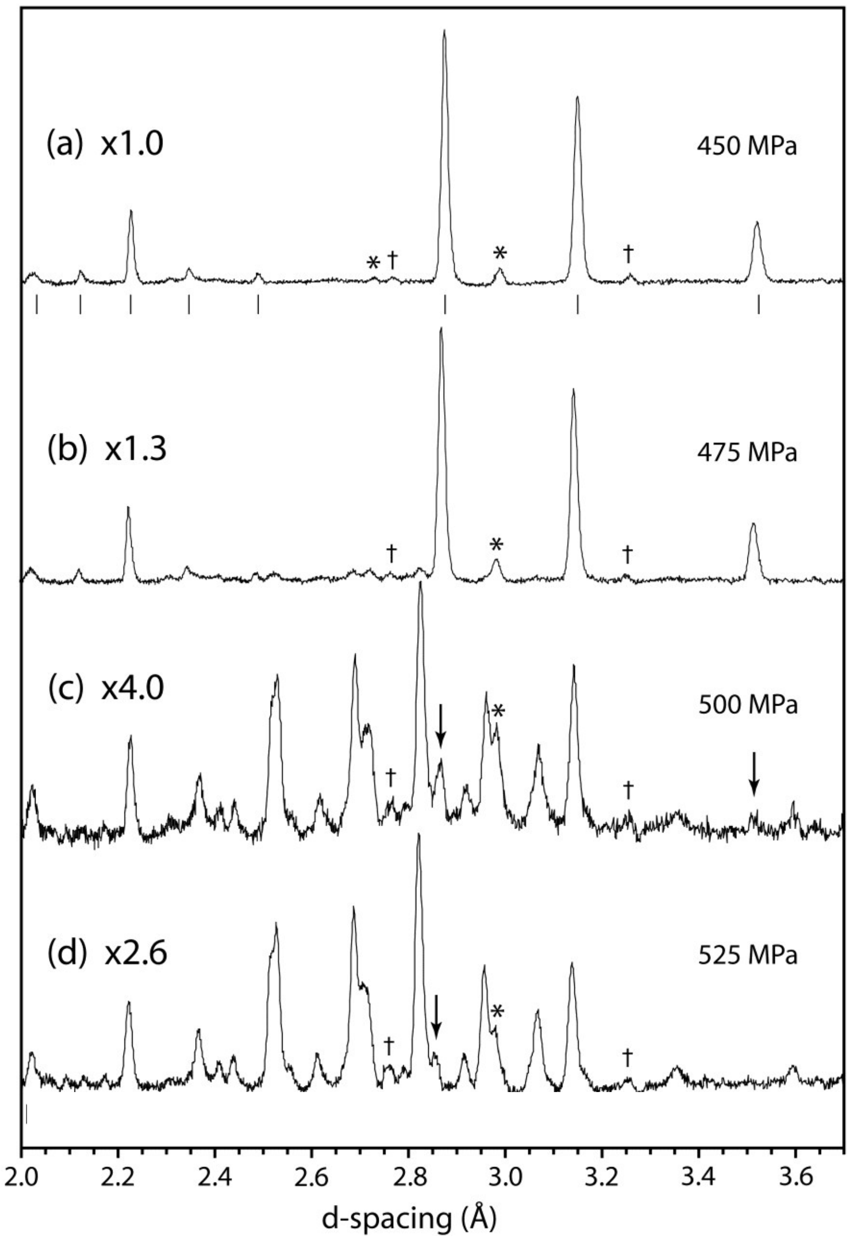
growth of ice II

↓

growth of ammonia hydrate(s)

ammonia dihydrate II
+
ammonia monohydrate II

Isothermal compression through a phase transition



Phase transition in ammonia dihydrate upon compression from 0.1 – 525 MPa

cubic phase I of ADH

↓

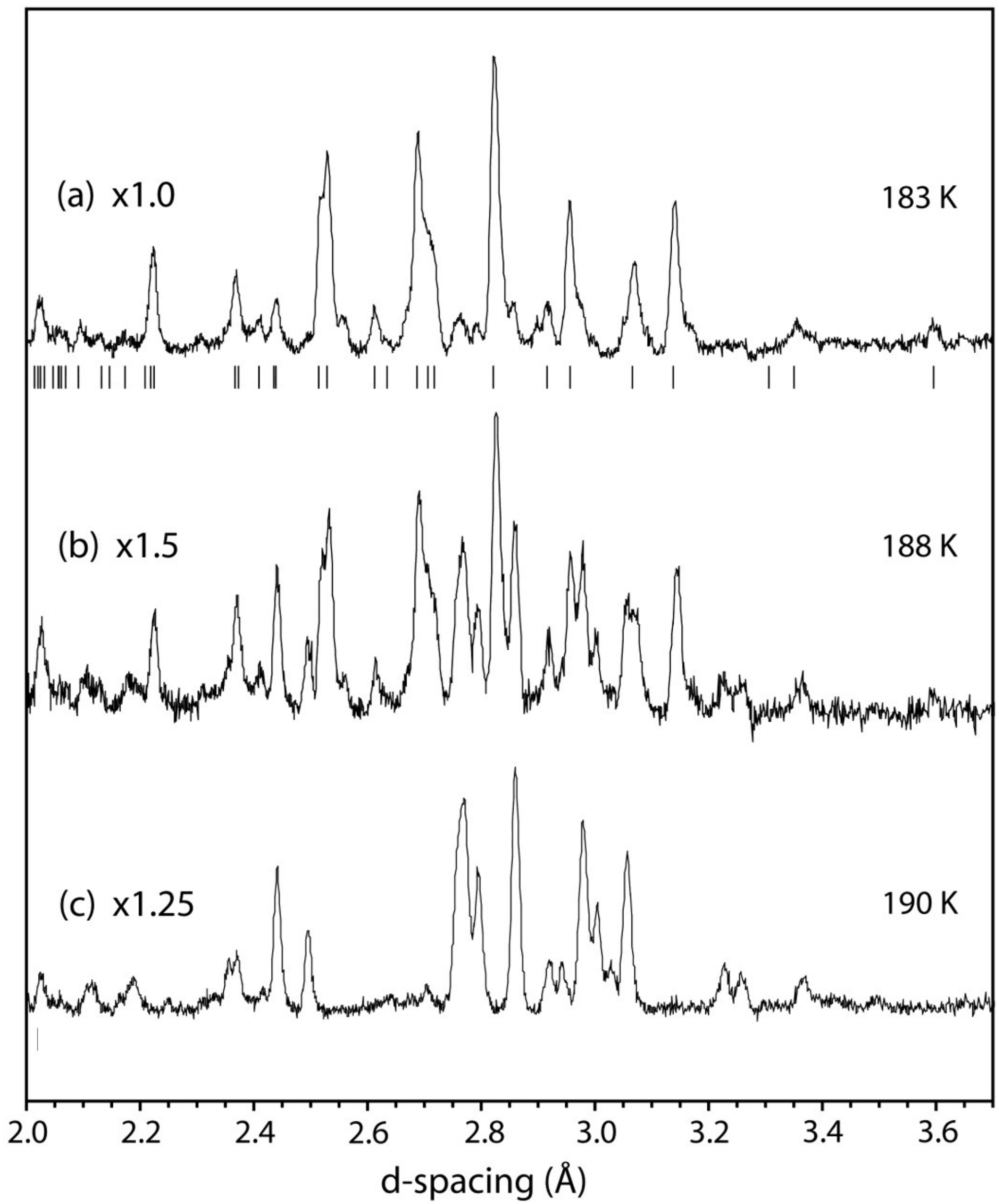
phase II of ADH

ADH II (monoclinic)
a = 7.7686(11) Å
b = 6.6947(11) Å
c = 6.0380(8) Å
β= 101.967(14) °

P = 546 MPa, T = 173 K
V = 307.20 Å^3 (Z = 4)
M(11) = 97.1
F(11) = 97.2 (0.0039, 29)

Systematic absences indicate space-groups, Pn, P2/n, or P2$_1$/n

Isobaric warming through a phase transition



Phase transition in ADH upon warming at 550 MPa

monoclinic phase II of ADH

(ADH II)

mono-phase, multi-phase???

Partial melting under high pressure

Partial melting of AMH + ice mixture upon warming at 550 MPa

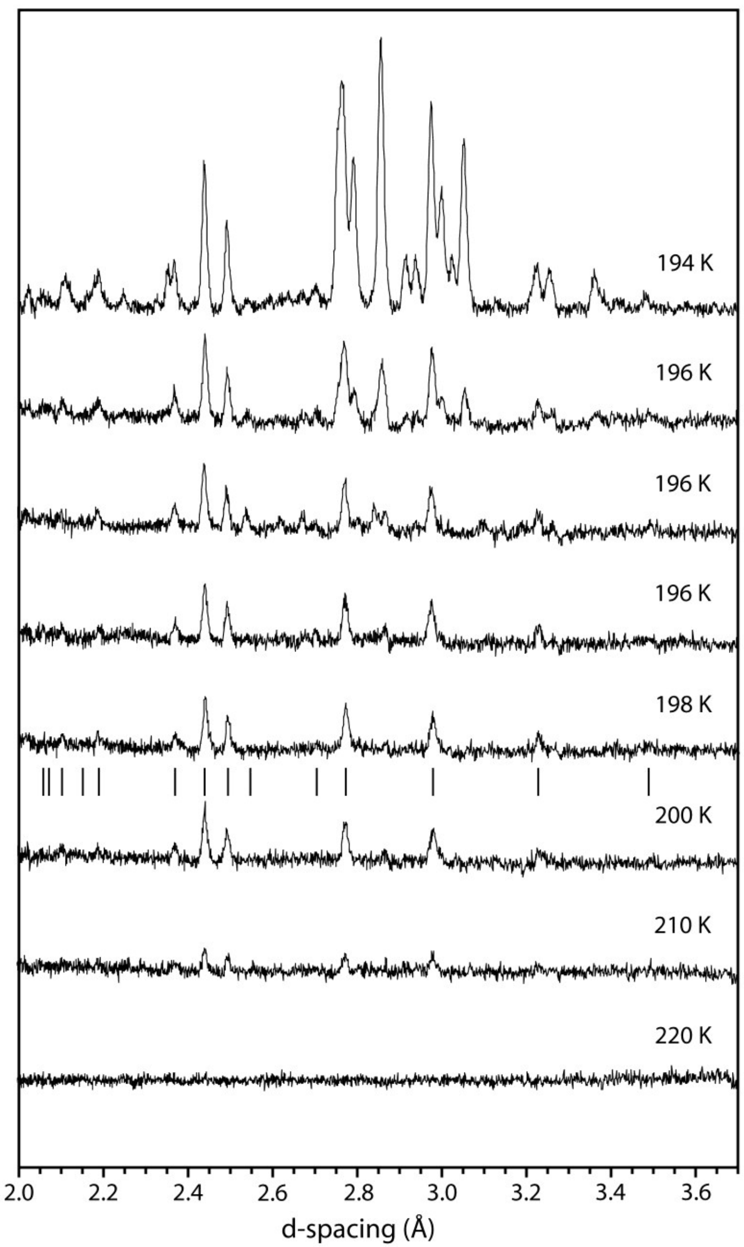
AMH II + ice II

↓

ice II + liquid

↓

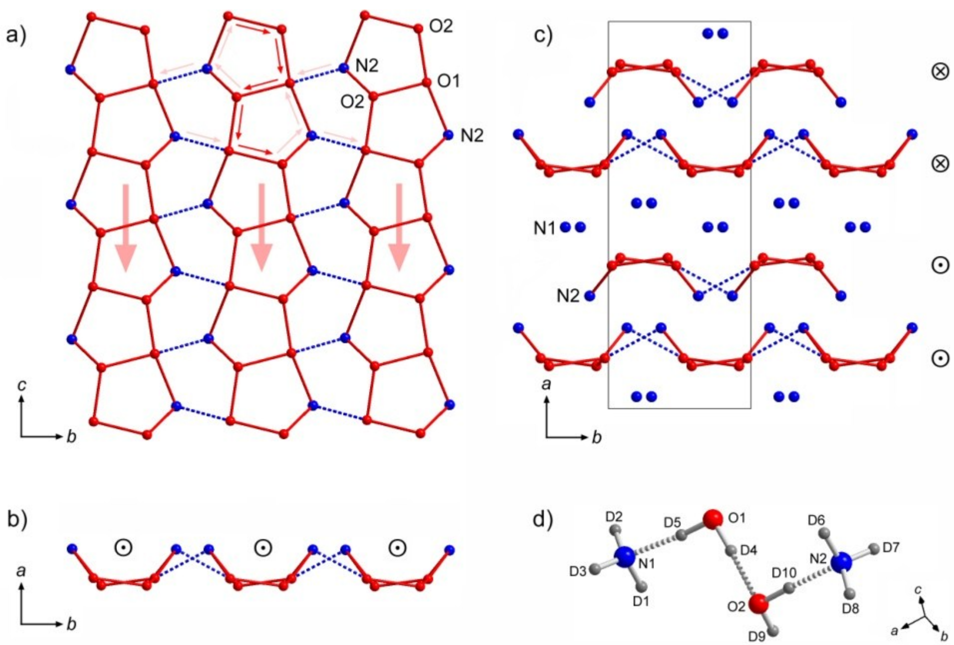
liquid

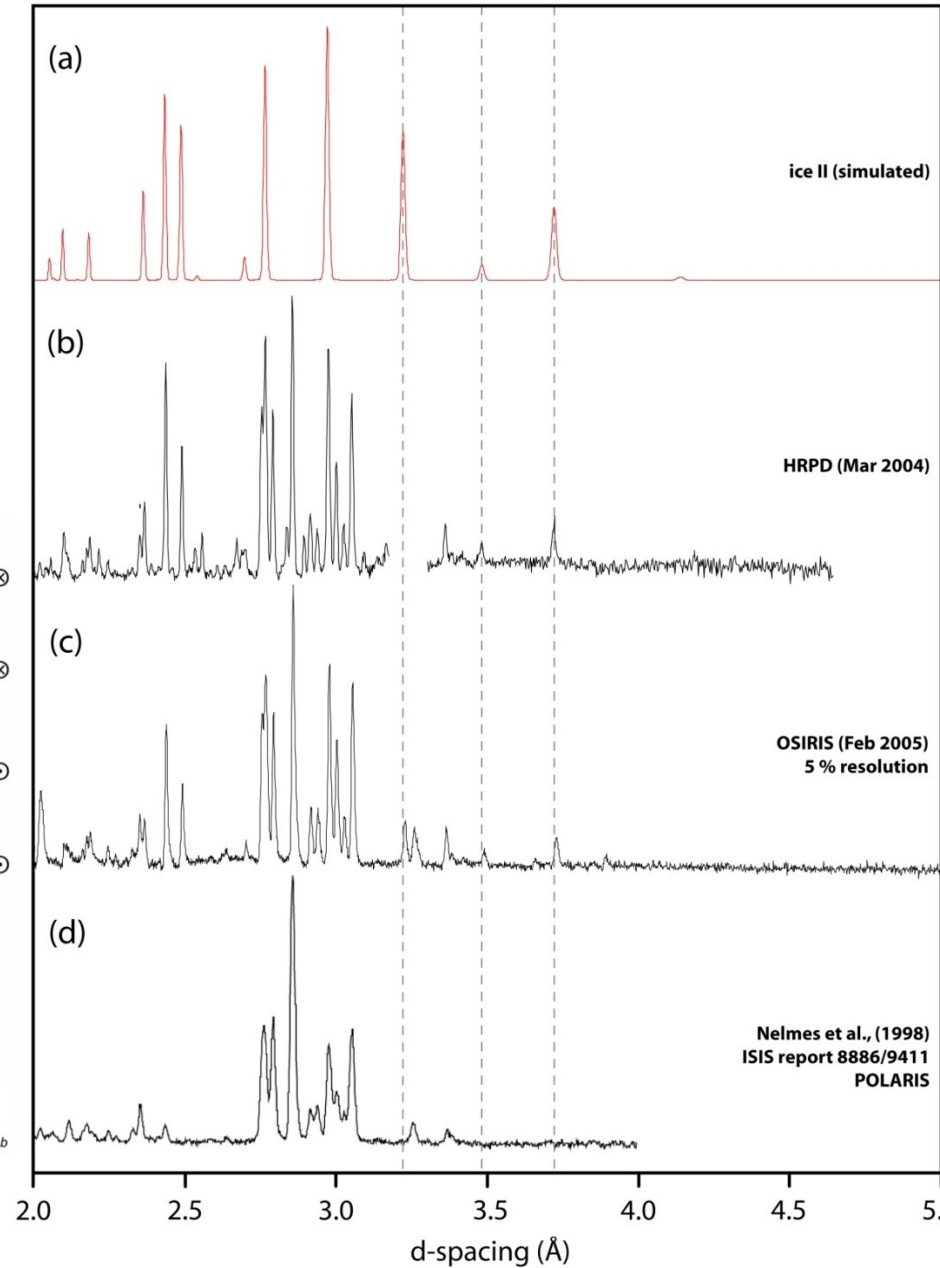


Powder indexing and solution of AMH II structure

AMH II (orthorhombic)	P = 550 MPa, T = 190 K
a = 18.8119(33) Å	V = 892.66 Å^3 (Z = 16)
b = 6.9400(10) Å	M(12) = 51.5
c = 6.8374(8) Å	F(12) = 65.7 (0.0041, 44)

Structure subsequently solved in space-group P*bca*. Consists of a pentagonally tessellated net similar to that found in tetragonal argon clathrate.

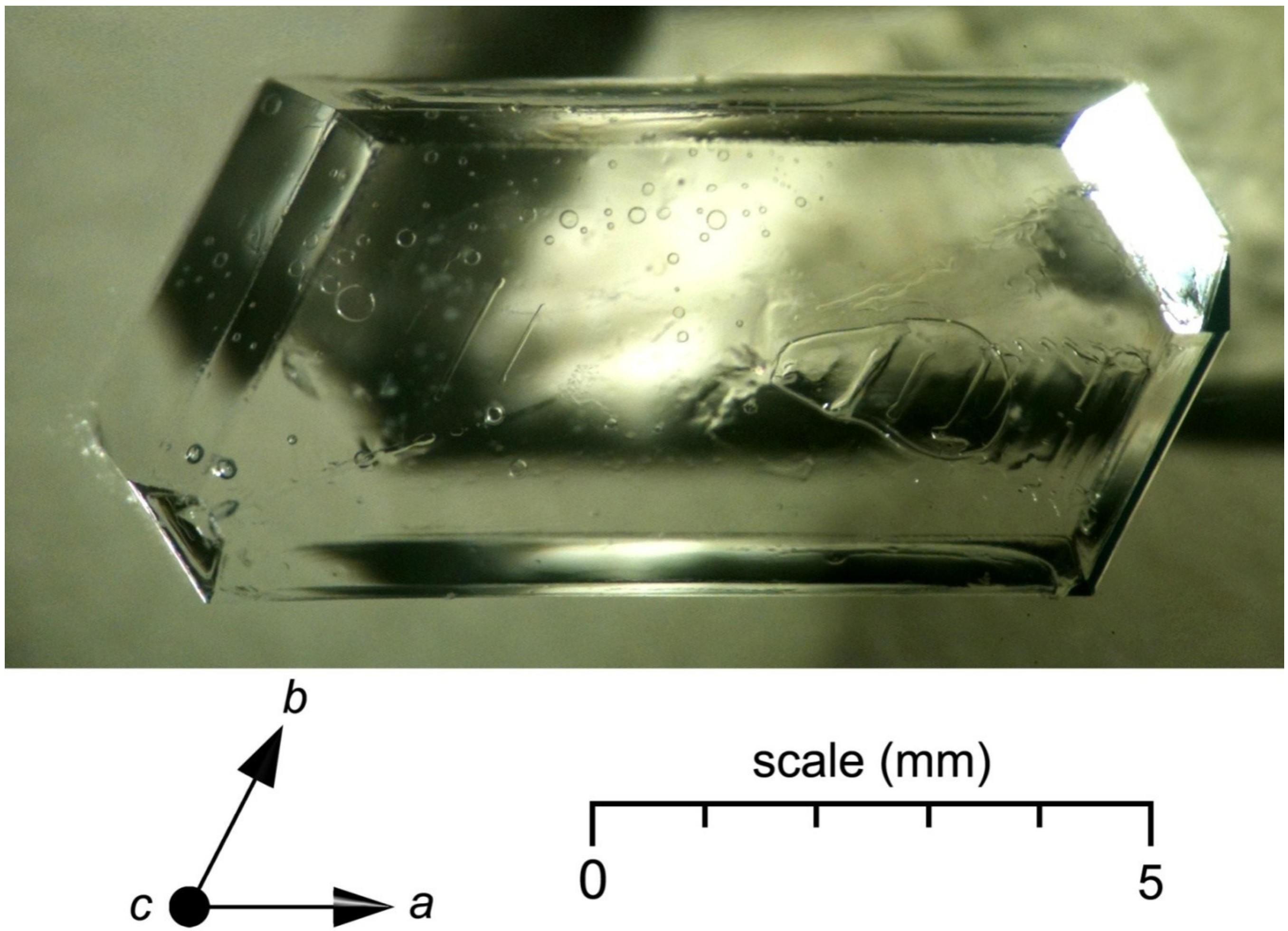




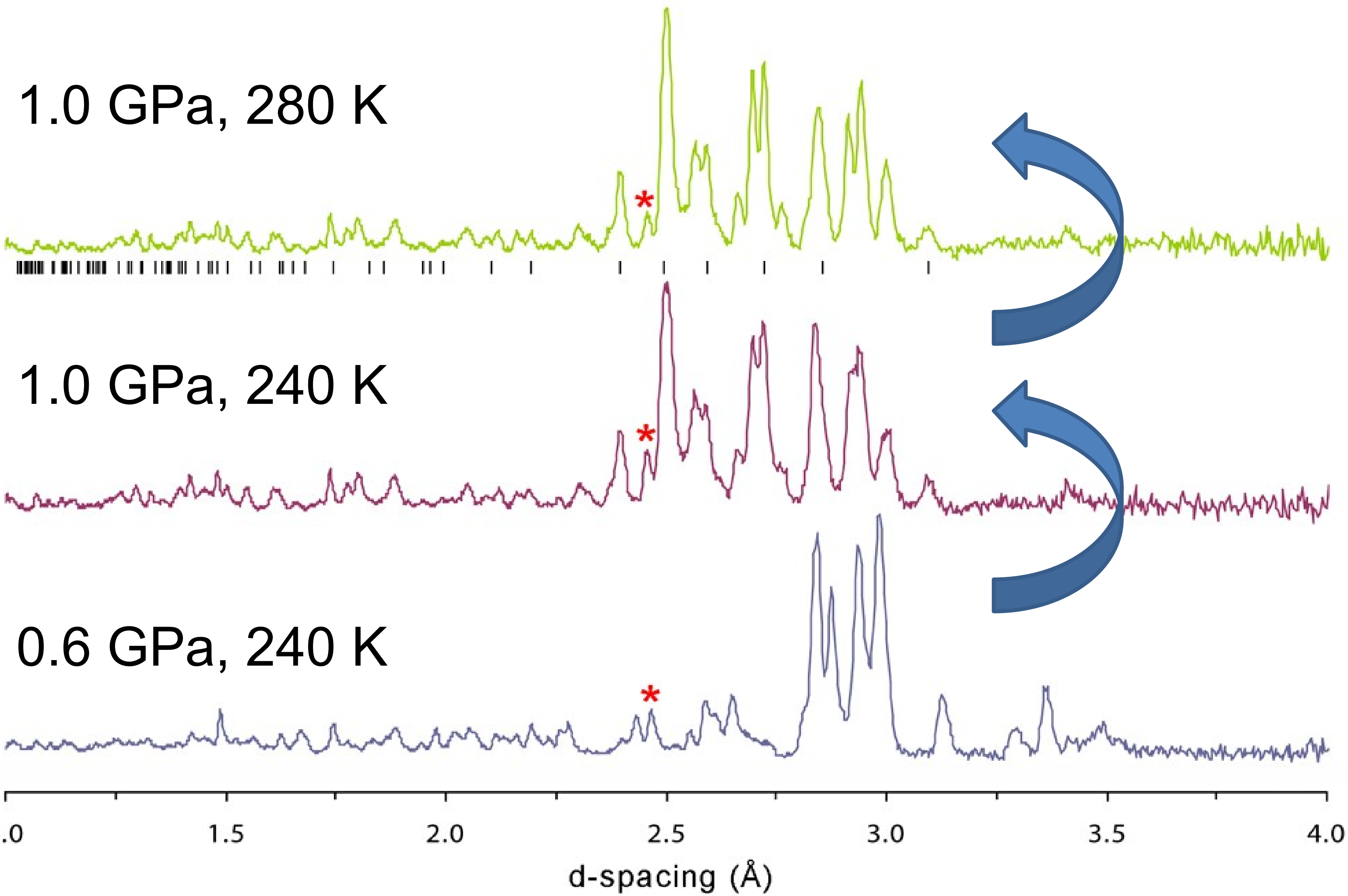
J. Am. Chem. Soc. **131**, 13508

Case study 2:

The high-pressure behaviour of meridianiite



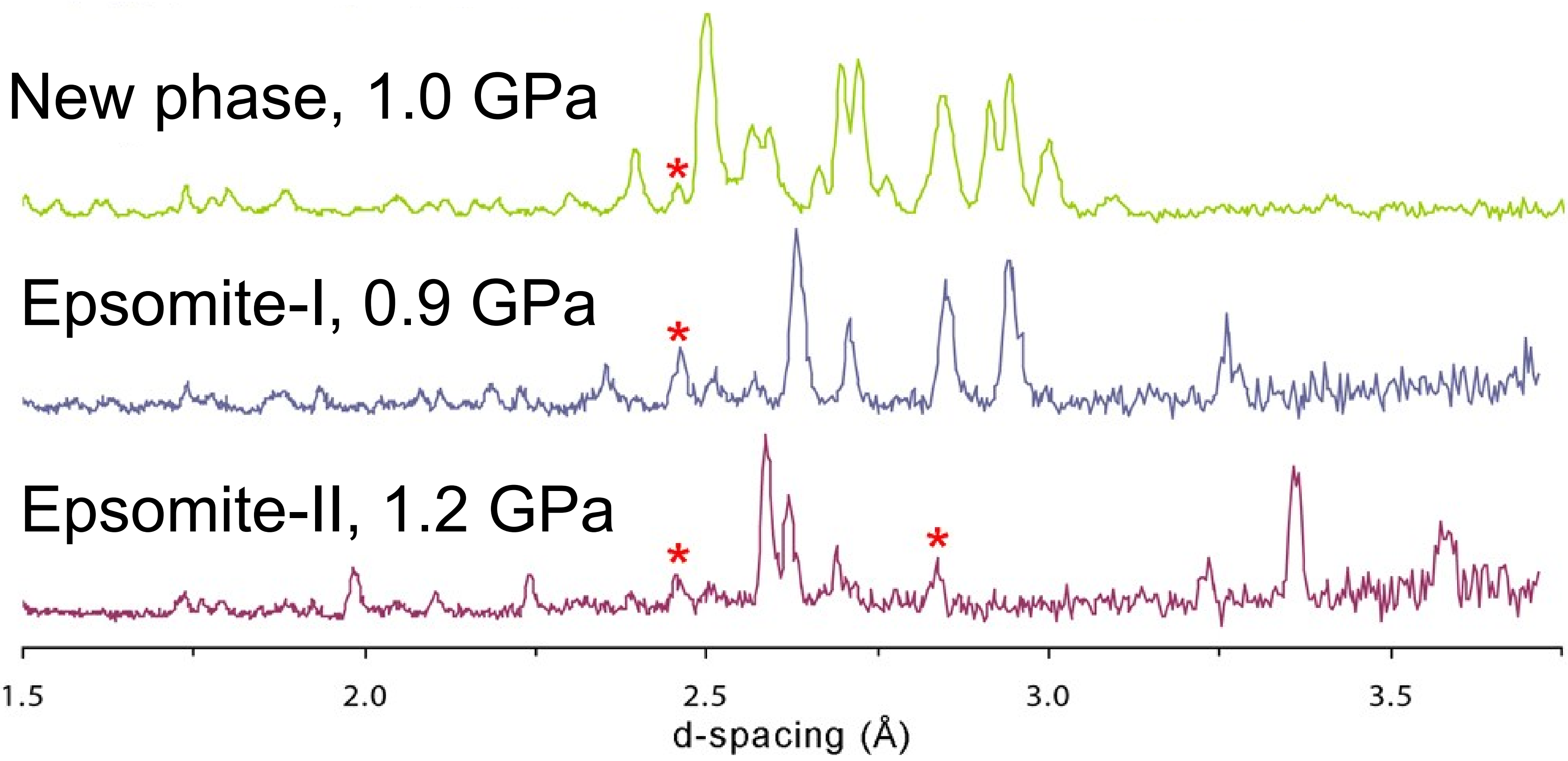
High-pressure transformation of meridianiite



The exsolution of ice indicates a change in hydration state

No obvious match to epsomite at high-pressure

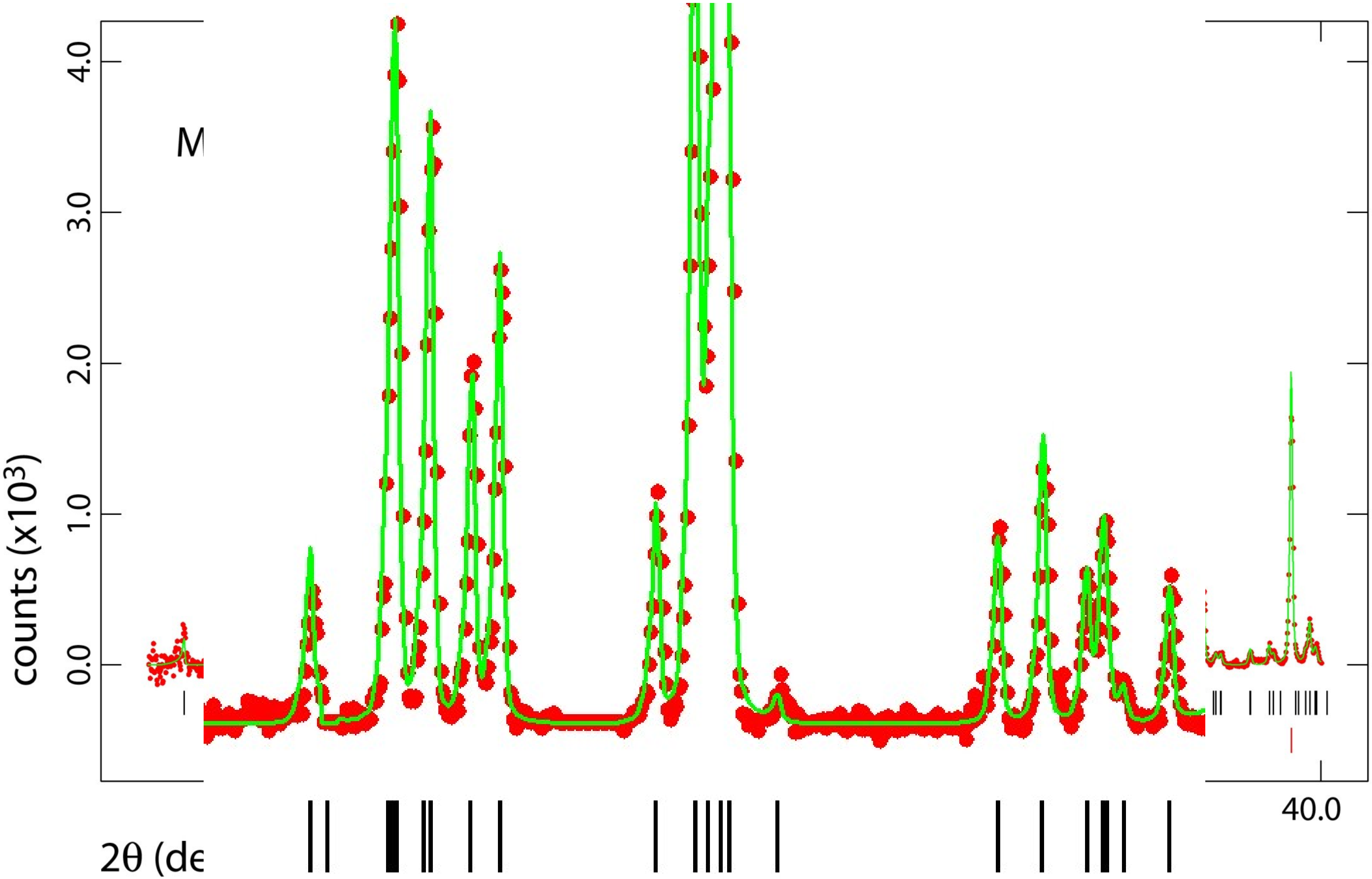
Suggests that the new phase has a hydration state between 7 and 11

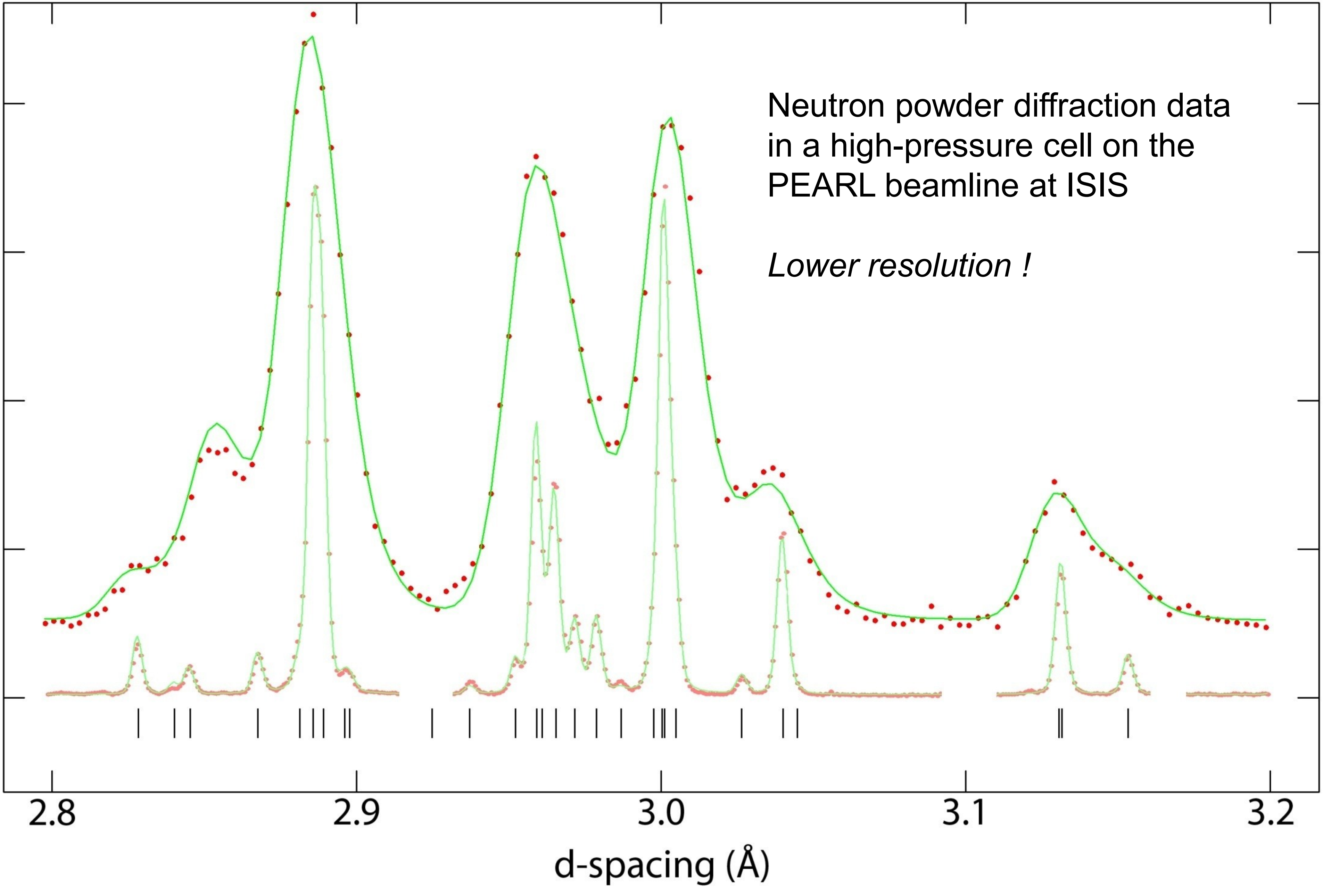


Gromnitskaya *et al.* (2013) Phys. Chem. Min. **40**, 271-285

High resolution X-ray powder data from a laboratory diffractometer

essential for indexing unknown phases





Neutron powder diffraction data in a high-pressure cell on the PEARL beamline at ISIS
Lower resolution !
2.8
2.9
3.0
3.1
3.2
d-spacing (Å)

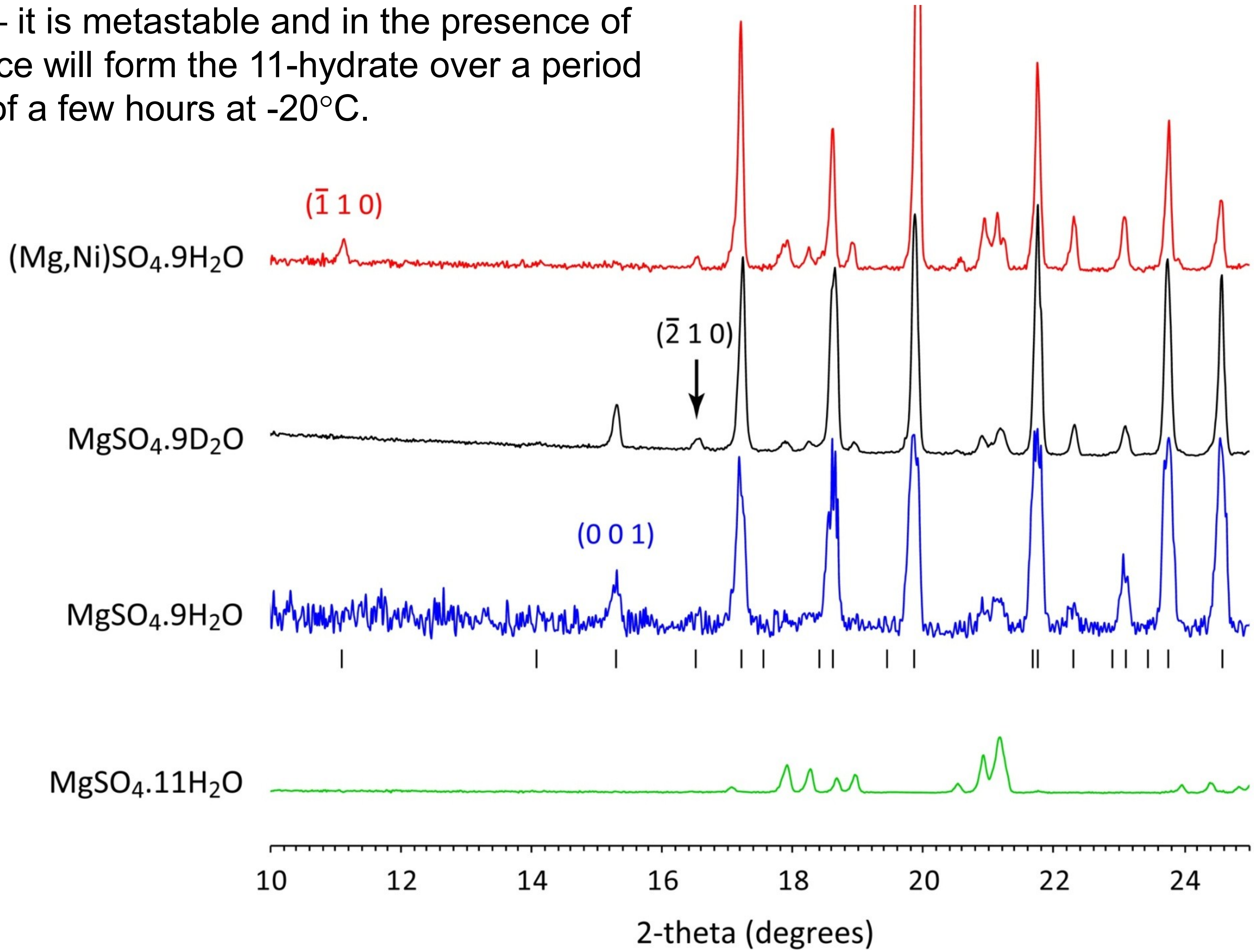
One solution to this problem is to seek structural analogues with different compositions, which might form novel hydrates under conditions where we can acquire high-resolution data.

Occurrence of known $MgX^{6+}O_4 \cdot nH_2O$ crystals

n =	4	5	6	7	8	9	10	11
SO_4	✓	✓	✓	✓		✓		✓
SeO_4	✓	✓	✓	✓		✓		✓✓
TeO_4				work in progress				
CrO_4		✓		✓		✓		✓
MoO_4		✓		✓	✓			
WO_4		✓		✓	only amorphous solids so far			

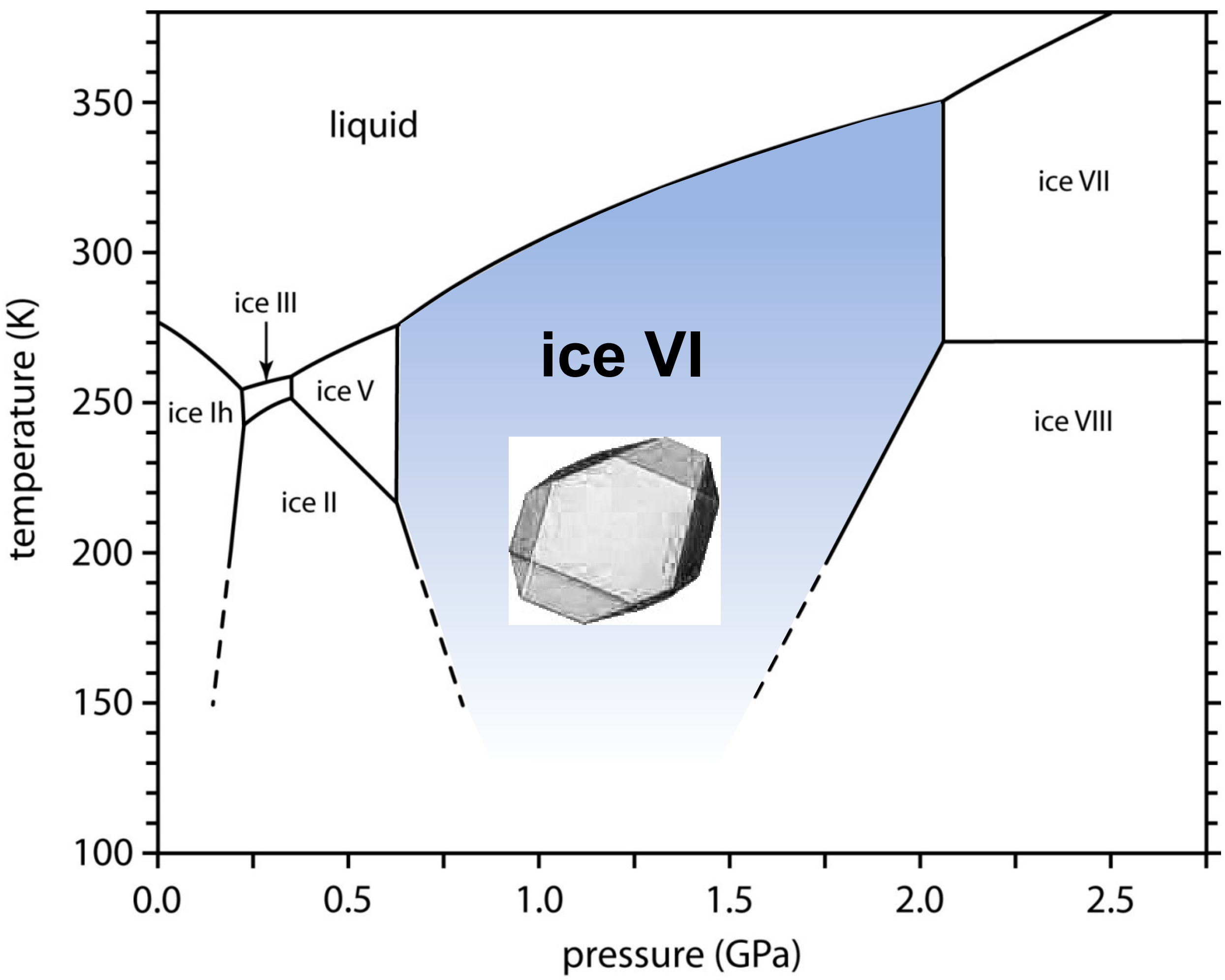
$MgSeO_4 \cdot 9H_2O$ is particularly interesting because this phase seems to be stable in aqueous solution, although it is not isostructural with any of the other 9-hydrates identified so far.

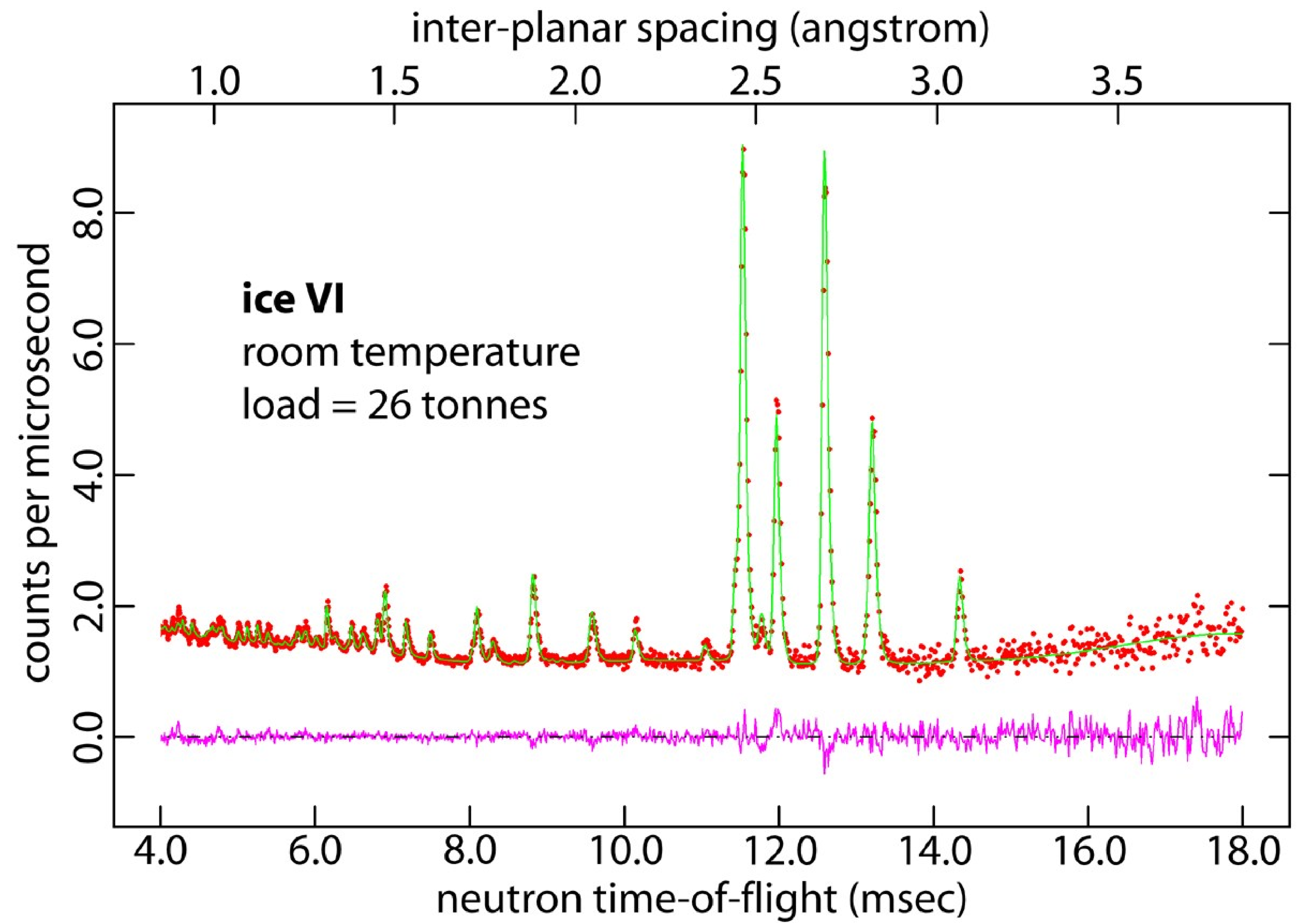
Pure $MgSO_4$ 9-hydrate can be formed by quenching small droplets in liquid nitrogen – it is metastable and in the presence of ice will form the 11-hydrate over a period of a few hours at -20°C.



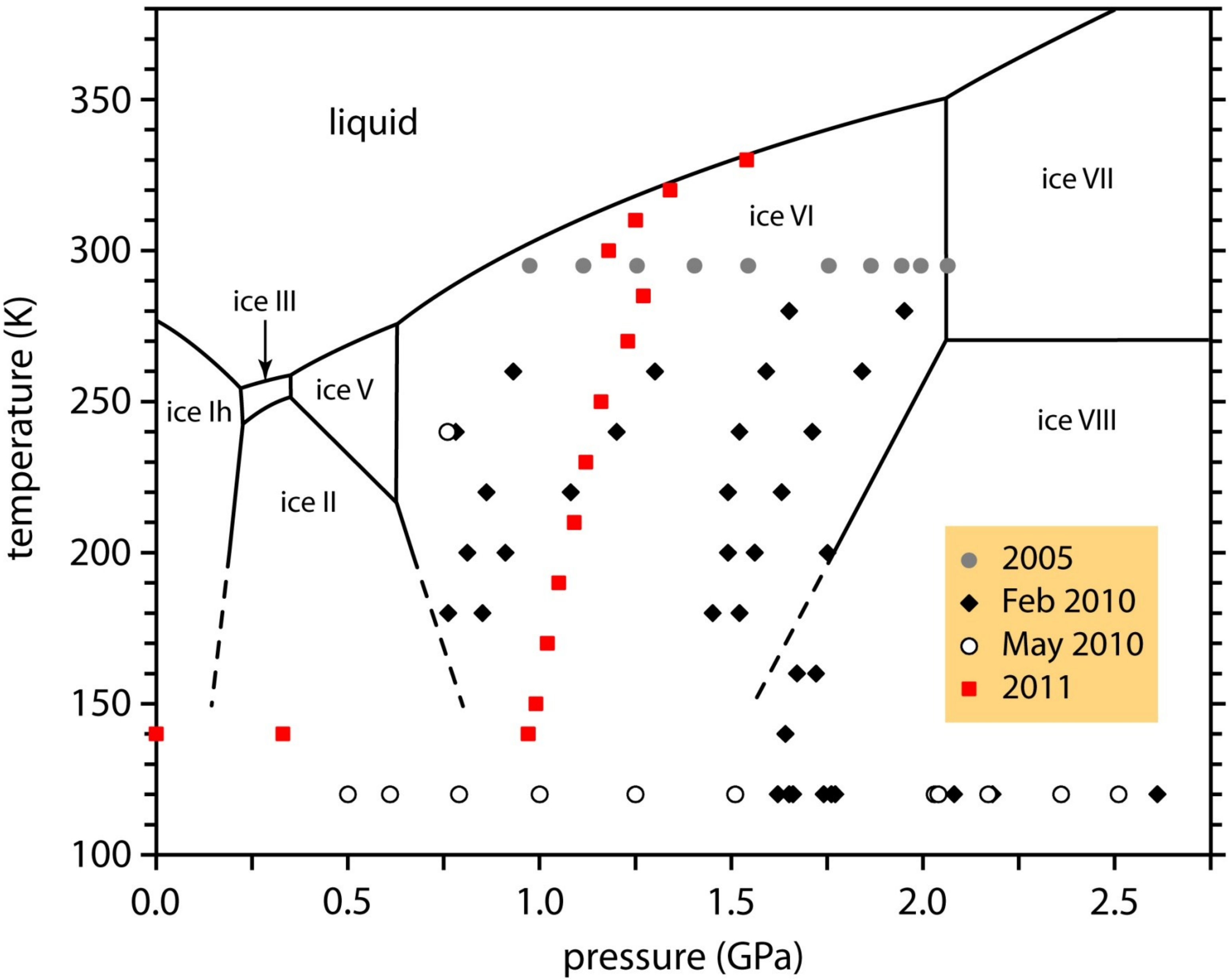
Case study 3:

P-V-T equation of state of ice VI

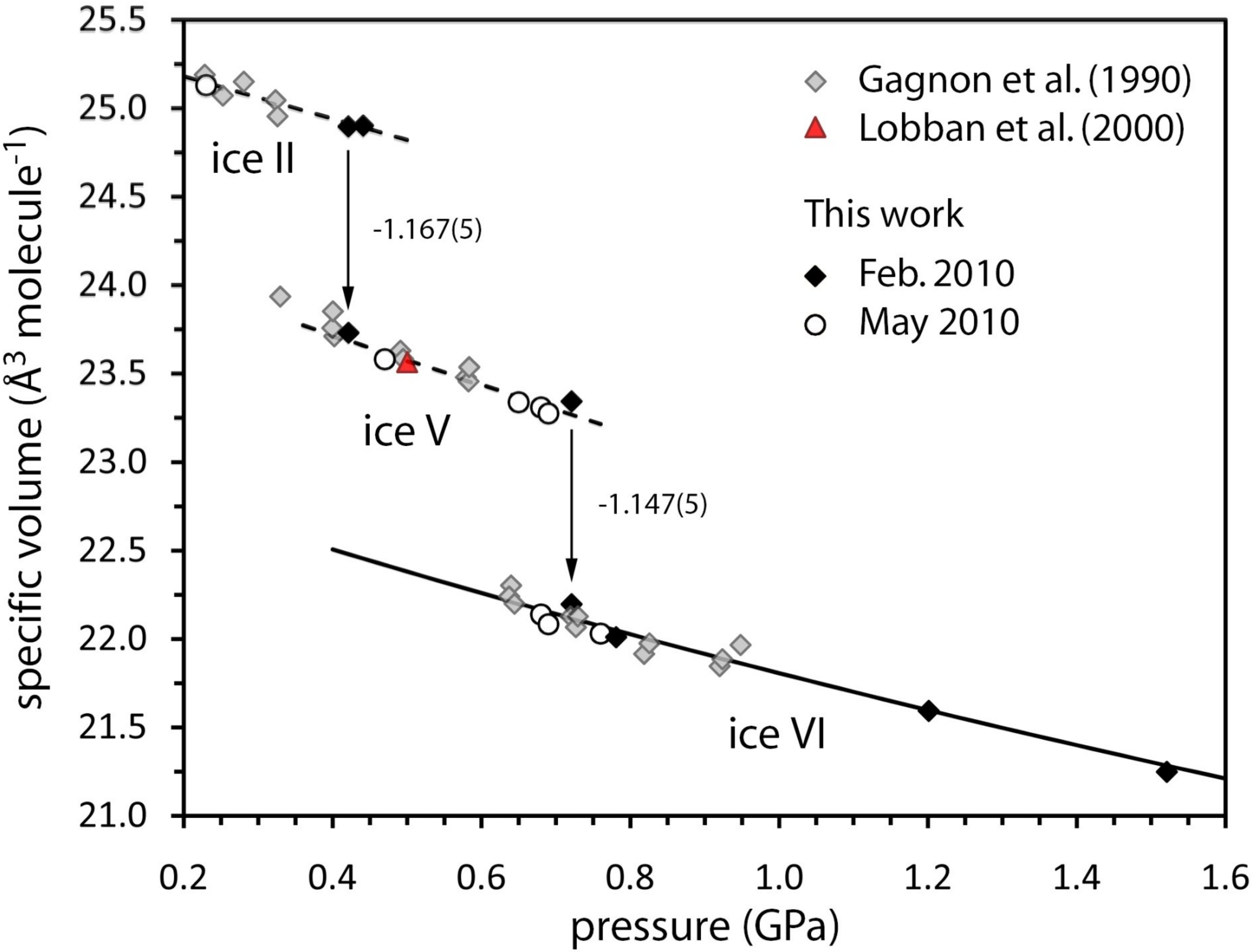



inter-planar spacing (angstrom)
1.0
1.5
2.0
2.5
3.0
3.5
8.0
6.0
4.0
2.0
0.0
counts per microsecond
ice VI
room temperature
load = 26 tonnes
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
neutron time-of-flight (msec)

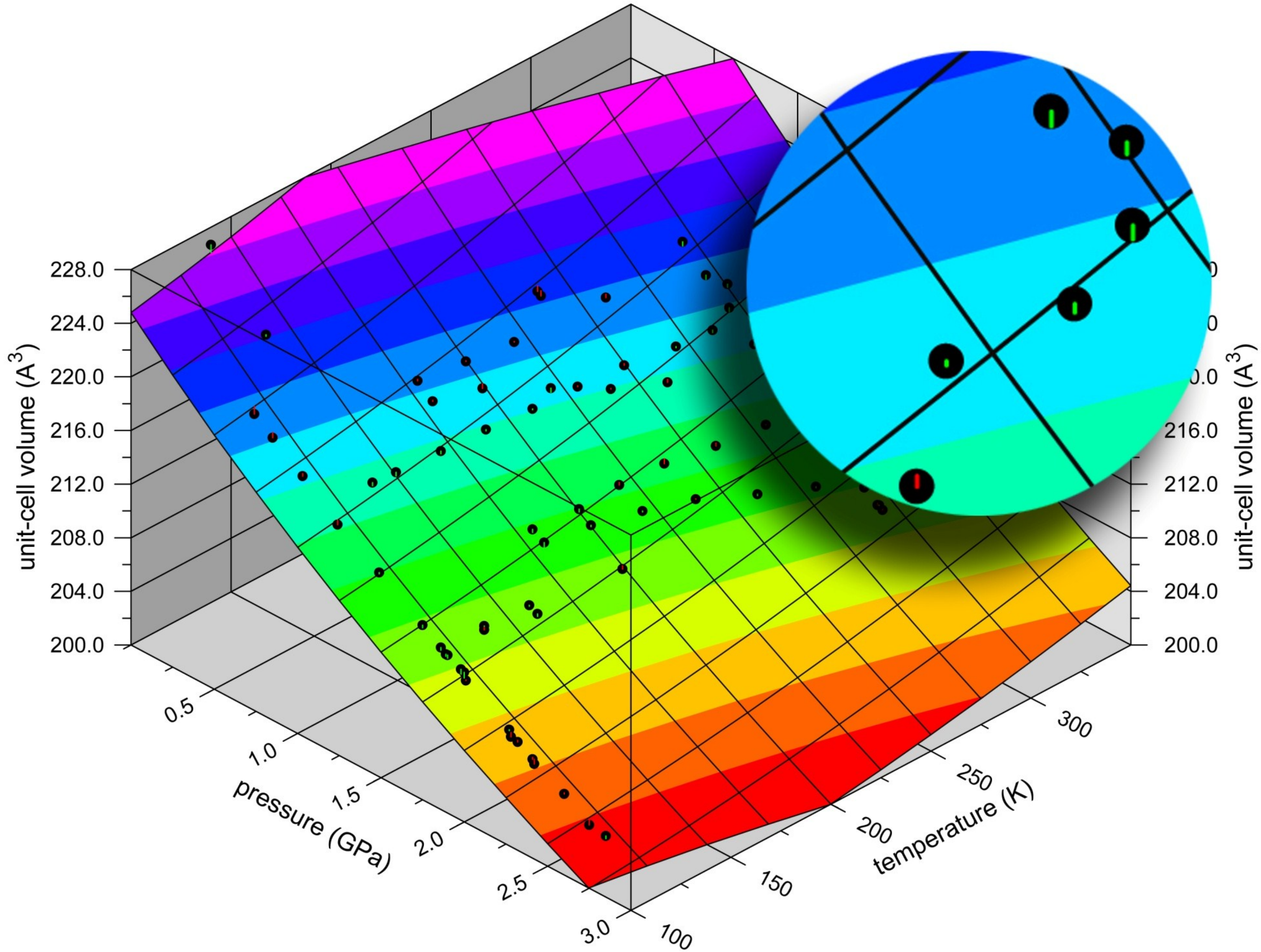
P-T distribution of measurements on ice-VI



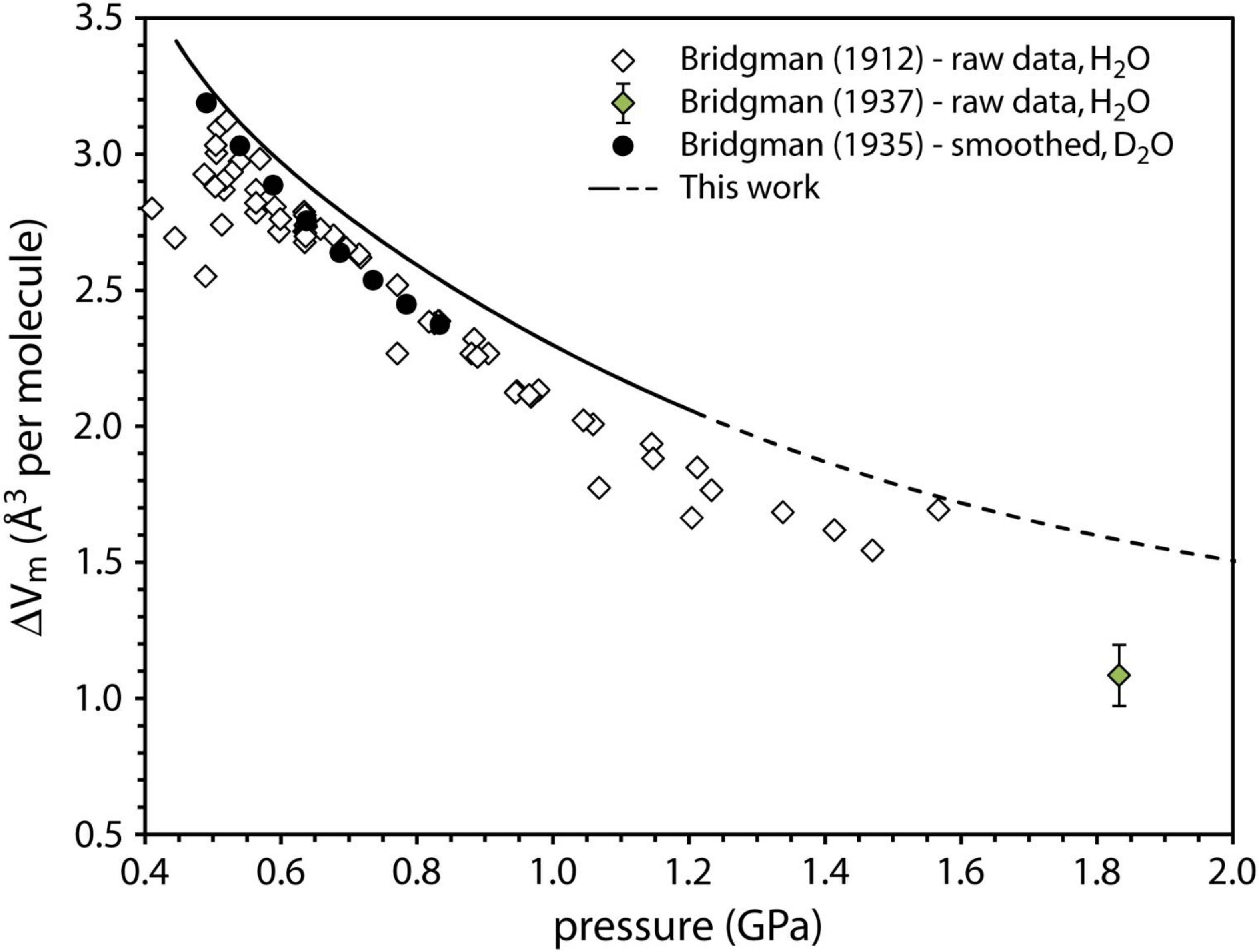
Measurements made en-route to ice-VI



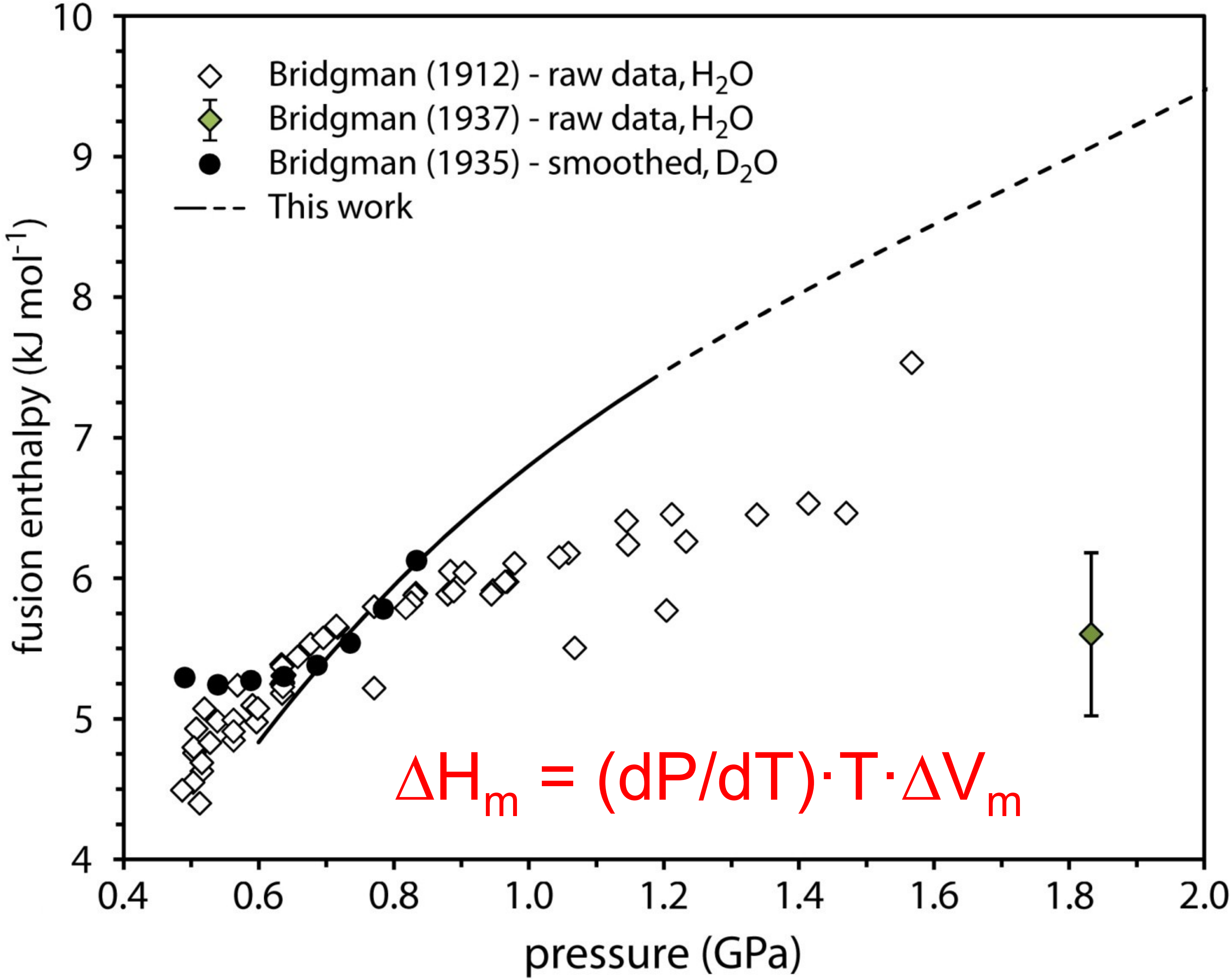
Pressure-Volume-Temperature (PVT) surface for ice-VI



Volume of fusion, ΔV_m calculated from the new equation of state



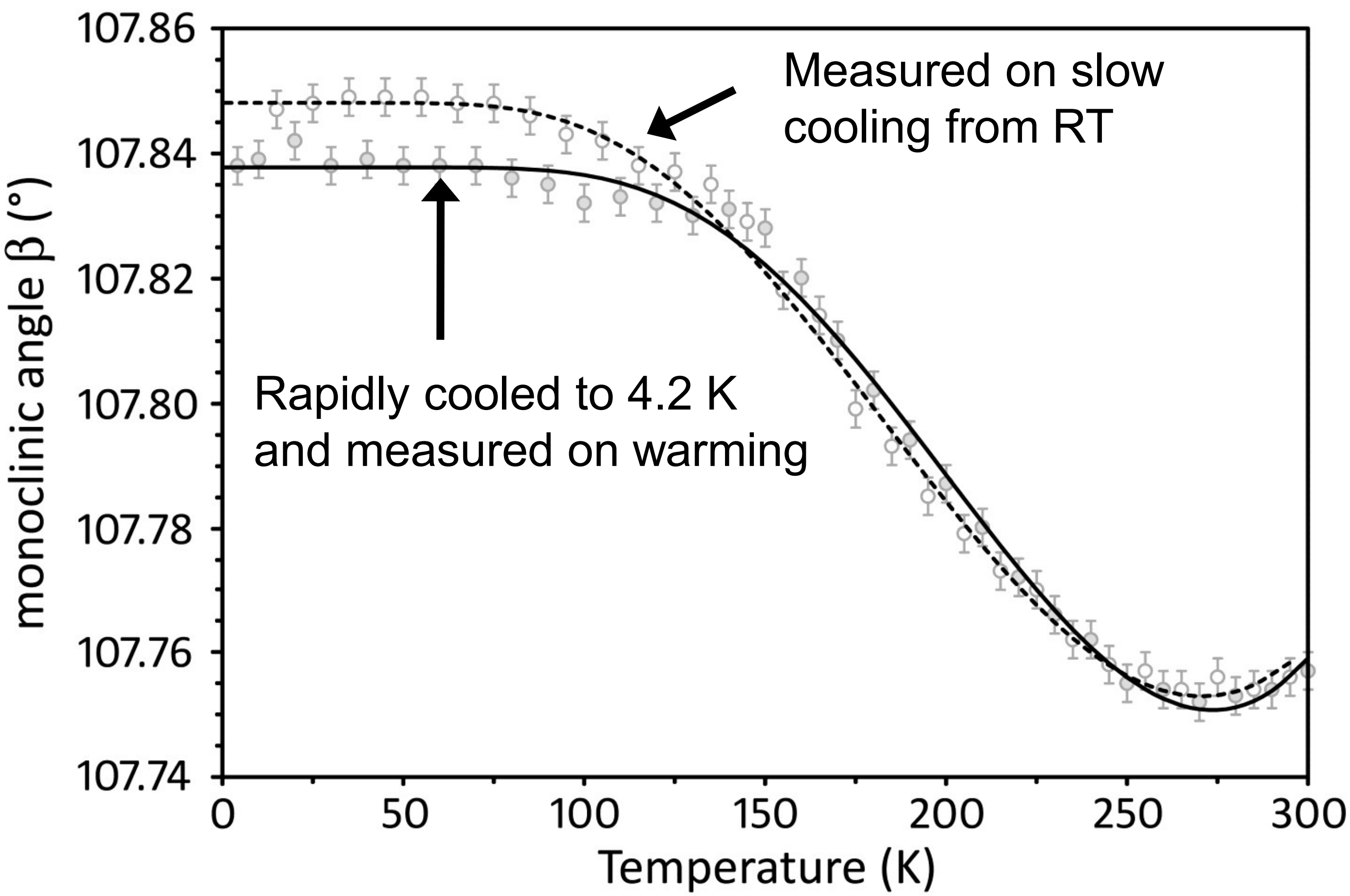
Enthalpy of fusion, ΔH_m calculated from the new equation of state



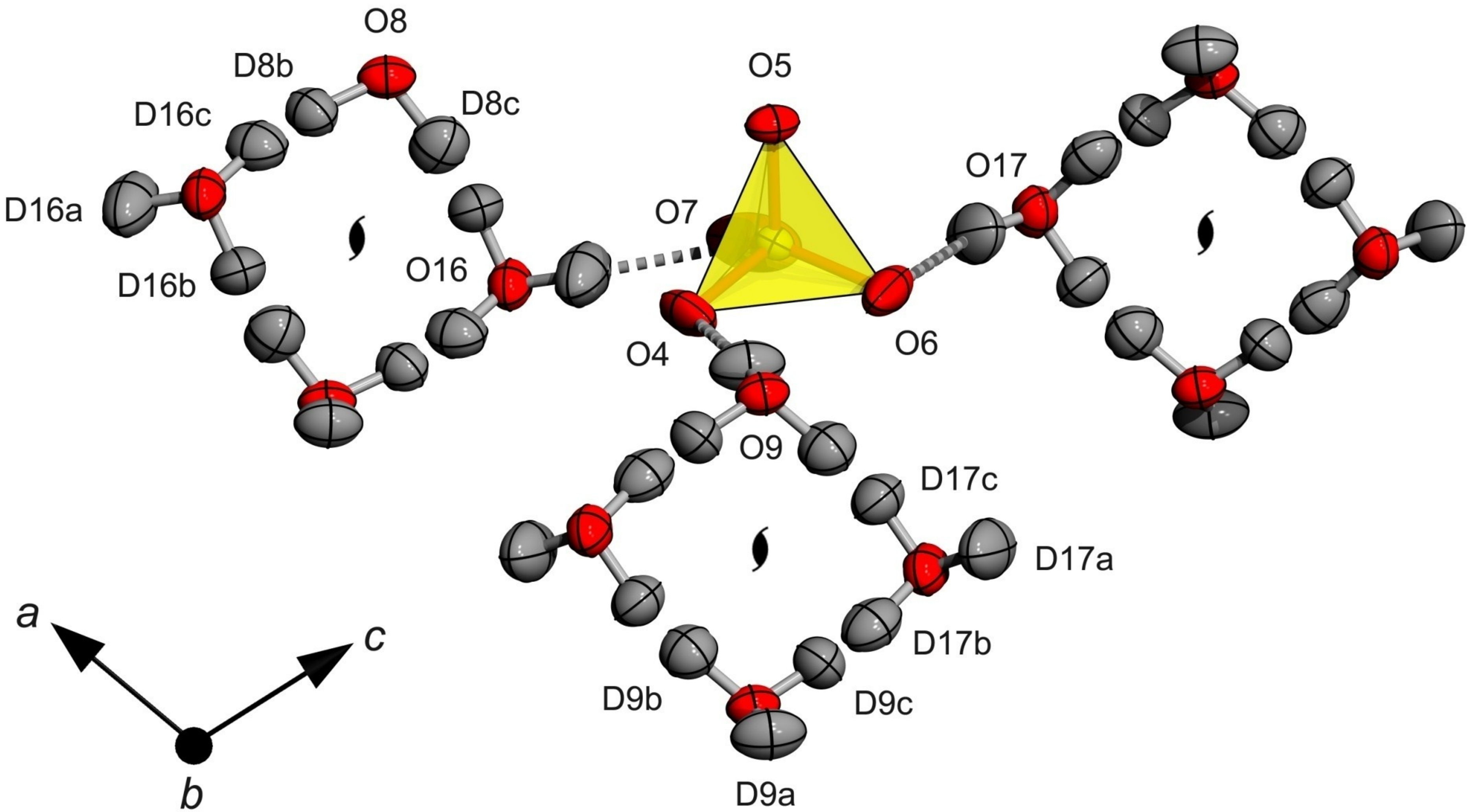
$$\Delta H_m = (dP/dT) \cdot T \cdot \Delta V_m$$

Case study 4:

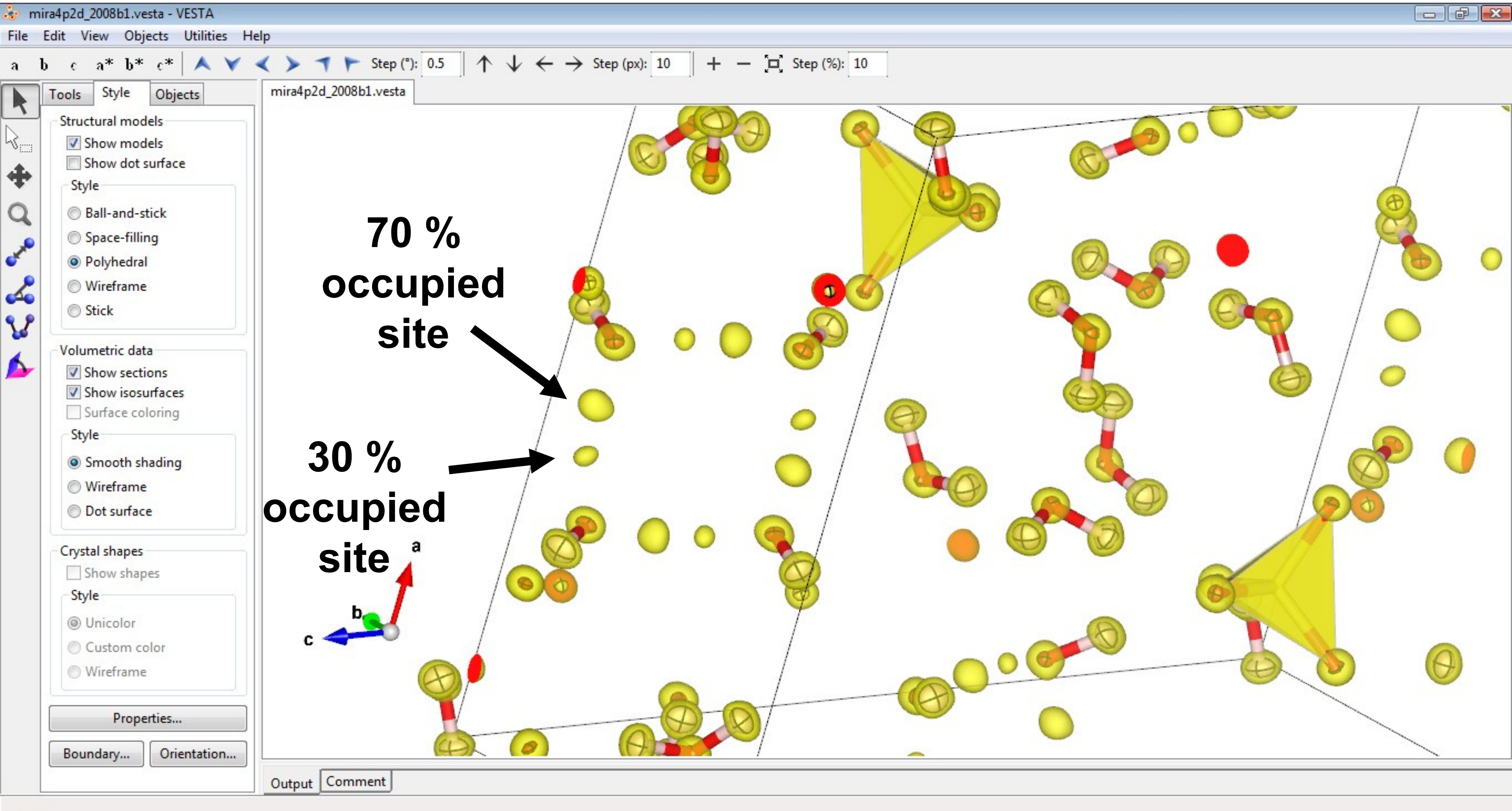
Understanding the thermal expansion of mirabilite from single-crystal data



The mirabilite structure contains two symmetry independent rings of orientationally disordered water molecules. At room T, the hydrogen atom sites in the rings are apparently half-occupied.



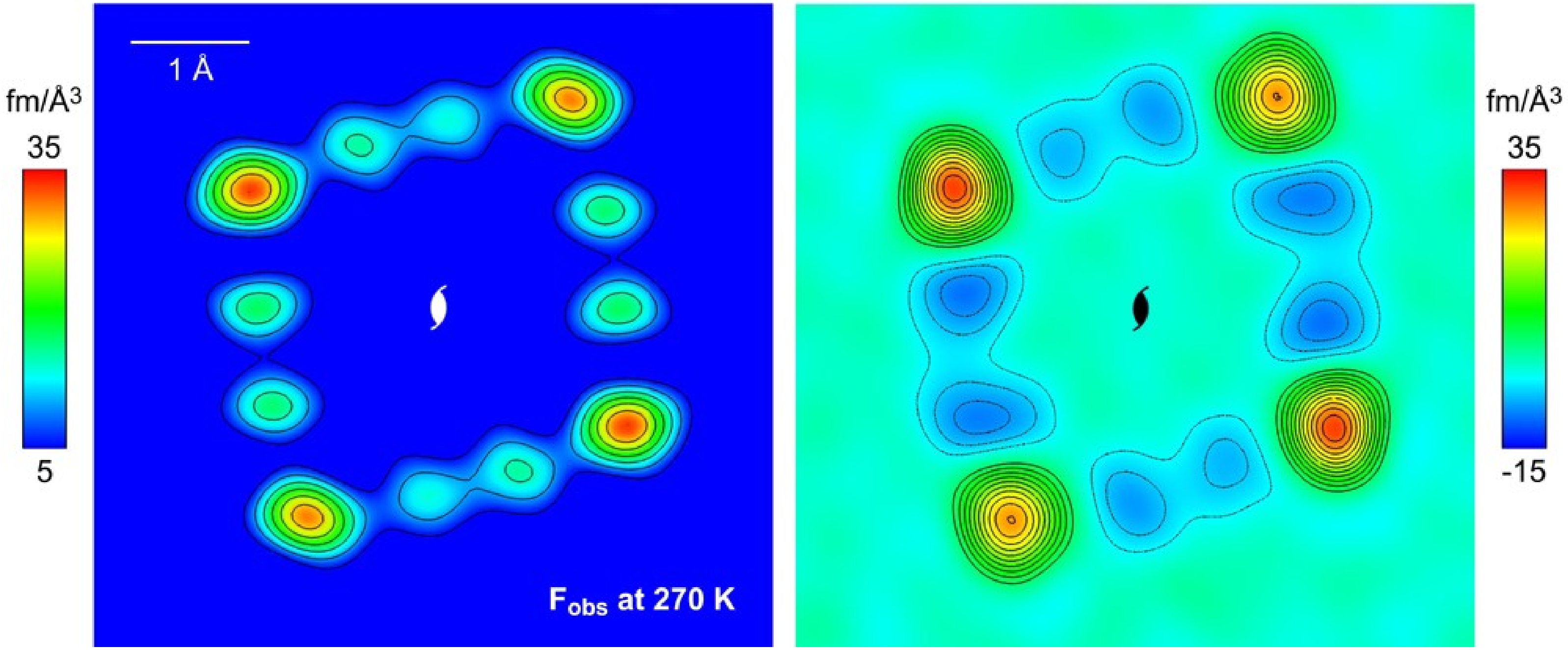
VESTA is a useful tool for visualising scattering density maps



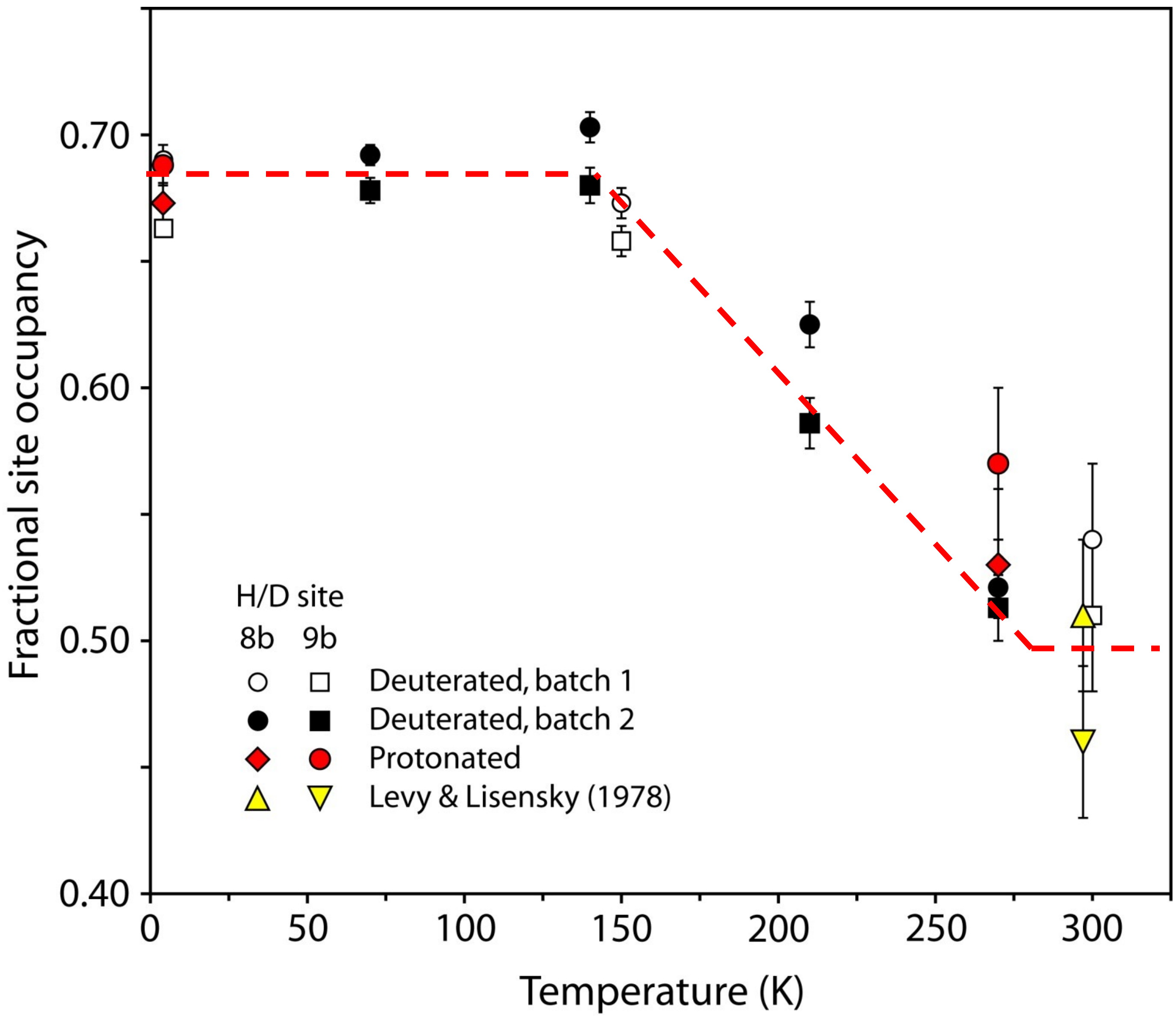
Results

Twenty degrees below room T, we find that the hydrogen atoms sites in the square rings are completely disordered (50 % occupancy) in both ordinary and heavy mirabilite

Note that deuterons produce positive peaks in the F_{obs} maps whereas protons (with a negative scattering length) produce holes, or negative peaks.



Variation in site occupancies as a function of temperature from SXD data



Thanks to all the colleagues who have made this work possible, including

Ian Wood, Matt Tucker, Bill Marshall, Kevin Knight, and the many ISIS Technical & Support staff.

Thanks also to the STFC ISIS Neutron Source for the beam-time required to carry out these measurements.


Thankyou!