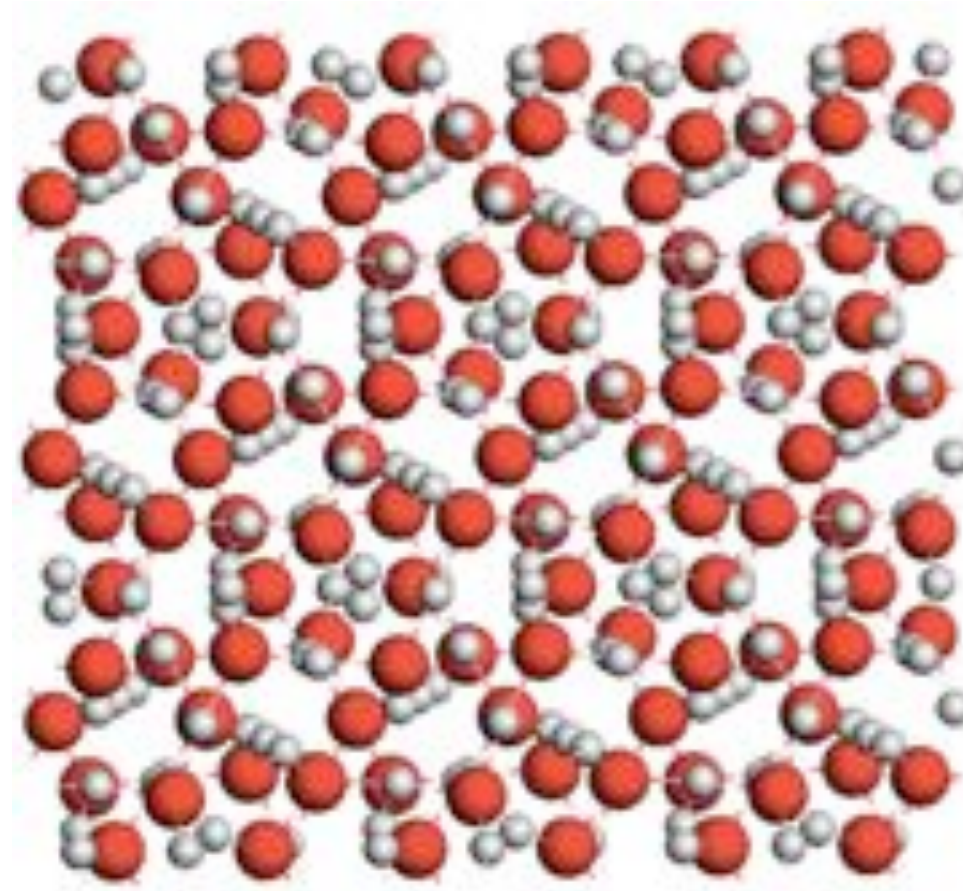


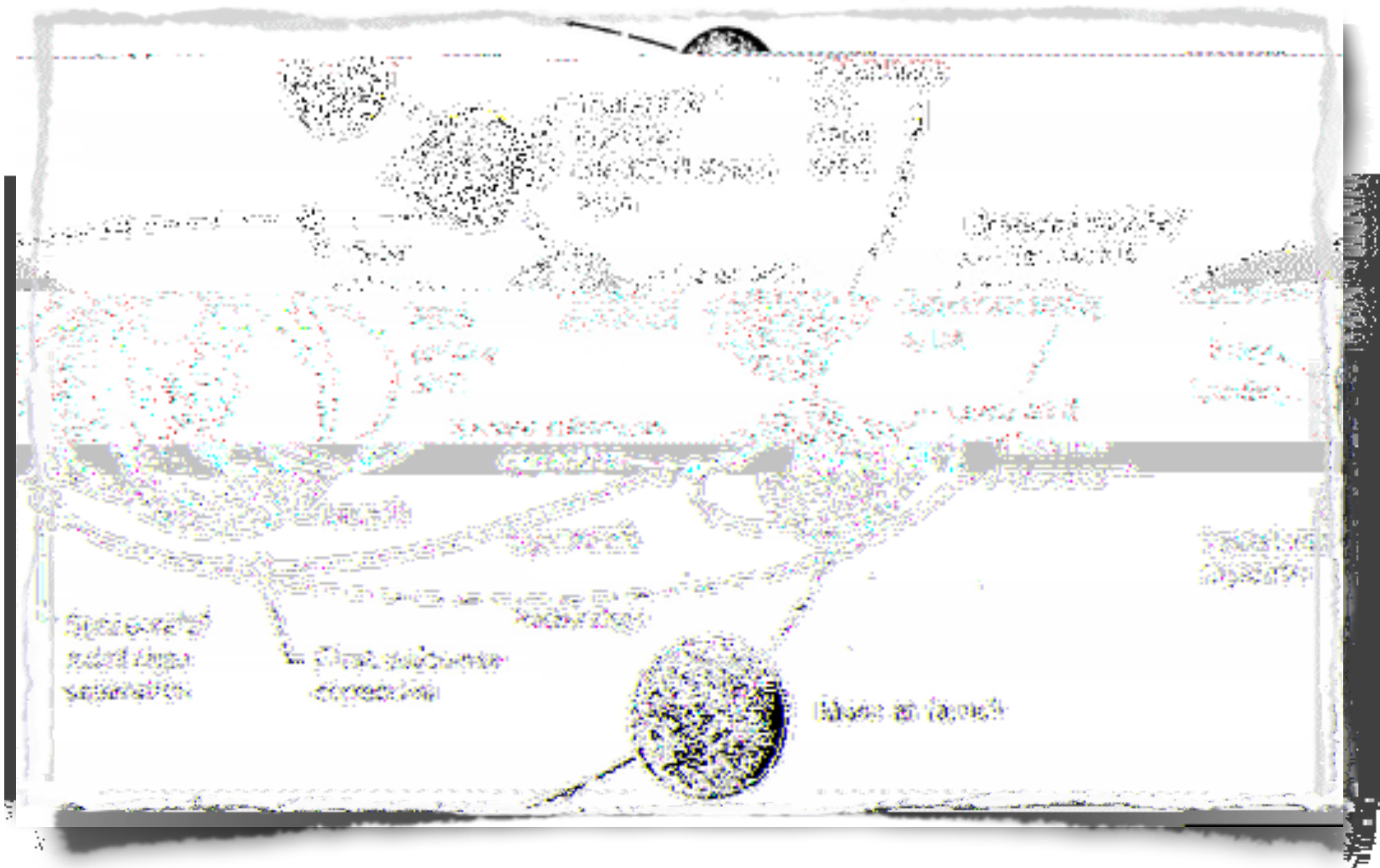
Random search: a tool for discovery and the end of water?



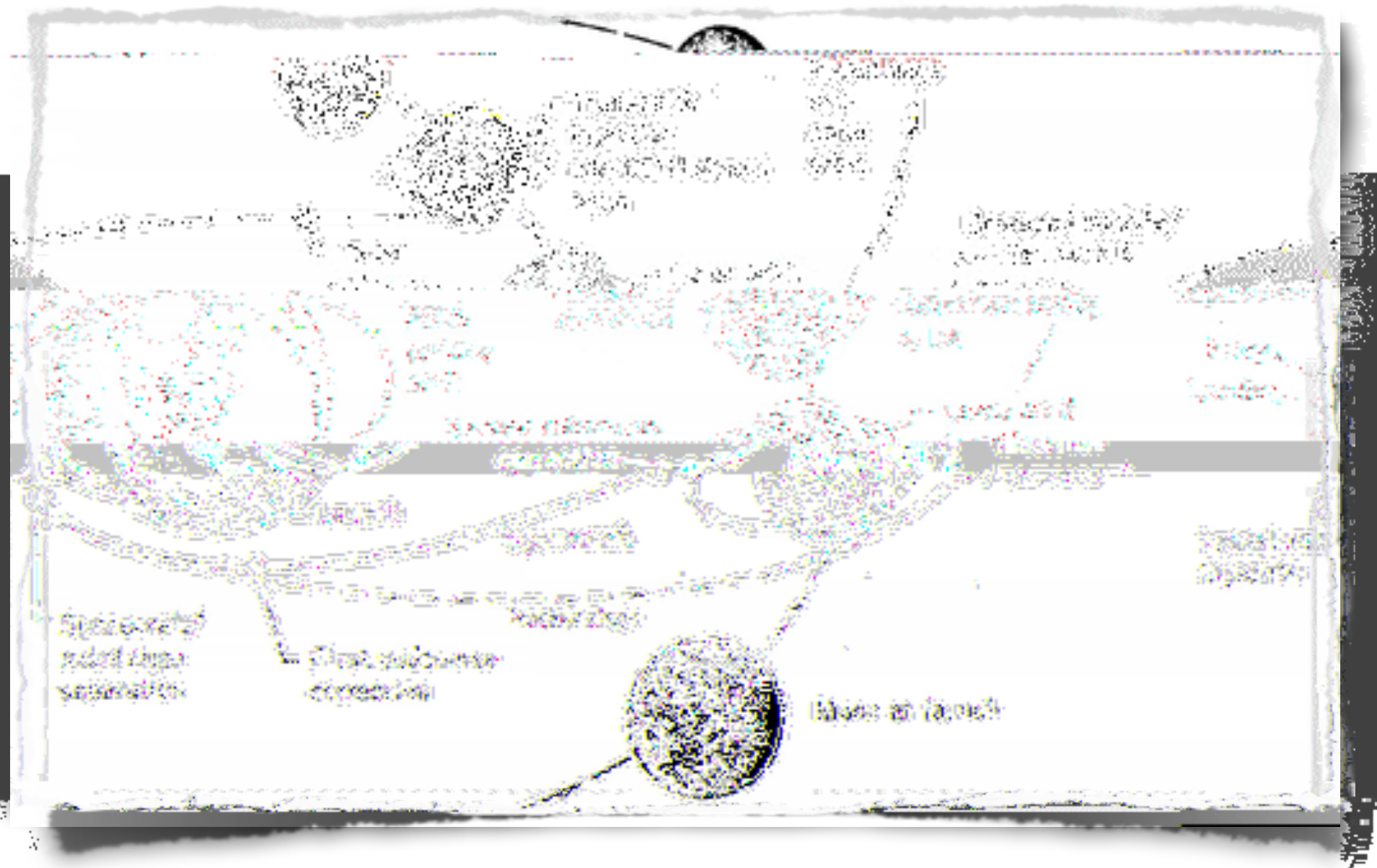
Chris J Pickard
University College London
&
London Institute for Mathematical Sciences



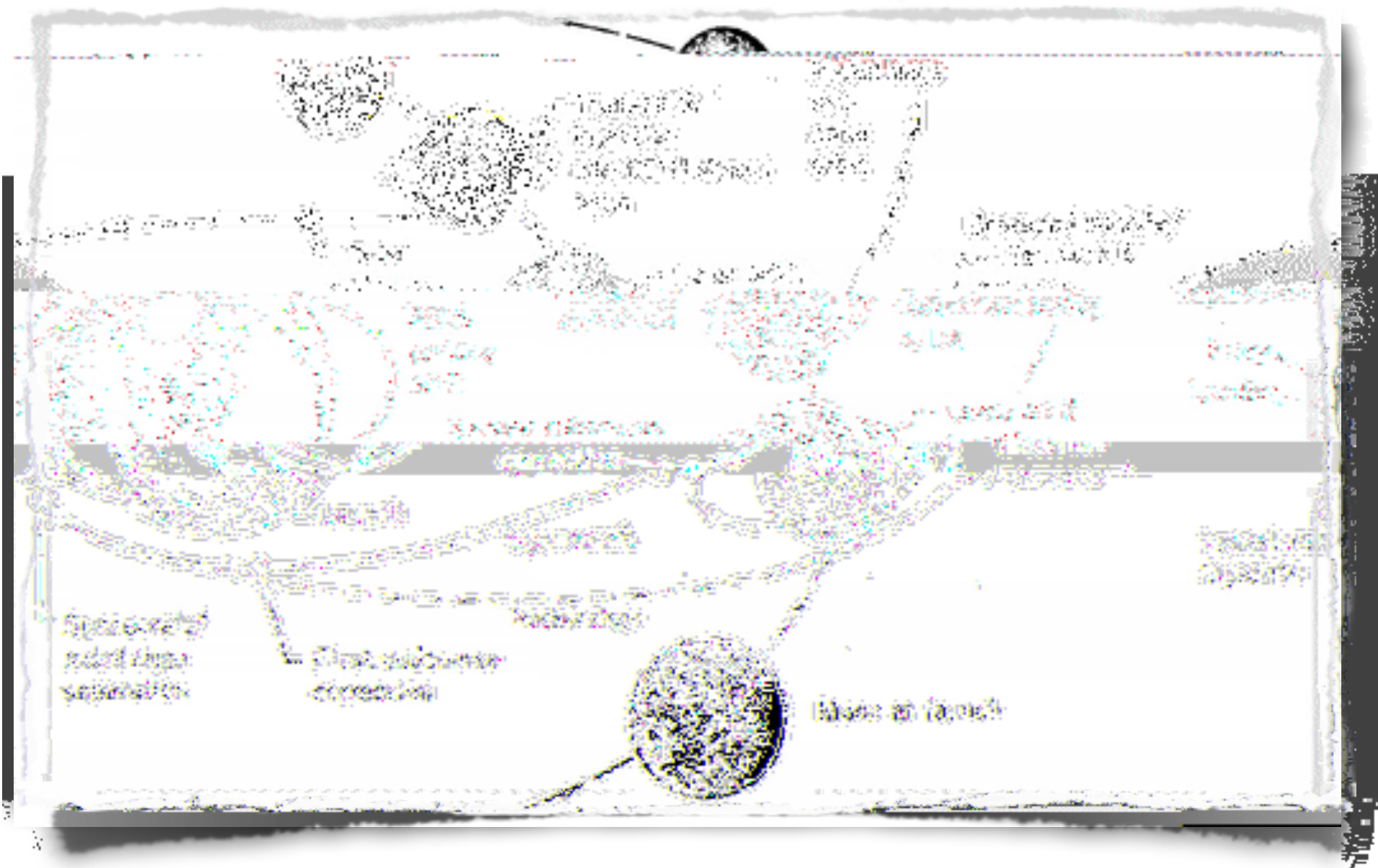
Moon Shot



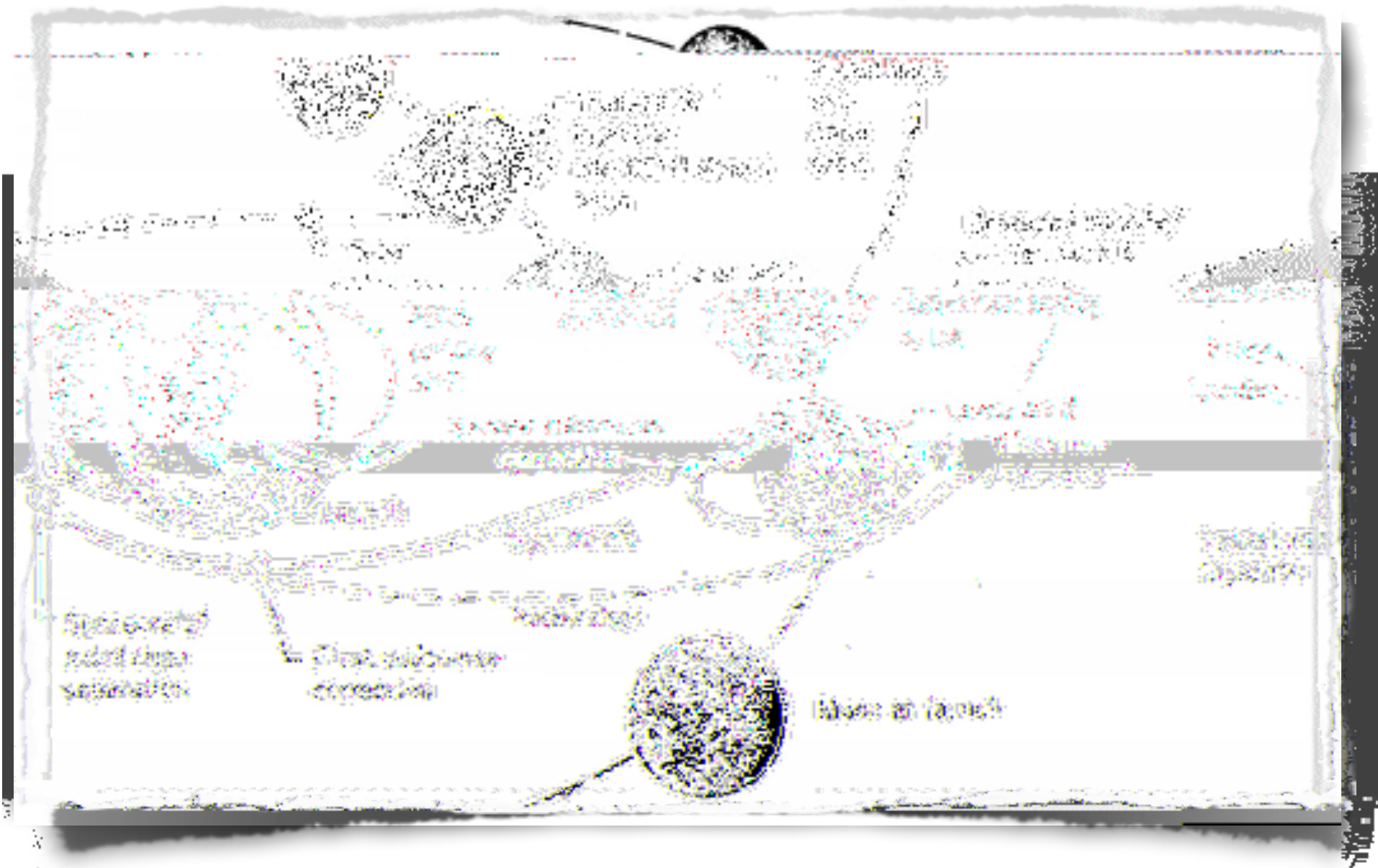
Moon Shot



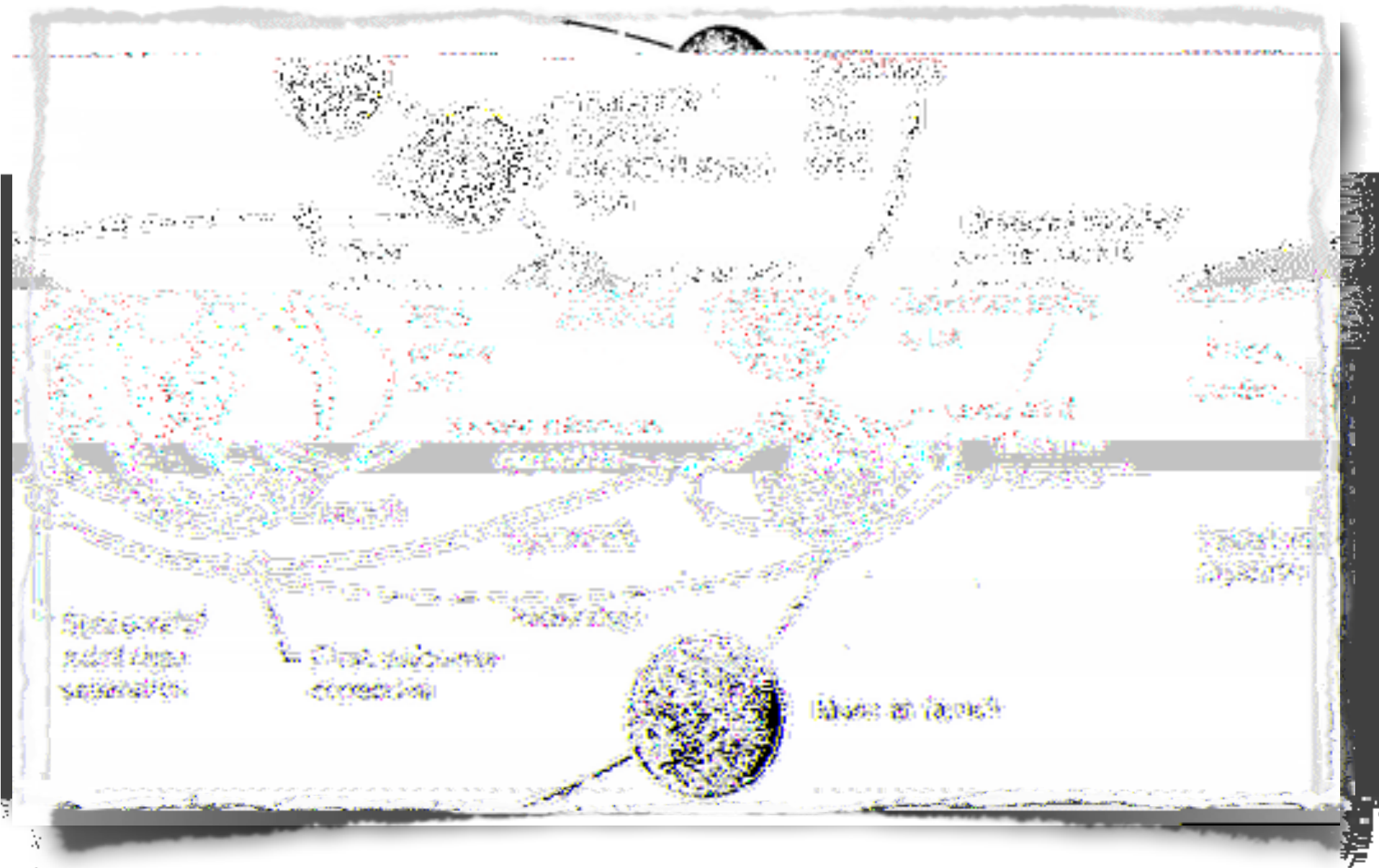
Moon Shot



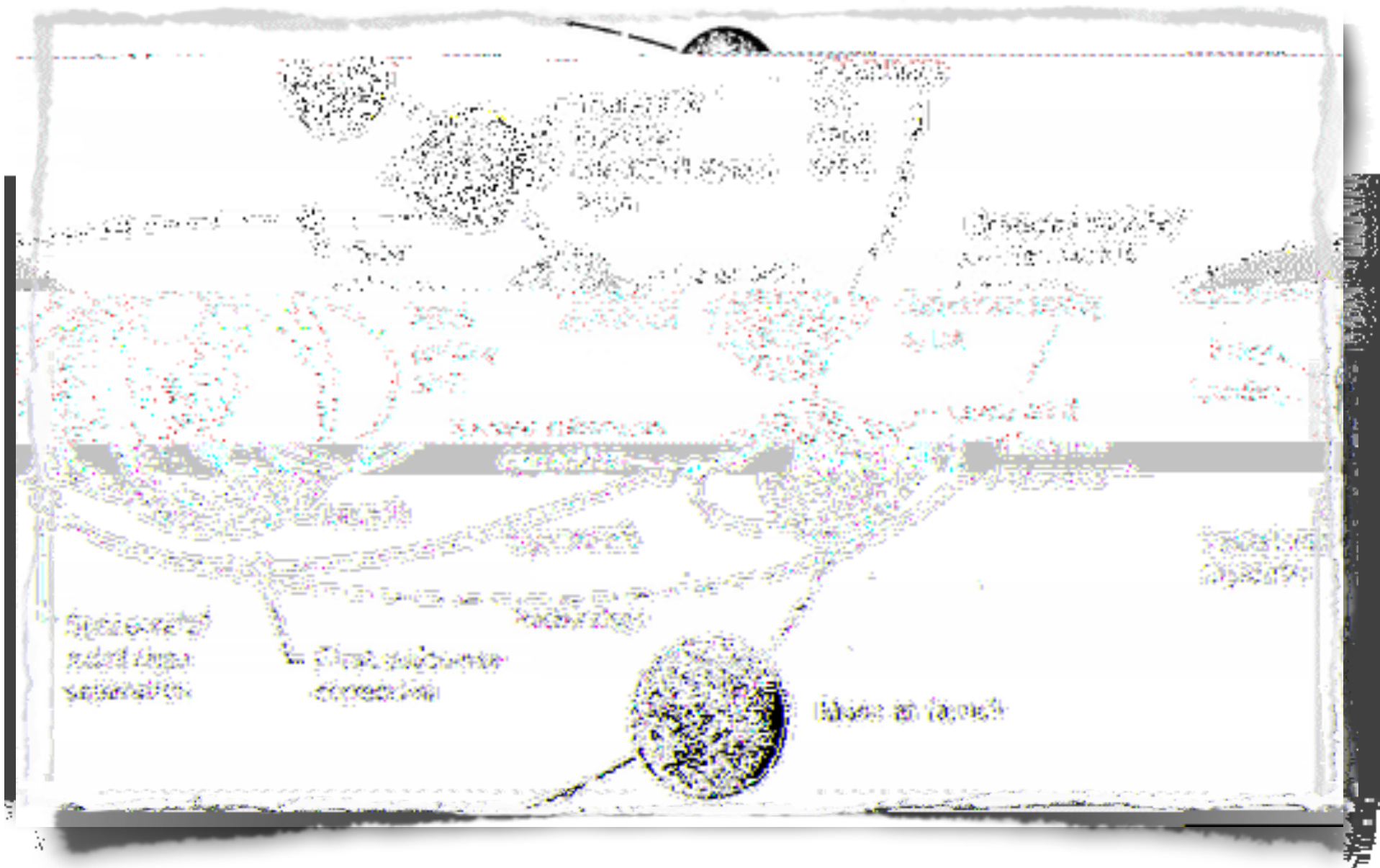
Moon Shot



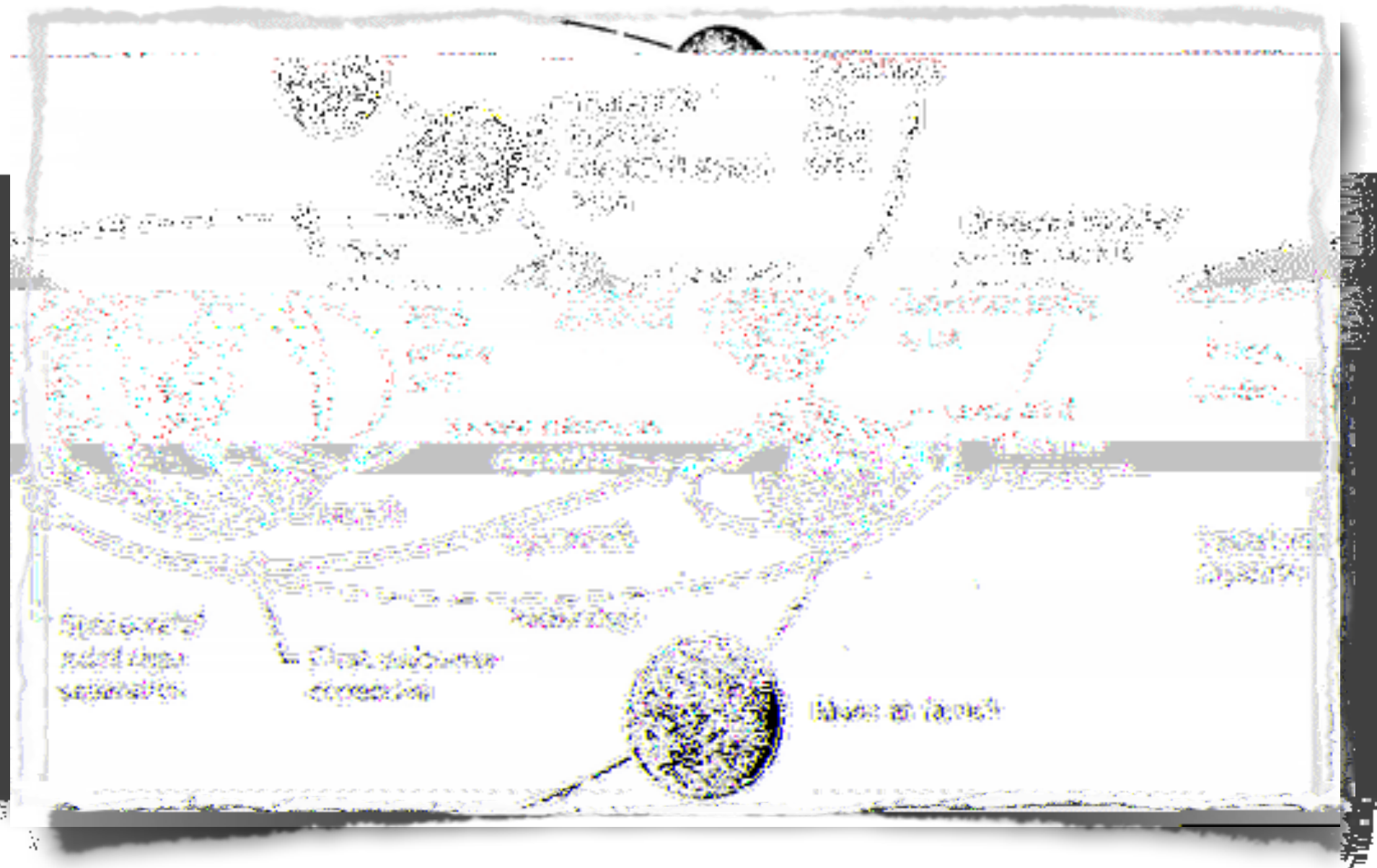
Moon Shot



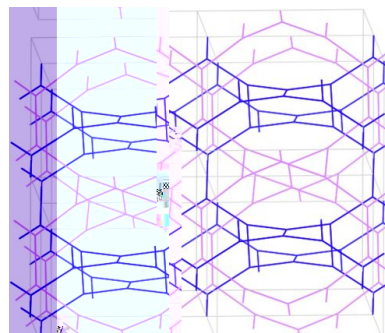
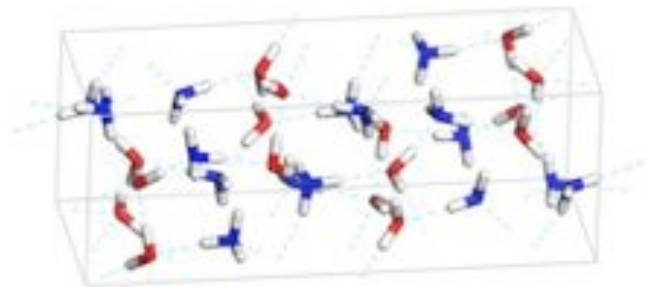
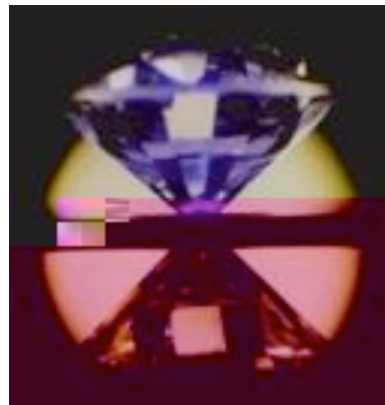
Moon Shot



Moon Shot



Condensed matter!

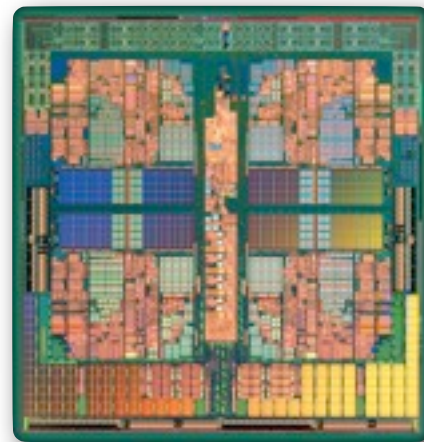


?

Theory

$$E[\rho] = F[\rho] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r}$$

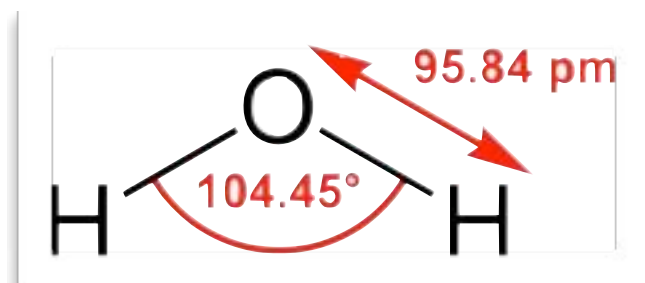
Computation



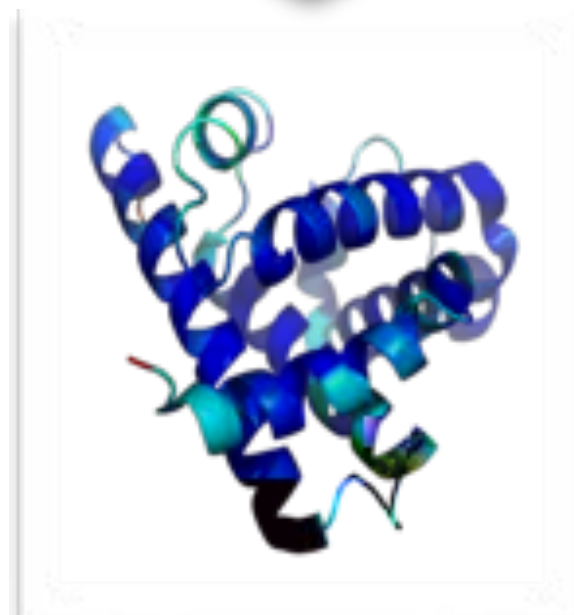
Software



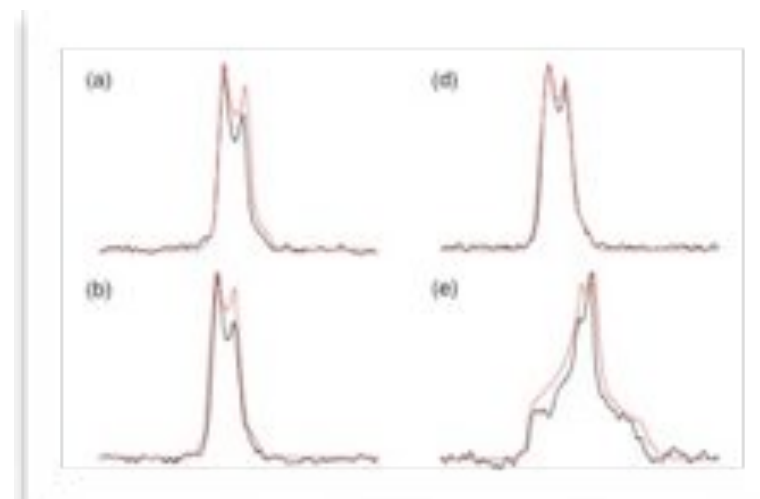
ion_atom.F90



Precision



Complexity

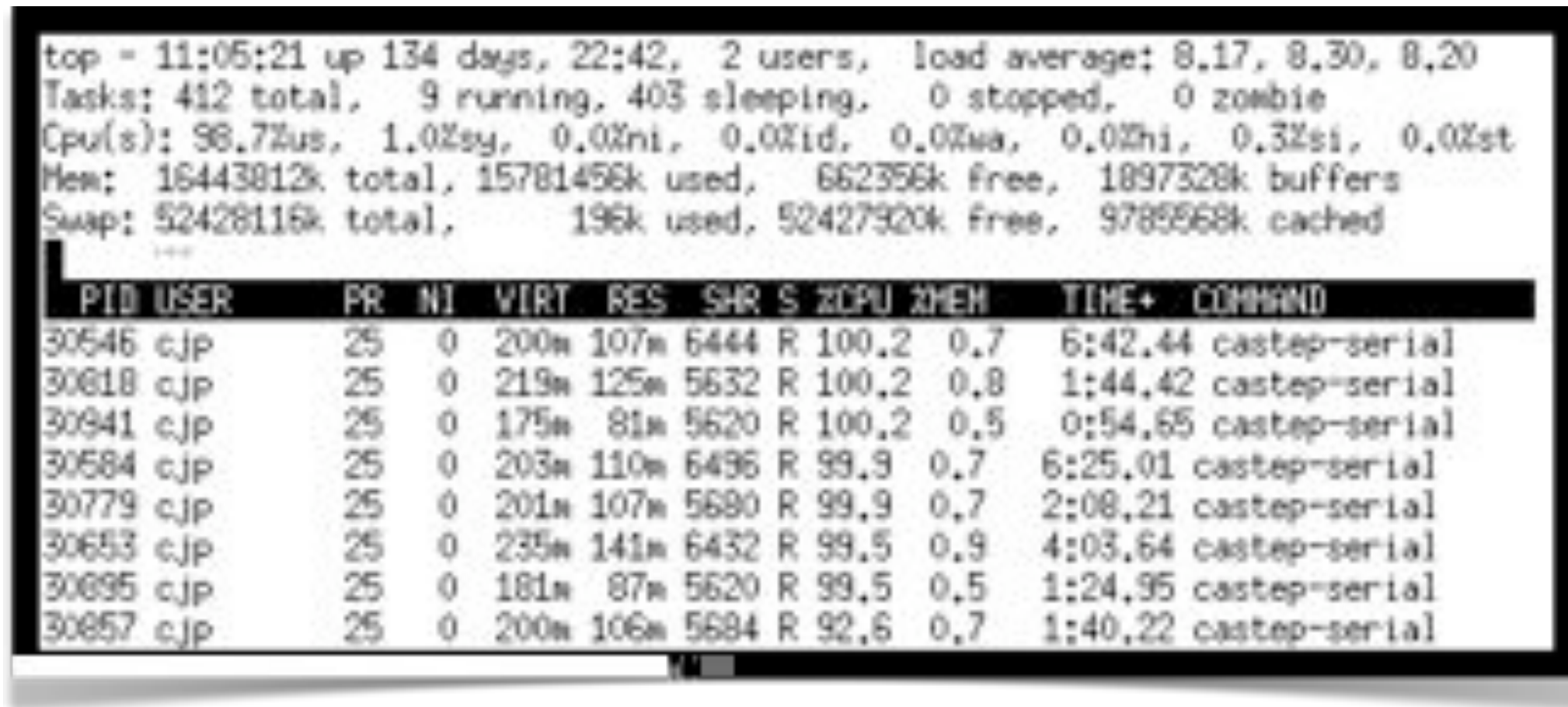


Properties

Computers



Many small calculations

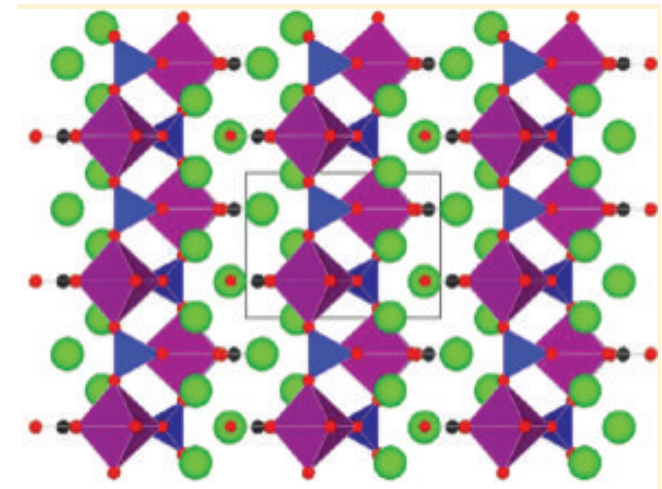


The image shows a terminal window displaying the output of the 'top' command. At the top, system statistics are listed: 'top - 11:05:21 up 134 days, 22:42, 2 users, load average: 8.17, 8.30, 8.20'. Below this, task and CPU statistics are shown: 'Tasks: 412 total, 9 running, 403 sleeping, 0 stopped, 0 zombie' and 'Cpu(s): 98.7%us, 1.0%sy, 0.0%ni, 0.0%id, 0.0%wa, 0.0%hi, 0.3%si, 0.0%st'. Memory and swap statistics follow: 'Mem: 16443812k total, 15781456k used, 662356k free, 1897328k buffers' and 'Swap: 52428116k total, 196k used, 52427920k free, 9785568k cached'. A table of processes is then displayed with columns: PID, USER, PR, NI, VIRT, RES, SHR, S, %CPU, %MEM, TIME+, and COMMAND. The table lists several processes with PID 30546 through 30857, all running as 'cjp' with priority 25 and NI 0. They are all running 'castep-serial' and show high CPU usage (92.6% to 100.2%) and varying memory usage (81m to 235m).

PID	USER	PR	NI	VIRT	RES	SHR	S	%CPU	%MEM	TIME+	COMMAND
30546	cjp	25	0	200m	107m	6444	R	100.2	0.7	6:42.44	castep-serial
30618	cjp	25	0	219m	125m	5632	R	100.2	0.8	1:44.42	castep-serial
30641	cjp	25	0	175m	81m	5620	R	100.2	0.5	0:54.65	castep-serial
30584	cjp	25	0	203m	110m	6496	R	99.9	0.7	6:25.01	castep-serial
30779	cjp	25	0	201m	107m	5680	R	99.9	0.7	2:08.21	castep-serial
30653	cjp	25	0	235m	141m	6432	R	99.5	0.9	4:03.64	castep-serial
30695	cjp	25	0	181m	87m	5620	R	99.5	0.5	1:24.95	castep-serial
30857	cjp	25	0	200m	106m	5684	R	92.6	0.7	1:40.22	castep-serial

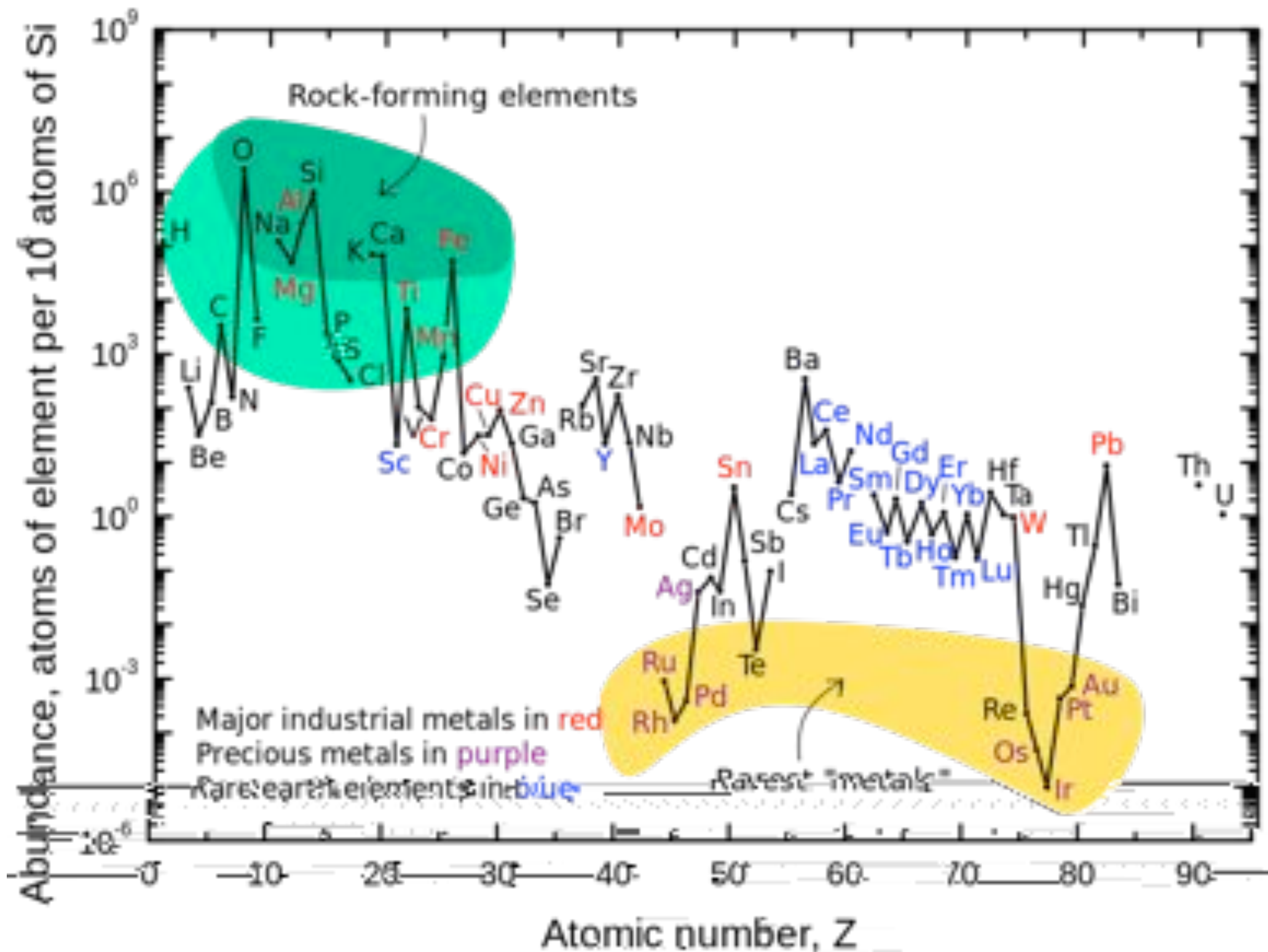
Lots of data

Materials science as search

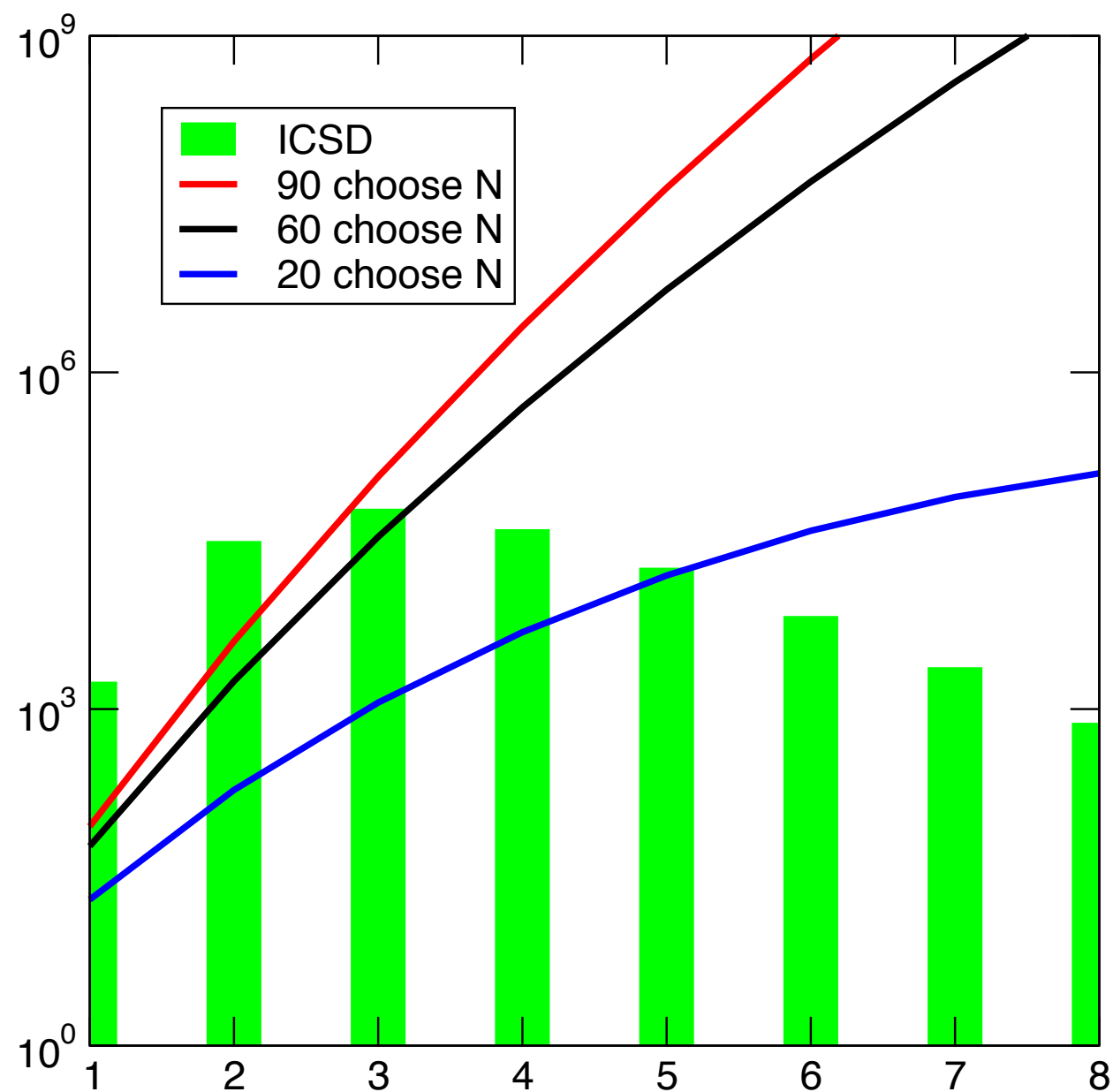


Materials Genome Initiative: A
Renaissance of American Manufacturing

The elemental palette

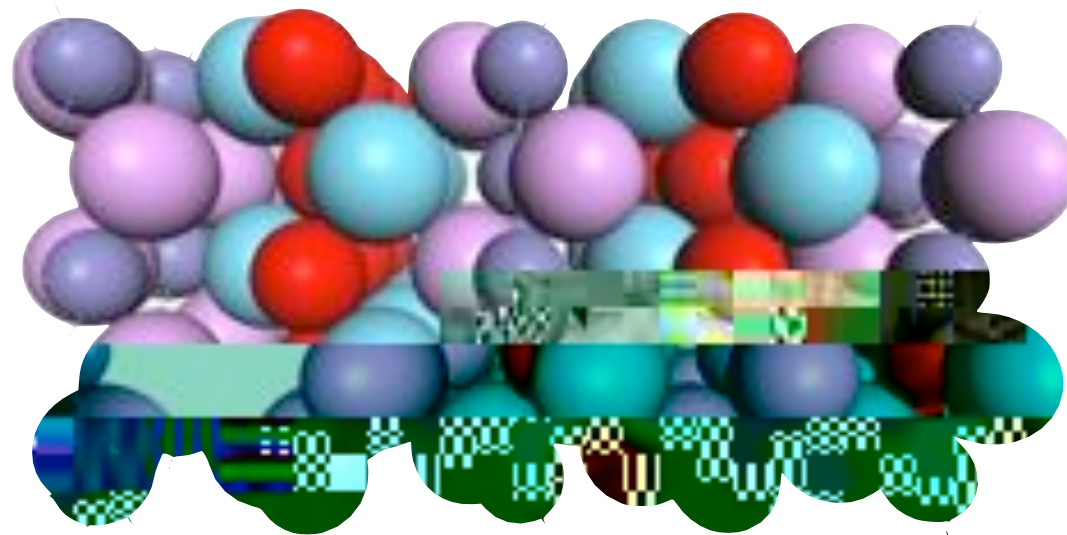


Is the ICSD empty?



A very important problem

What will a collection of atoms do? What will he do?

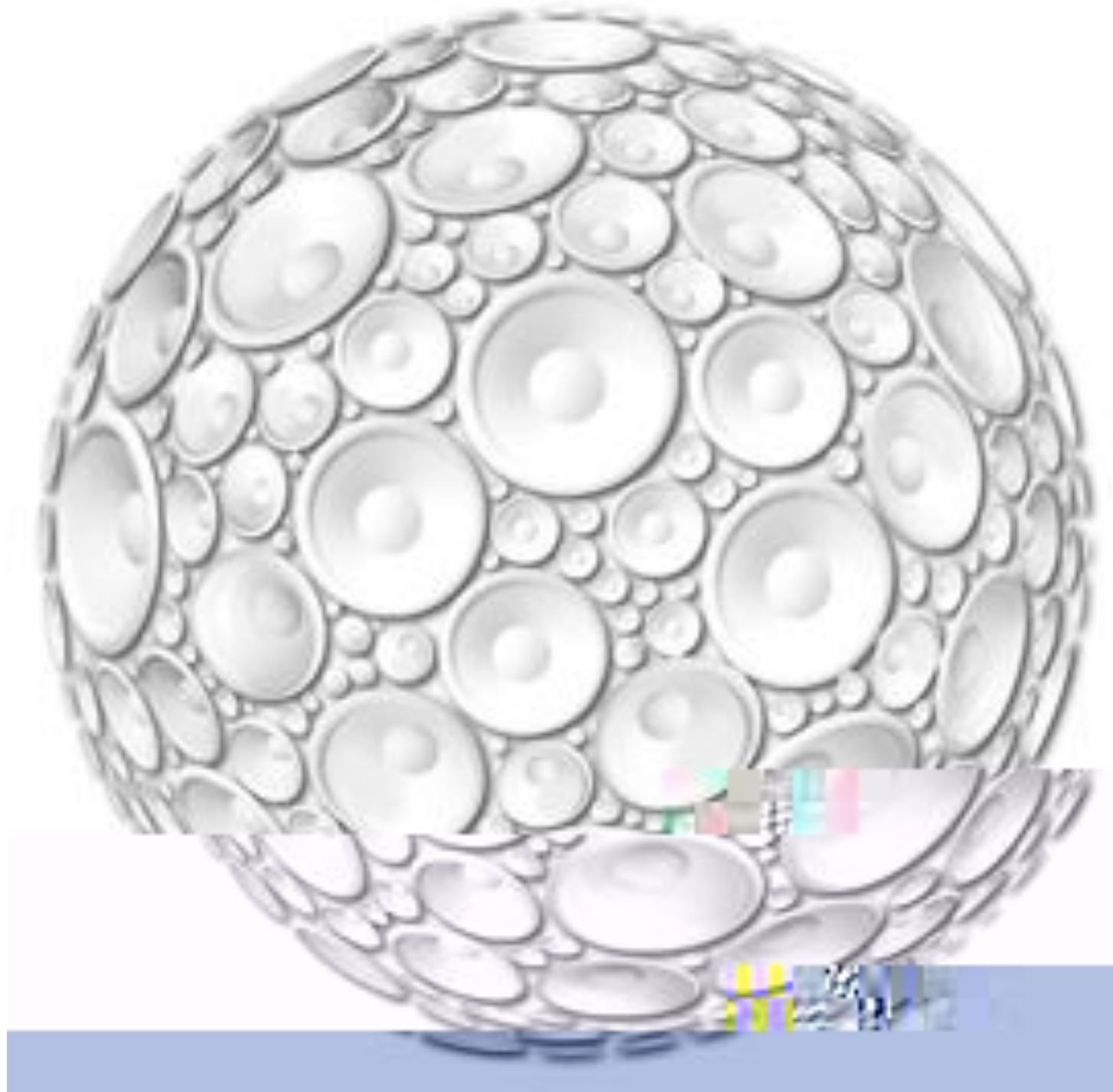


Material

Typically answered by experiment

AIRSS

Ab initio random structure searching

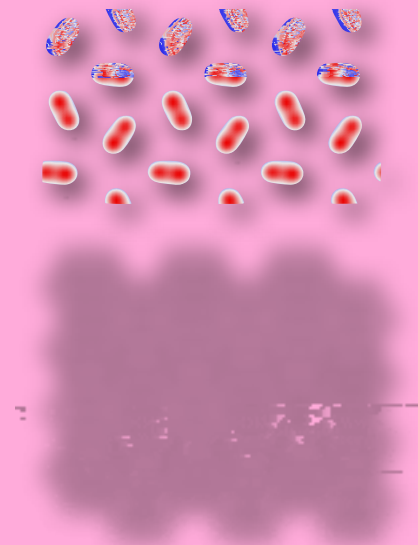


Pickard & Needs, PRL 2006 and JPCM 2011

Discovery through virtual experiments

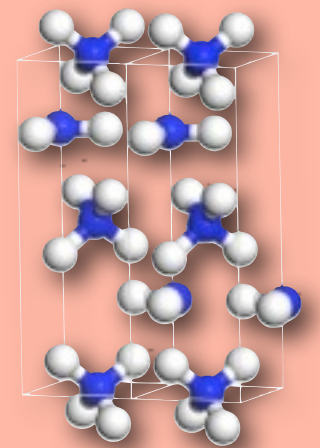
**Hydrogen is
polar and
“graphene”**

Nature Physics, 2007



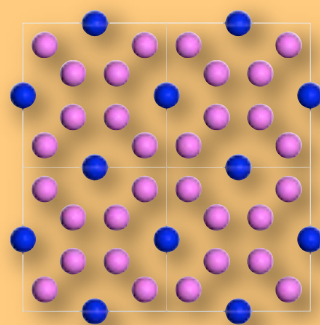
Ammonia is ionic

Nature Materials, 2008



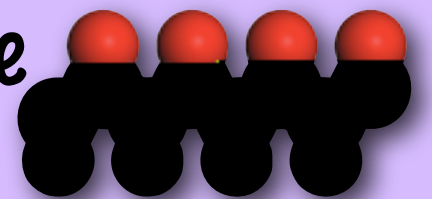
Aluminium is complex

Nature Materials, 2010

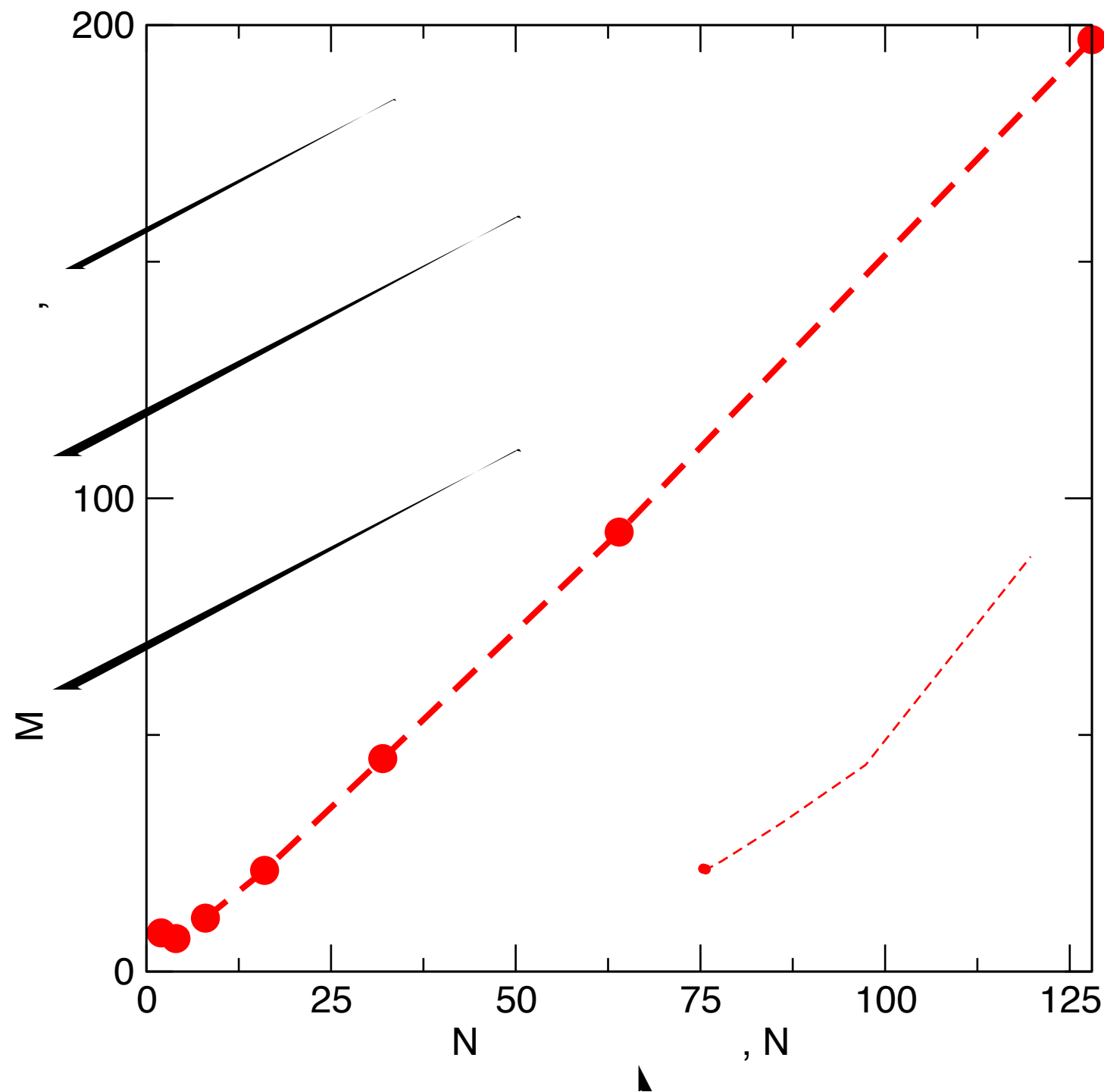


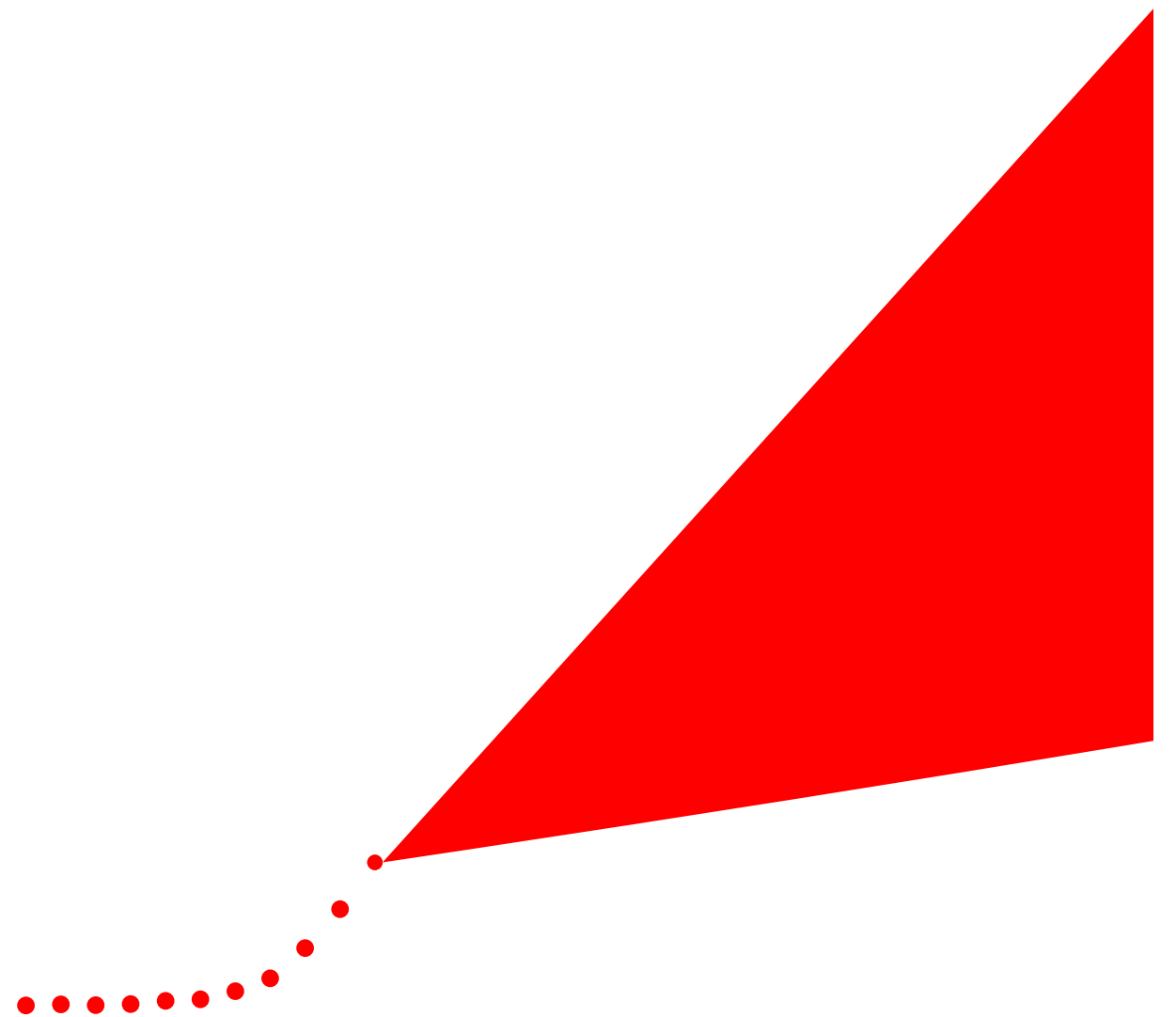
CO is not a molecule

Physical Review Letters, 2011



HCP Lennard-Jones Crystal





Constraints

Hard and soft

Stoichiometry

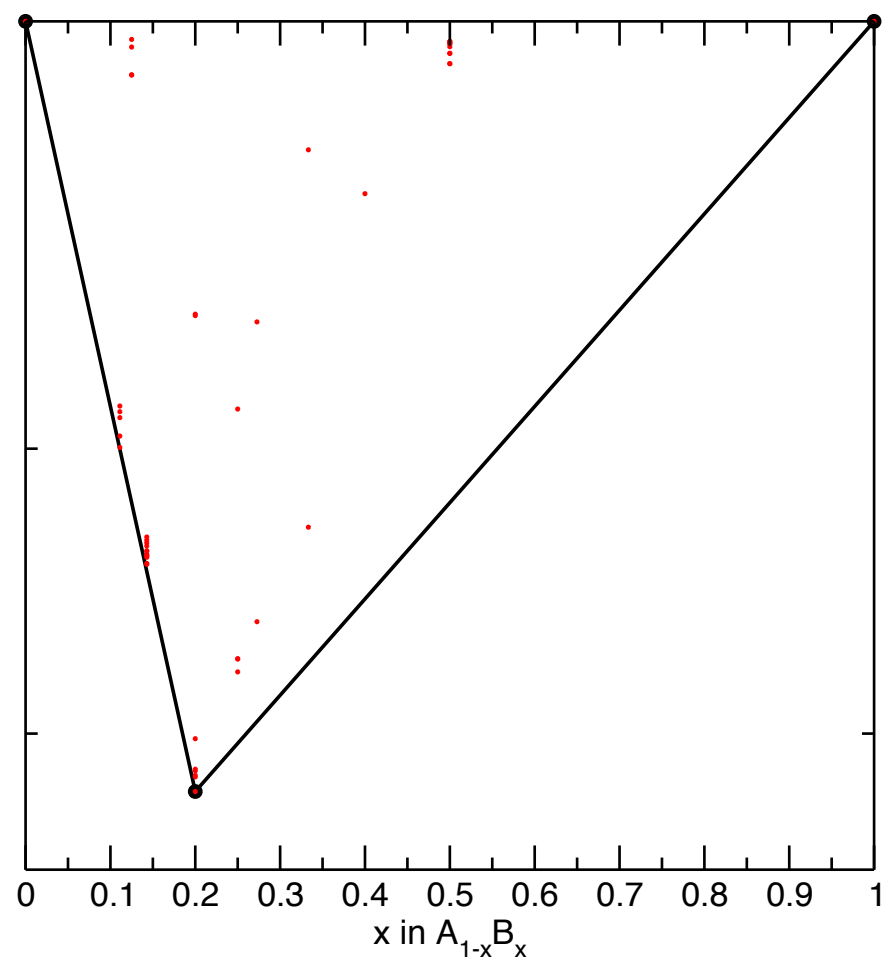
Symmetry

Structural Units

Energy

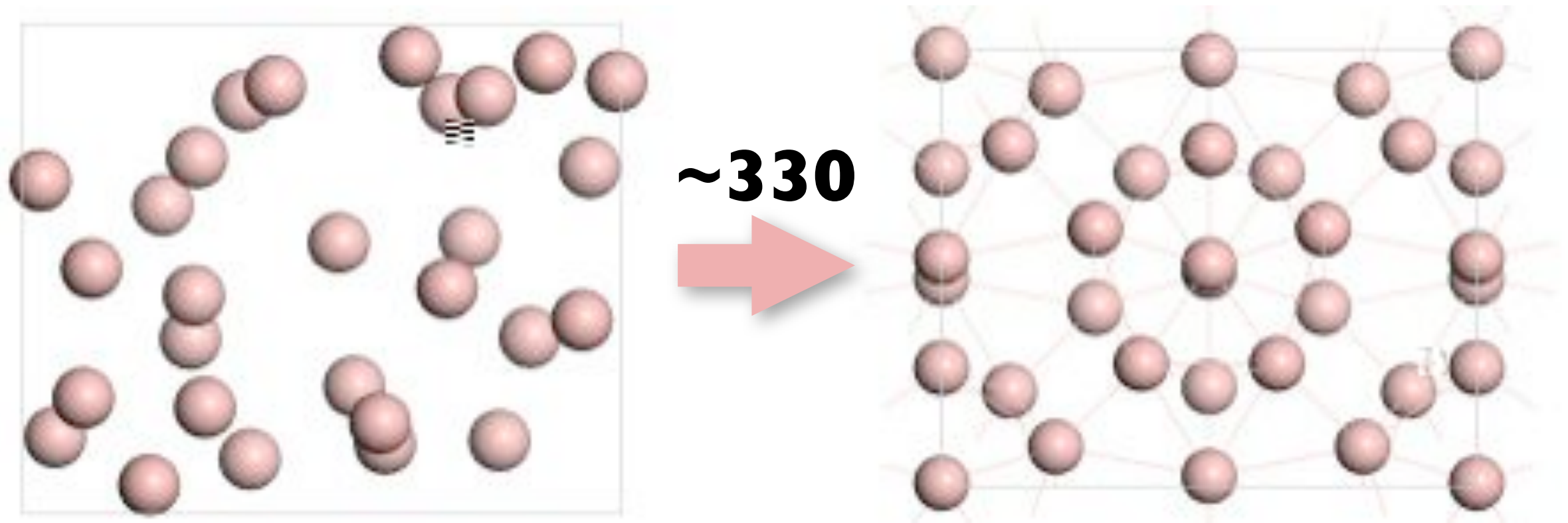
Cell shape

Experiment



Cell shape

gamma-Boron 28 atoms

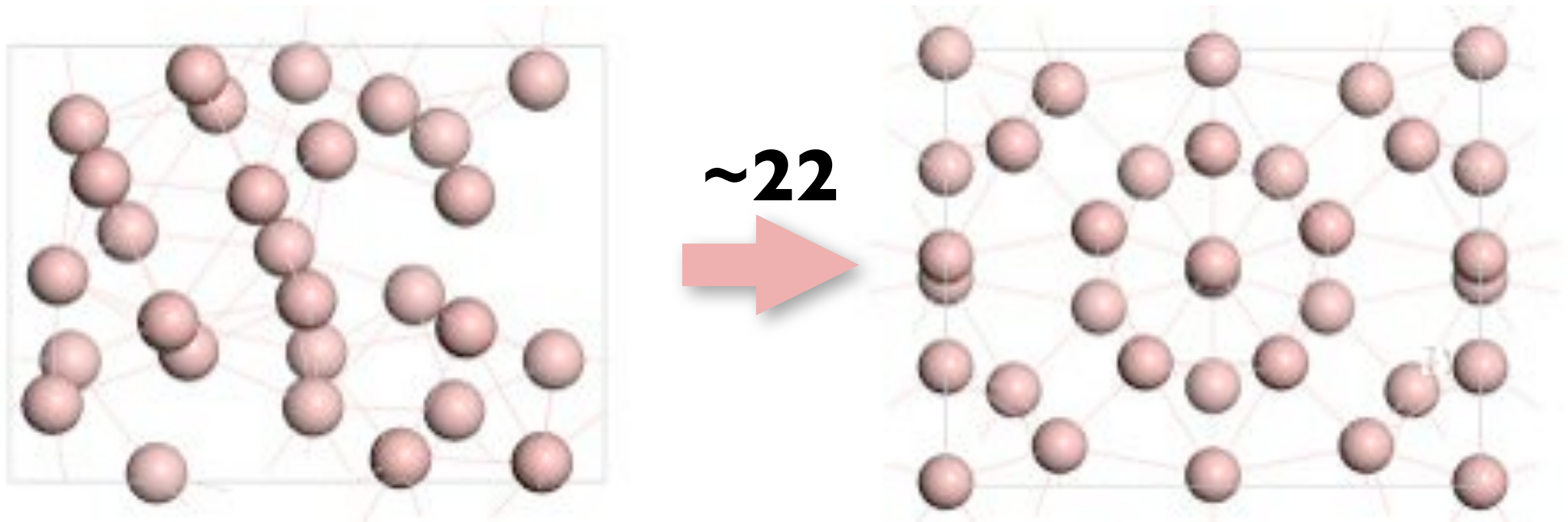
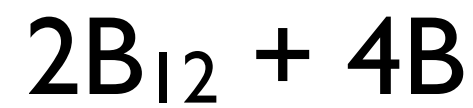


Comparing to EAs

Oganov et al *Na* e 2009 ~**550**

Ji, Wang & Ho *PCCP* 2010 ~**288**

Units



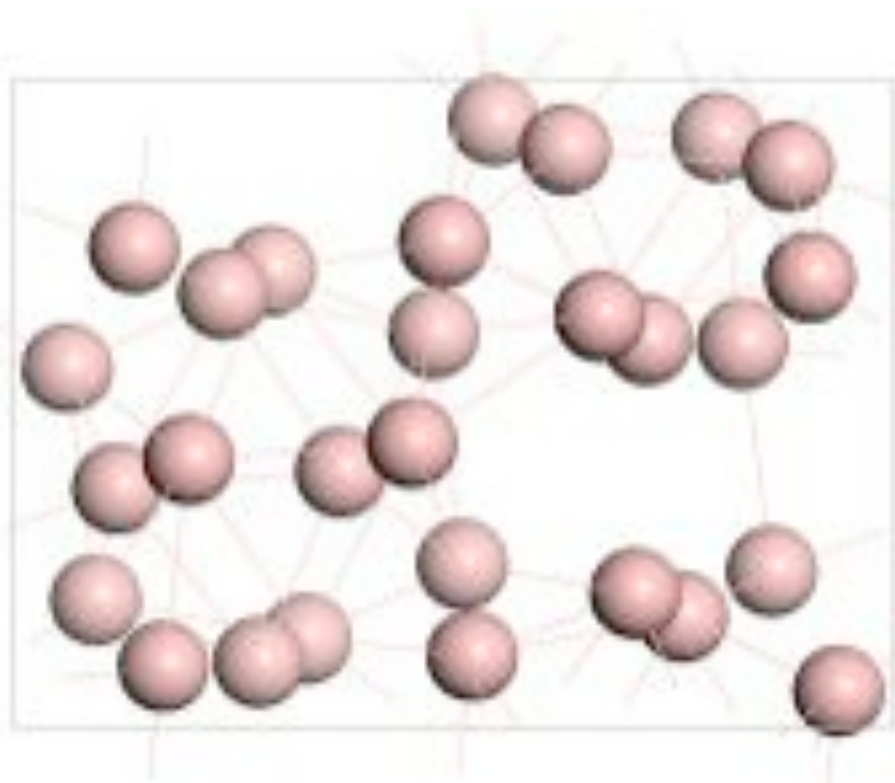
Comparing to EAs

Oganov et al *Na* e 2009 ~**550**

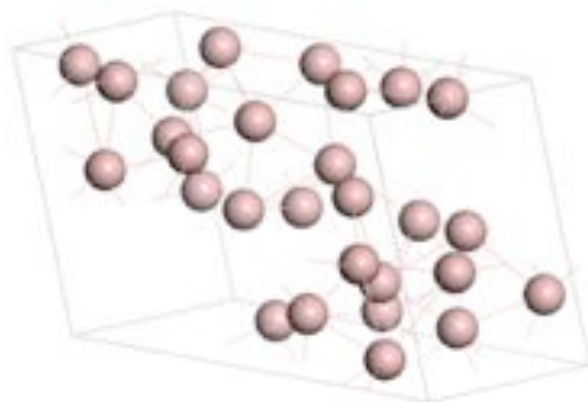
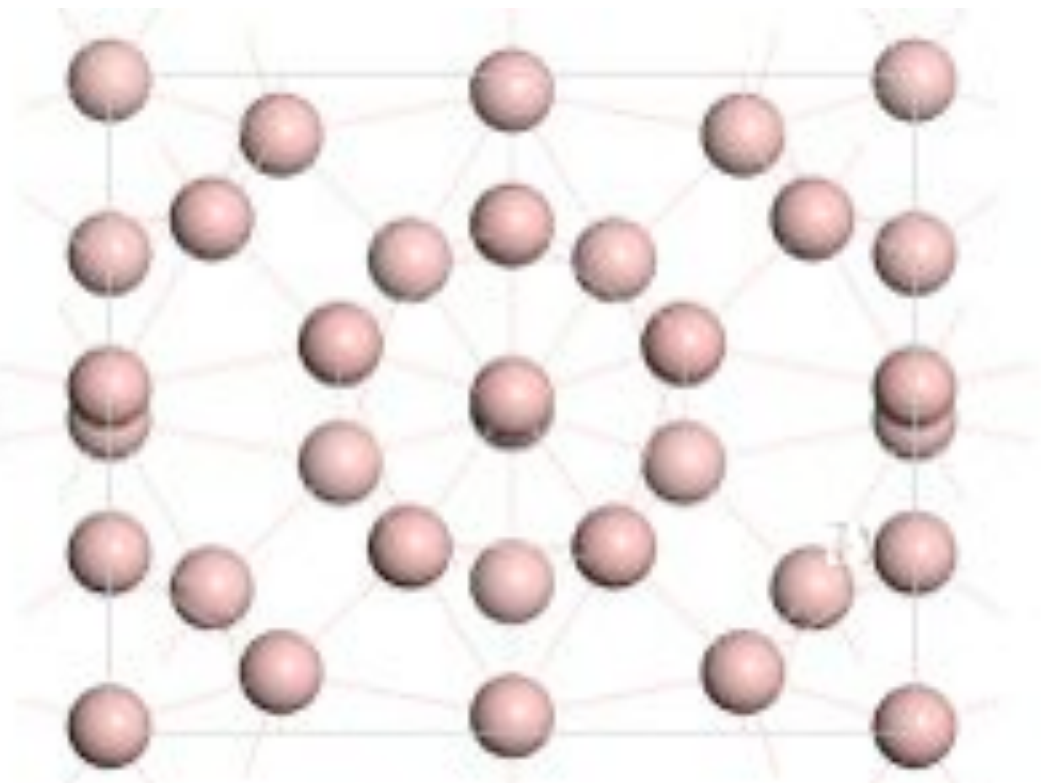
Ji, Wang & Ho *PCCP* 2010 ~**288**

Symmetry

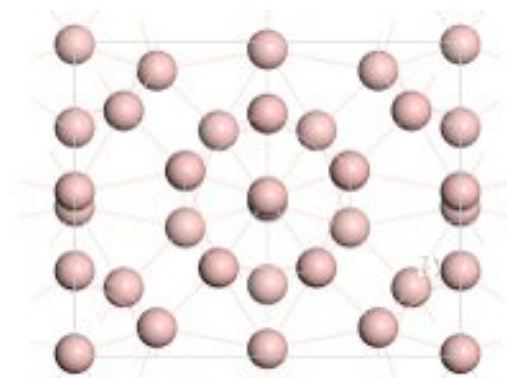
$B_{12} + 2B$, 2 symm ops



~12
Fixed cell



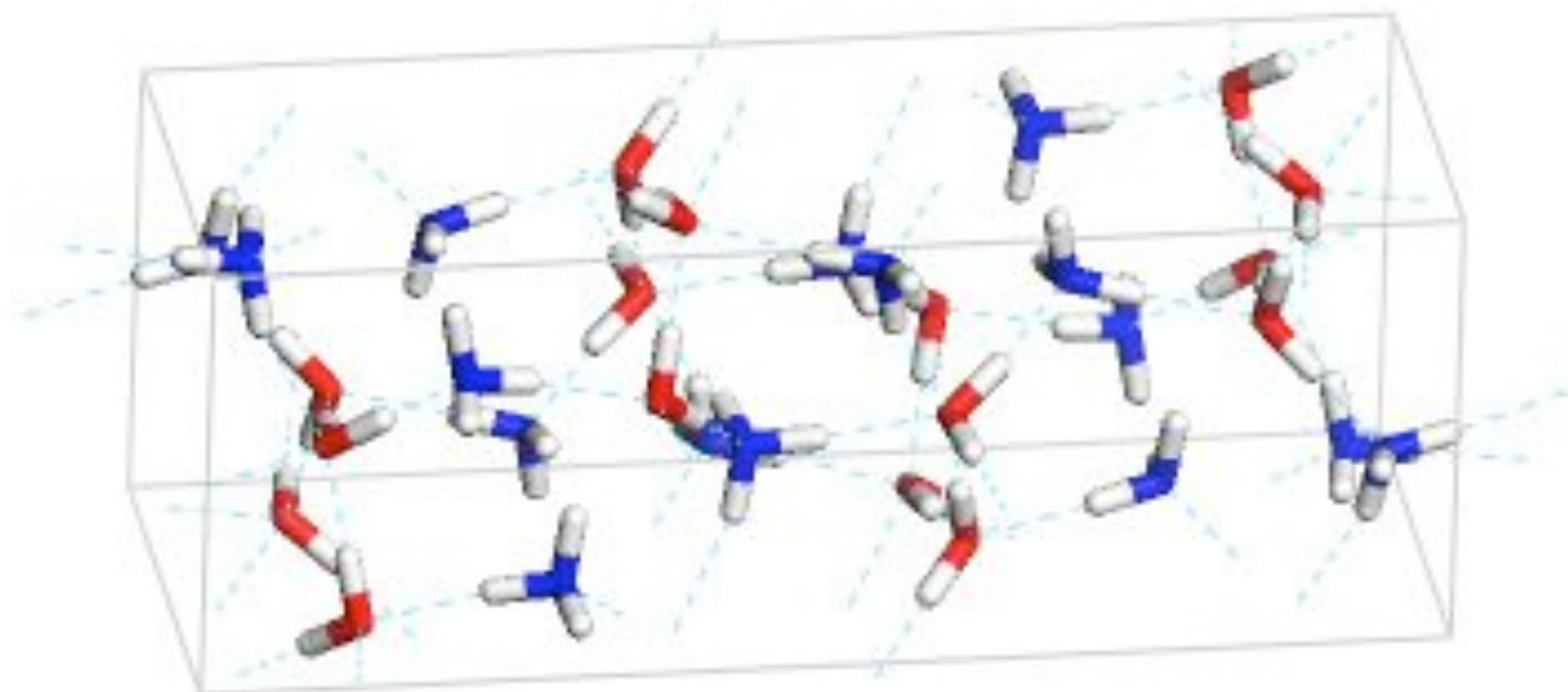
~108
Free cell



Experiment

Ammonia monohydrate

JACS, 2009 with Dom Fortes



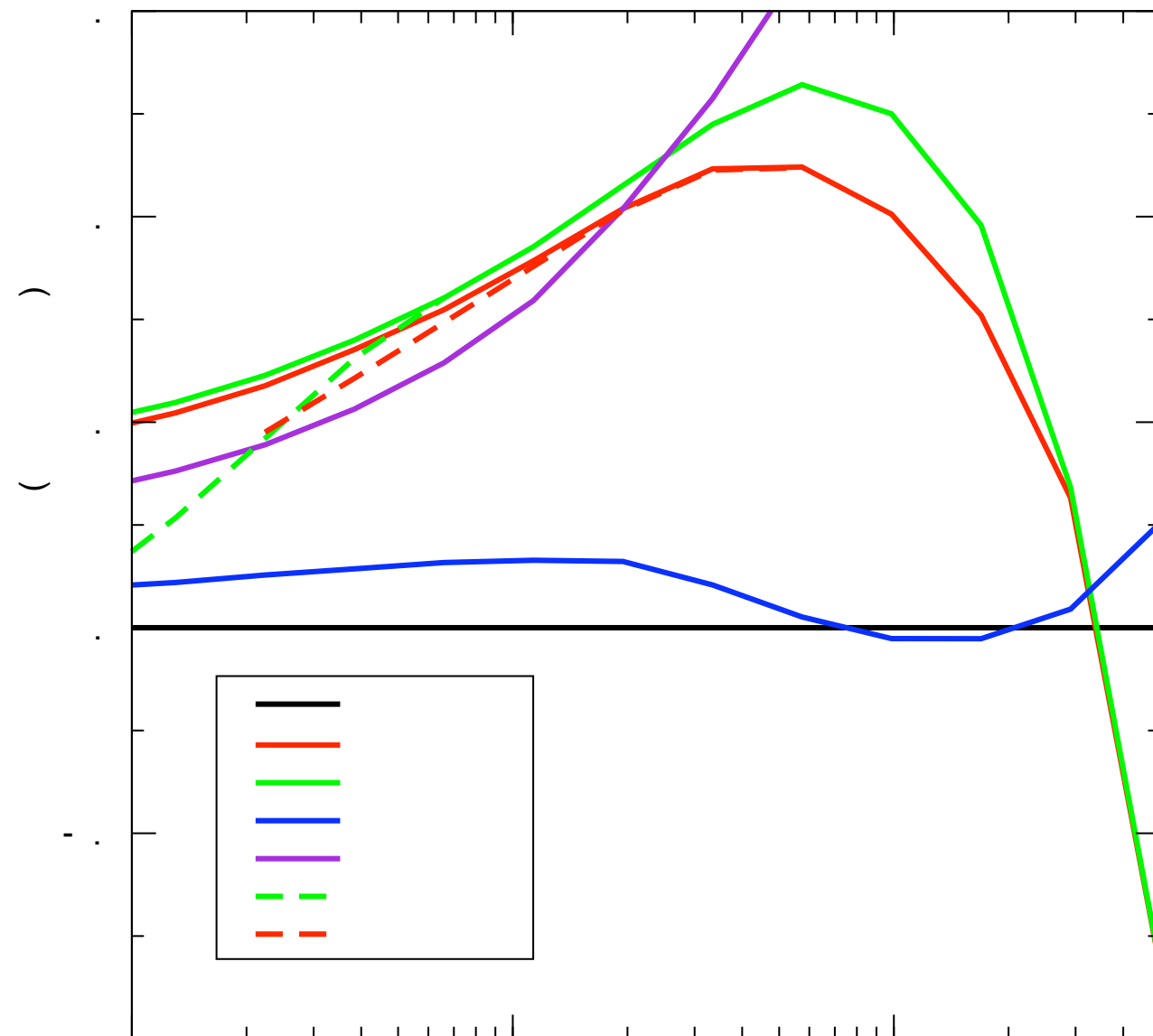
Input lattice parameters and density

Output solved crystal structure containing 112 atoms

“easy experiment, easy theory - new science”

Iron at extremes

You need good PSPs
but DFT should be fine ...



Packing fractions:
fcc/hcp 74.05%
bcc 68.01%

s-d transfer

Earth

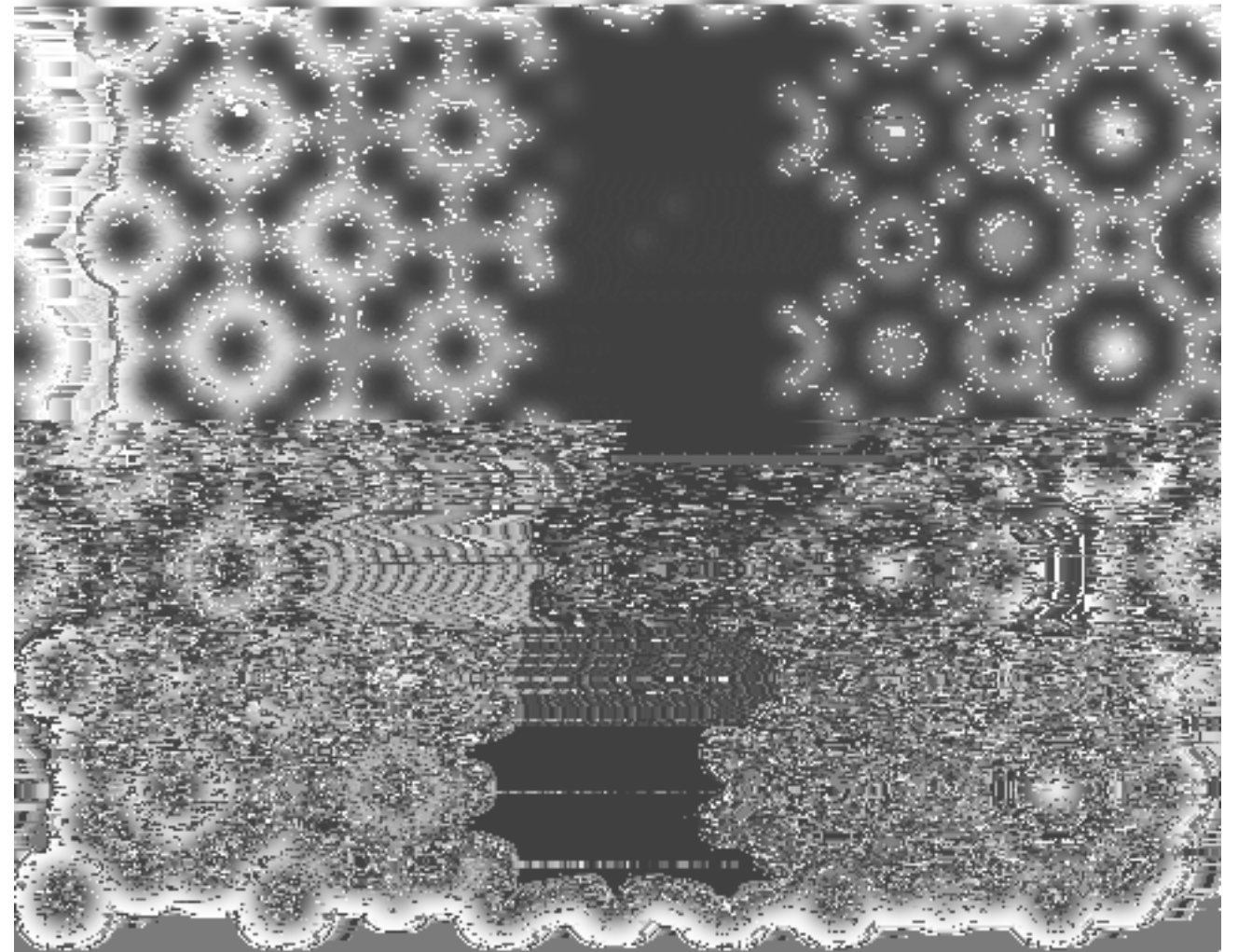
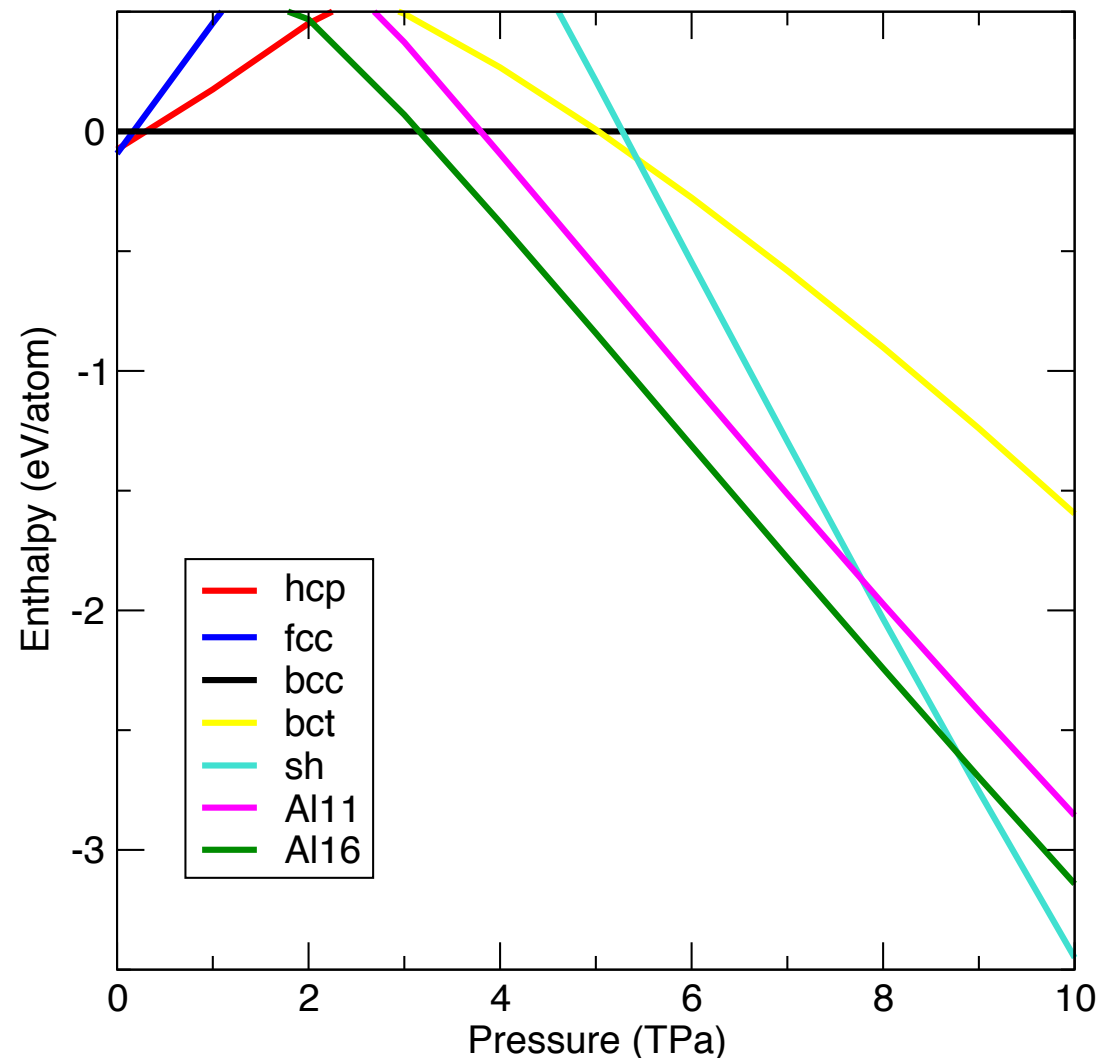
Jupiter

Exoplanets

Neutron stars

Pickard & Needs, *JPCM*, 2009

Aluminium at Terapascals



Ba-IV and Rb-IV united

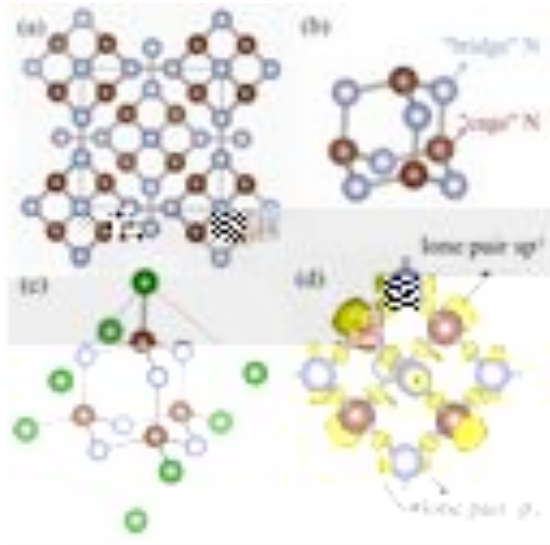
fcc - hcp - bcc - Ba-IV - sh -

Pickard & Needs, *Nature Materials*, 2010

Boron

Carbon to PPa

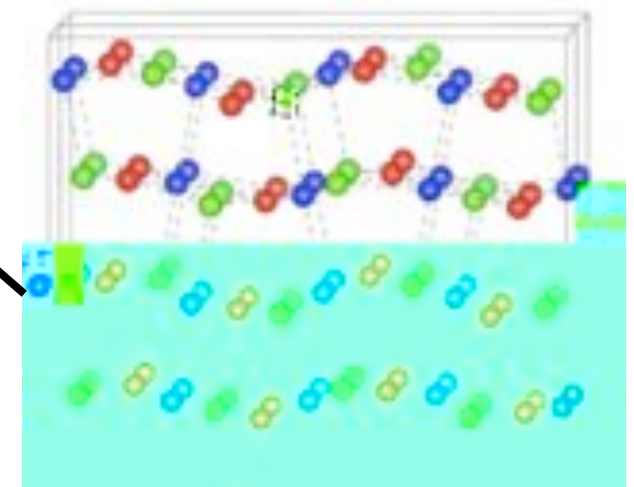
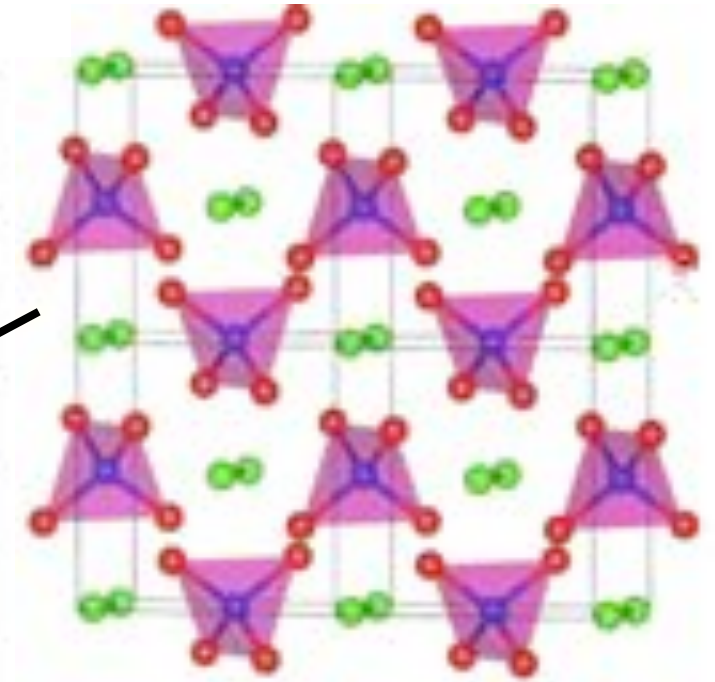
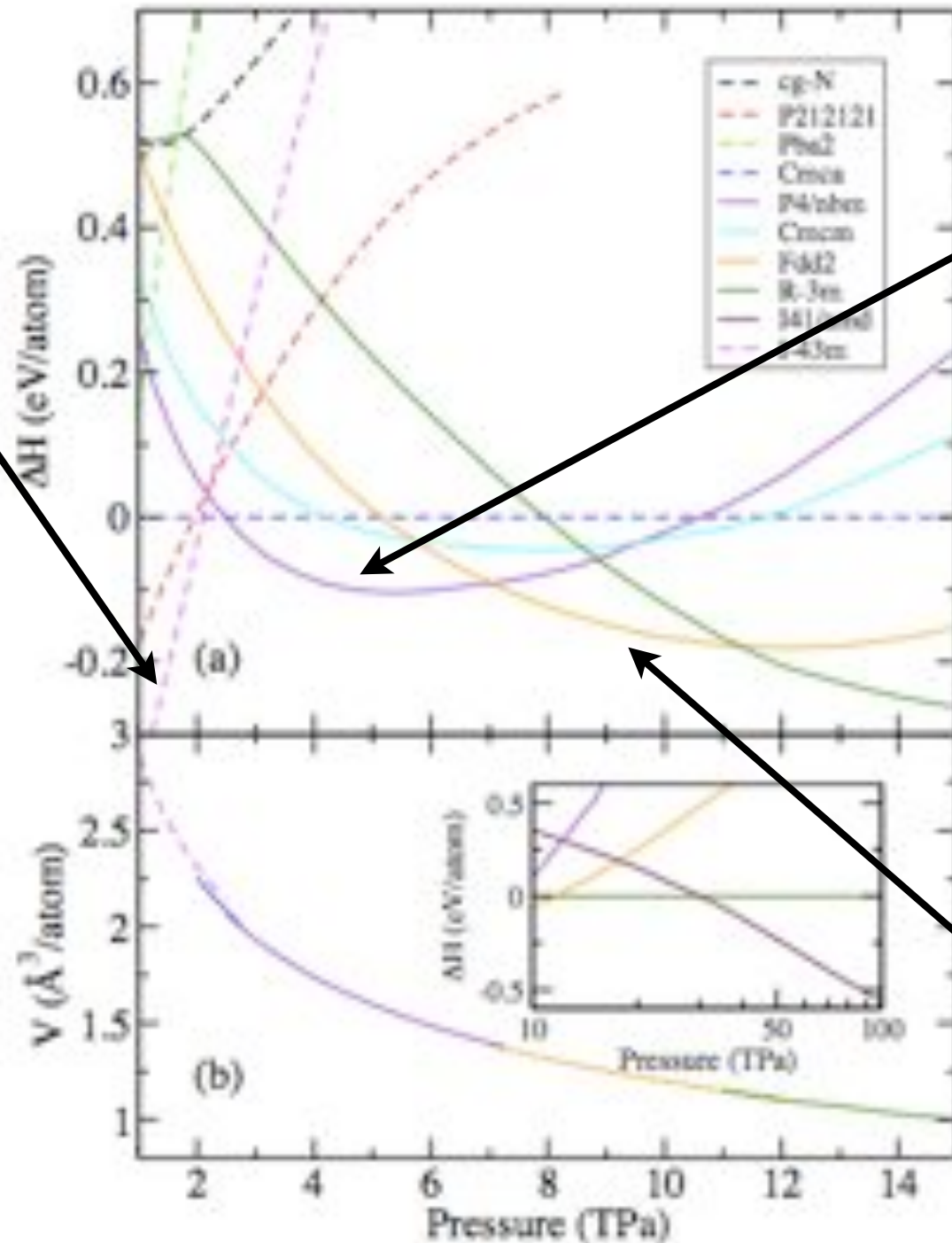
Nitrogen: from cages to salt to waves



Diamondoid
Nitrogen

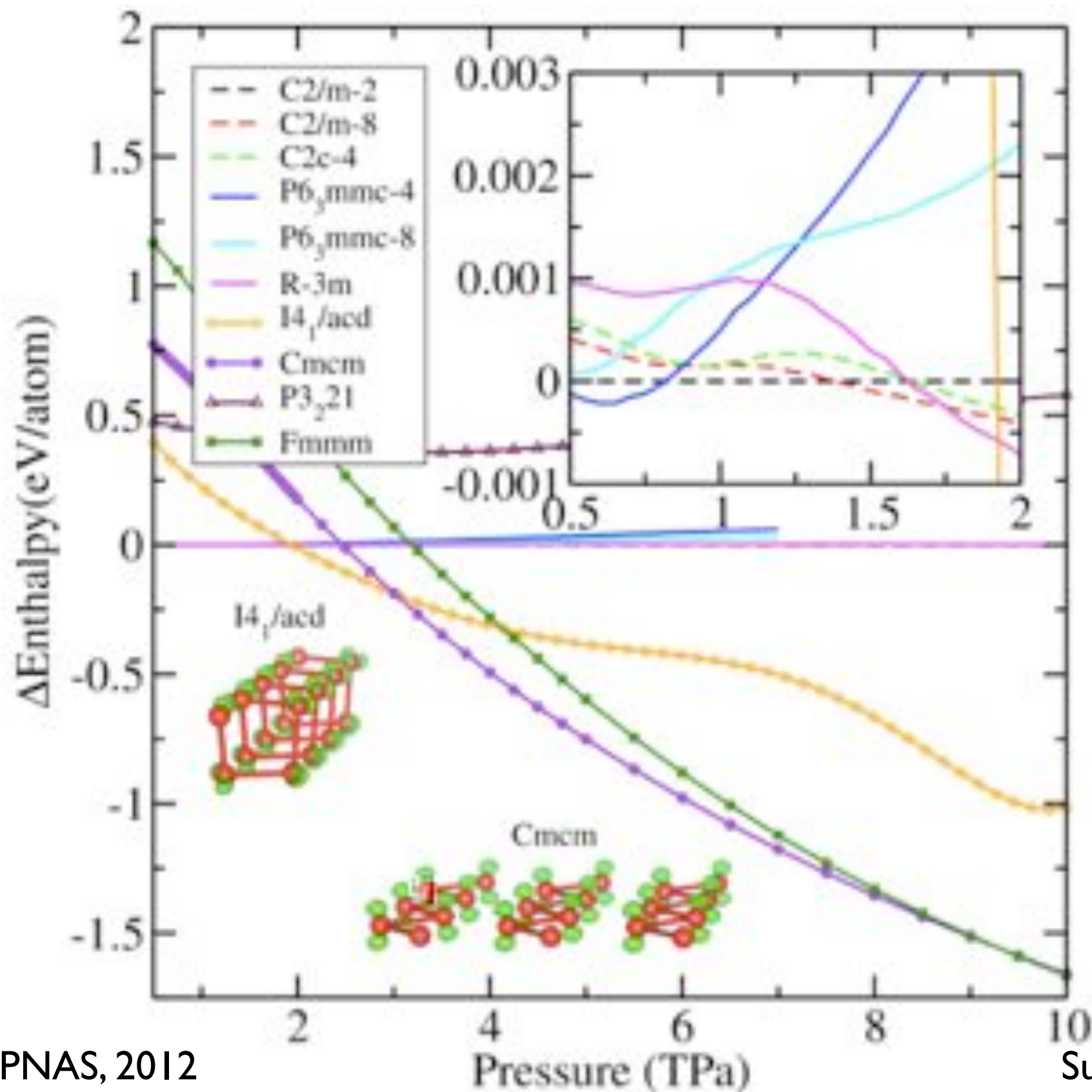
Wang *et al.*, PRL, 2012

Remarkably
rich behaviour
at terapascals



Sun *et al.*, condmat, 2012

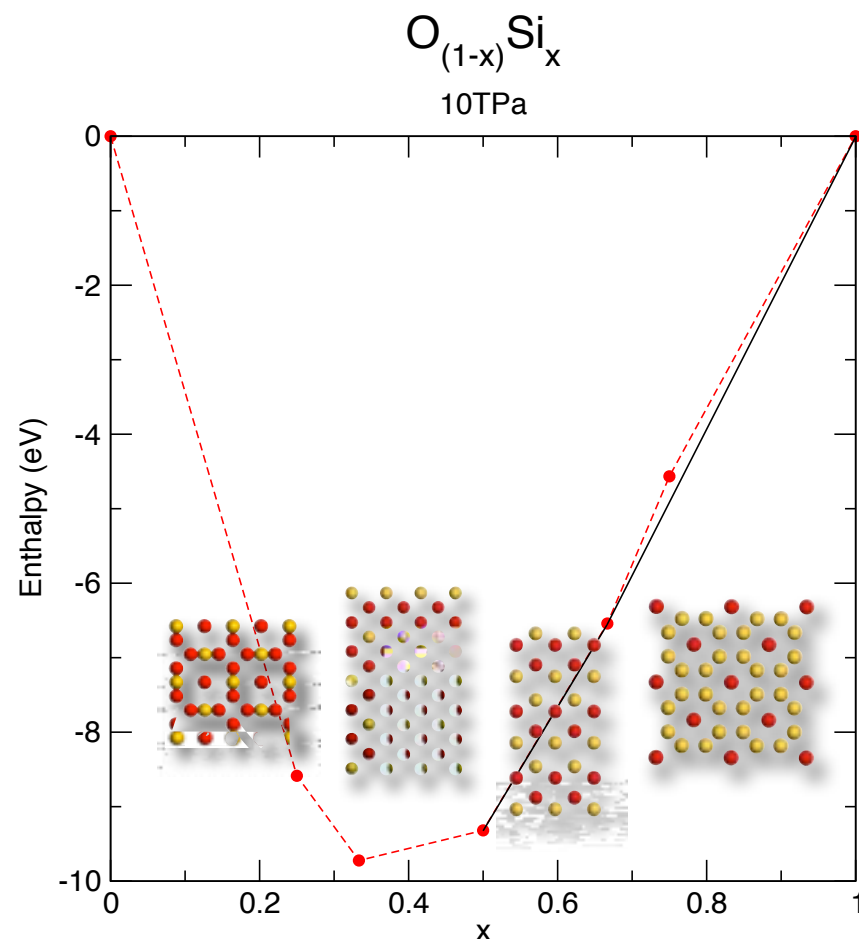
Oxygen: defeating O₂



Dense rock

O, Mg, Al, Si, Ca, Fe

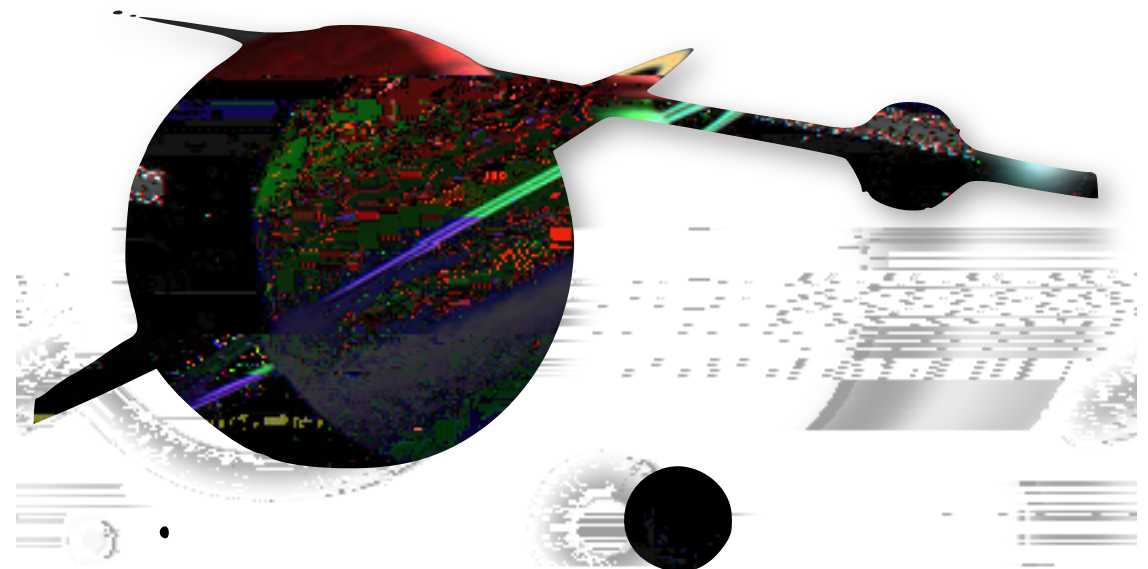
and squeeze (theoretically) to 10TPa



$2 \times \text{Fe} + 50 \times \text{O} + 19 \times \text{Si} + 17 \times \text{Mg} + 1 \times \text{Al} + 2 \times \text{Ca}$
 $0.5 \times \text{Al}_2\text{O}_3 + 17 \times \text{MgO} + 12.5 \times \text{SiO}_2 + 6.5 \times \text{SiO}_3 + 2 \times \text{FeCa}$

$2 \times \text{Fe} + 25 \times \text{O} + 19 \times \text{Si} + 17 \times \text{Mg} + 1 \times \text{Al} + 2 \times \text{Ca}$
 $1 \times \text{AlO} + 17 \times \text{MgO} + 7 \times \text{Si}_2\text{O} + 5 \times \text{Si} + 2 \times \text{FeCa}$

Calculate binary convex hulls
using AIRSS

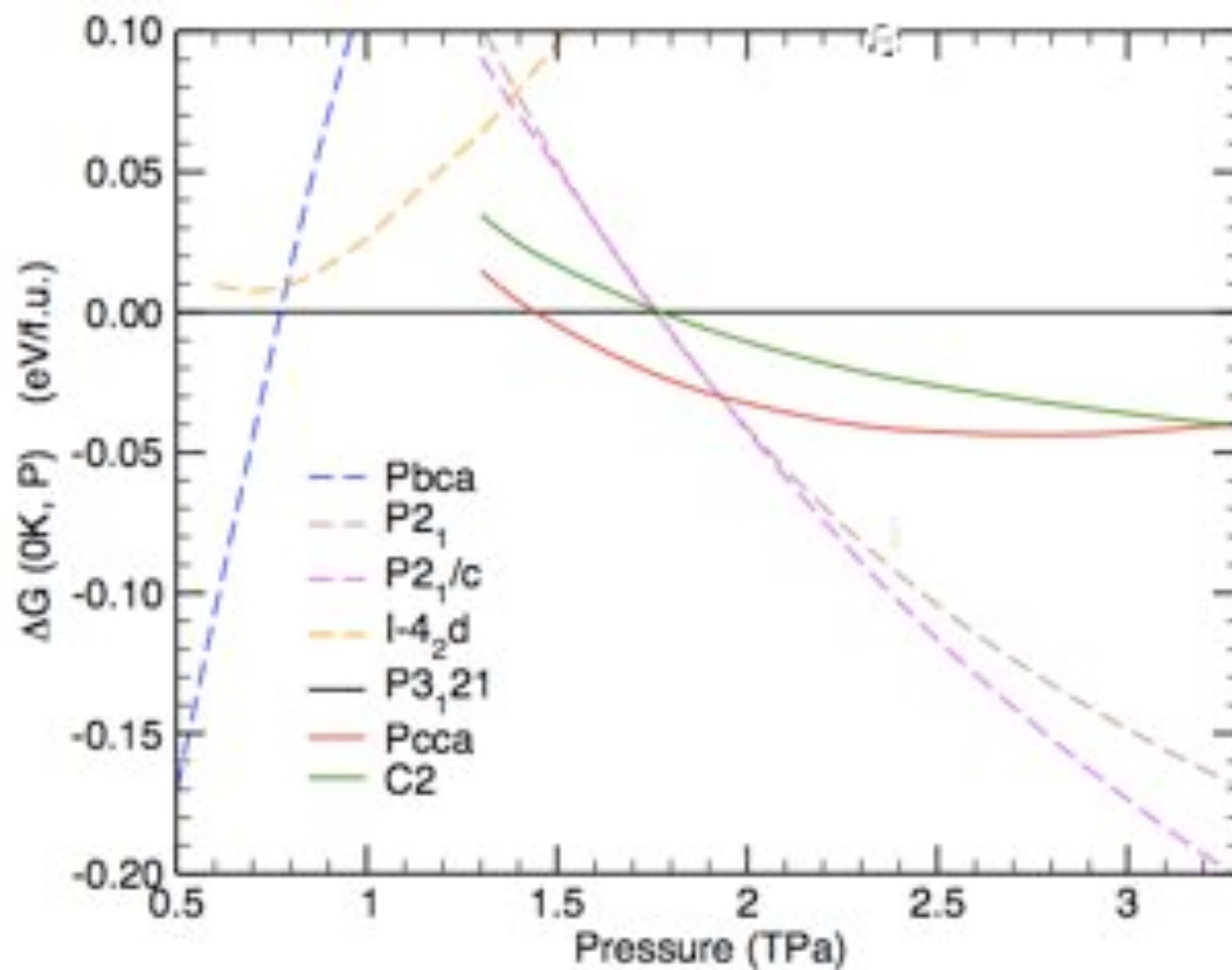


H₂O at TPa

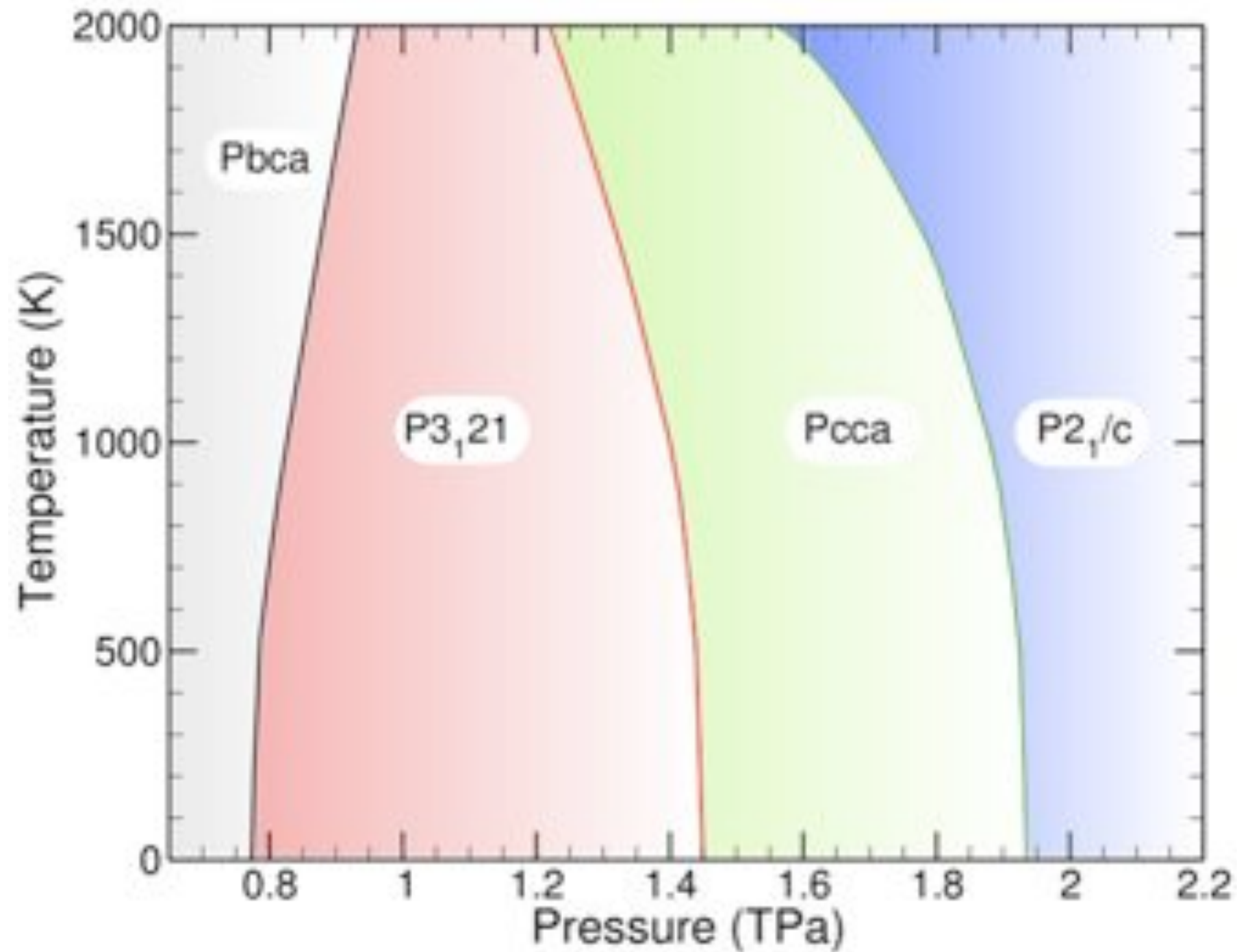
Space group	Stability range (TPa)	No. fu	Source
Ice X	−0.30	2	Ref. [12]
<i>Pbcm</i>	0.30–0.71	4	Ref. [13]
<i>Pbca</i>	0.71–0.78	8	Ref. [14]
<i>P3₁21</i>	0.78–2.01	12	This work
<i>Pcca</i>	2.01–2.24	12	This work
<i>C2</i>	2.24–2.36	12	This work
<i>P2₁</i>	2.36–2.75	4	Ref. [15–17]
<i>P2₁/c</i>	2.75–6.06	8	Ref. [16]
<i>C2/m</i>	6.06–	2	Ref. [15]

<i>P</i> (TPa)	Phase	density (g/cm ³)
0	ordered-Ih	0.917 (expt)
0.1	X	3.18
0.5	<i>Pbcm</i>	4.87
0.8	<i>Pbca</i>	5.70
1.0	<i>P3₁21</i>	6.29
2.0	<i>Pcca</i>	8.16
2.25	<i>C2</i>	8.55
2.5	<i>P2₁</i>	8.94
3.25	<i>P2₁/c</i>	9.93
6.0	<i>C2/m</i>	12.84

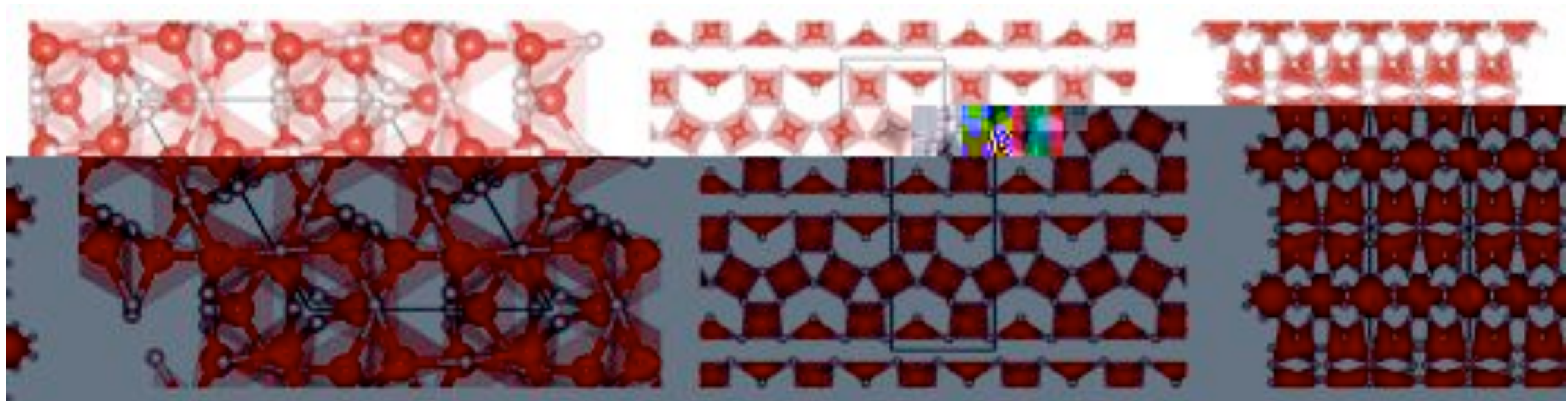
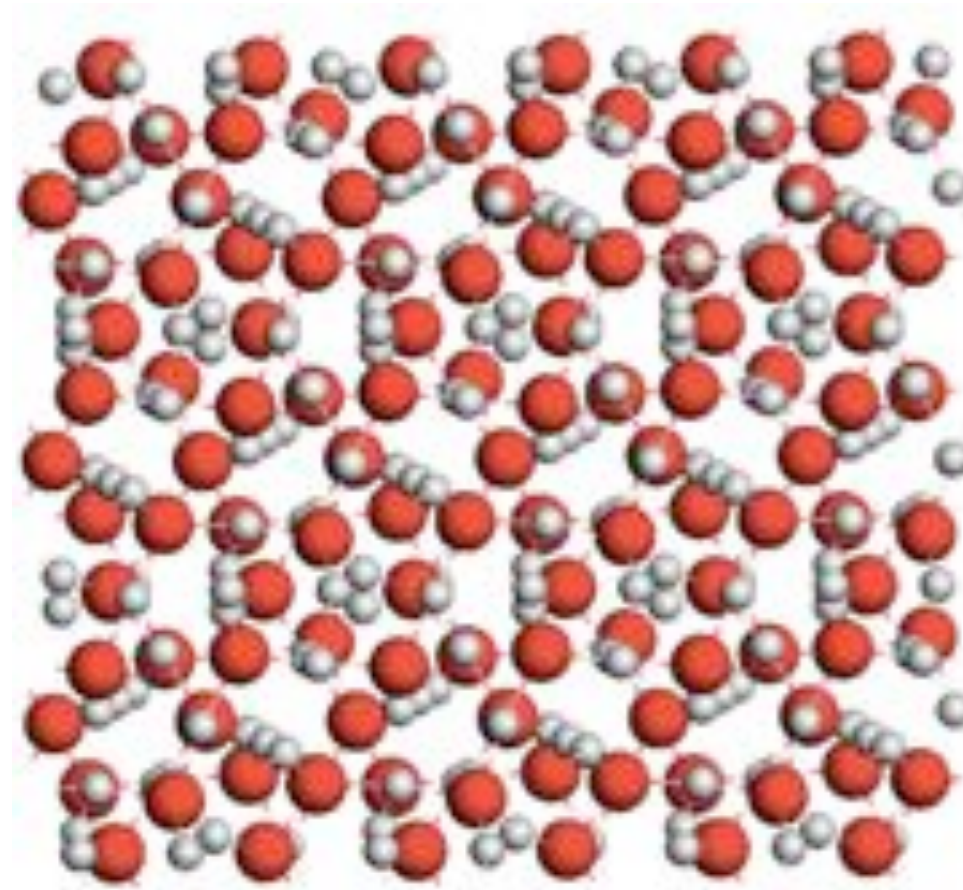
Enthalpies



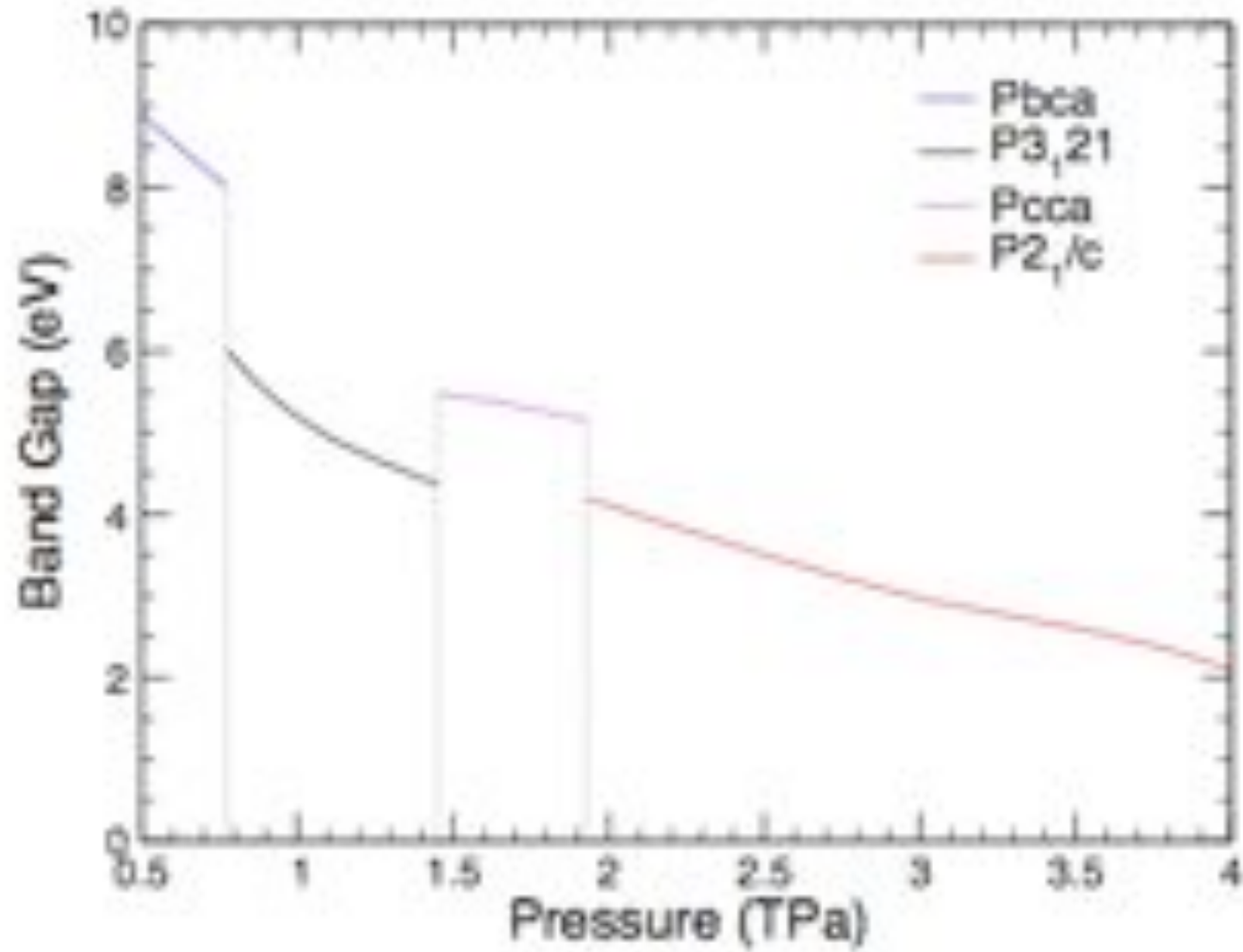
Phase Diagram



Structures

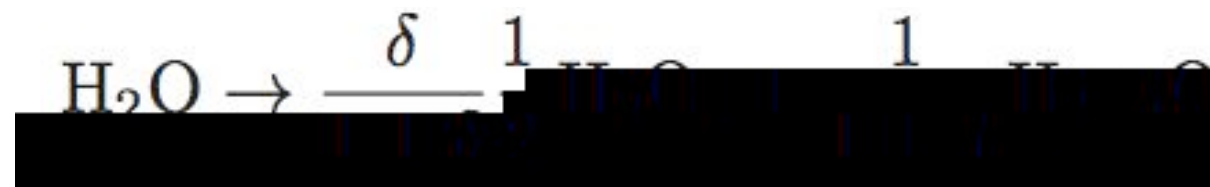
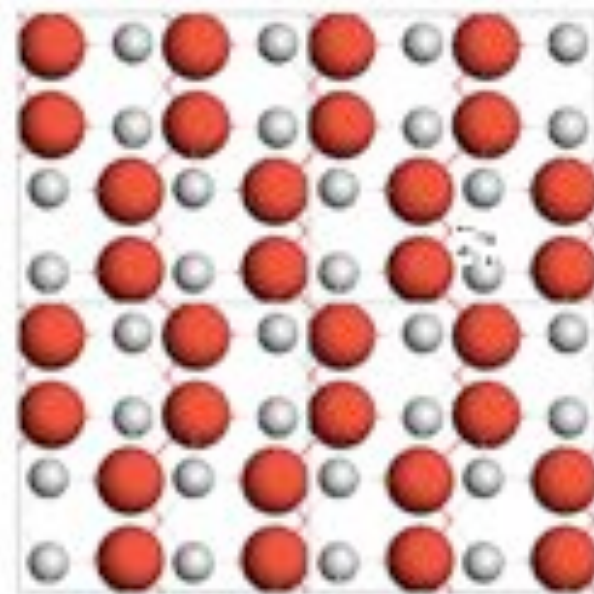


Electronic properties

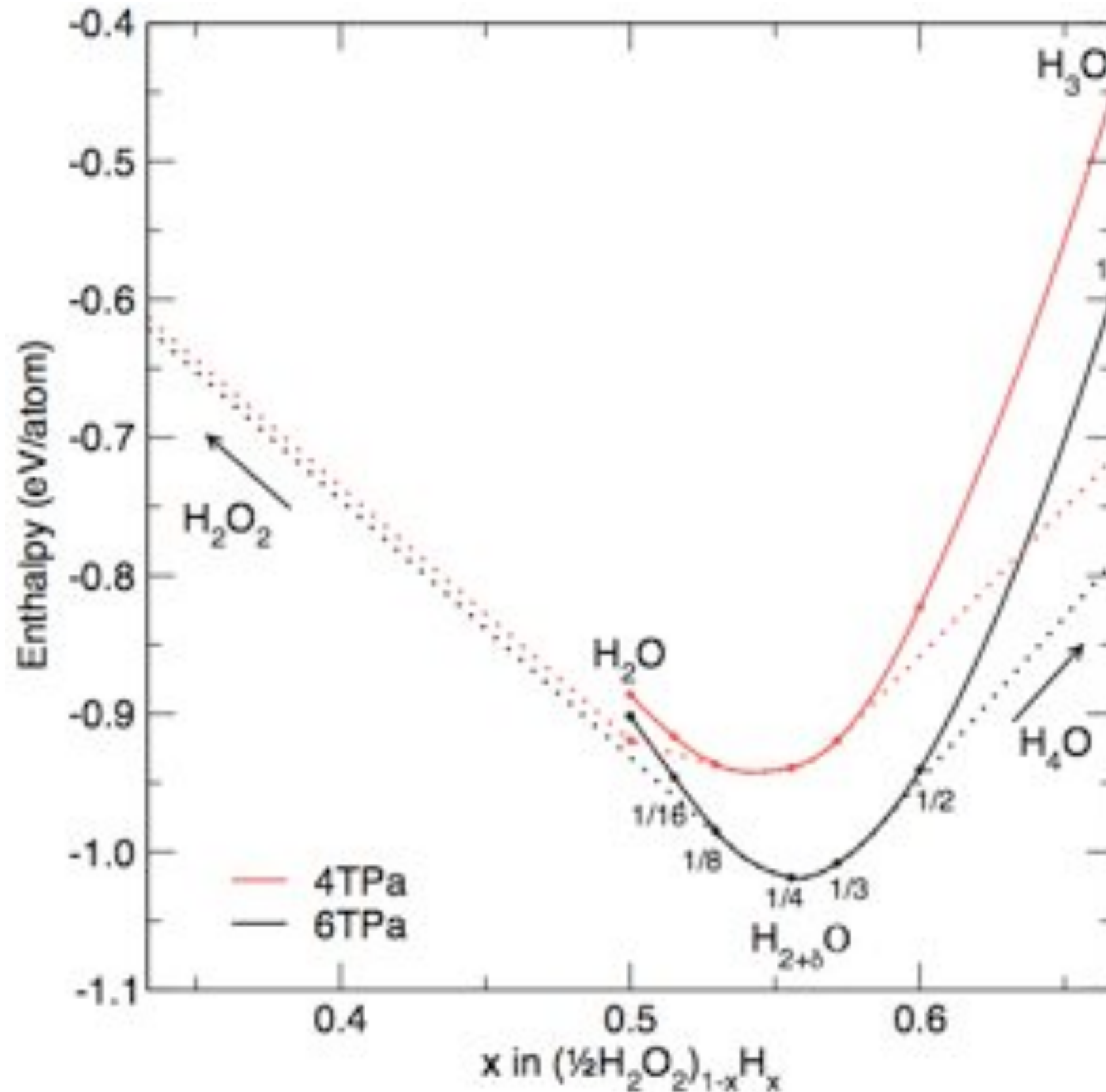


Does H_2O exist?

Maybe not - H_2O_2 is very stable

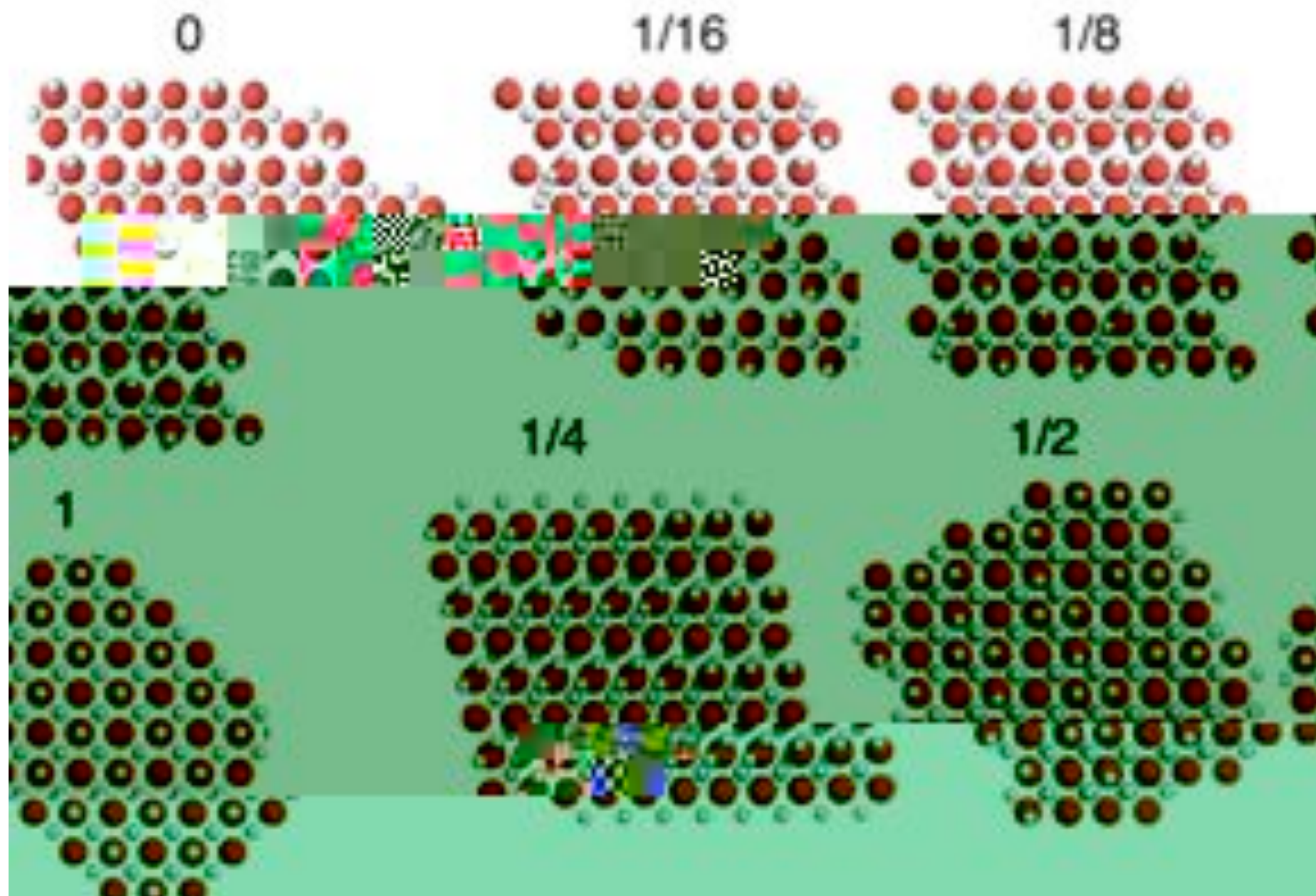


Decomposition of H₂O

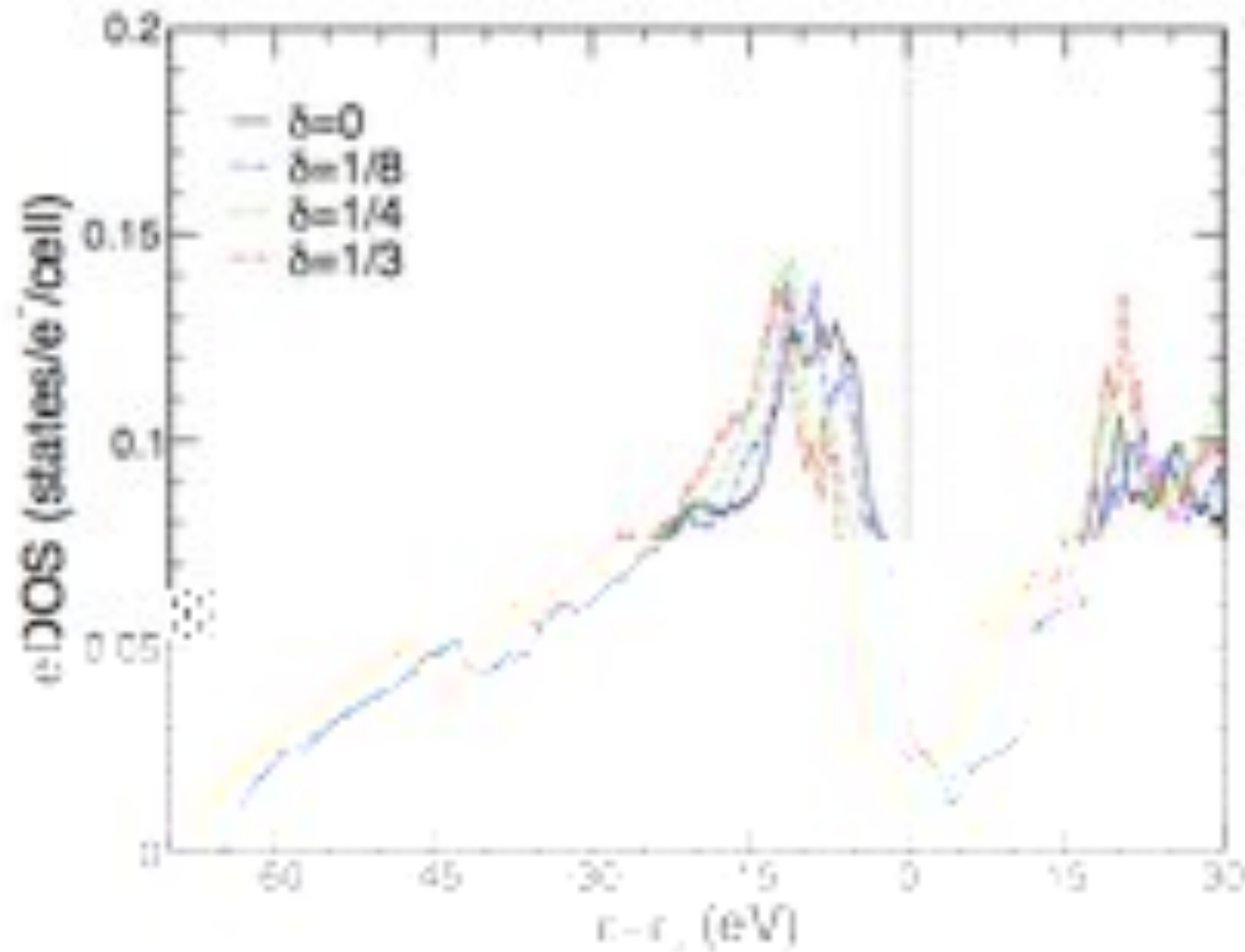


H₂O is not a thermodynamically stable composition above 5TPa

A hydrogen sponge



Fermi surface effects



The doping of C2/m with H moves E_f to a minimum in the eDOS

Perspective

Virtual experimentation

Acknowledgements