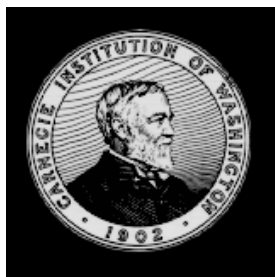


Brijuni Conference, Matter Under Extreme Conditions, Sept. 2, 2004

Materials Under Pressure: New Findings and Phenomena

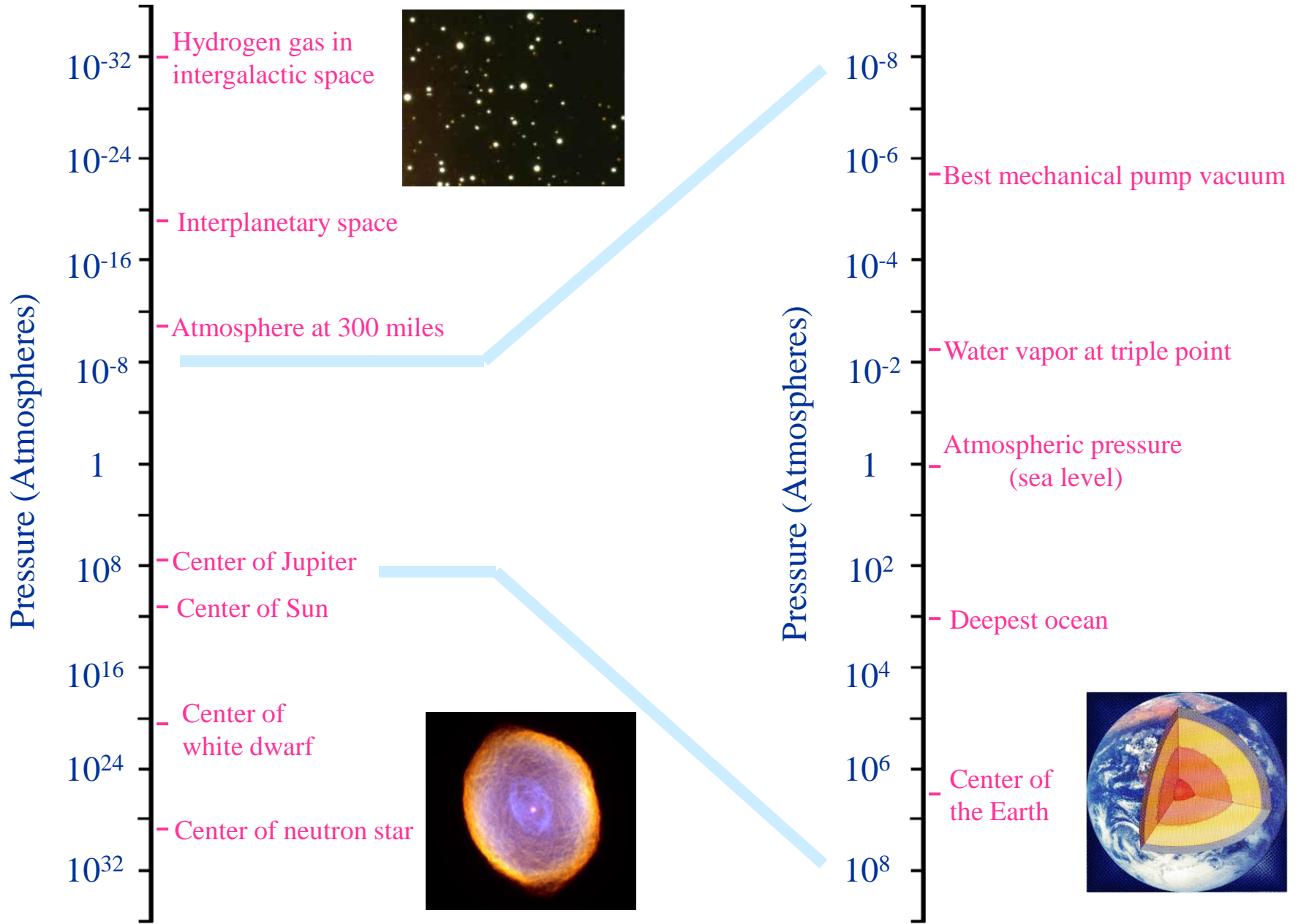
Russell J. Hemley



***Geophysical Laboratory
Carnegie Institution of Washington
Washington, DC***

CDAC, Carnegie/DOE Alliance Center

RANGE OF PRESSURE IN THE UNIVERSE



There have been great advances in our ability to generate static high pressures and temperatures in the laboratory



PRESSURE UNITS

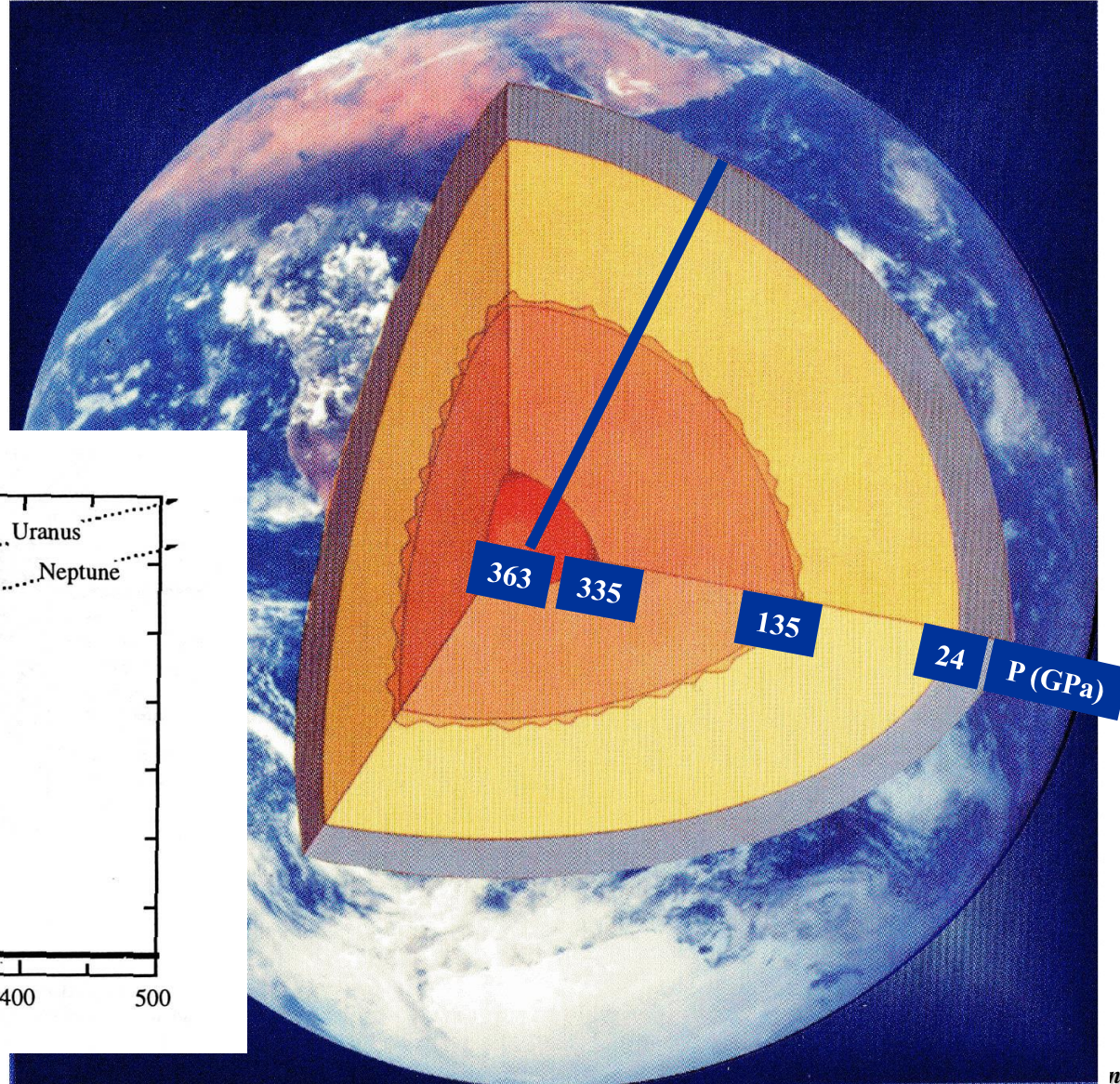
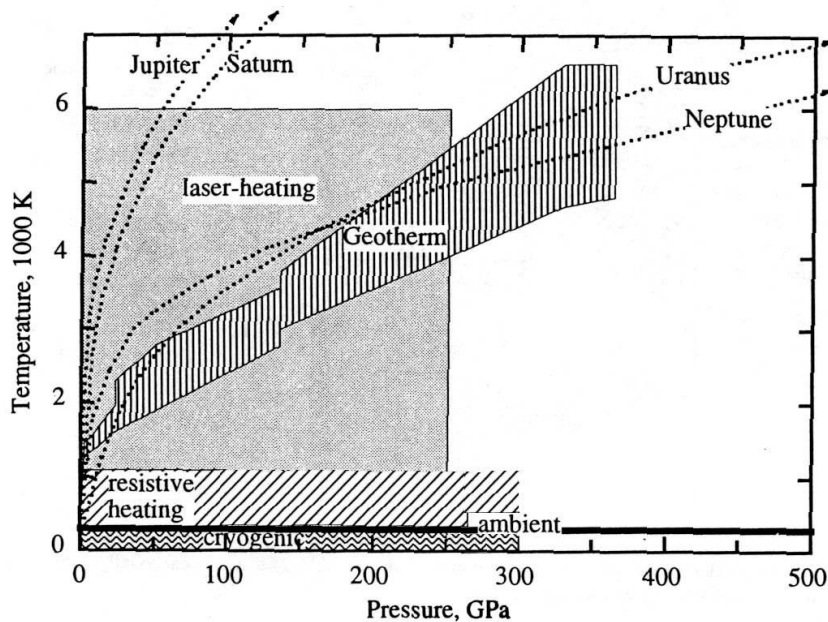
$10^3 \text{ atm} \approx \text{kbar}$

$10^6 \text{ atm} \approx \text{Mbar}$

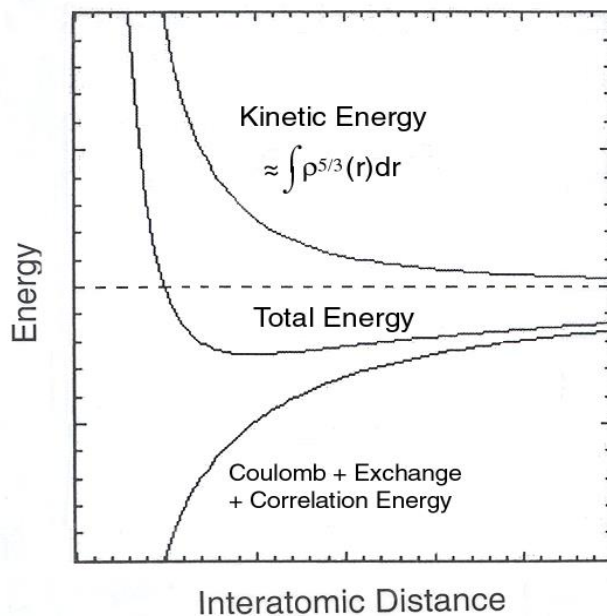
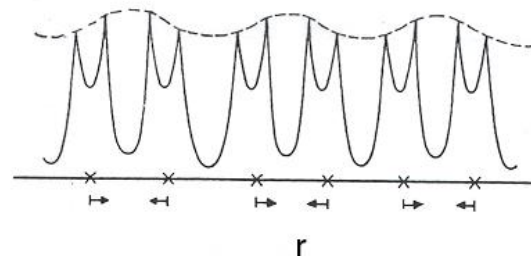
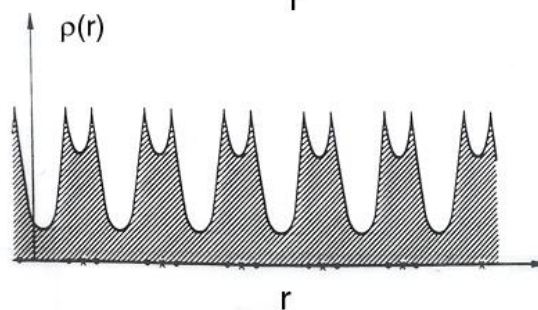
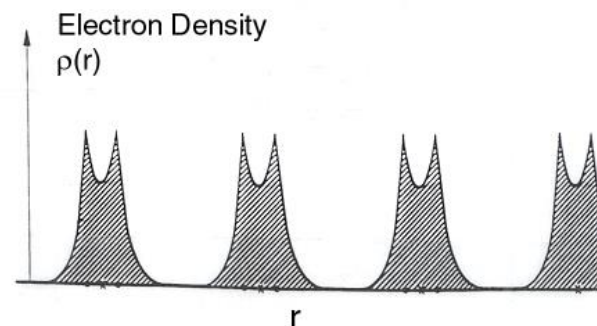
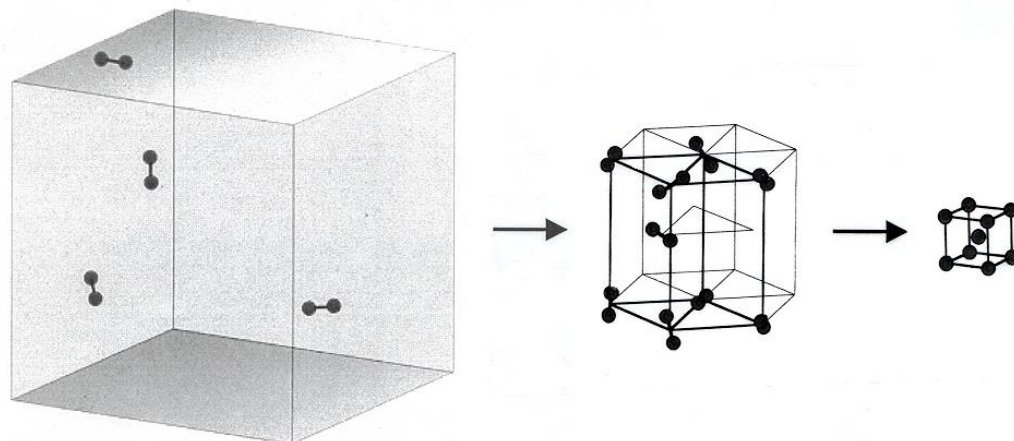
$10 \text{ kbar} = 1 \text{ GPa}$

$1 \text{ Mbar} = 100 \text{ GPa}$

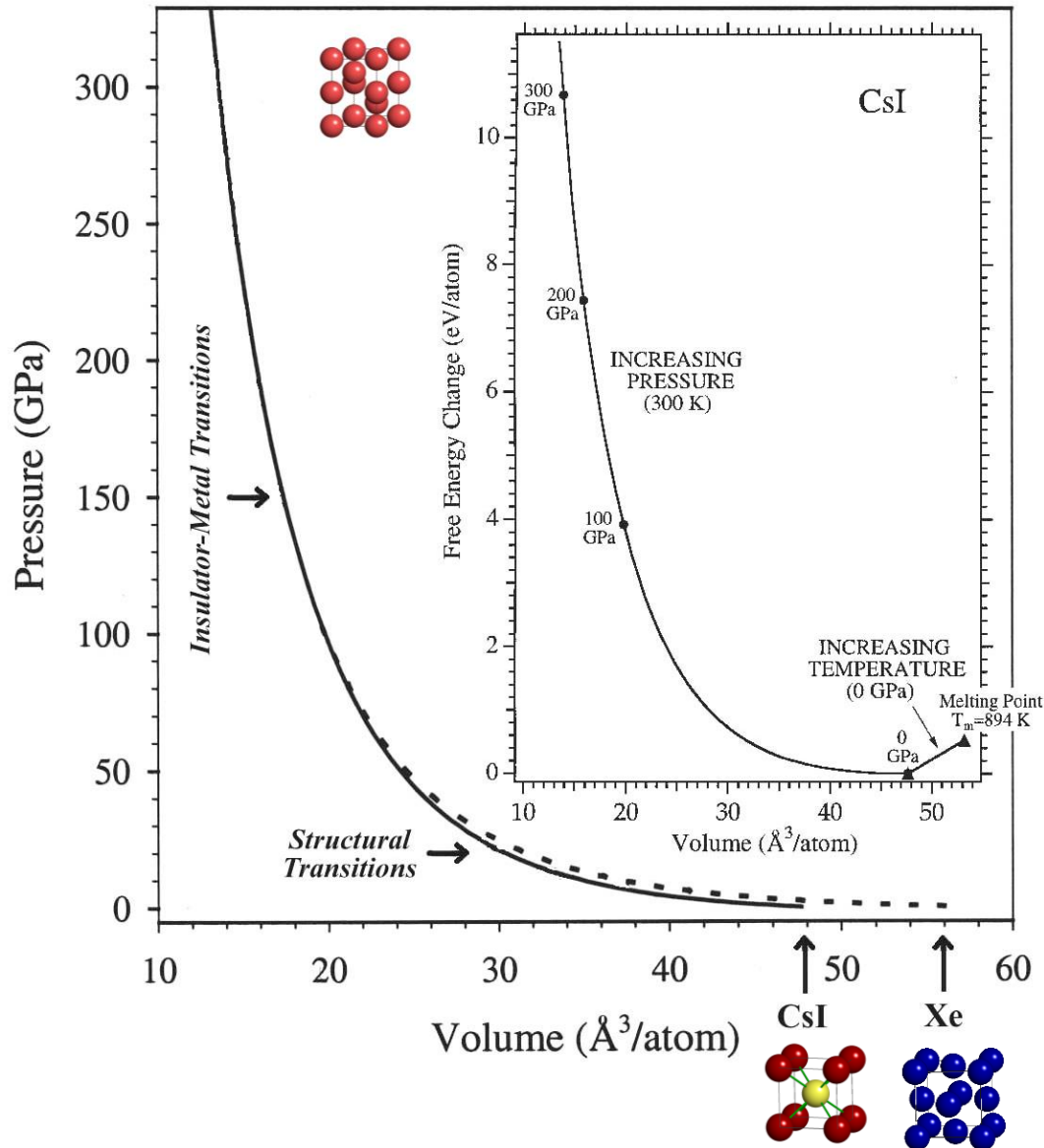
$1 \text{ Gigapascal} = 10^9 \text{ N/m}^2$



Effect of strong compression on molecules and 'ultimate' state of matter



Pressure induces major changes in free energies and therefore chemical bonding



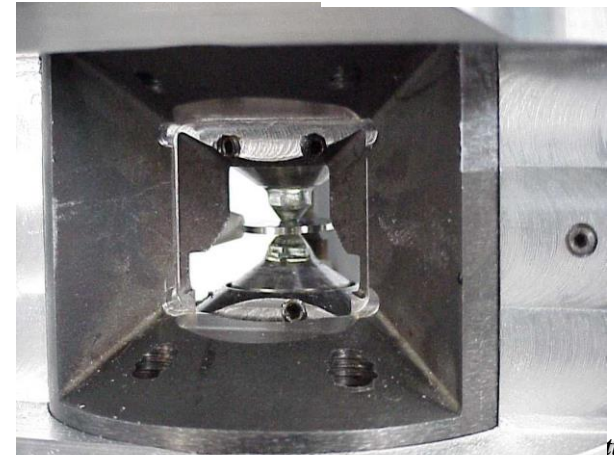
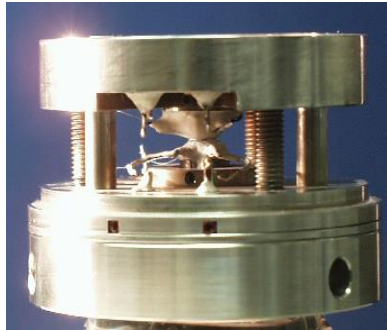
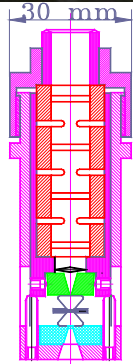
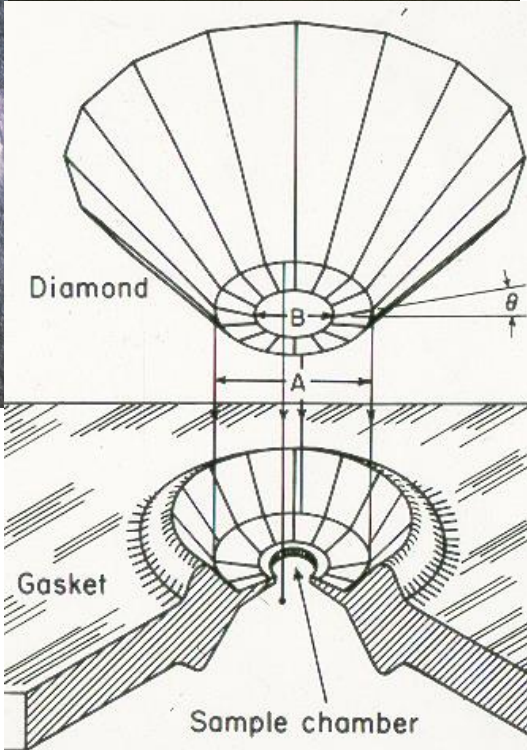
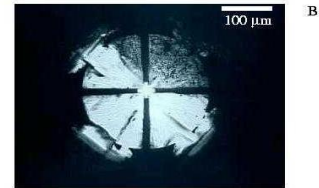
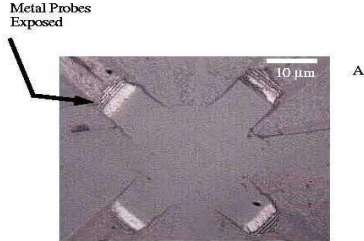
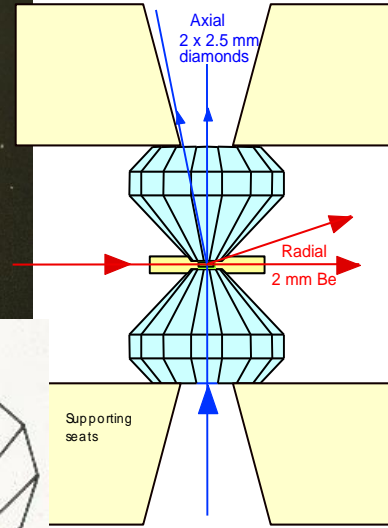
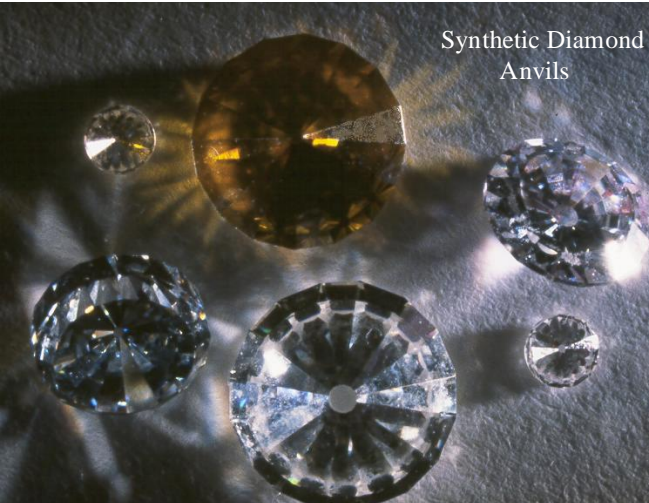
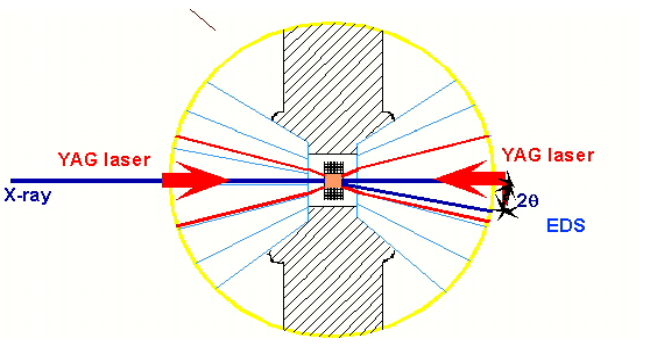
Pressure Alchemy: Xe-CsI Convergence

- *P-V* work can exceed binding energies
- Dramatic changes in bonding and electronic states
- New reaction pathways, mechanisms, transition states
- Stored energy in metastable phases

[Hemley and Ashcroft,
Physics Today 51, 26 (1998)]

Carnegie Institution

Recent advances result from the development of a plethora of devices based on diamond anvil cells



OVERVIEW: *Selected Recent Examples*



1. **The Elements: Hydrogen and its Analogs**
2. **Novel Semiconductors, Metals, Superconductors**
3. **Water and Molecular Systems**
4. **New Findings for the Earth**
5. **Technical Developments**

THEMES

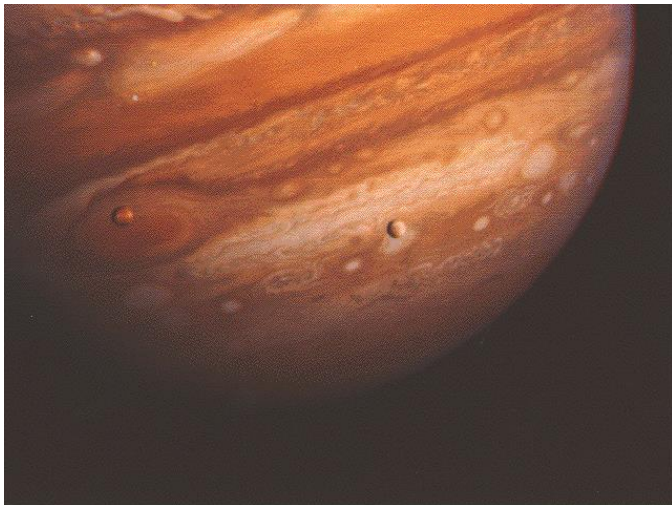
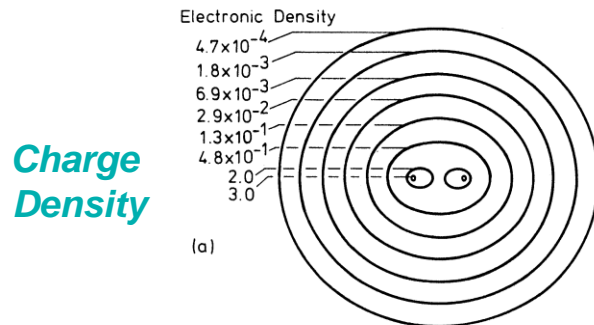
- *“Simplicity” versus “complexity”*
- *Integration of techniques*
- *Tests of theory*
- *Broad implications*

The behavior of hydrogen under pressure is a key problem in physics and astrophysics



ISOLATED H_2 MOLECULE

- Strong covalent bond: 4.5 eV
- Nearly spherical electron density
- 14 bound vibrational states
- “Halogen” not “alkali” like



HIGH-PRESSURE PREDICTIONS

- Pressure-induced dissociation/metallization?
[Wigner & Huntington, *J. Chem. Phys.* **3**, 764 (1935)]
- Exotic properties: High T_c and liquid ground state?
[Ashcroft, *Phys. Rev. Lett.* **21**, 1748 (1968)]
- Intermediate transitions (e.g., band overlap)?
[Friedli & Ashcroft, *Phys. Rev. B* **21**, 662 (1977)]

EXPERIMENT

- ‘Low-temperature’ solid 300 GPa:
Transformations, structures, optical response, conductivity, . . .
- New questions about high P - T behavior:
Interactions? Equation of state? Melting? Bonding state?

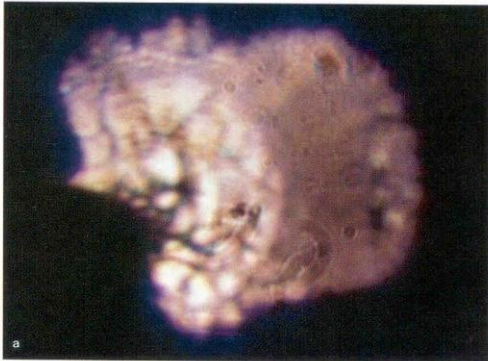
A wealth of unexpected phenomena were documented for the low-temperature (<300 K) solid up to megabar pressures



pressures

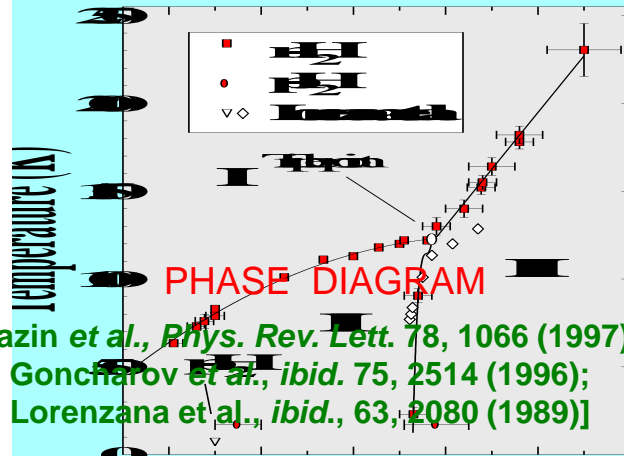
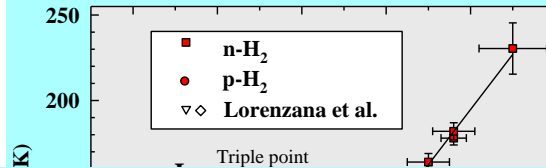
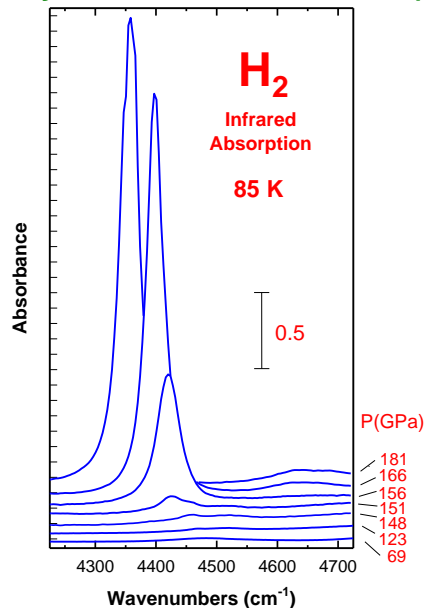
OPTICAL ABSORPTION >250 GPa

[Mao & Hemley, *Science* 244, 1462 (1989)]

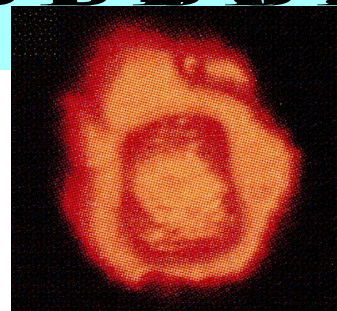
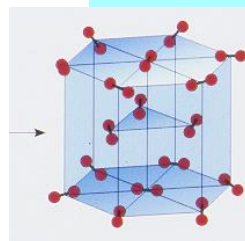


CHARGE-TRANSFER STATE

[Hemley et al., *Nature* 369, 384 (1994)]



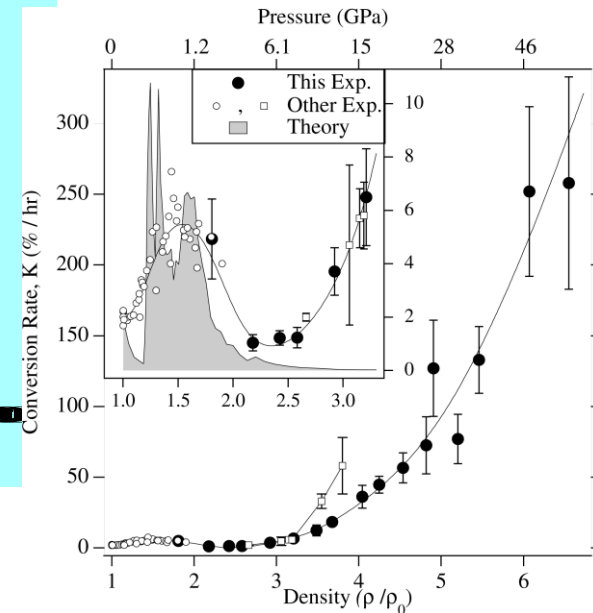
[Mazin et al., *Phys. Rev. Lett.* 78, 1066 (1997);
Goncharov et al., *ibid.* 75, 2514 (1996);
Lorenzana et al., *ibid.*, 63, 2080 (1989)]



X-RAY DIFFRACTION >100 GPa [Loubeyre et al., *Nature* 383, 702 (1996)]

ORTHO-PARA CONVERSION

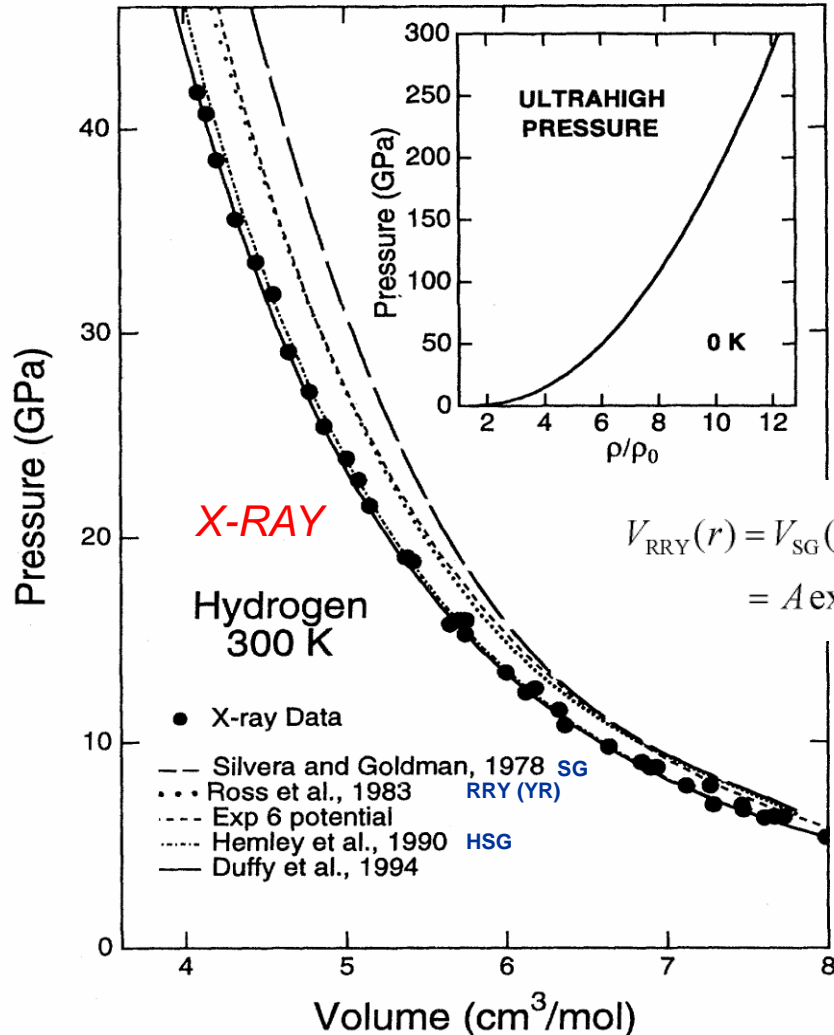
[Eggert et al., *Proc. Nat. Acad. Sci.* 96, 12269 (1999); Pravica & Silvera, *Phys. Rev. Lett.* 81, 4180 (1998); Strzhemechny et al., *Phys. Rev. B* 66, 014103 (2002)]



The pressure-volume equation of state provides detailed information about intermolecular interactions



[Mao & Hemley, *Rev. Mod. Phys.* **66**, 761 (1994)]



- Effective pair potential fits to EOS
- Need for softening at high pressure (*many-body exchange, He, Ne,..*)

SG: (*fit to solid to 2.5 GPa*)

$$V_{SG}(r) = \exp(\alpha - \beta r - \gamma r^2) - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right) f(r) + \frac{C_9}{r^9} f(r)$$

RRY (YR): (*fit to shock wave Hugoniot*)

$$V_{RRY}(r) = V_{SG}(r), \quad r \geq r_c,$$

$$= A \exp[-B(r-r_c) - C(r-r_c)^2 - D(r-r_c)^3 - E(r-r_c)^3(r-r_1)], \quad r < r_c$$

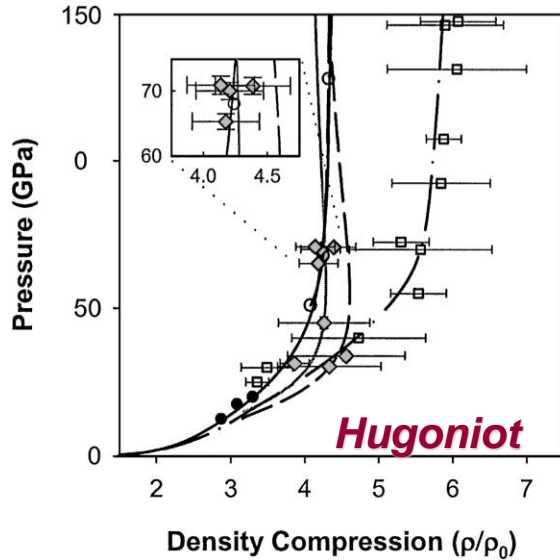
HSG: (*fit to x-ray/solid to 26 GPa*)

$$V_{HSG}(r) = V_{SG}(r) + V_{SR}(r)$$

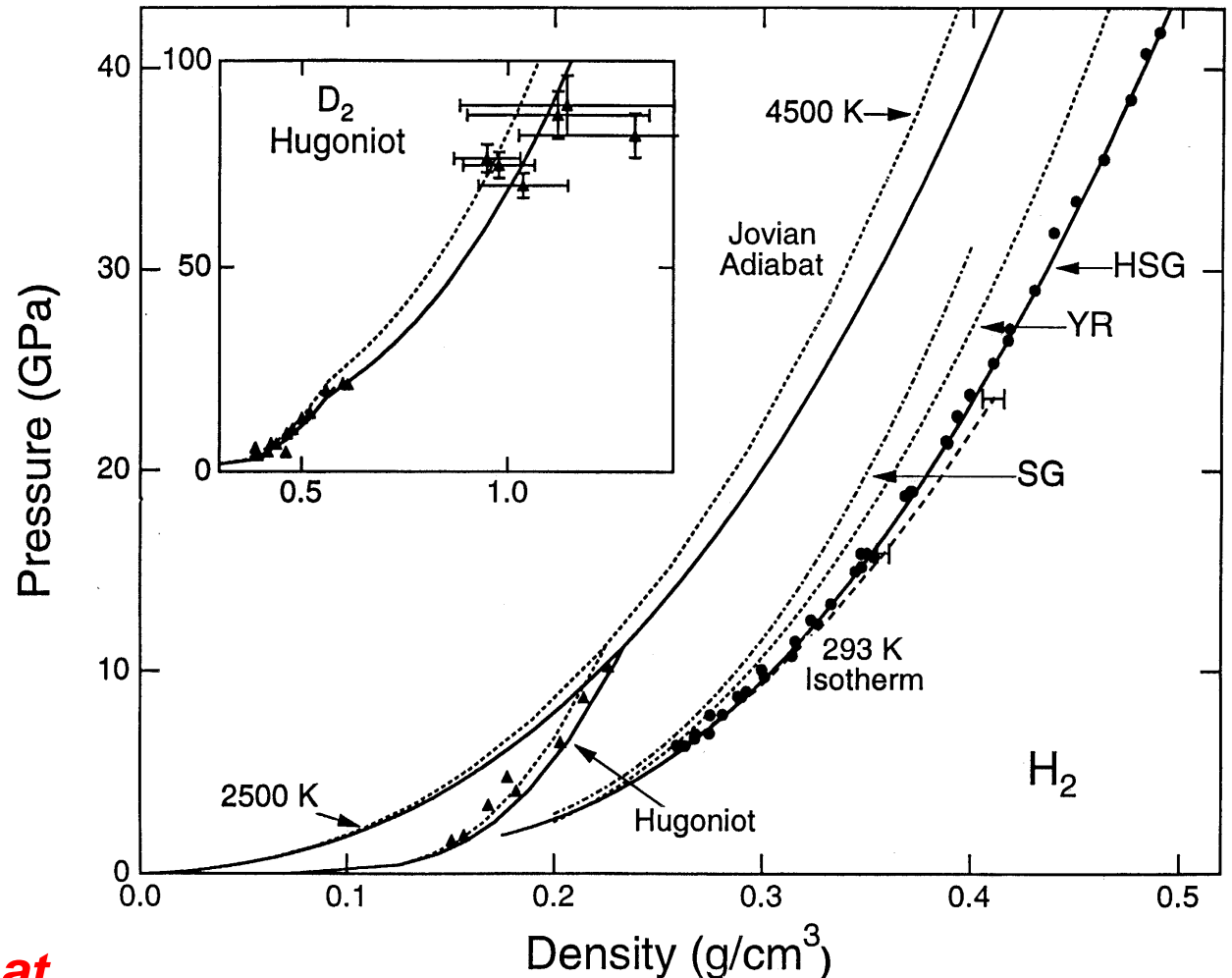
$$V_{SR}(r) = a_1(r-r_c)^3 + a_2(r-r_c)^6, \quad r \leq r_c$$

$$= 0, \quad r > r_c.$$

The effective pair potentials can be used to calculate the P - V - T EOS, Hugoniot, and Jovian adiabat



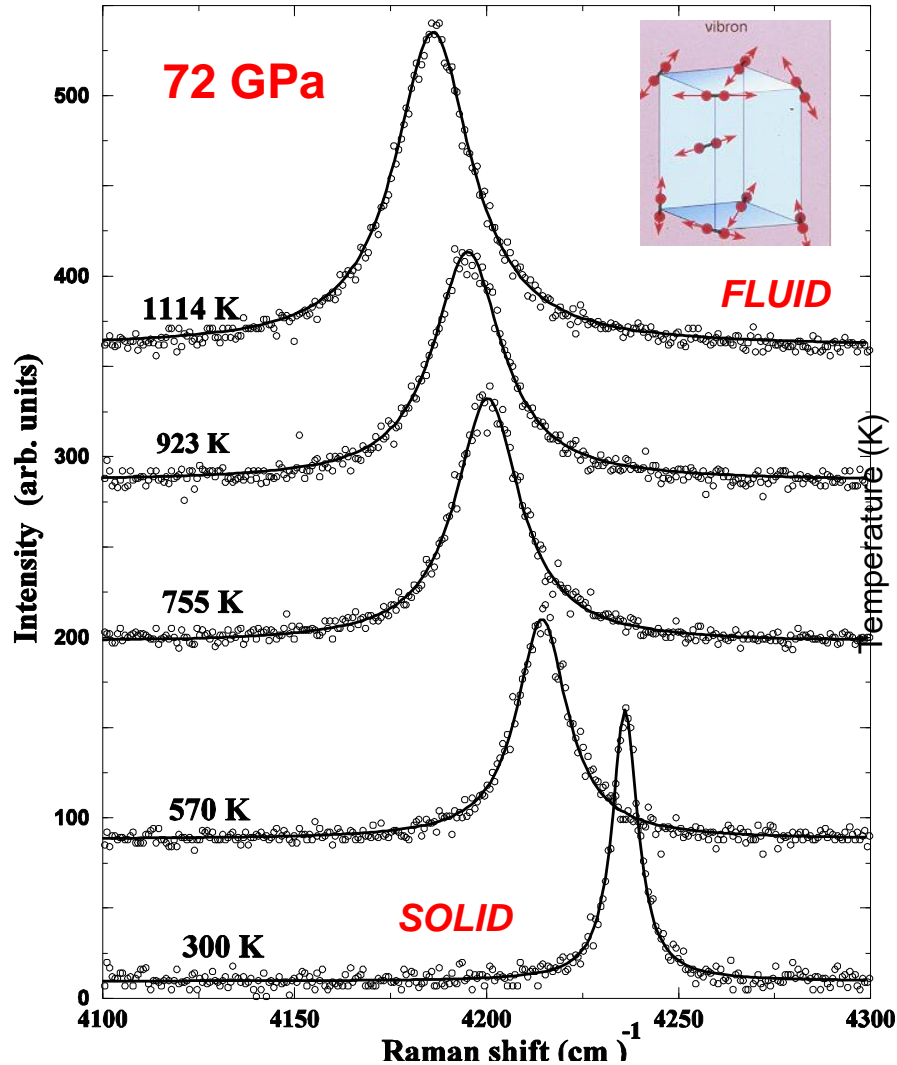
[Cauble *et al.*, *Science* 281, 1178 (1998);
Knudson *et al.* *Phys. Rev. Lett.* 87, 225501 (2001)]



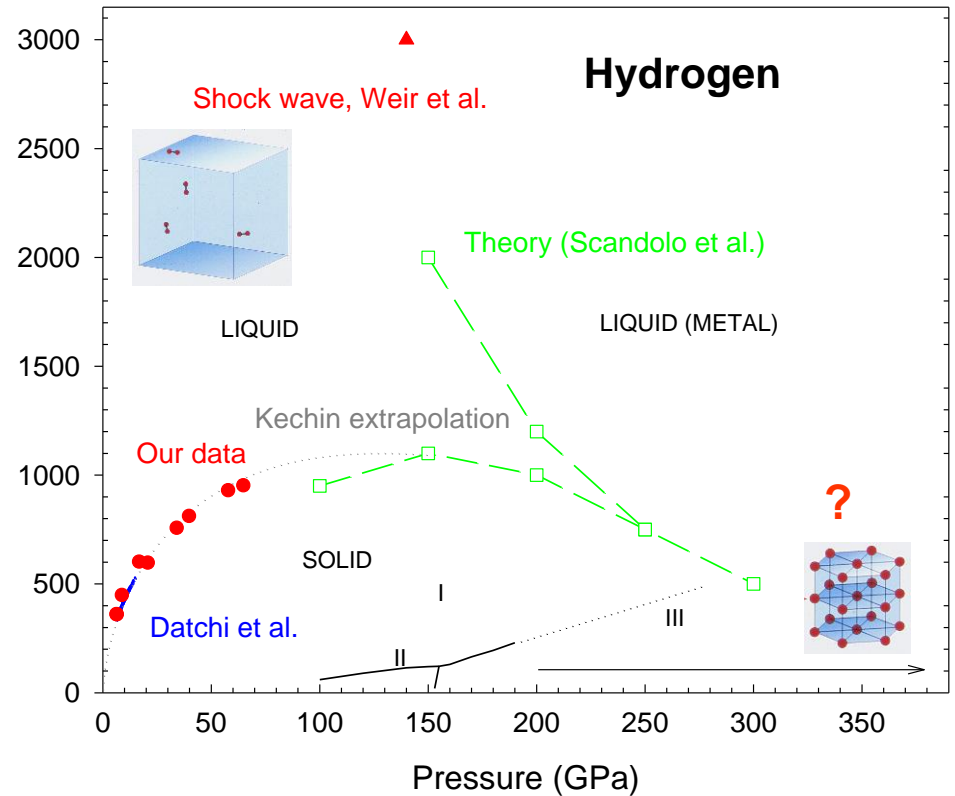
- Solid-state data provide baseline

➤ Bonding changes at high P and T ?

High P - T Raman measurements reveal new findings but now raise several new questions



- Persistence of molecular state
- Bond weakening and anharmonicity
- Possible melting maximum

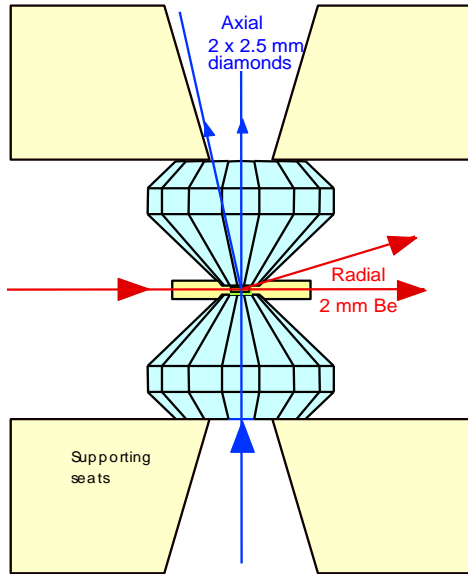


- *Ground state?*
- *Probe electronic structure by inelastic x-ray scattering?*

The pressure dependence of bonding and electronic structure can be probed by inelastic x-ray scattering



- Diamond window is opaque above 5 eV.
- Need to examine $\Gamma \neq 0$
- Scatter into excited electronic states

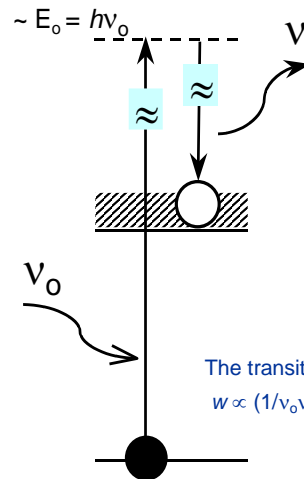


e.g., Si [555]
87° 9899.2 eV



Application to graphite

[W. Mao et al. Science, 302, 425 (2003)]

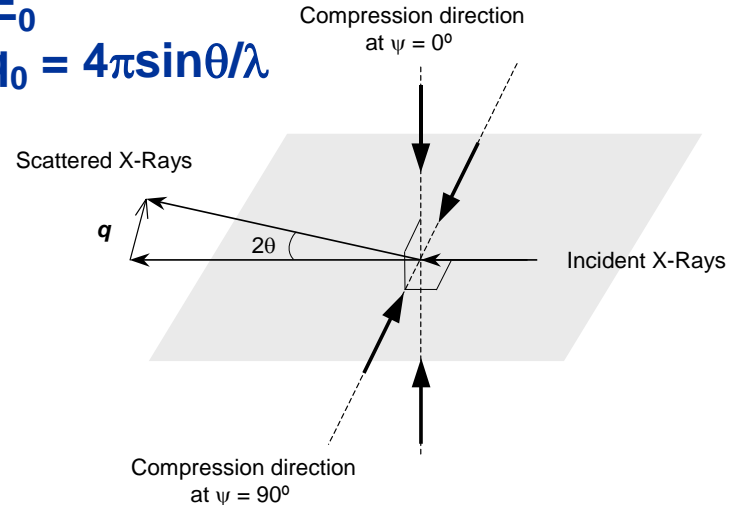


$$\Delta E = E - E_0$$

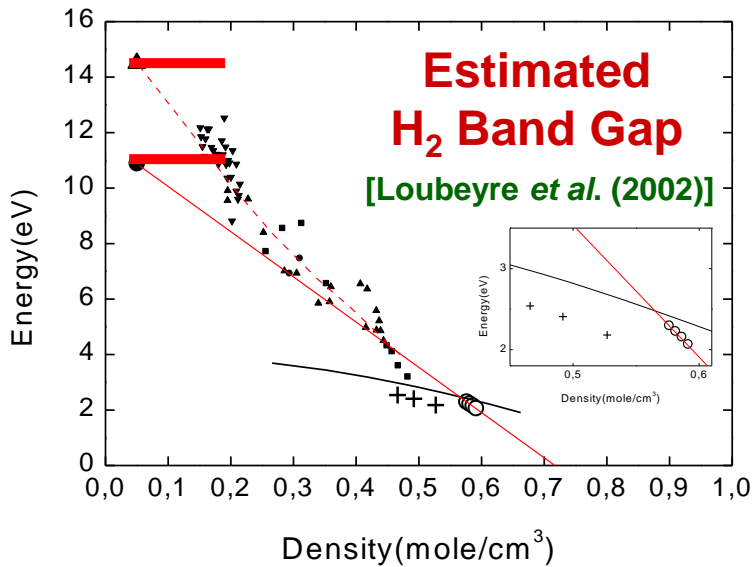
$$\Delta q = q - q_0 = 4\pi \sin\theta / \lambda$$

$2\pi r / \lambda_0 < 1$
 $h\nu_0 > \text{ionization energy}$
 r – orbital radius of bound electron.

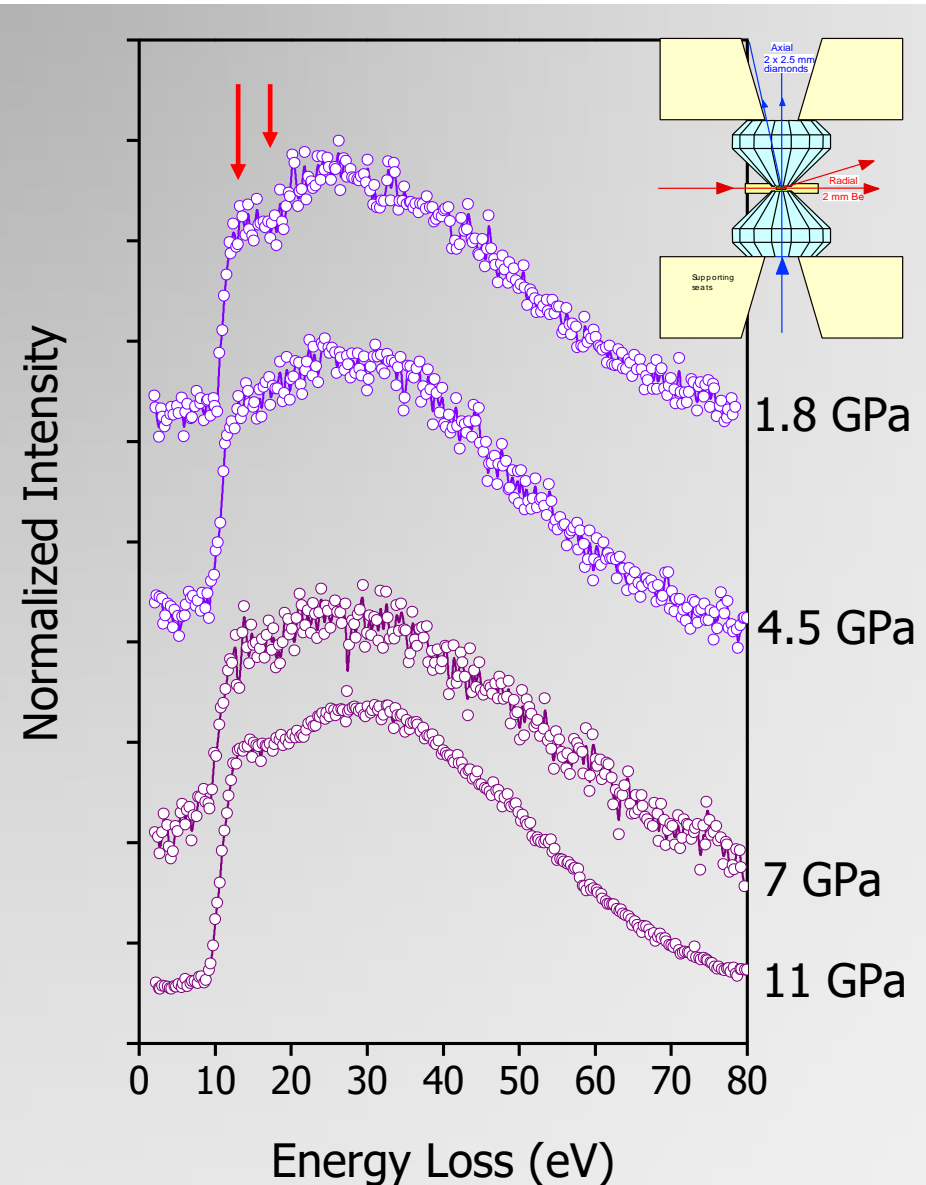
The transition probability of XRS:
 $w \propto (1/\nu_0\nu)(1+\cos^2\theta)\langle i | \exp(iqr) | j \rangle^2$



The hydrogen band gap under pressure has been directly measured by inelastic x-ray scattering



- Indirect probes (refractive index measurements; indications of darkening ~300 GPa)
[Mao & Hemley (1989); Loubeyre et al. (2002)]
- Absorption threshold above the diamond absorption edge
- Probe by IXS (inelastic x-ray scattering; “x-ray Raman”)
- No pressure shift to 11 GPa (4 x compression)



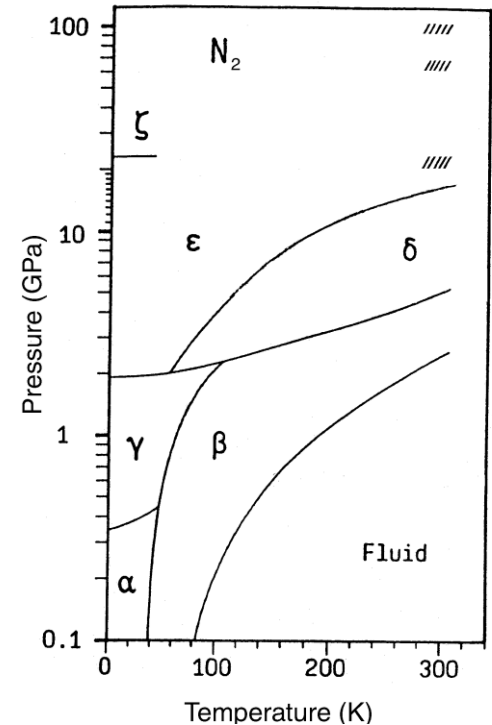
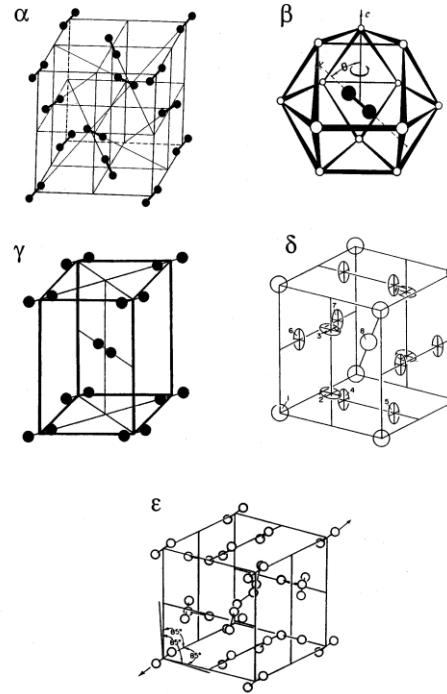
Do related transformations occur in other diatomic systems?



Nitrogen as an analog
(9.8 eV vs. 4.5 eV E_b)

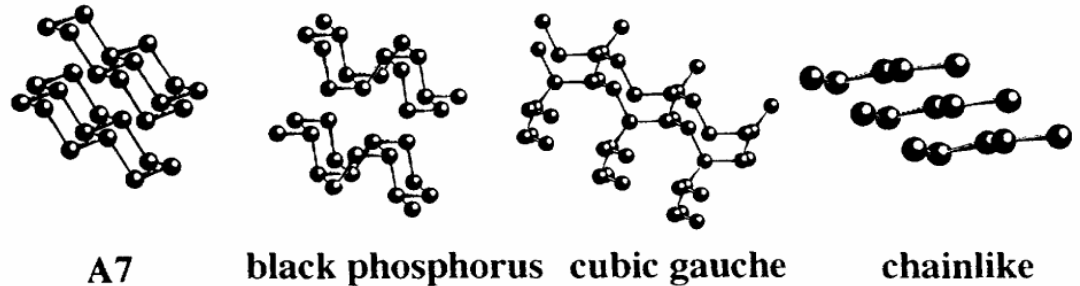
MOLECULAR PHASES
(<100 GPa)

[after Mills et al., 1980;
Freiman, *Physics of Cryocrystals* (1997)]



PREDICTED NON-MOLECULAR PHASES
(>50 GPa)

[McMahan and LeSar (1985), Martin & Needs (1986); Mailhot et al. (1992)]

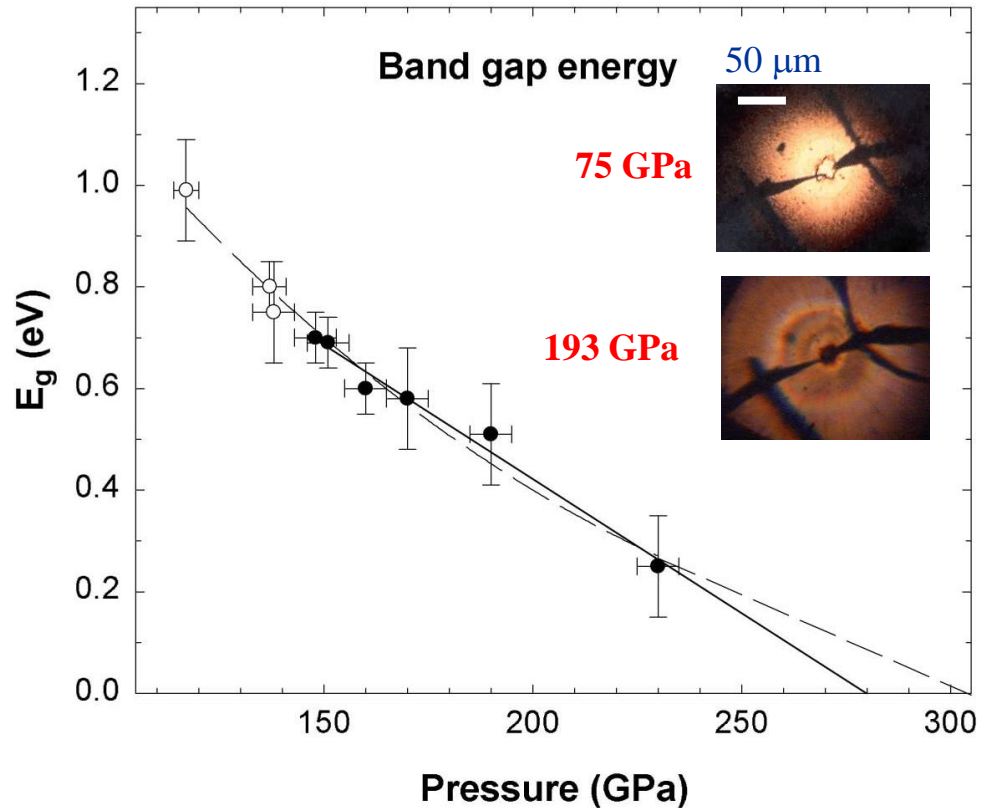
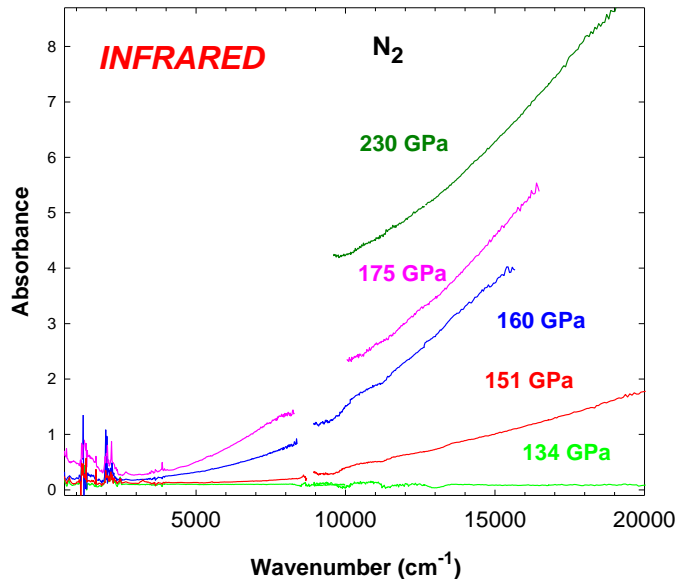
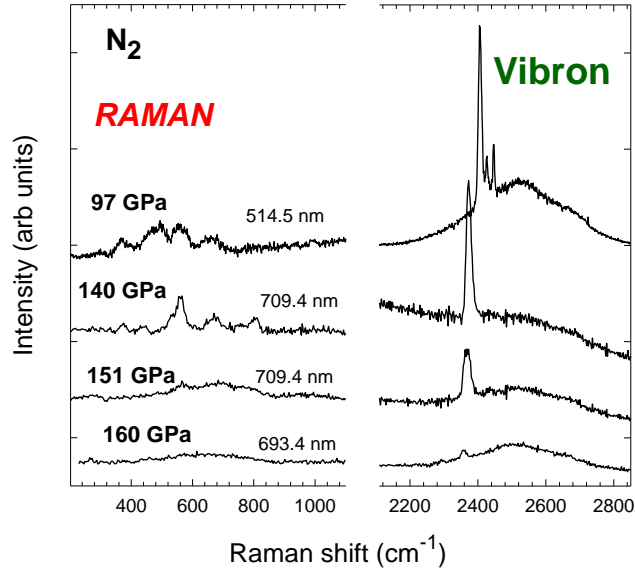


Nitrogen is a non-molecular semiconductor from 150 to >230 GPa

[Goncharov *et al.*, *Phys. Rev. Lett.* 82, 1262 (2000); Eremets *et al.*, *Nature* 411, 170 (2001)]



GPa

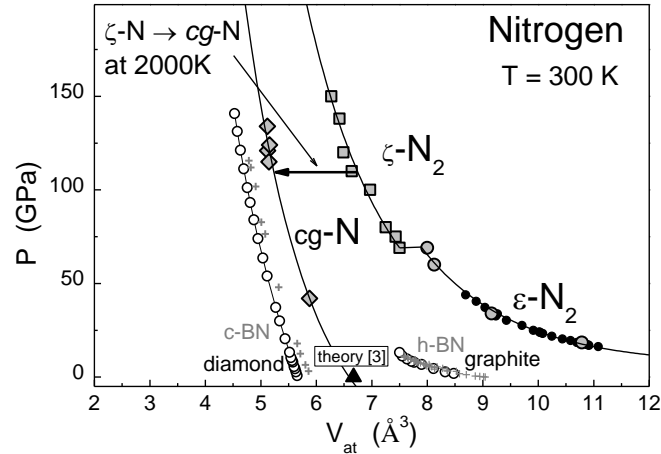
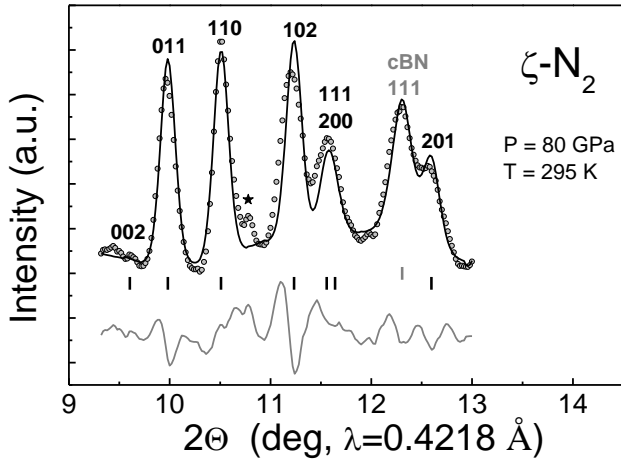


- 'Polymeric' phase identified (150 GPa)
- Semiconducting to 230 GPa
- Consistent with electrical conductivity

➤ **Crystal structure?**

Recent x-ray diffraction measurements reveal the structure of framework “polymeric” nitrogen

ESRF
APS

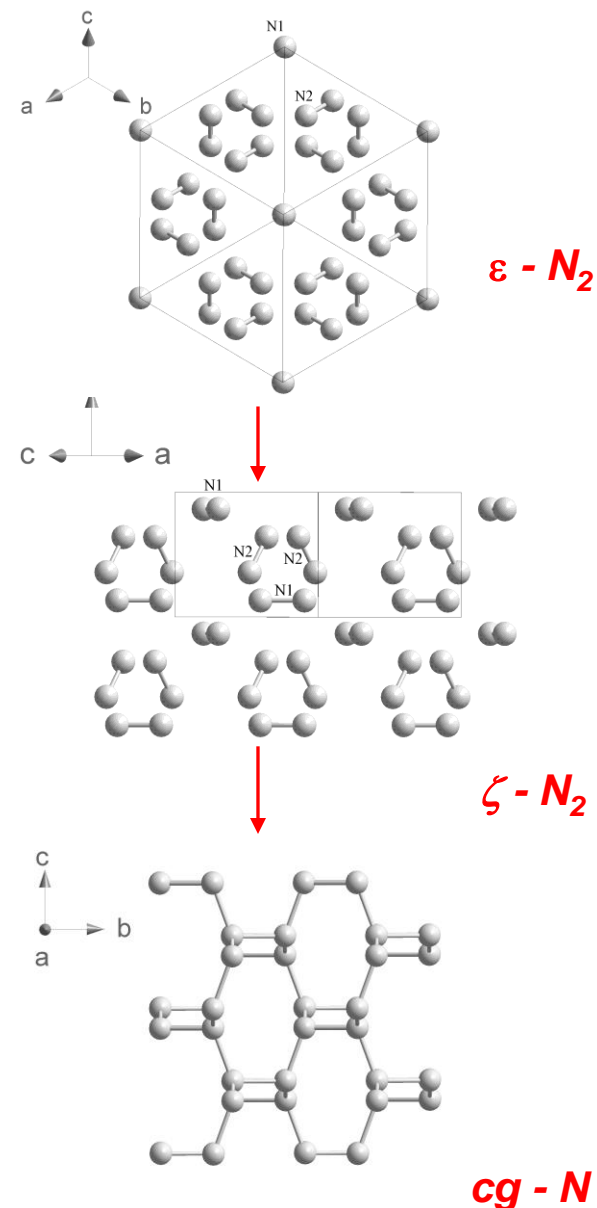
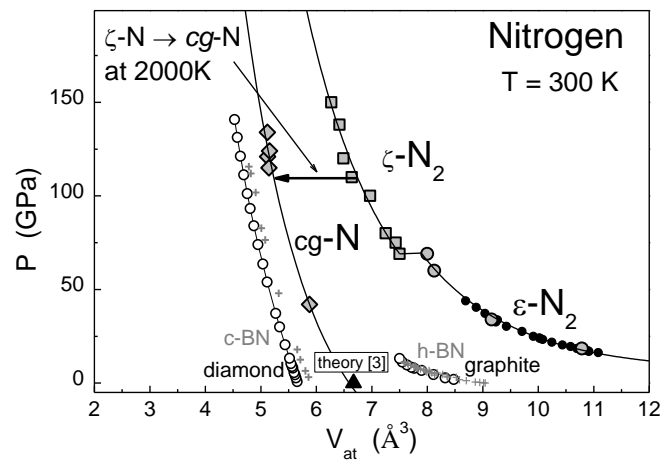
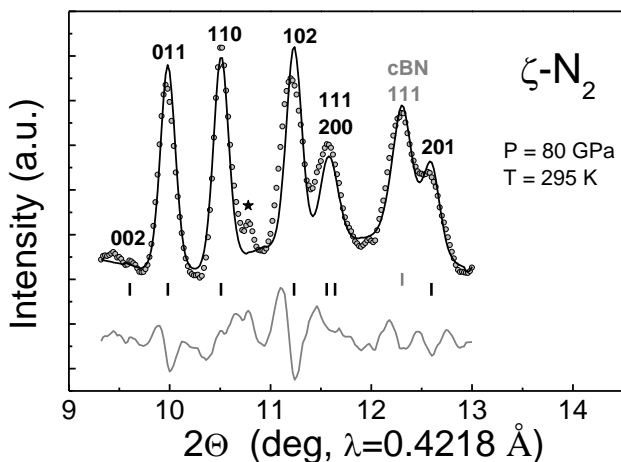


- Transition at 60 GPa from (*R3c*) ϵ -N₂ to the (*P222*₁) ζ -N₂ phase
- Near 110 GPa (with heating) the single-bonded framework phase forms
- Identified as the *cubic gauche* structure (*cg*-N) with a density increase of 22%.

[Eremets et al., *Nature Materials* 3, 558 (2004);
Eremets et al., *J. Chem. Phys.*, submitted]

Recent x-ray diffraction measurements reveal the structure of framework “polymeric” nitrogen

ESRF
APS

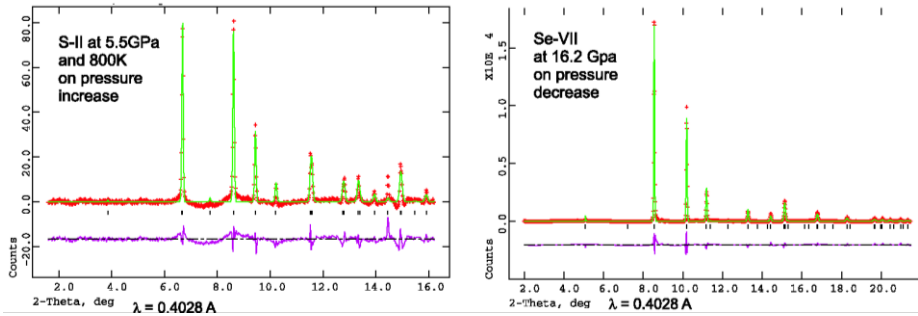


- Transition at 60 GPa from ($R3c$) $\epsilon - N_2$ to the ($P222_1$) $\zeta - N_2$ phase
- Near 110 GPa (with heating) the single-bonded framework phase forms
- Identified as the *cubic gauche* structure ($cg - N$) with a density increase of 22%.

[Eremets et al., *Nature Materials* 3, 558 (2004);
Eremets et al., *J. Chem. Phys.*, submitted]

X-ray diffraction reveals new classes of structures in Group VI element

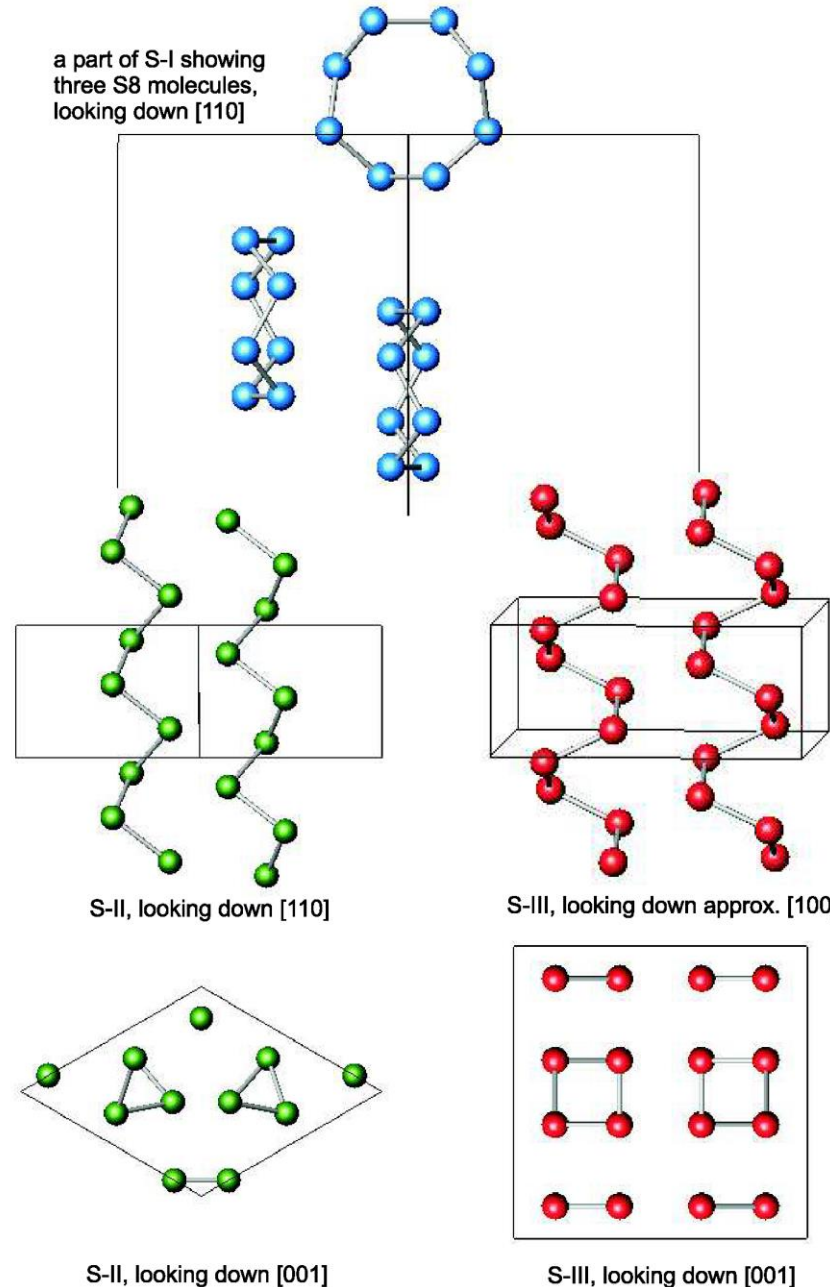
Sulfur: up to 17 phases reported and most structures unknown. The high-pressure phases above 90 GPa are superconducting



- **New chain structures (to 90 GPa)**
 - **Simplified phase diagram**
- **Higher pressure behavior?**

[Degtyareva et al., *Nature Materials*, submitted;
Phys. Rev. Lett., submitted]

a part of S-I showing three S₈ molecules, looking down [110]



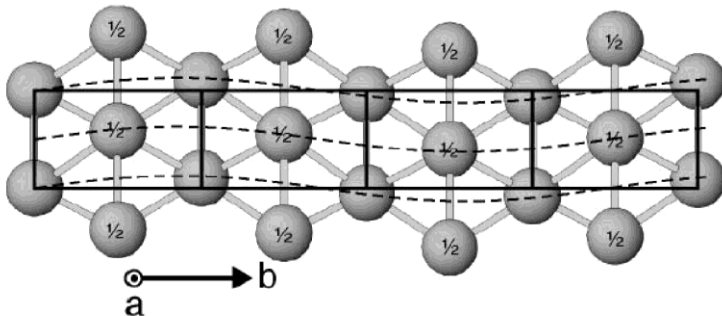
The chalcogens form a family of superconductors and their high-pressure structures are complex



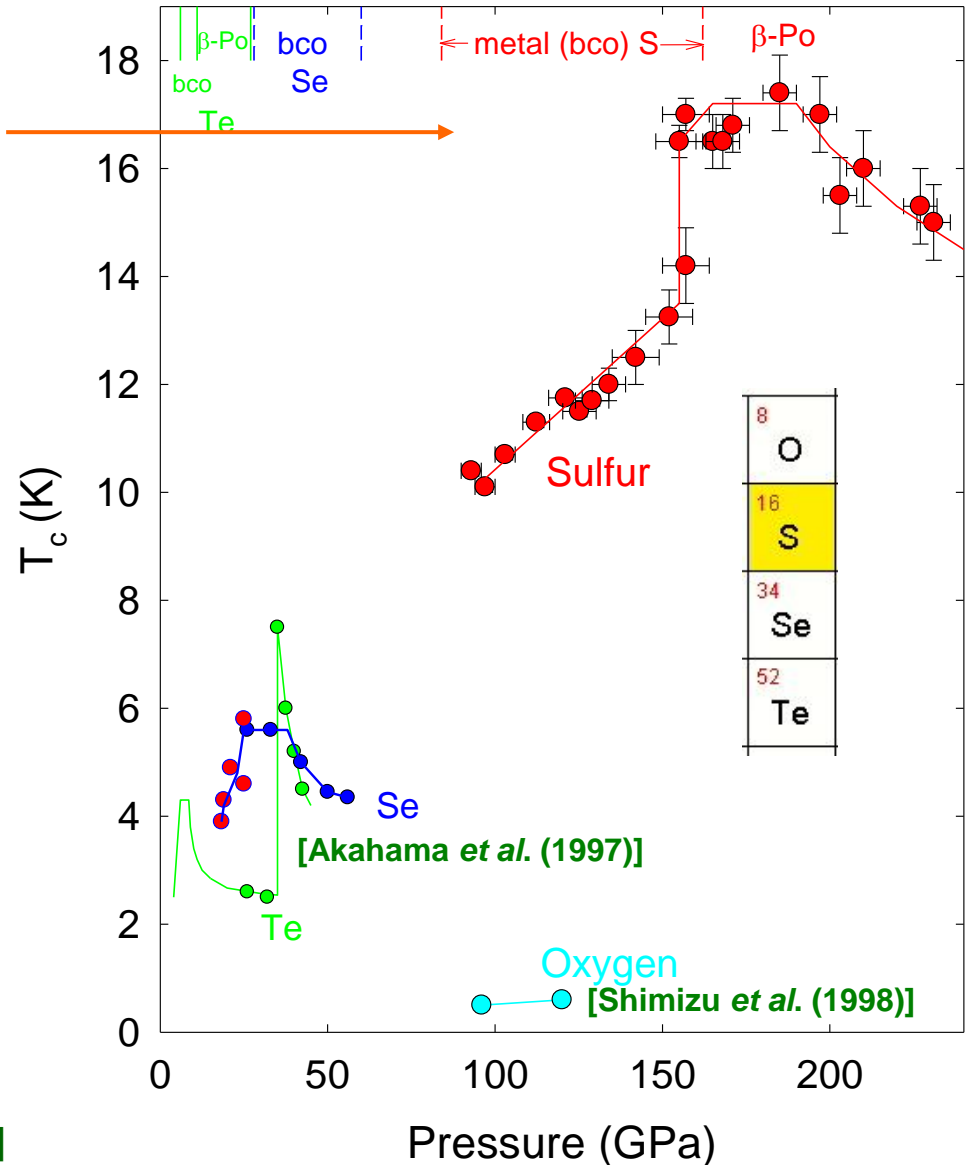
MAGNETIC SUSCEPTIBILITY TECHNIQUE

[Gregoryanz *et al.*, *Phys. Rev. B* 65, 06504 (2002)]

- Superconducting phase is incommensurate phase (not bco)



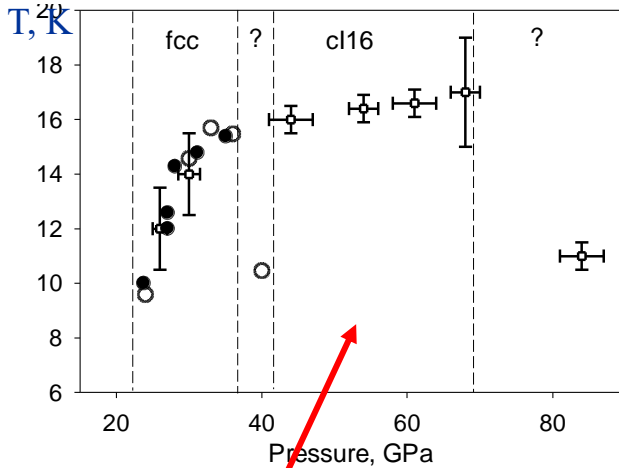
[Degtyareva *et al.*, *Phys. Rev. Lett.*, submitted]



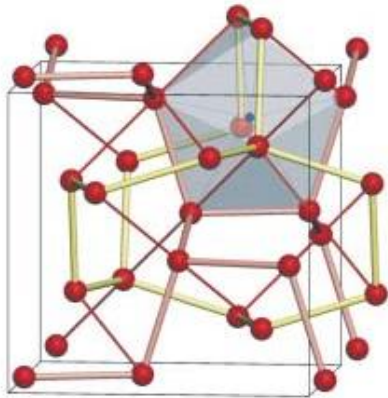
A growing number of novel metals and superconductors are being uncovered in high-pressure experiments



Lithium
High- T_c ->
"molecular"
metal?



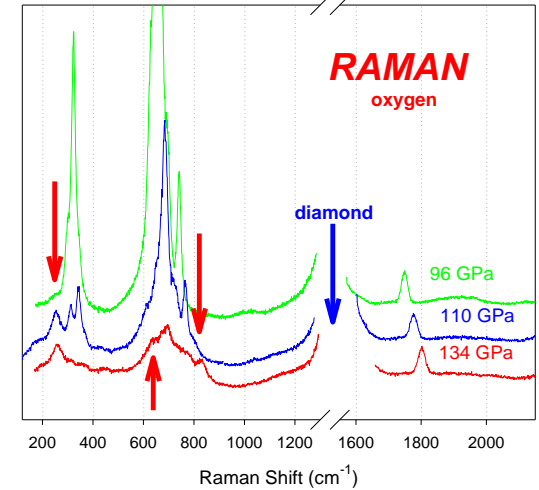
[Neaton & Ashcroft (2001); Shimizu *et al.* (2002); Struzhkin *et al.* (2002); Hanfland *et al.* (2002)]



[Hanfland *et al.* (2000)]

Oxygen
molecular
superconductor

[Shimizu *et al.* (1998); Weck *et al.* (2002); Goncharov *et al.* (2003)]



Periodic Table of Superconductors

H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Ru 104	Ha 105	Unh 106	Uns 107	Uno 108	Une 109									
Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71				
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103				

■ P = 0
■ P > 0

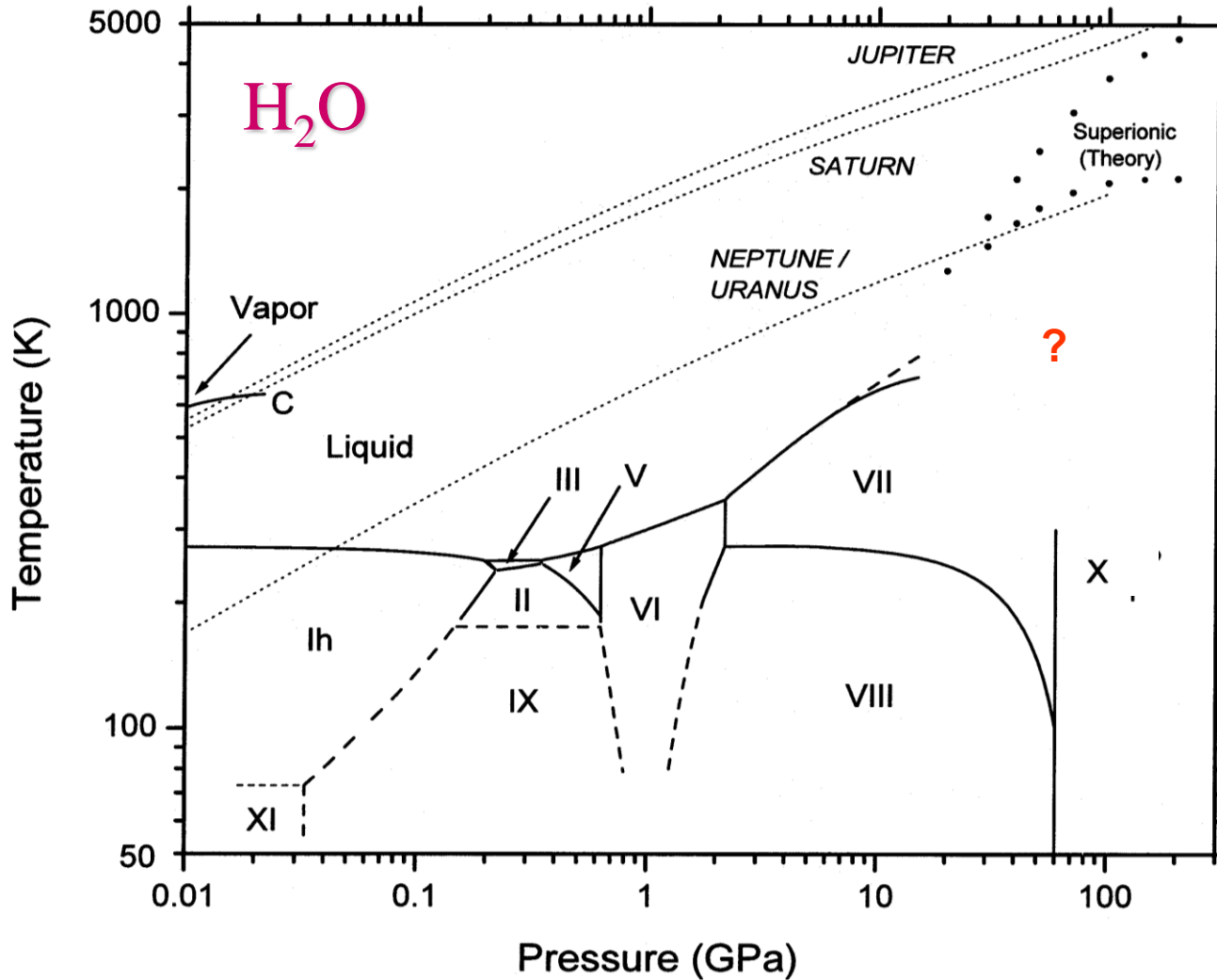
[Hemley & Mao (2002); Ashcroft (2002)]

Highest T_c (164 K at 30 GPa)



[Gao *et al.*, (1994); Lokshin *et al.* (2002)]

The high-pressure behavior of water continues to present new questions and surprises

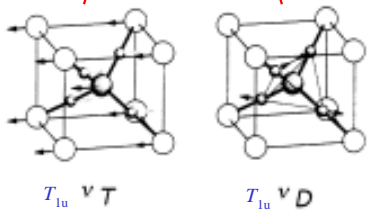
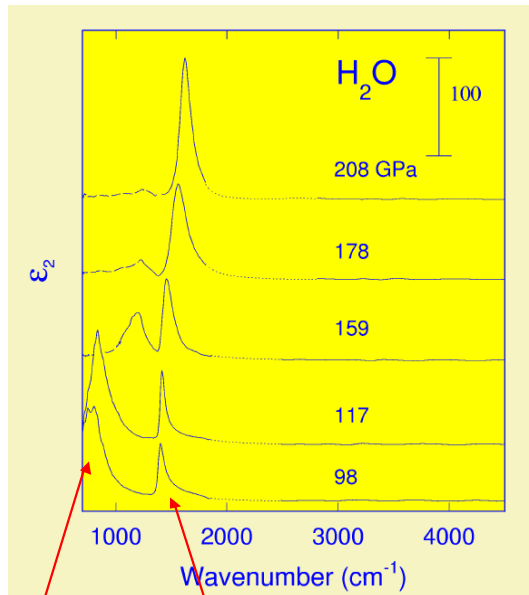


- ~20 stable and metastable phases
- Novel transitions
 - non-molecular
 - amorphization
 - liquid/liquid trans?
- High P - T fluid

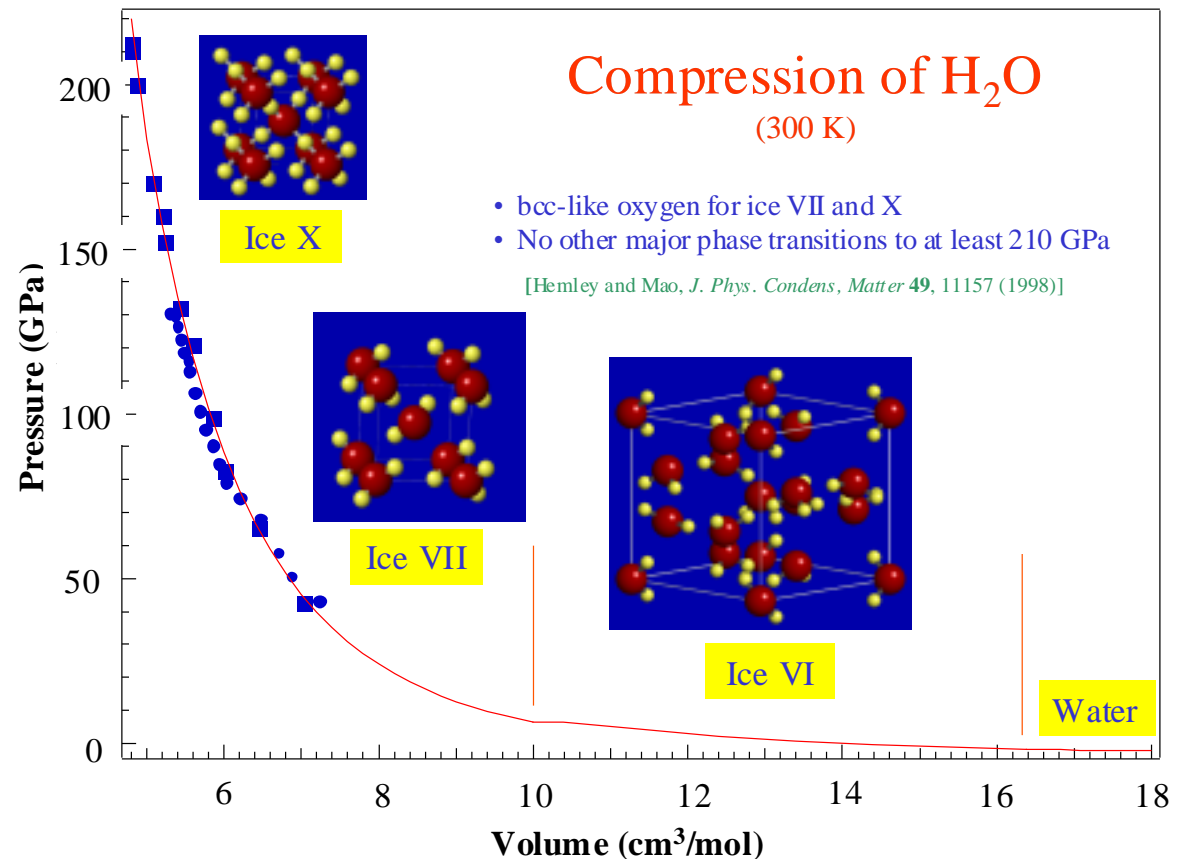
H₂O transforms to a symmetric hydrogen-bonded phase (non-molecular ice X) near 60 GPa



HIGH PRESSURE SPECTRA Synchrotron Infrared Reflectivity



[Goncharov *et al.*, *Science* 273, 218 (1996)]



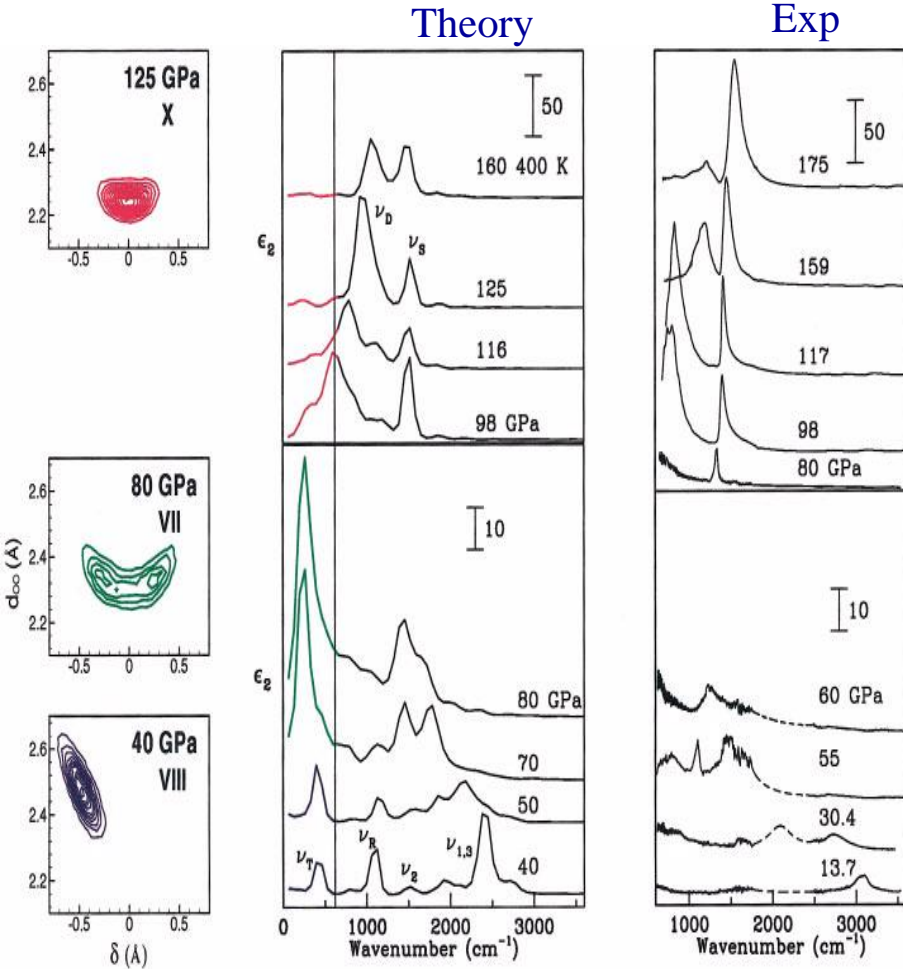
- Non-molecular ice first identified by IR reflectivity above 60 GPa
- X-ray confirms spectroscopic data: bcc-based structure

First-principles calculations predict unusual dynamics in ice under pressure

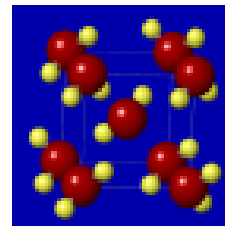
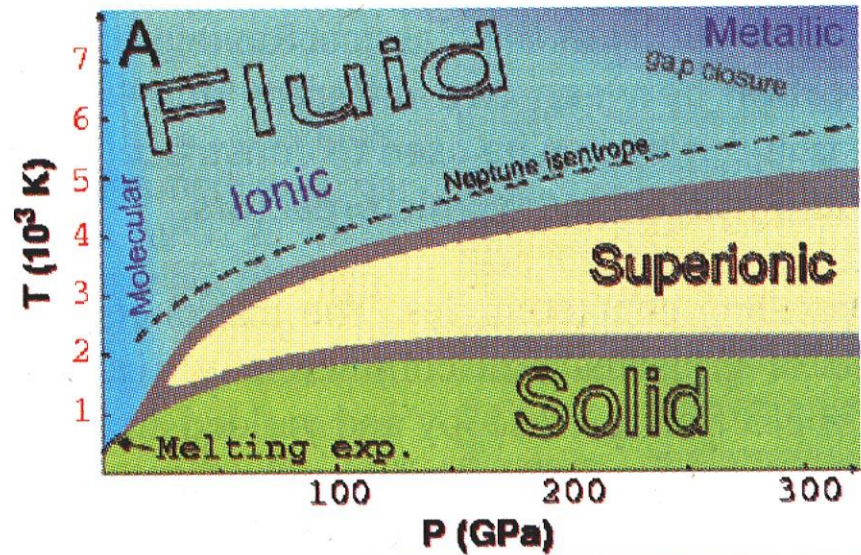


Car-Parinello simulations

Infrared spectrum across transition



'Superionic' phase of ice VII

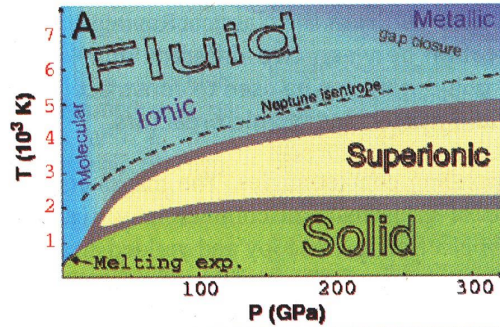


bcc oxygens with diffusive protons

[Bernasconi et al., *Phys. Rev. Lett.* 81, 1235 (1998)]

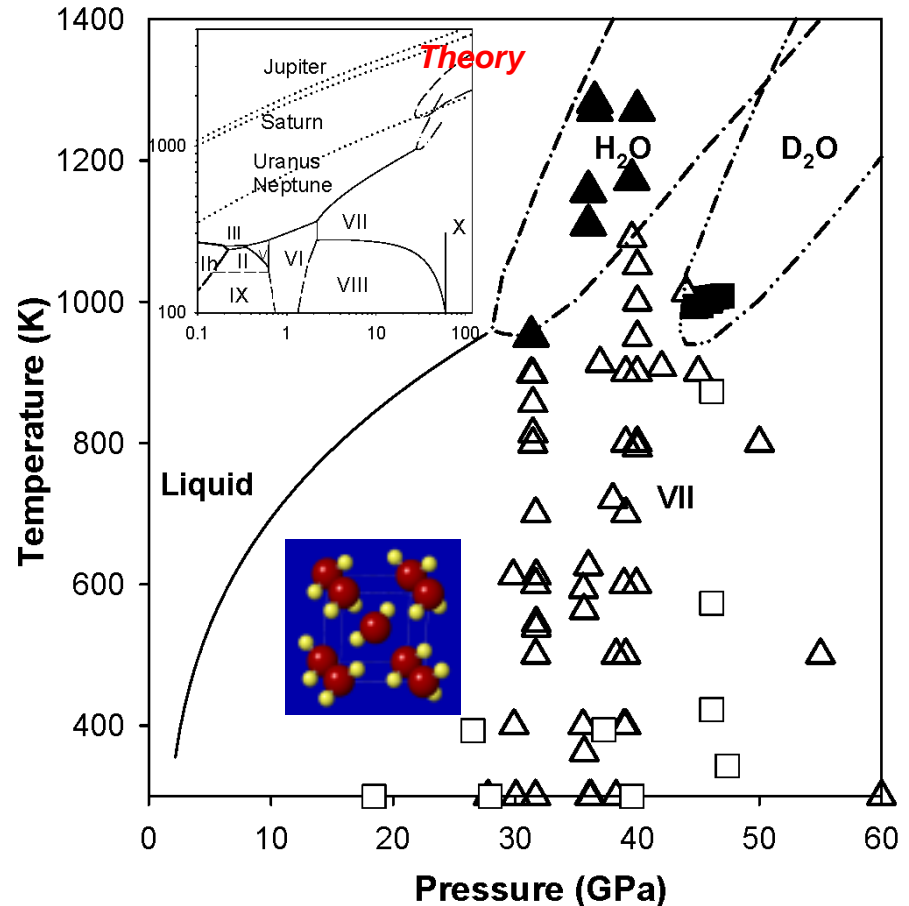
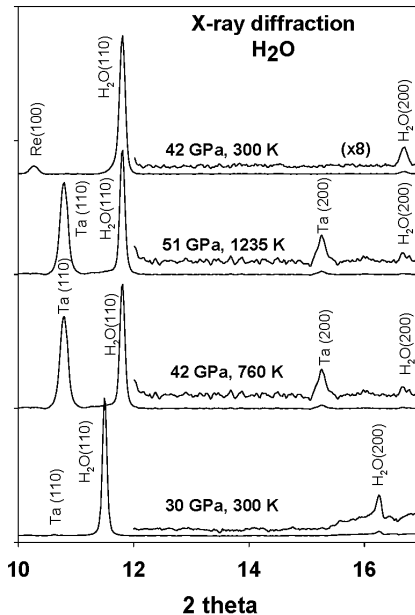
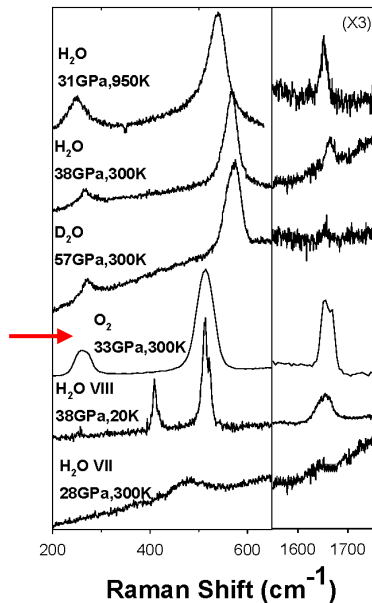
[Cavazzoni et al., *Science* 283, 44 (1999)]

High P - T x-ray diffraction and spectroscopy reveal a new transformation in H_2O : more than superionic ice



RAMAN

X-RAY



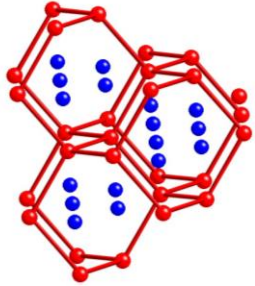
- Breakdown of water to form oxygen-rich and hydrogen-rich 'alloys'
- $H_{2+x}O$ superionic phase?
- Phase diagram of H-O?

[Lin et al., Nature, submitted]

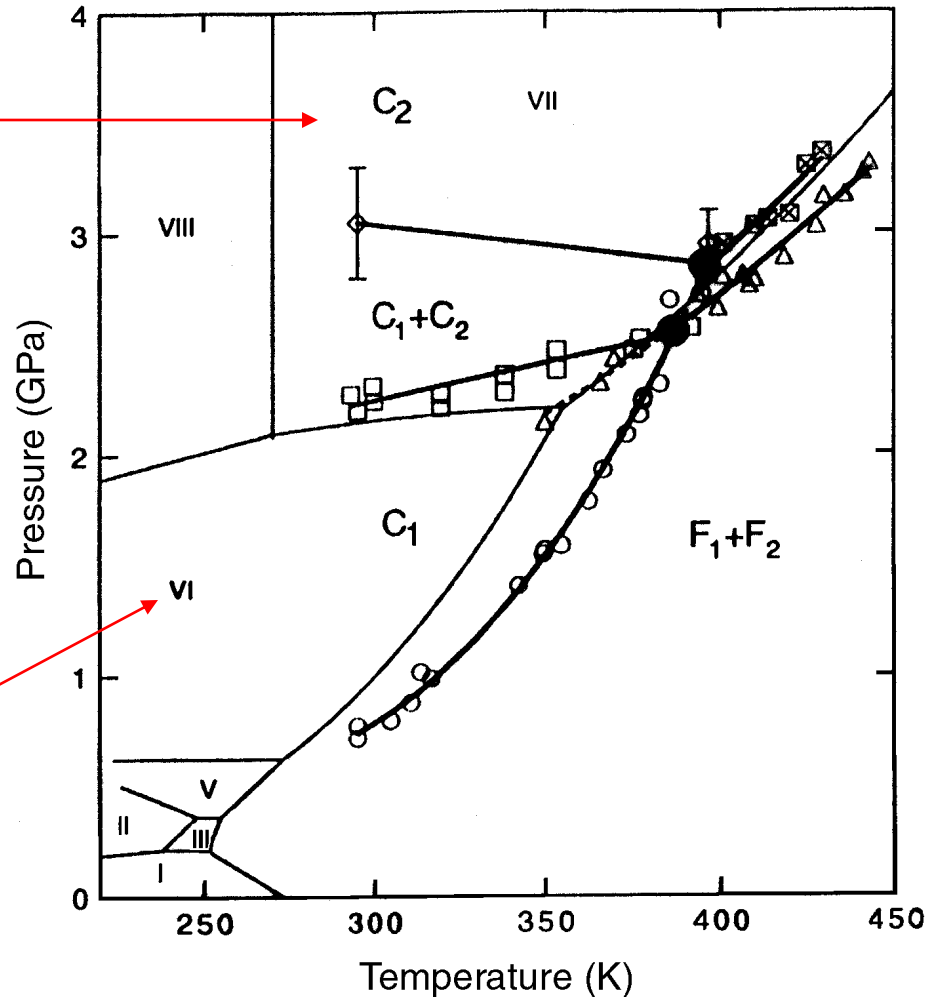
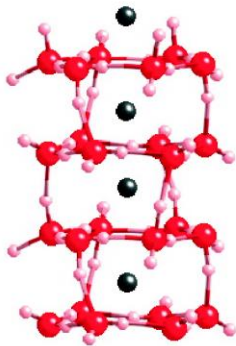
New classes of molecular compounds form in simple molecular systems under pressure: H₂-



H₂O



- “Filled ices”
- C₁ ice II-like
- C₂ ice VII-like



➤ *Can they be recovered on decompression?*

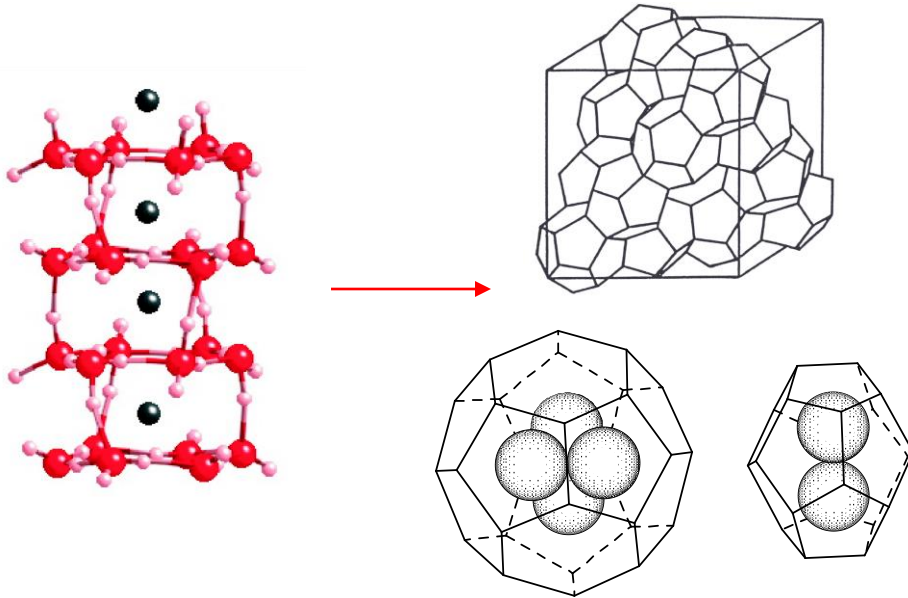
SINGLE-CRYSTAL NEUTRON DIFFRACTION

[Guthrie et al., to be published]

The low-pressure H₂-H₂O clathrate has been characterized by variable *P-T* spectroscopy, neutron and x-ray diffraction

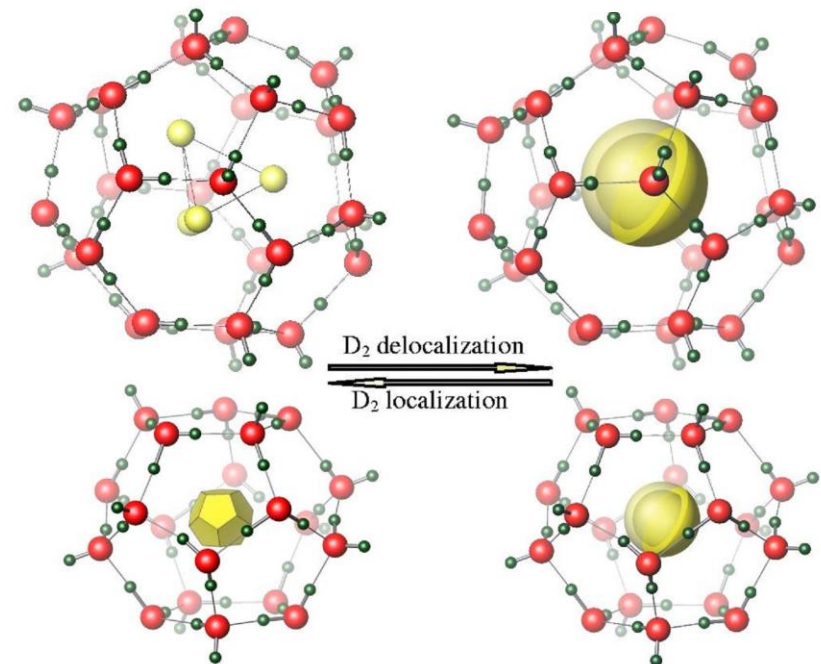
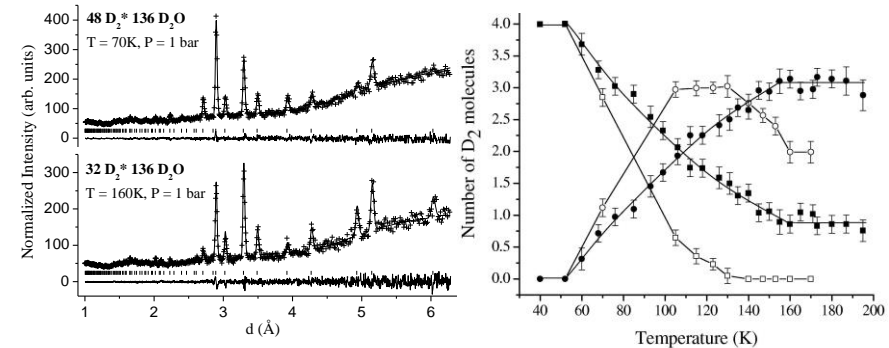


Low-temperature Decompression of C₁ clathrate



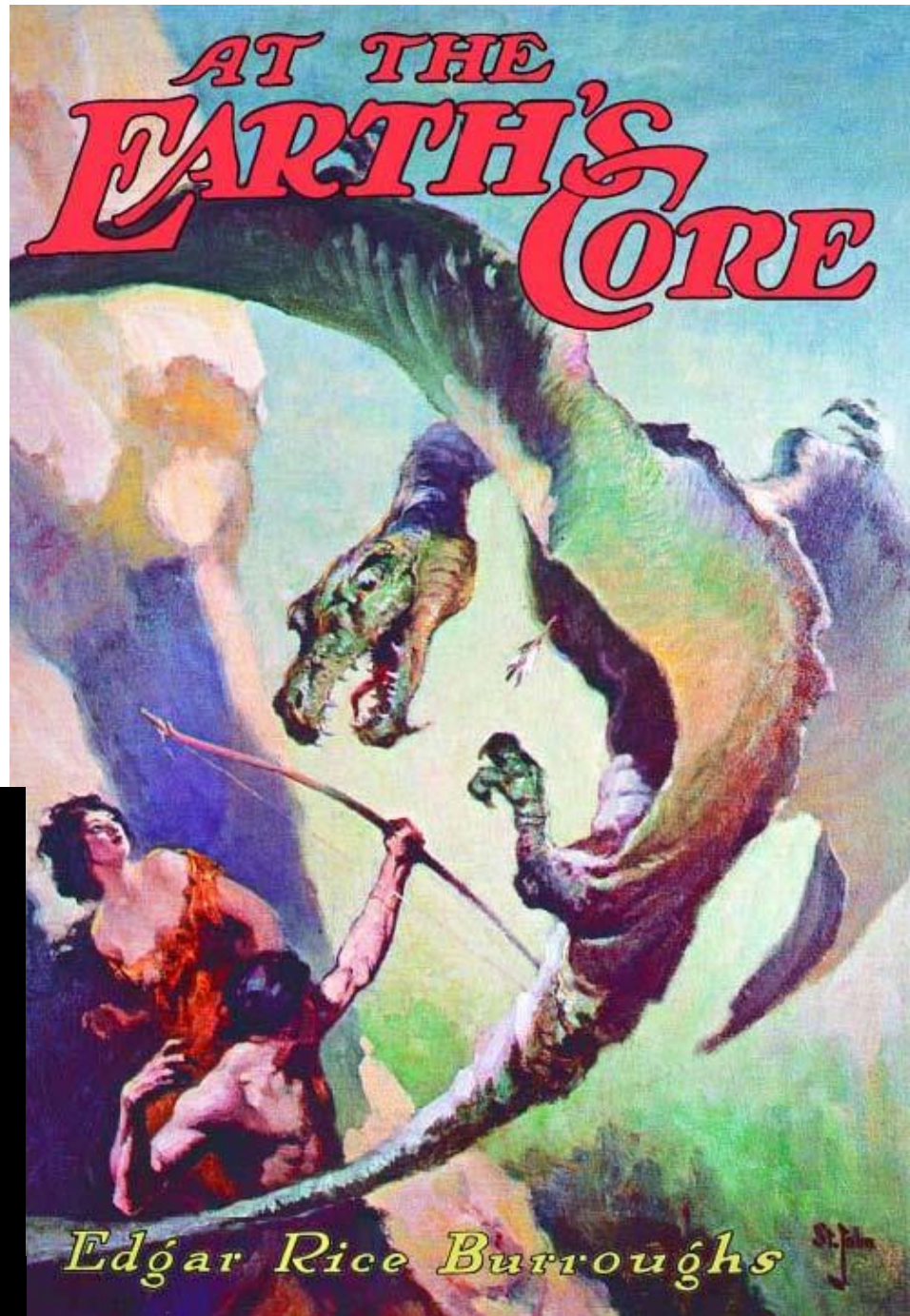
- Structure II clathrate
- Novel H₂ (D₂) clusters
- Stable at ambient pressure (<145 K)
- Spectrum match H₂ in interstellar clouds
- Hydrogen storage (5.3 wt % H₂)

[W. Mao *et al.*, *Science* 297, 2247 (2002)]



POWDER DIFFRACTION (LANSCE)
Gas Cell

[Lokshin *et al.*, *Phys. Rev. Lett.*, in press]



EARTH HAS A DEADLINE

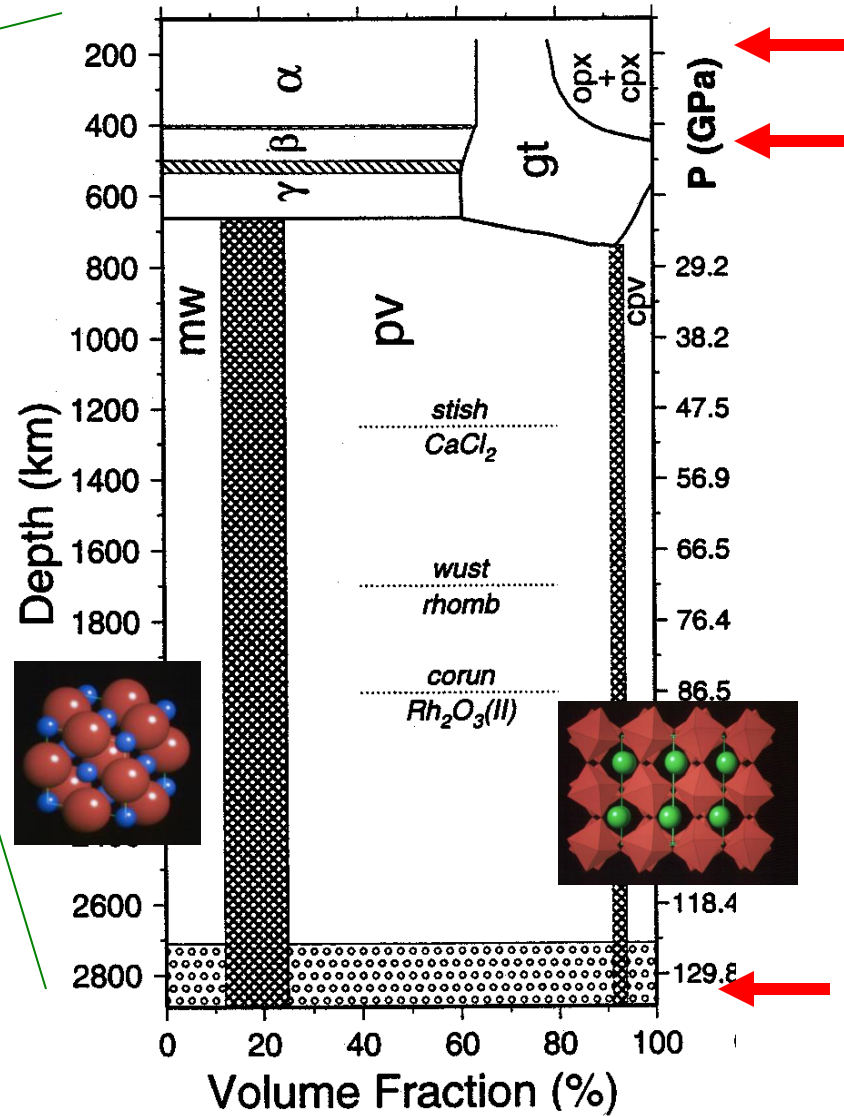
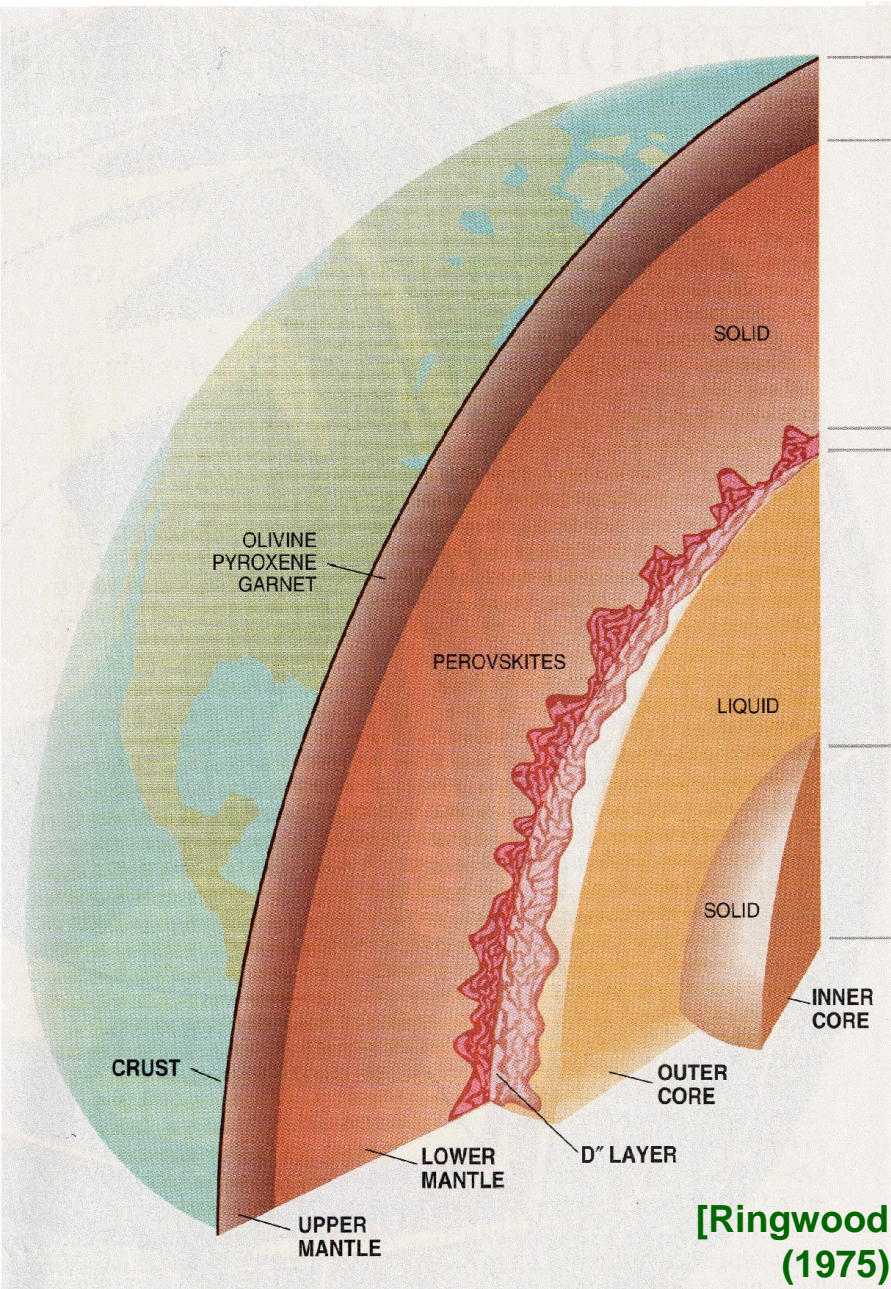


THE ONLY WAY OUT IS IN

Edgar Rice Burroughs

Carnegie Institution

Solid Earth geophysics has its standard model



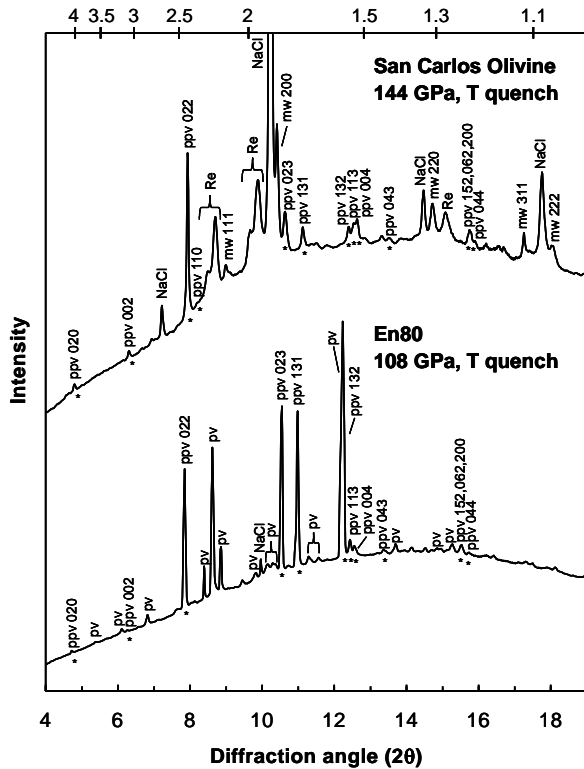
Earth's Interior: "Pyrolite" Model

[Ringwood, *Composition and Petrology of the Earth's Mantle* (1975); Bina, *Ultrahigh Pressure Mineralogy* (1998)]

Discovery of new Fe-bearing silicate phases at 100 GPa: post-perovskite (Mg,Fe)SiO₃

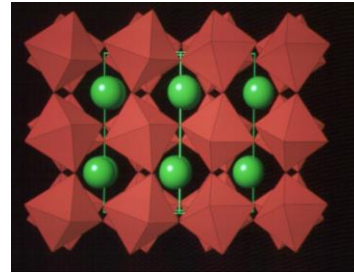


X-ray at 108 GPa (300 K) after laser-heating (Fe,Mg) olivine to 2000 K

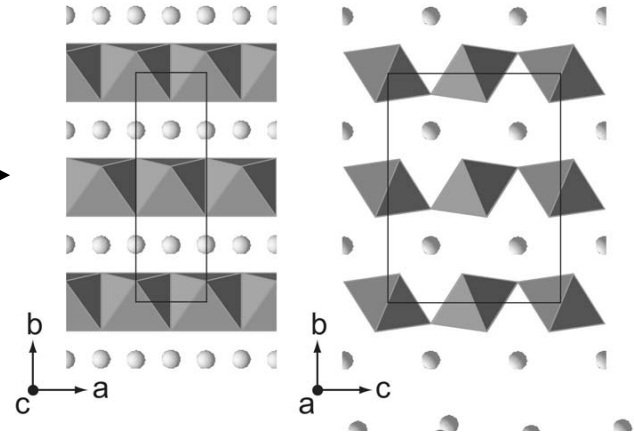


Evidence for a post-perovskite phase

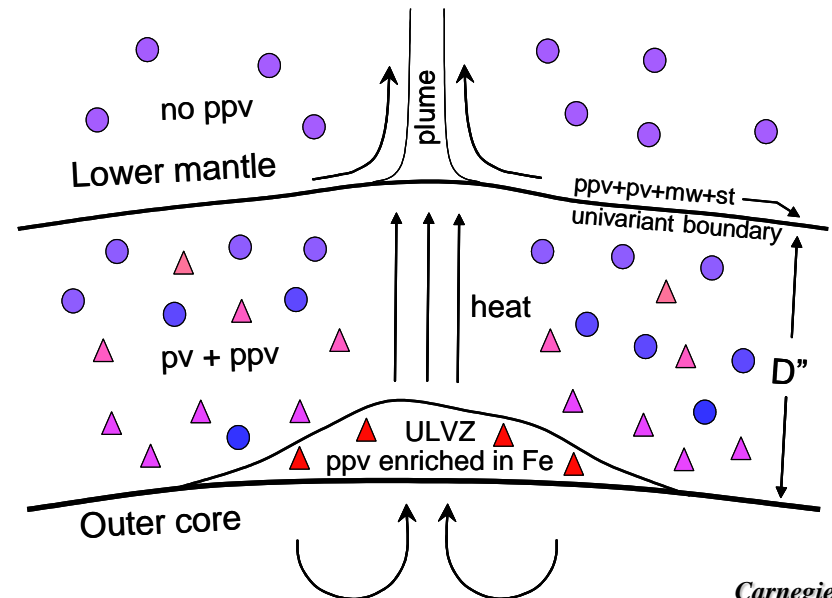
[Murakami et al., Science, in press]



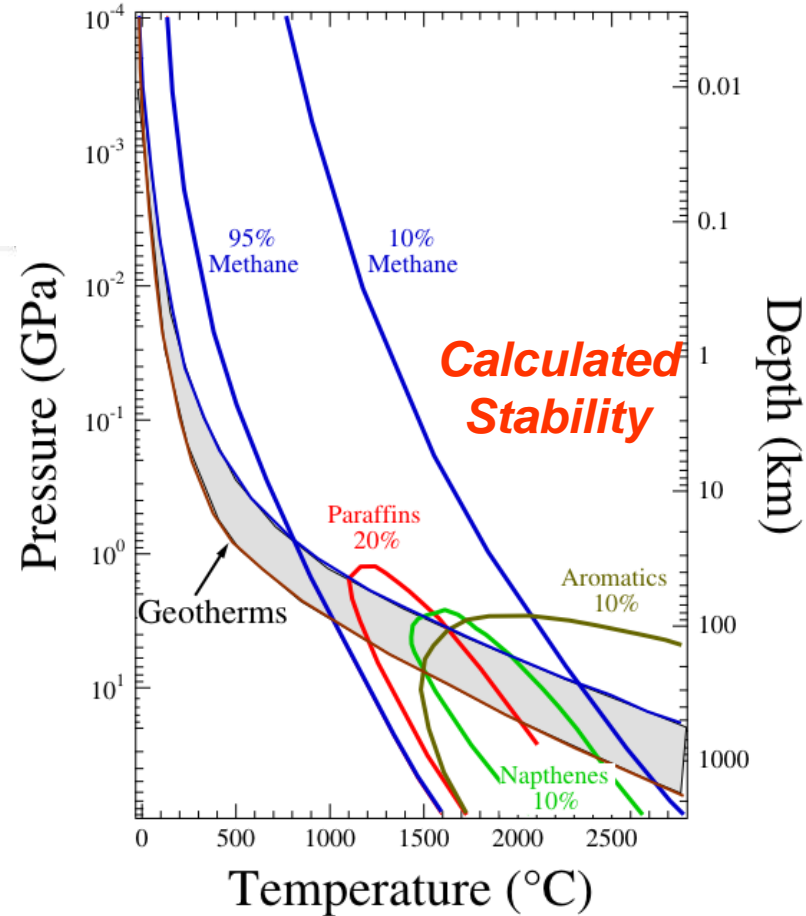
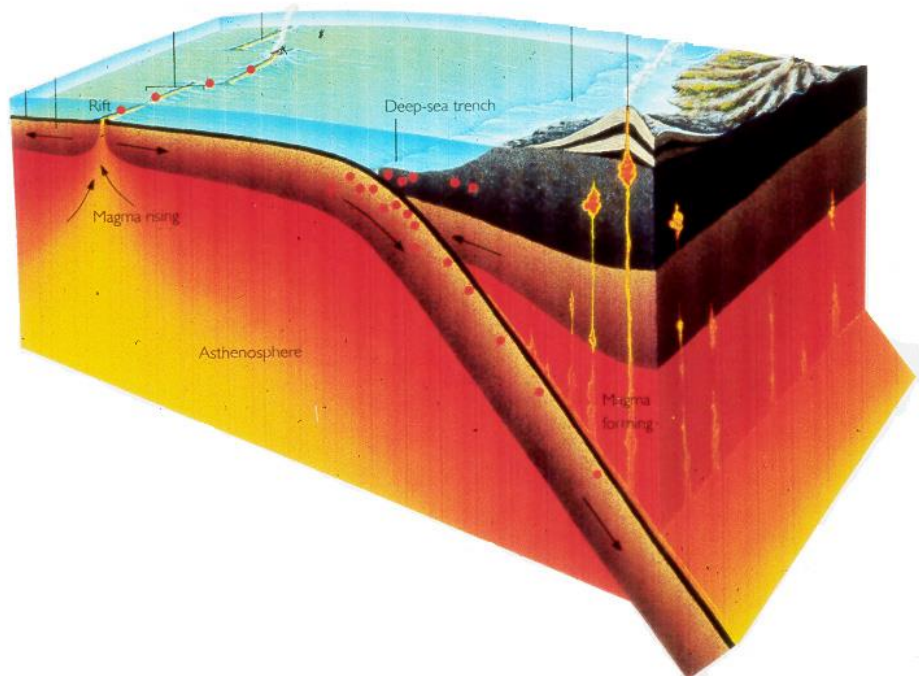
[W. Mao et al., Science, submitted]



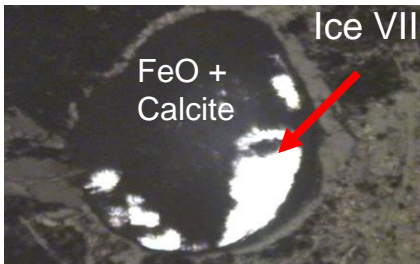
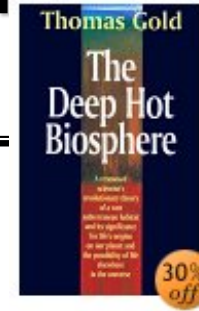
- The phase 'soaks' up iron
- Enlarges 'ppv' stability field
- Core-mantle reactions
- Explains seismic signatures



Chemistry at shallower depths: Can hydrocarbons form abiogenically in the mantle?

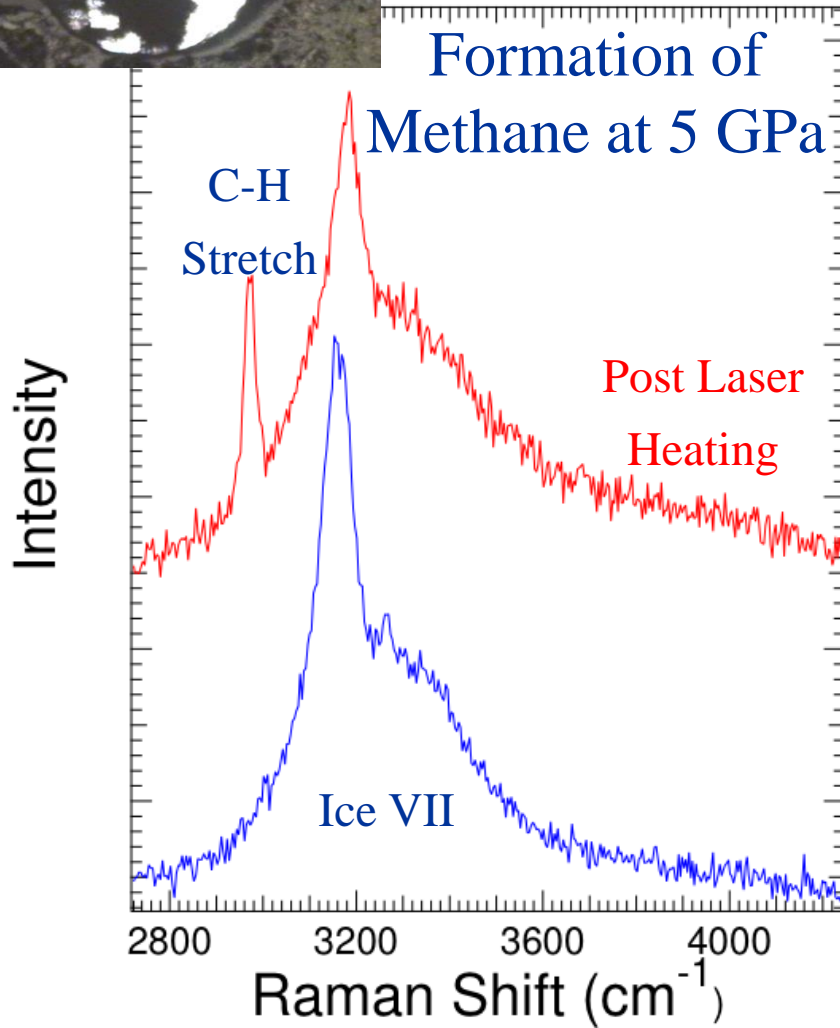


Chemistry at shallower depths: Can hydrocarbon form abiogenically in the mantle?

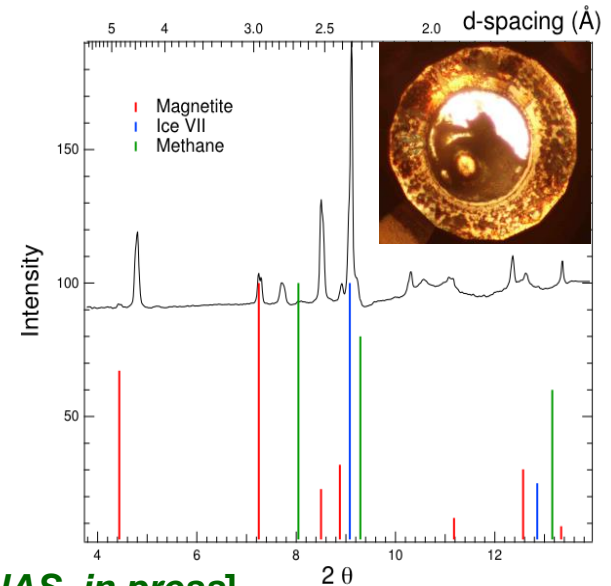


Laser heating calcite, FeO and H₂O at 5.1 GPa

Formation of Methane at 5 GPa



- **Copious methane produced**
- **In situ diffraction identifies the solid phases and reaction**



[Scott et al., PNAS, in press]

Can these techniques be used to directly examine life

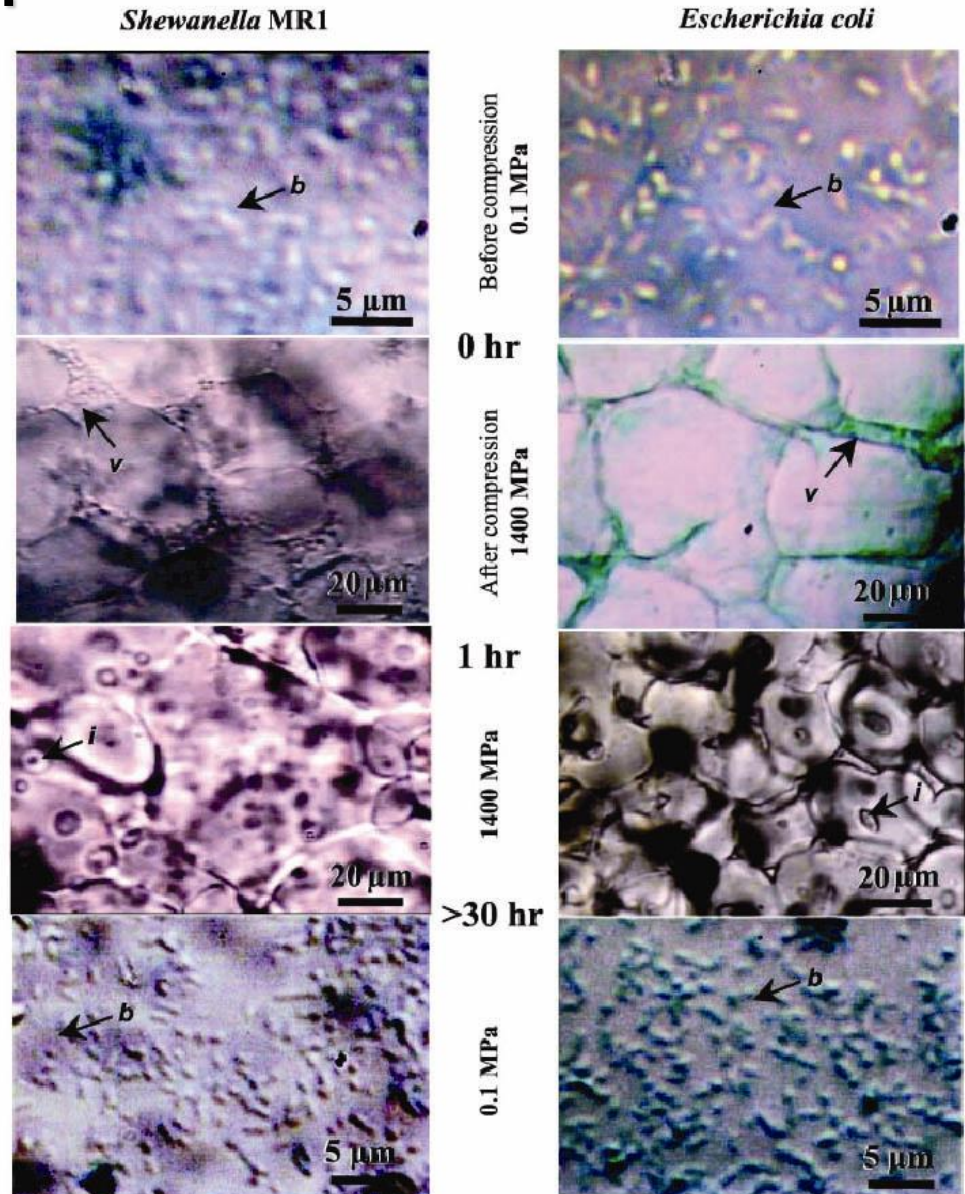
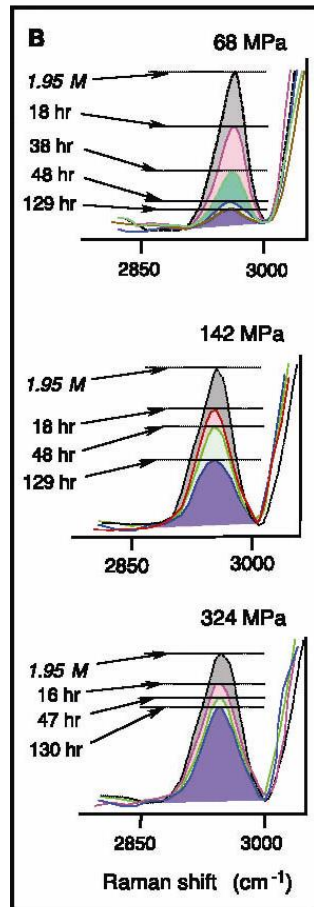
~~under 'extreme' pressures?~~



OBSERVATIONS OF MICROBIAL ACTIVITY UP TO 1.6 GPa (300 K)

[Sharma, Scott, et al., *Science* 295, 1514 (2002)]

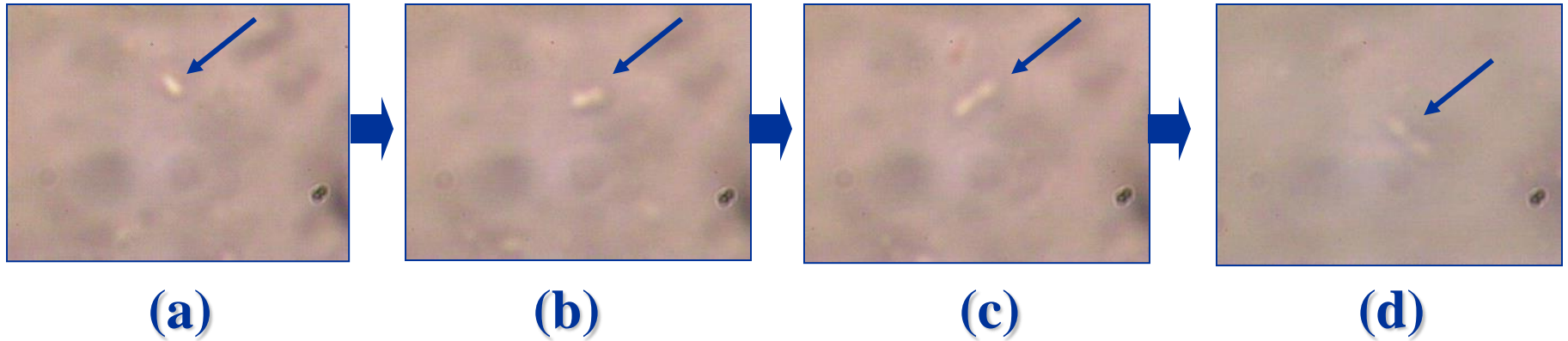
Formate Raman



Cell division after exposure to 1.4 GPa further demonstrates viability



A single *Shewanella* MR1 cell replicating after decompression from 1.4 GPa. The observed cells are on the diamond surface of the opened diamond anvil cell.



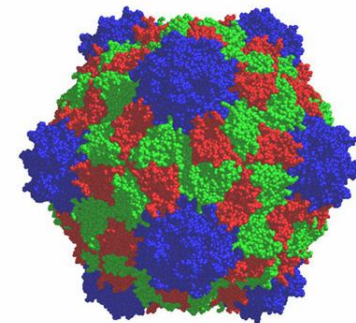
[Sharma, Cody, Scott & Hemley, *Chemistry Under Extreme Conditions*, in press]

In situ techniques are now needed to probe structure-property relations in this new *P-T* domain

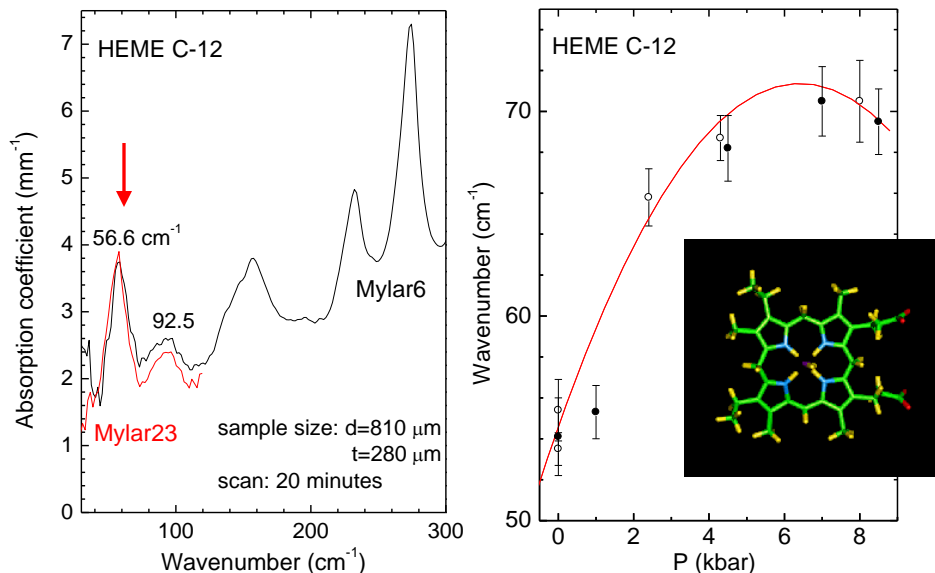


New techniques provide unprecedented accuracy for structure/dynamics studies of complex biomolecules

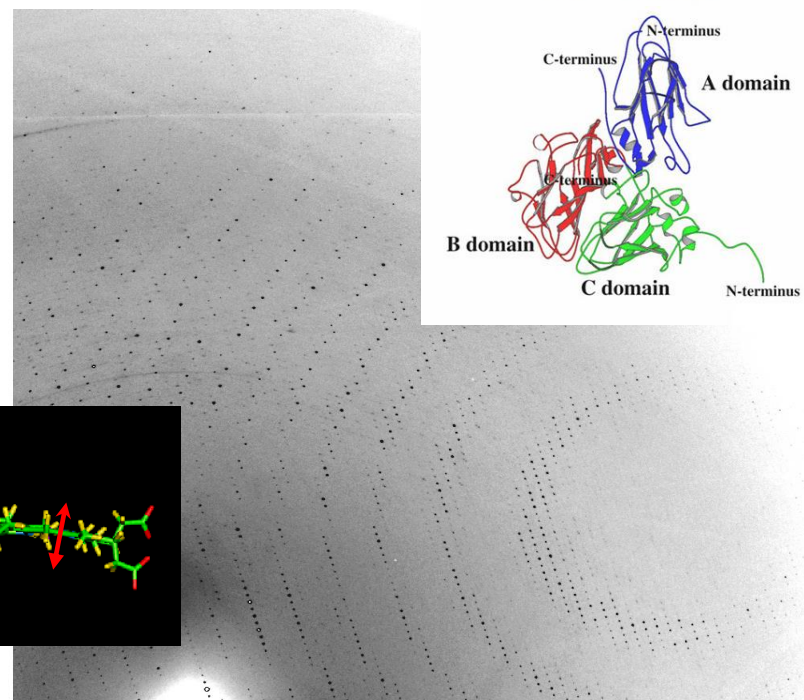
Single Crystal Diffraction of Cow Pea Mosaic Virus



Heme "Doming Mode" by Far-IR Spectroscopy



[Klug *et al.*, *PNAS* 99, 12526 (2002)]



3.5 kbar

[Lin *et al.*, *to be published*]

We are extending these experiments with the development of new materials and instrumentation

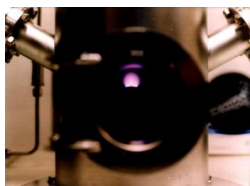


GOALS FOR STATIC HIGH PRESSURE:

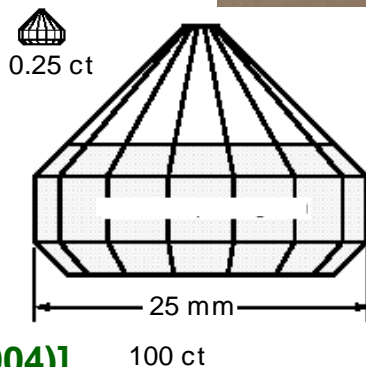
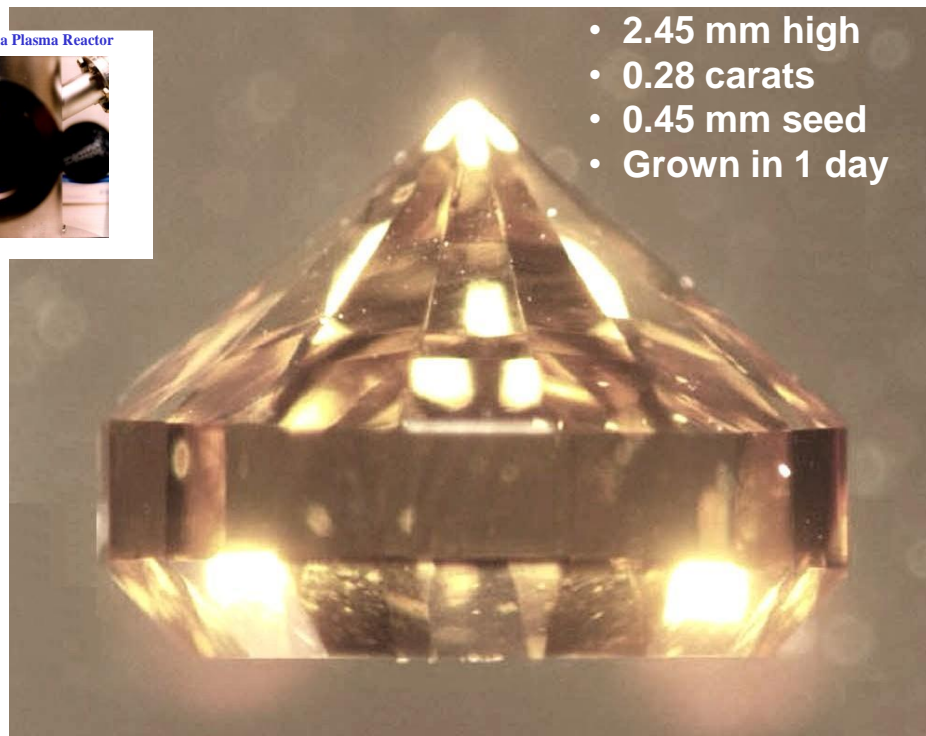
- Higher pressures (1 TPa or 10 Mbar) and temperatures (>1 eV)
- Larger sample volumes needed (e.g., neutron and x-ray inelastic scattering, THz spectroscopy, NMR)
- Further improve accuracy/precision and applications of multiple simultaneous

Fabrication of Single Crystal Diamond by CVD

Diamond Growing in a Plasma Reactor



- 2.45 mm high
- 0.28 carats
- 0.45 mm seed
- Grown in 1 day



- Large samples
- Harder/tougher material
- Electrical/magnetic studies
- IXS, INS, NMR spectroscopies

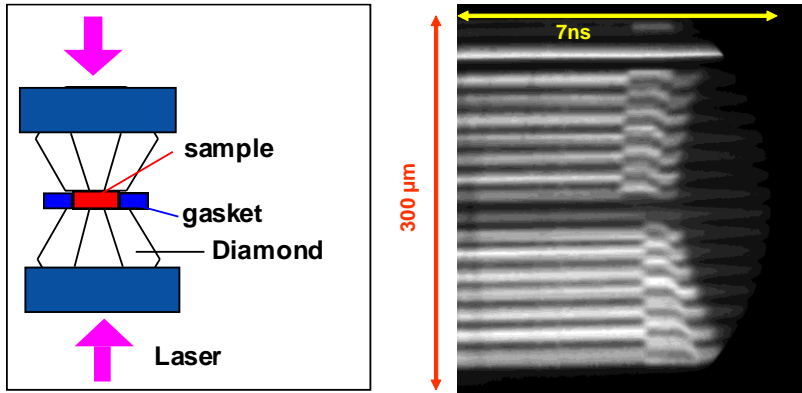
[Yan *et al.* *PNAS* 99, 12523 (2002)]

[Yan *et al.* *Phys. Stat. Sol.* 201, R27 (2004)]

Static/dynamic compression methods can be combined

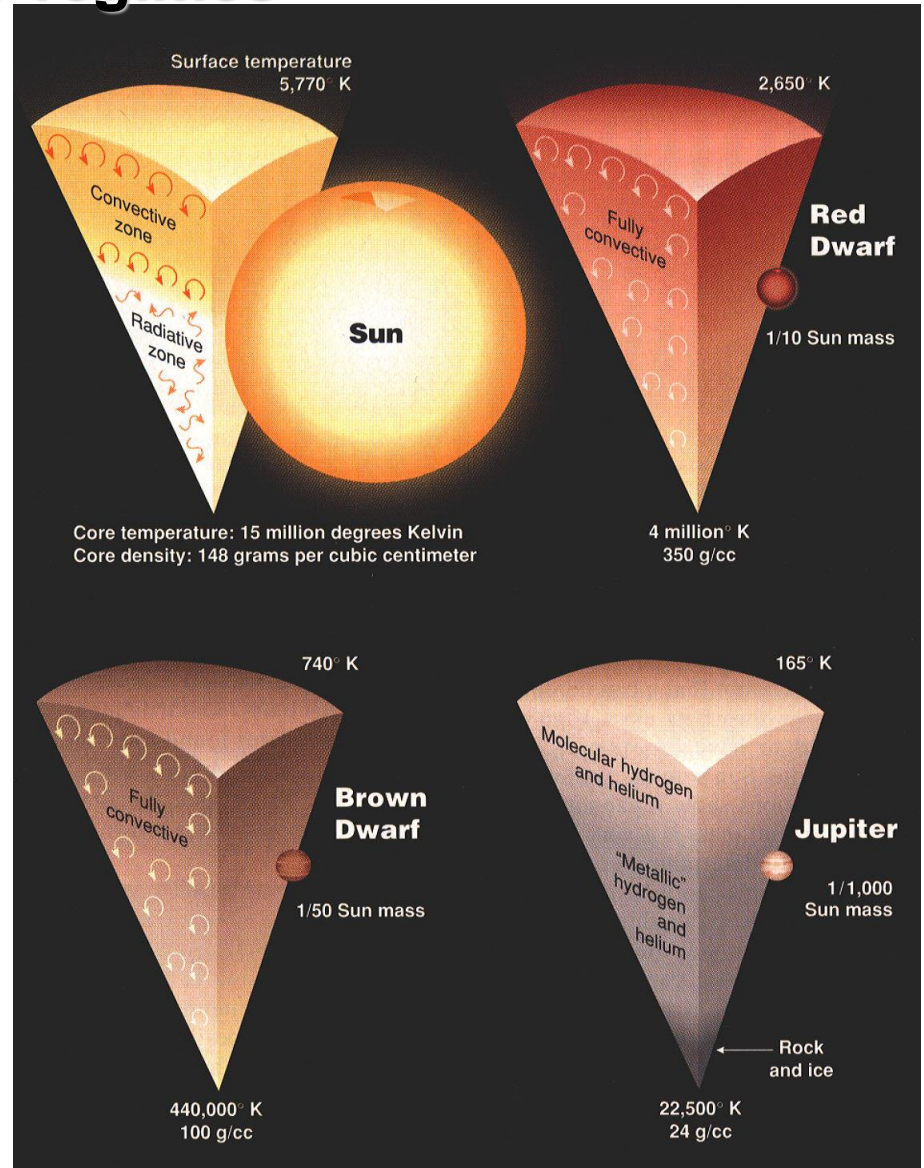
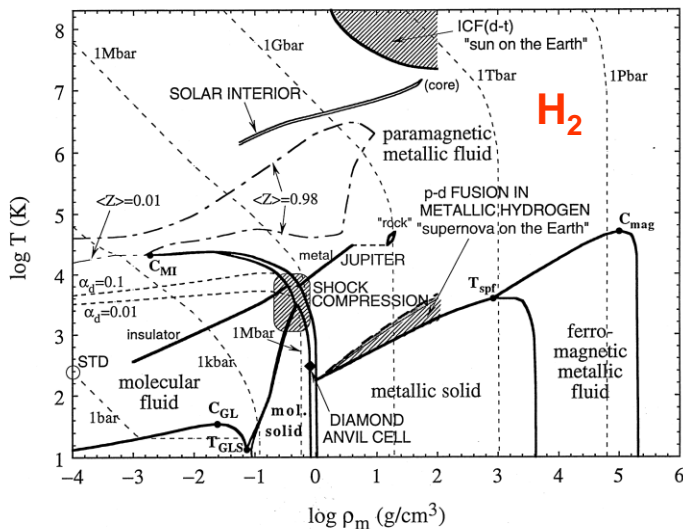
~~to access altogether new P - T regimes~~

Anvil-Cell/Laser Shock Techniques



Metallization of Fluid H_2O Omega, NIF

[Lee et al., to be published]



CONCLUSIONS AND OUTLOOK



- High-pressure science is a rapidly developing field, particularly in combination with variable temperature methods.
- A diversity of phenomena is being revealed over a broad range of pressure and temperature.
- Understanding these phenomena continues to challenge our understanding of chemical bonding, condensed matter theory, and even accepted precepts in biology.
- Important new techniques are coming on line that are taking the science to the next level.

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