

# Dry High-Pressure Methods

**Chemistry at the Earth's surface at 100 kPa**

**Chemistry in the Universe at high pressures and temperatures deep within the planets and stars**

**Laboratory:**

**Pressures up to 250 GPa, high temperatures  $\sim 7000$  °C**

**1 bar = 100 kPa      1 Mbar = 100 GPa**

**p-V work during compression to 1 Mbar equivalent to approx. 1 eV chemical bond energy**

**In-situ observations by diffraction, spectroscopy to probe chemical reactions, structural transformations, crystallization, amorphization, phase transitions**

**Methods of obtaining high pressures**

**✘ Anvils, diamond, tetrahedral and octahedral**

**✘ Shock waves ( $\text{km s}^{-1}$ )**

**✘ Explosions, projectiles**

**✘ Go to another planet: Jupiter**

**(hydrogen is metallic at 100 Gbar)**

# Earth

Core 3.4 Mbar = 340 GPa, 6000 K  
 $\epsilon$ -Fe hcp

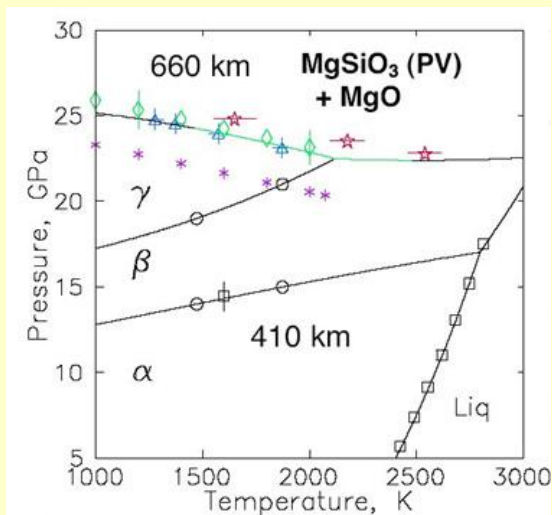
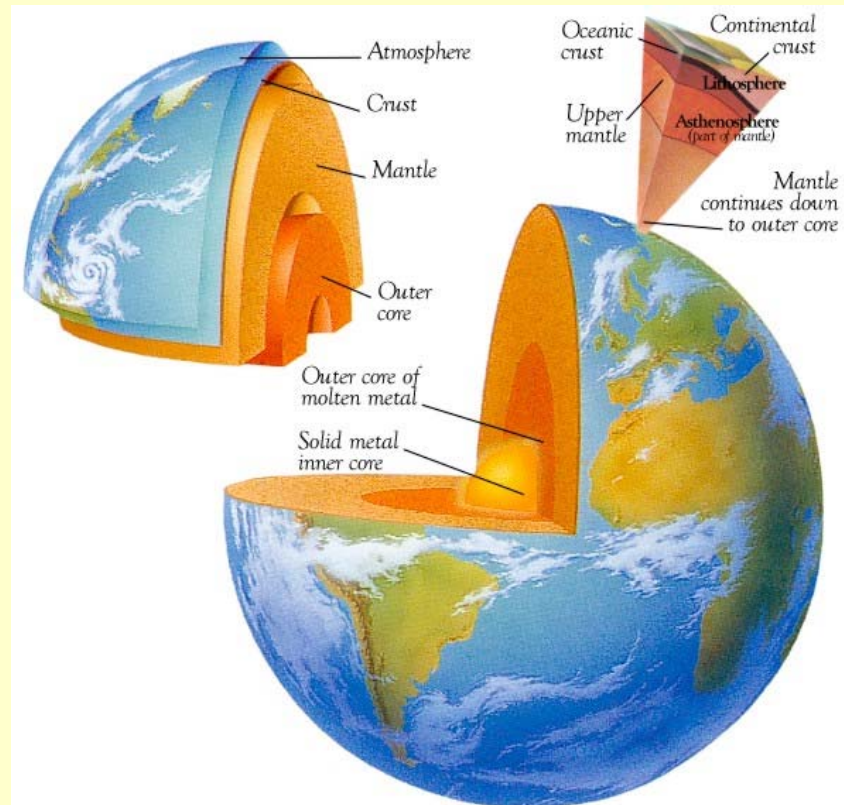
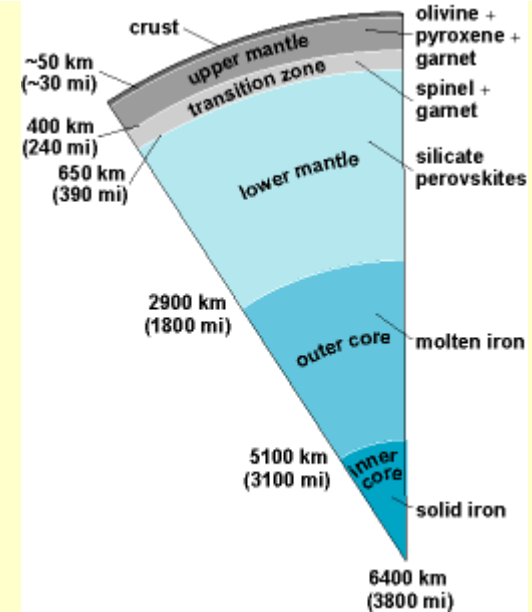
**MgSiO<sub>3</sub>** most abundant silicate mineral within our planet !

Olivine Mg<sub>2</sub>SiO<sub>4</sub> >

pyroxene (silicate chains) > spinel Mg<sub>2</sub>SiO<sub>4</sub>

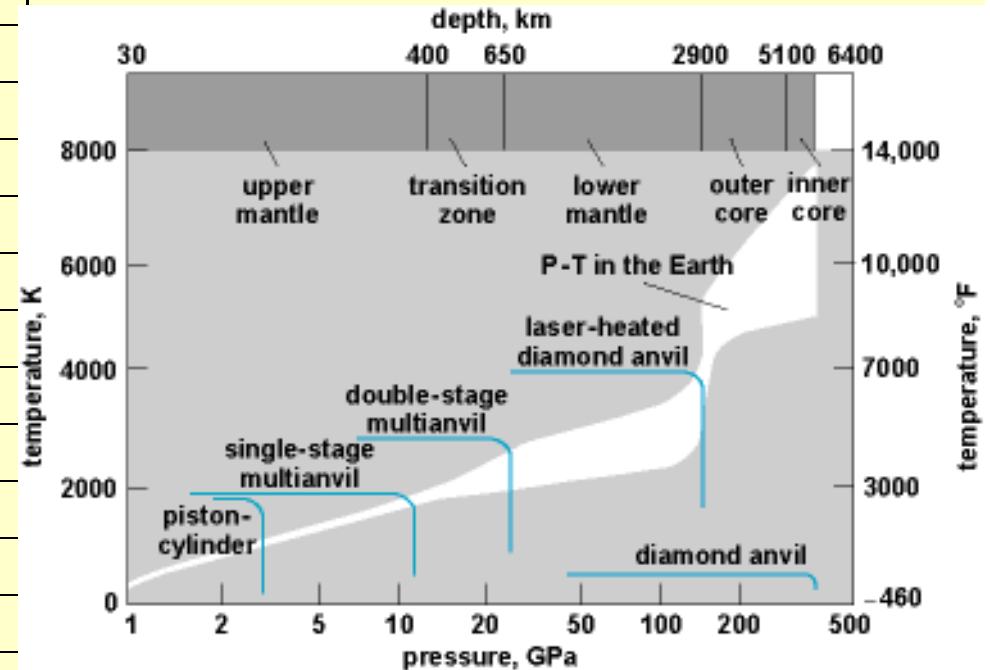
ilmenite > garnet (HT) >

perovskite MgSiO<sub>3</sub> Si CN = 6



## PRESSURE SCALE

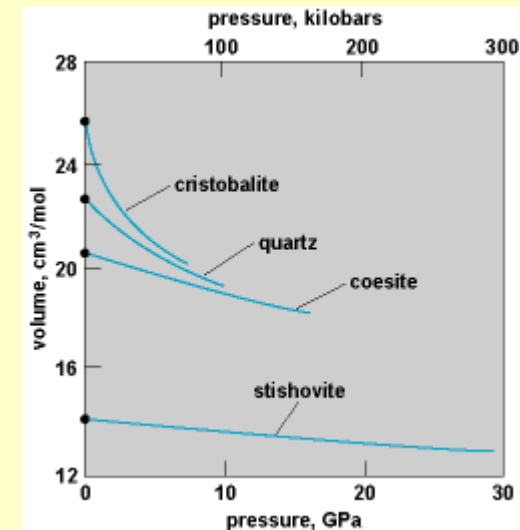
Pressure, bar	System
	1 Mbar = 100 GPa
$10^{-12}$	high vacuum chamber
1	atmospheric pressure
1.5	kitchen pressure cooker
2.0	car tire
50	a lady in stilleto heels
60	breakdown of human nervous system - divers
73.8	critical pressure of CO <sub>2</sub>
150	autoclave (safety burst disc)
221.2	critical pressure of H <sub>2</sub> O
$10^3$	pressure at the bottom of the ocean (11 km)
$2.10^3$	LDPE
$10^4$	Earth crust (30 km)
$10^5$	synthetic diamond production
$3.4.10^6$	pressure at the center of the Earth (6378 km)
$10^7$	Saturn, Jupiter, metallic hydrogen
$10^8$	neutron stars



# Dry High-Pressure Methods

Pressure techniques useful for synthesis of unusual structures  
TD metastable yet kinetically stable when pressure released  
= pressure and temperature quenching  
reconstructive transformation hindered at low temperature  
insufficient thermal energy for bond-breaking

- high pressure phases
- higher density
- higher coordination number
- higher symmetry
- transition to from nonmetal to metal
- band mixing

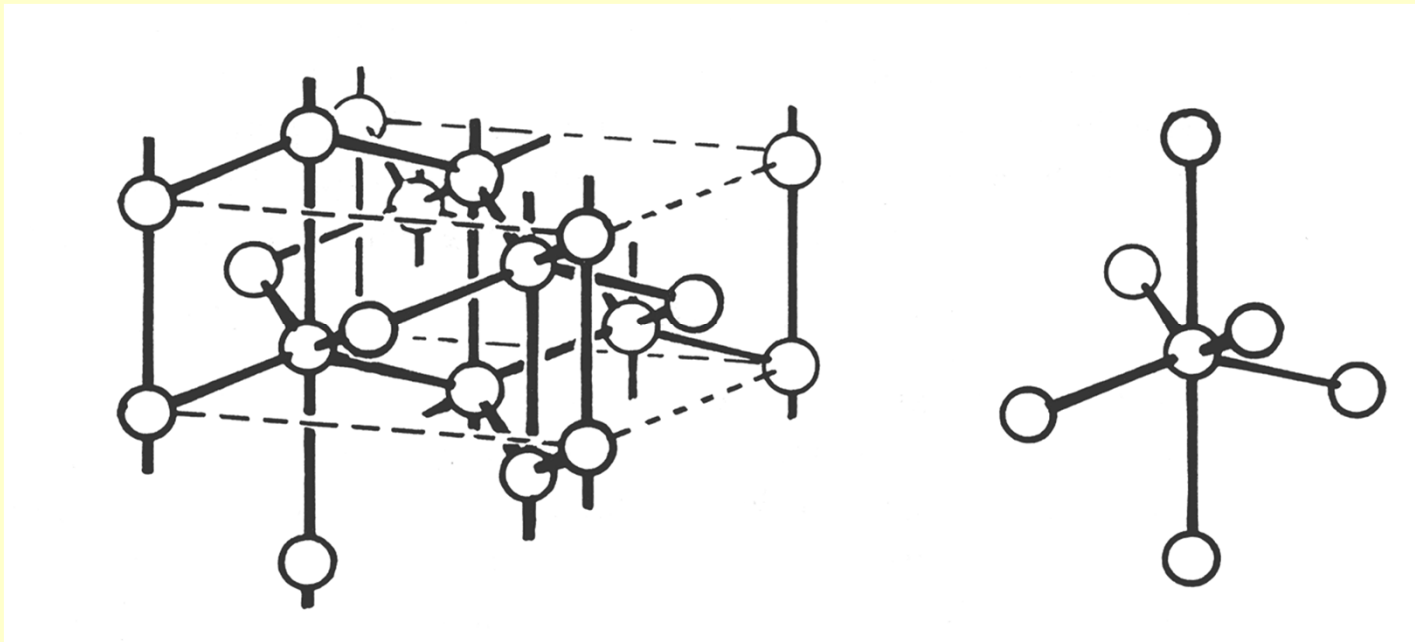


**Pressure/Coordination Number Rule: increasing pressure – higher CN**  
**Pressure/Distance Paradox: increasing pressure – longer bonds**

## Dry High-Pressure Methods

**Gray Sn (diamond type, stable below 13 °C, semiconductor)**  
**Coordination number 4, Sn-Sn bond length 281 pm**

**White Sn (metallic)**  
**Coordination number 6, Sn-Sn bond lengths 302 and 318 pm**

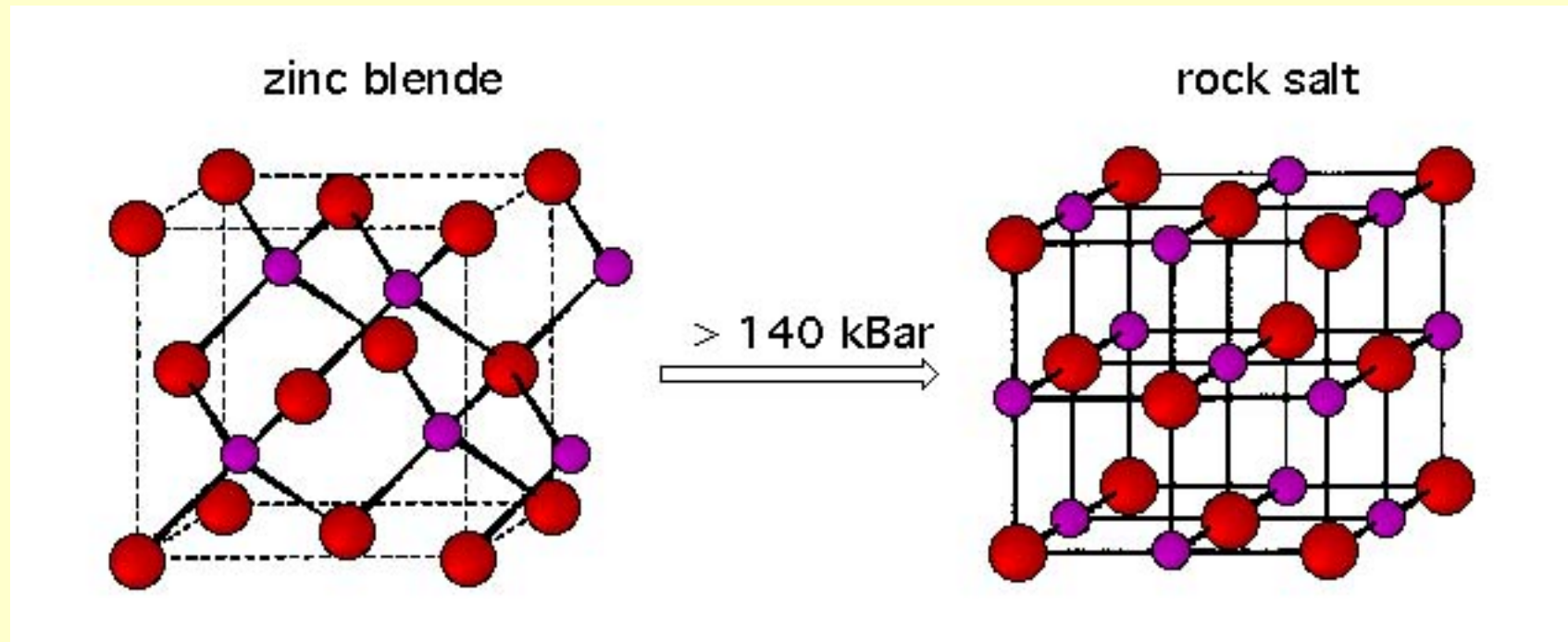


# Dry High-Pressure Methods

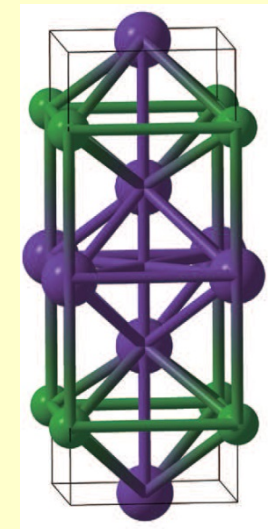
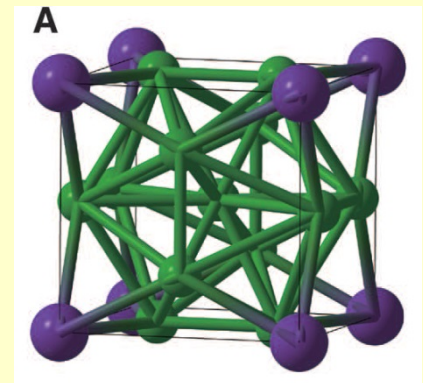
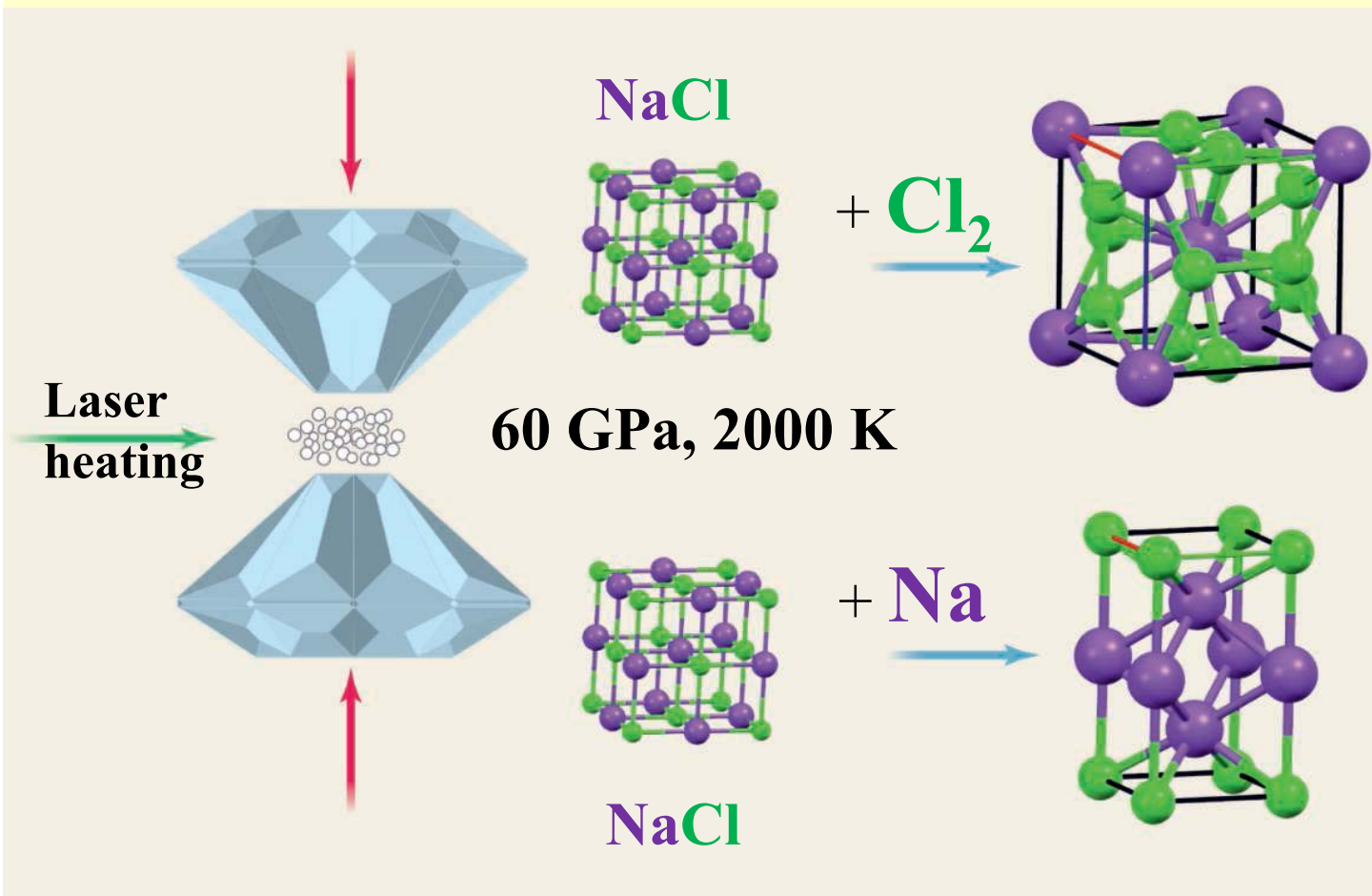
Examples of high pressure polymorphism for some simple solids

<b>Solid</b>	<b>Normal structure and coordination number</b>	<b>Typical transformation conditions P(kbar)</b>	<b>Typical transformation conditions T(°C)</b>	<b>High pressure structure and coordination number</b>
<b>C</b>	<b>Graphite 3</b>	<b>130</b>	<b>3000</b>	<b>Diamond 4</b>
<b>CdS</b>	<b>Wurtzite 4:4</b>	<b>30</b>	<b>20</b>	<b>Rock salt 6:6</b>
<b>KCl</b>	<b>Rock salt 6:6</b>	<b>20</b>	<b>20</b>	<b>CsCl 8:8</b>
<b>SiO<sub>2</sub></b>	<b>Quartz 4:2</b>	<b>120</b>	<b>1200</b>	<b>Rutile 6:3</b>
<b>Li<sub>2</sub>MoO<sub>4</sub></b>	<b>Phenacite 4:4:3</b>	<b>10</b>	<b>400</b>	<b>Spinel 6:4:4</b>
<b>NaAlO<sub>2</sub></b>	<b>Wurtzite 4:4:4</b>	<b>40</b>	<b>400</b>	<b>Rock salt 6:6:6</b>

# High-Pressure Phase Transformations

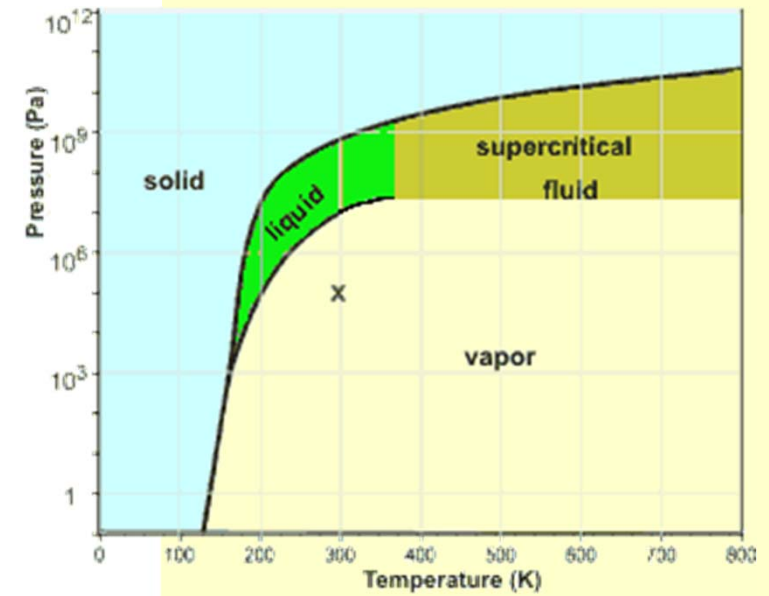
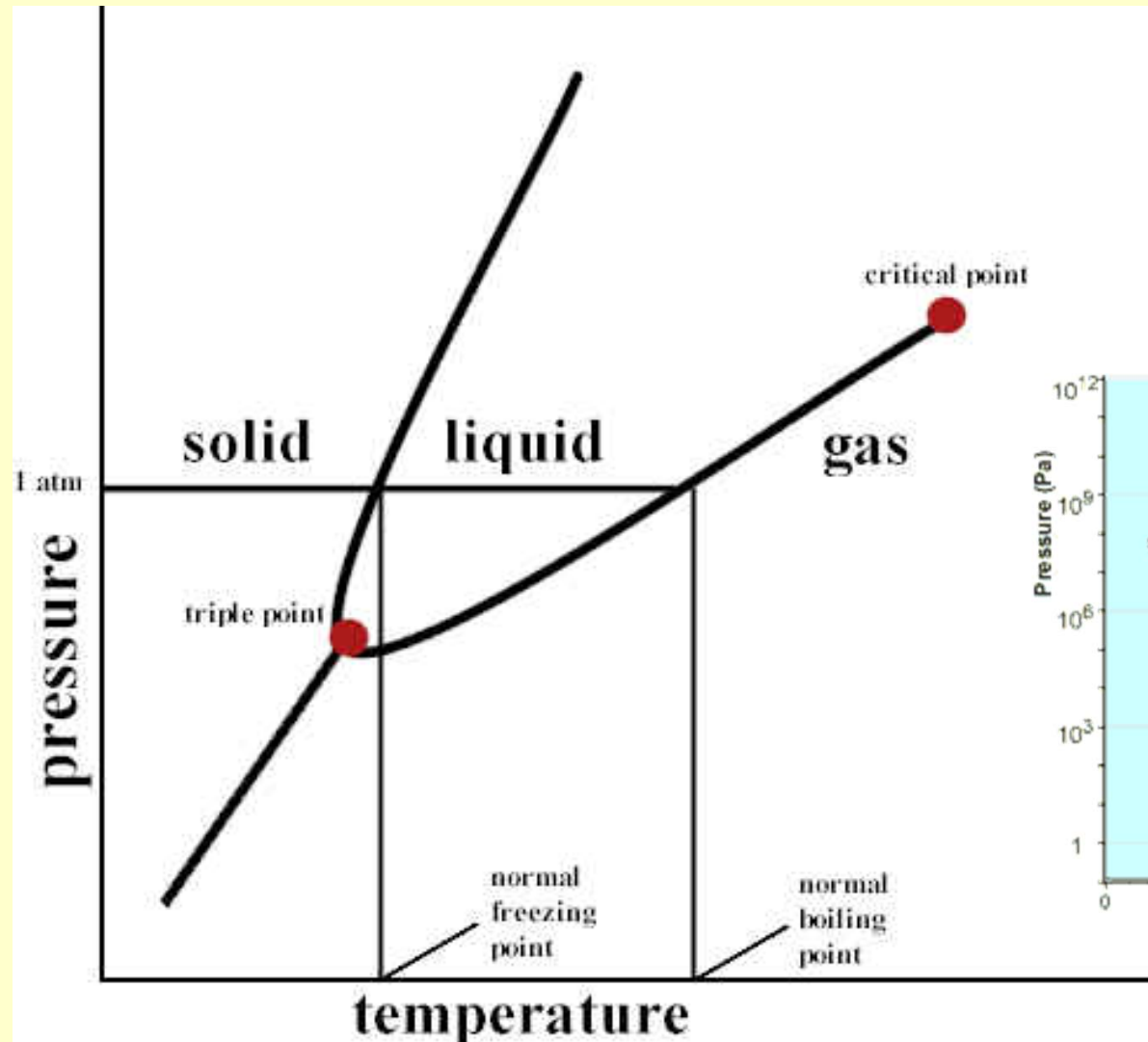


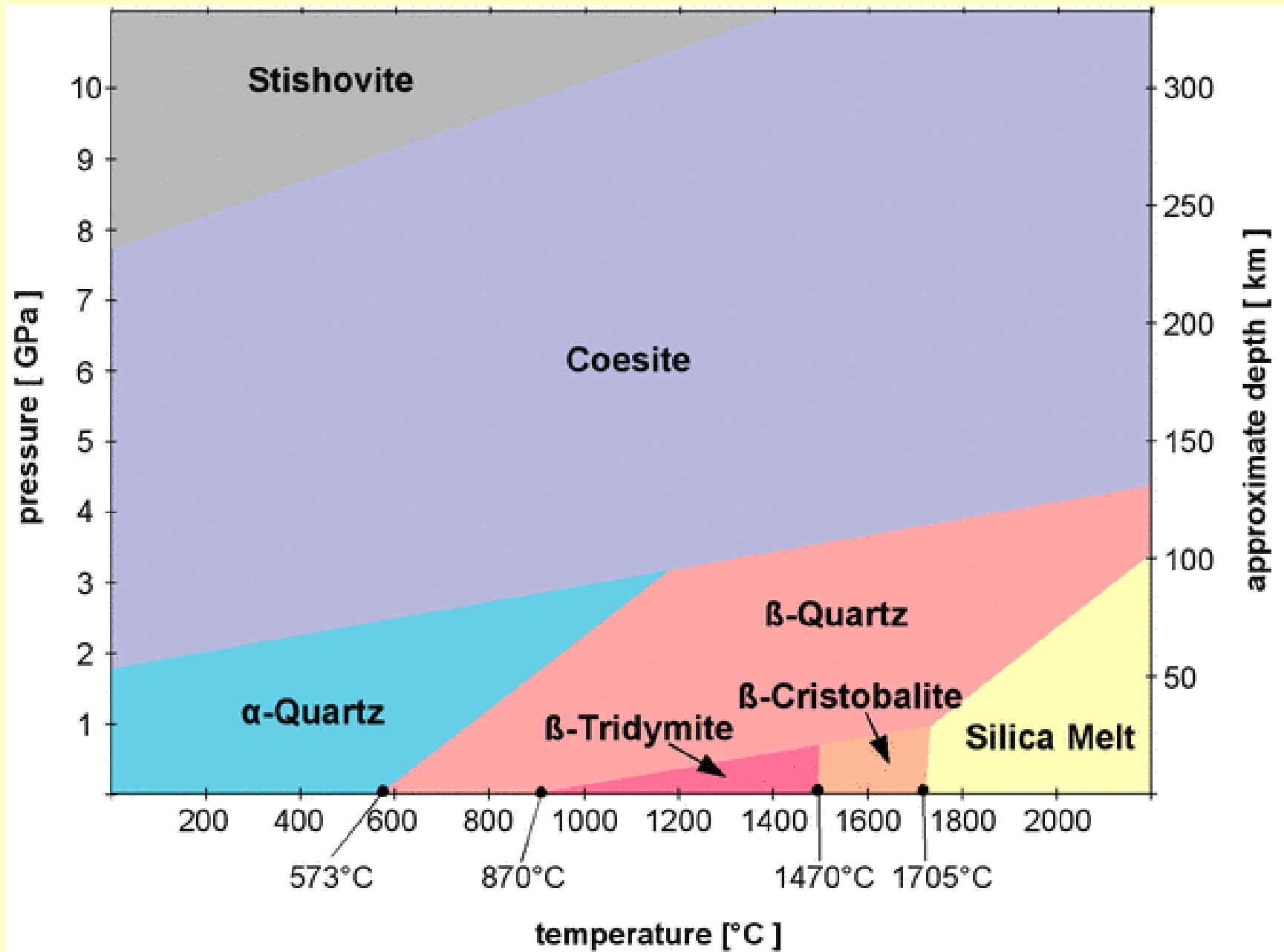
# Unusual Stoichiometries under High-Pressure

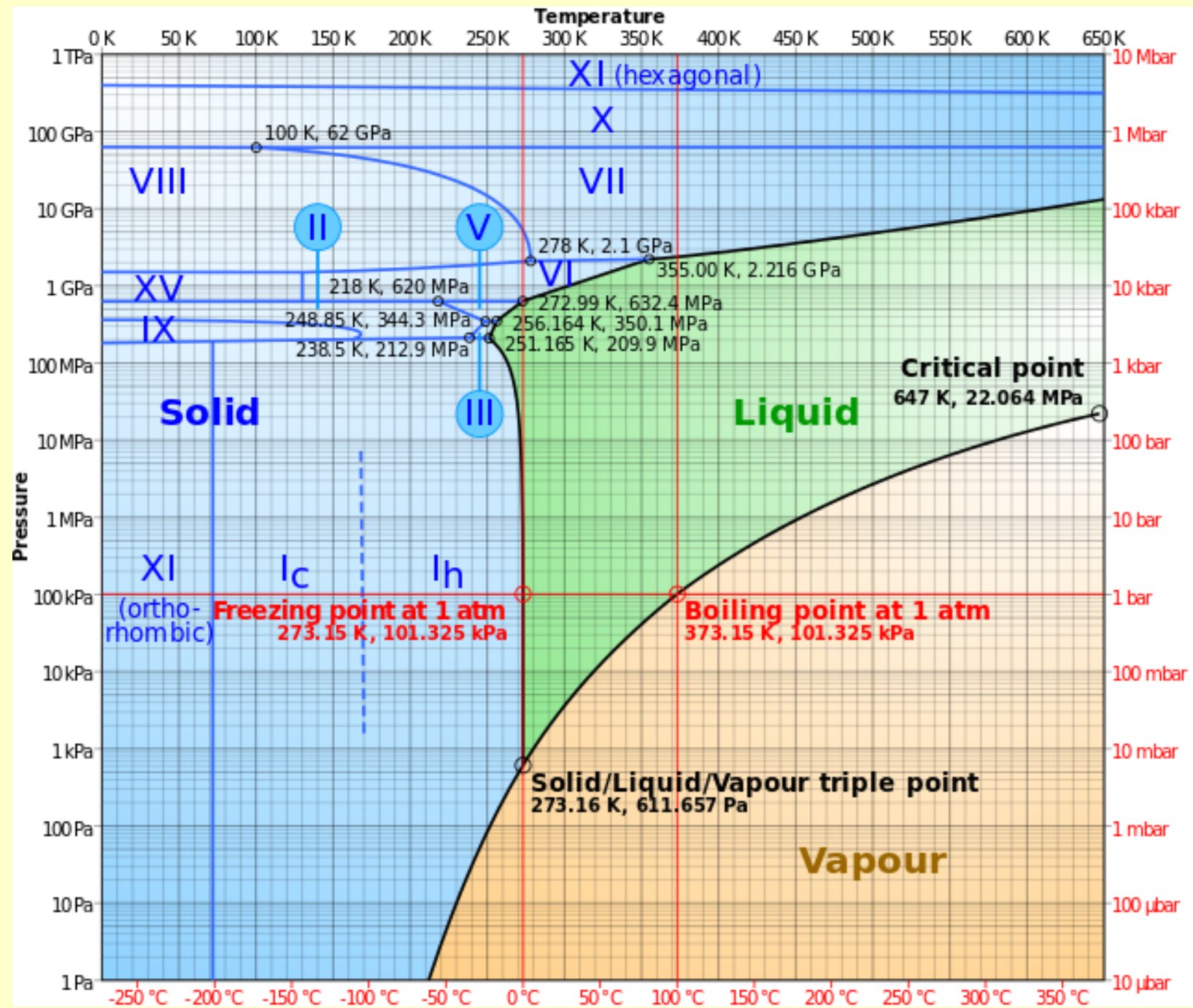




# p-T Phase Diagrams







## Water

17 phases of ice

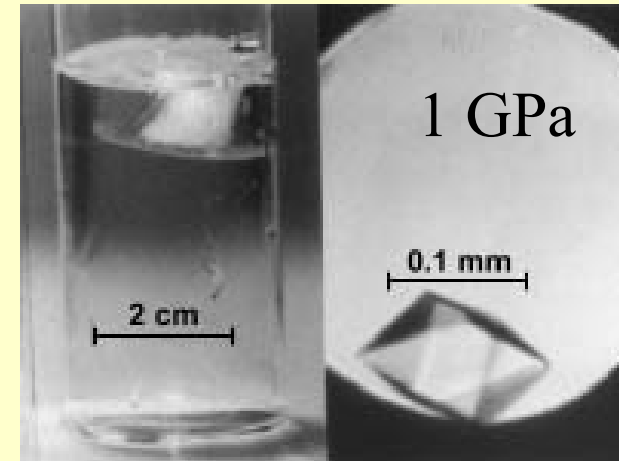
Ice-VII m.p. 100 °C

Ice-X fluorite, ionically conductive above 10 GPa

Equalization of O-H covalent

and hydrogen bonds above 60 GPa

Max pressure attained for water 210 GPa



floats

sinks

## Ca

ccp at ambient pressure

bcc (!) above 20 GPa 4s-3d mixing, Ca become a transition metal

**MgSiO<sub>3</sub>** most abundant silicate mineral within our planet !

pyroxene (silicate chains)

ilmenite > garnet > perovskite Si CN = 6

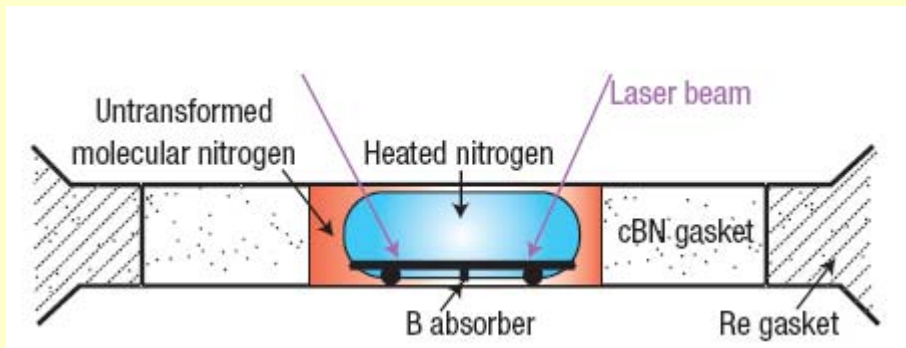
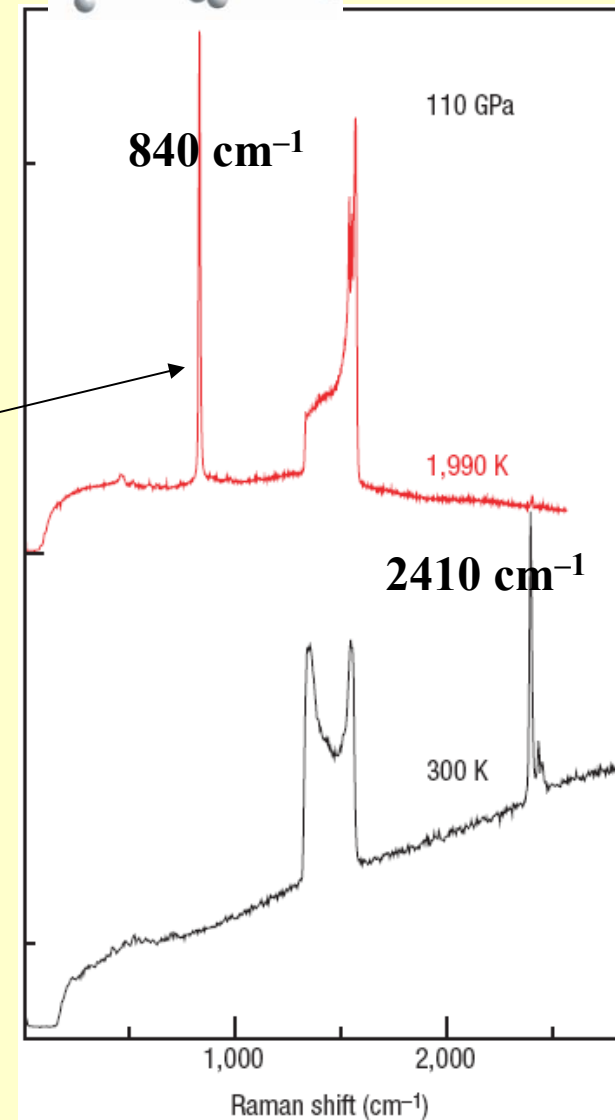
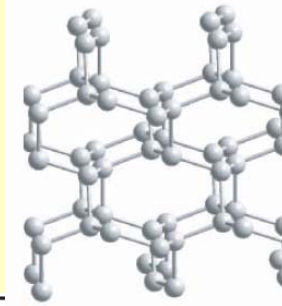
# Condensed gases

$\text{H}_2$  metallic conductivity in dense fluid hydrogen

$\text{H}_2^+ \text{H}_2^-$

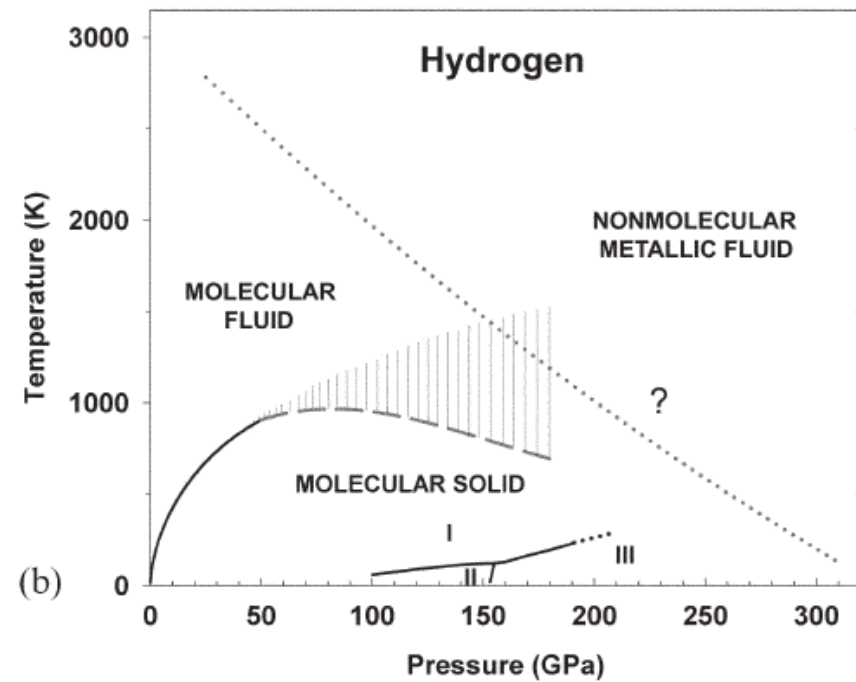
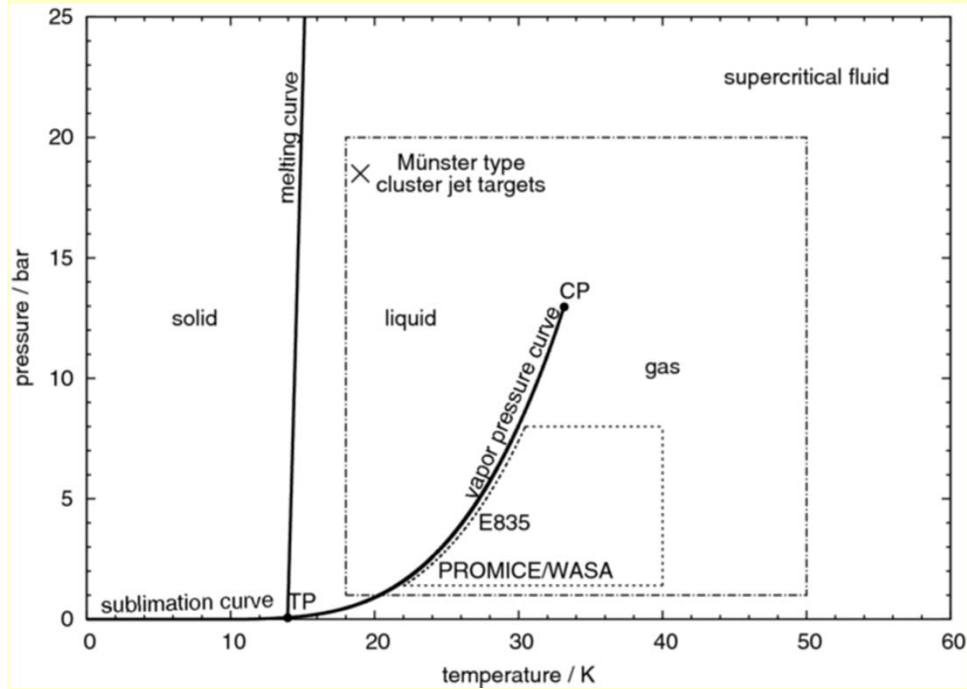
$\text{NO}_2 + \text{N}_2\text{O} \quad \text{NO}^+ \text{NO}_3^-$  calcite

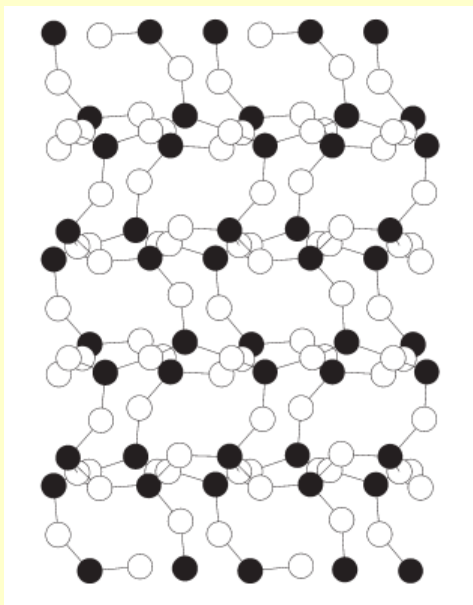
$\text{N}_2$  semiconducting oligomers  $(-\text{N}-)_x$  at 100-240 GPa  
cubic diamond 110 GPa, 2000 K



Heating: 1- $\mu\text{m}$  B plate (absorber of laser radiation rests on c-BN pieces that thermally insulate the plate from the bottom anvil. The sample squeezed between the anvils is surrounded by the c-BN/epoxy gasket followed by the metallic (Re) supporting ring.

# Phase Diagram of Hydrogen

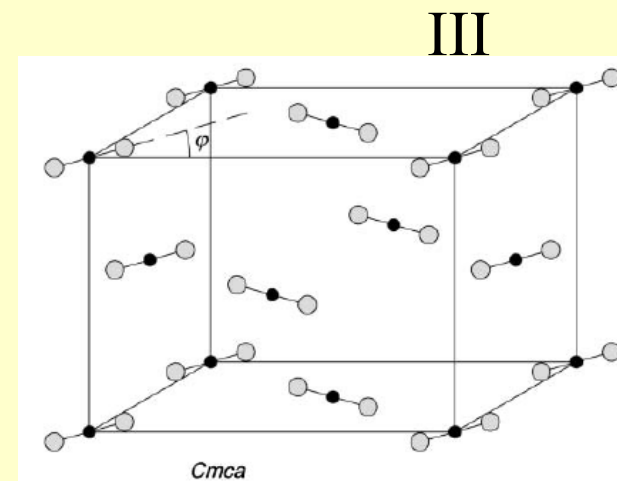
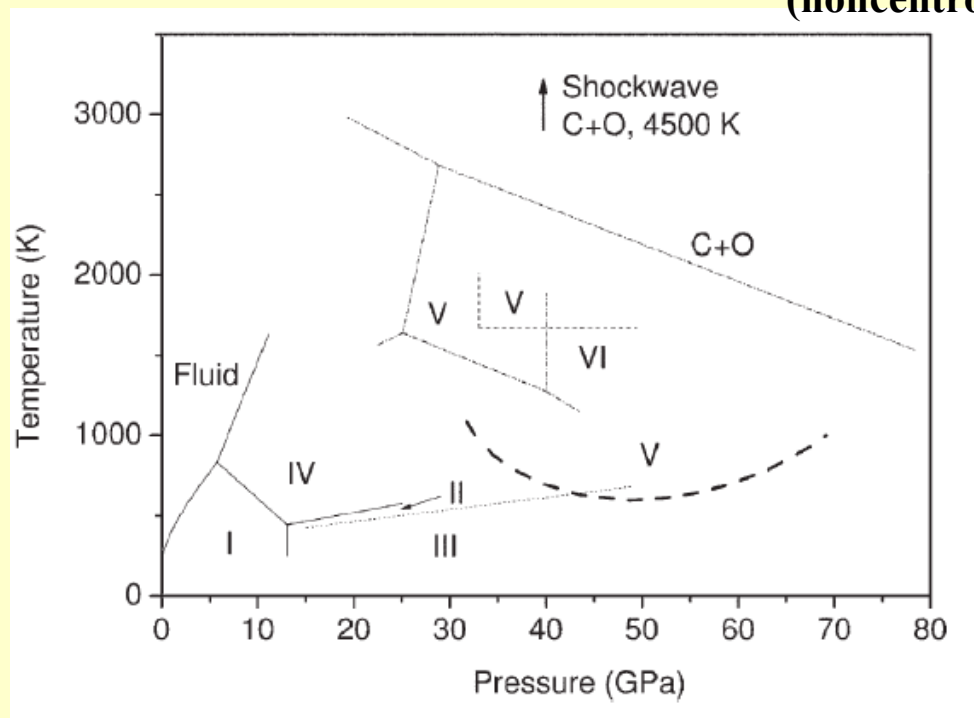
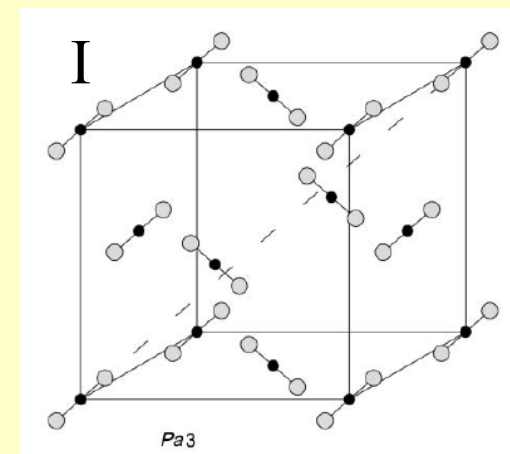




# Phase Diagram of CO<sub>2</sub>

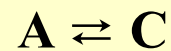
CO<sub>2</sub>-V  
 Quartz  
 superhard

CO<sub>2</sub> heating at 10-20 GPa  
 sp<sup>3</sup> bonded CO<sub>4</sub>  
 cristobalite, tridymite  
 40 GPa quartz  
 (noncentrosymmetric)



# Reaction Equilibrium and Pressure

The reaction volume  $\Delta V^0$  = the volume difference between the products (A) and the reactants (C)



$$K = \frac{C}{A}$$

$$\Delta G^0 = -RT \ln K$$



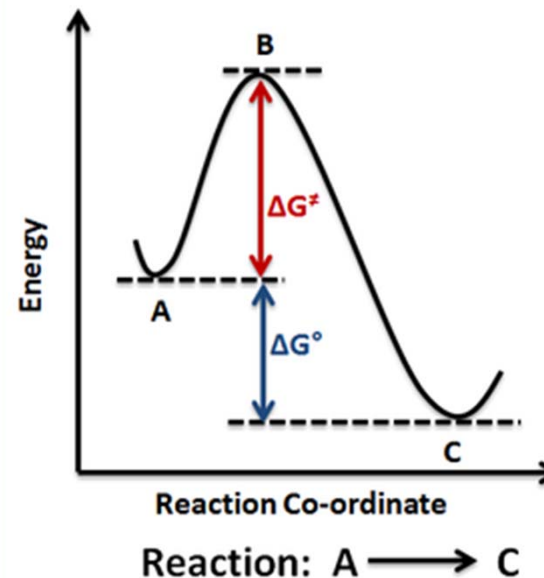
$$\left( \frac{\partial RT \ln K}{\partial P} \right)_T = -\Delta V^0$$

Associative type = negative  $\Delta V^0$

K increases with increasing pressure

Dissociative type = positive  $\Delta V^0$

K decreases with increasing pressure



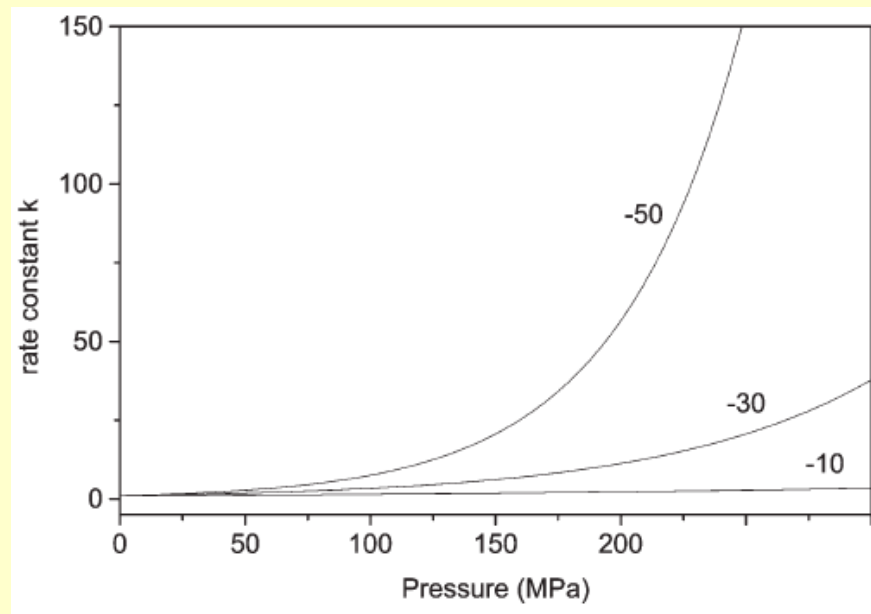


$$\left(\frac{\partial \ln k}{\partial T}\right)_P = -\frac{E_a}{RT}$$

## Reaction Kinetics

The activation volume  $\Delta V^\ddagger =$  the volume difference between the transition state complex and the reactants

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT}$$



Room-temperature pressure dependence of the rate constant for different activation volume  $\Delta V^\ddagger$  values (in  $\text{cm}^3 \text{mol}^{-1}$ )

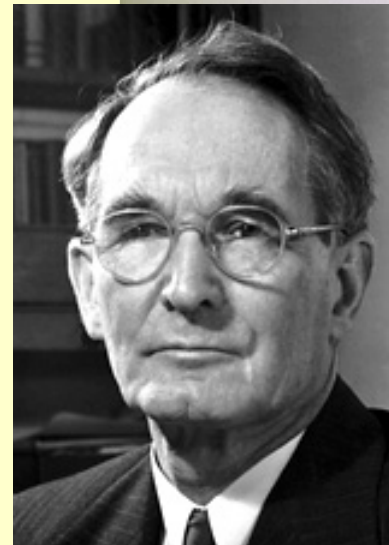
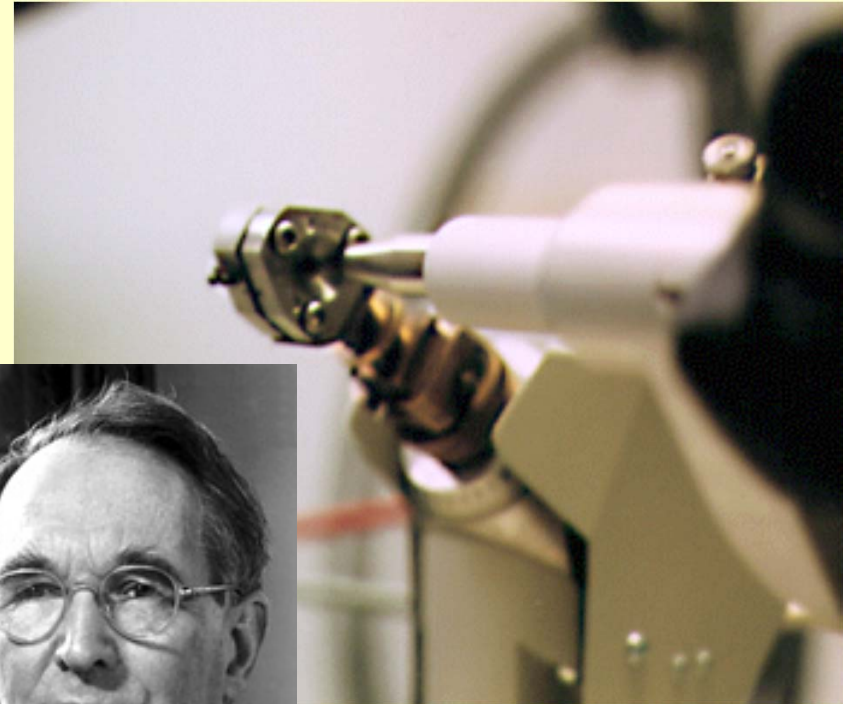
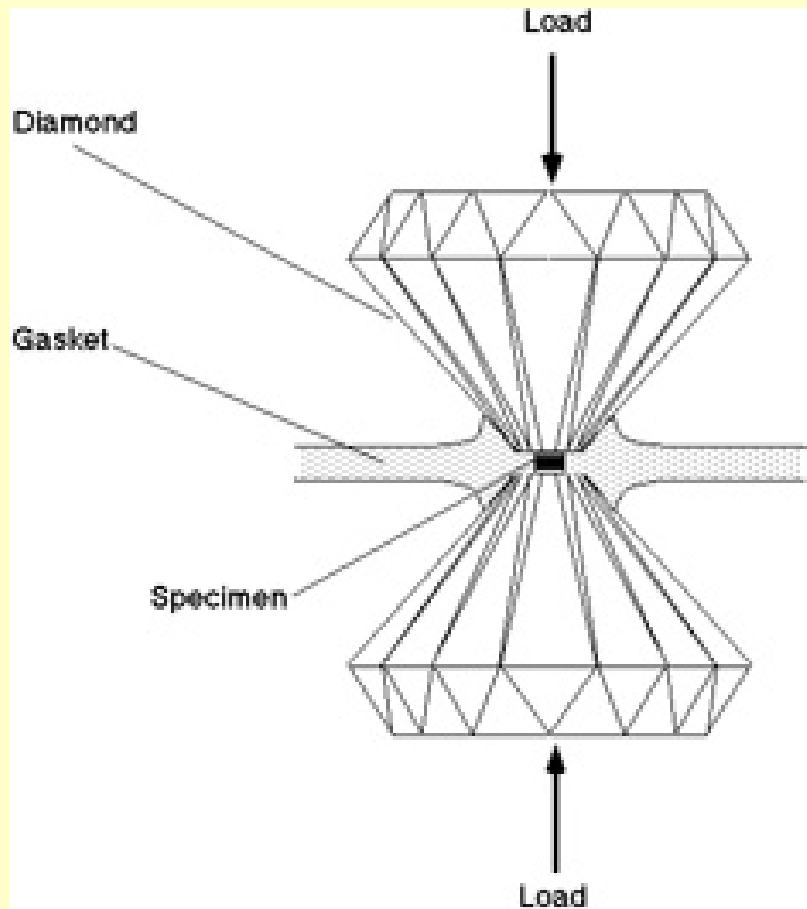
**Associative type = the rate determining step involves the formation of a covalent bond**

**negative  $\Delta V^\ddagger \rightarrow$  reaction rate increases with increasing pressure**

**Dissociative type = the breaking of a covalent bond**

**positive  $\Delta V^\ddagger \rightarrow$  reaction rate decreases with increasing pressure**

# Diamond Anvil Cell



**Percy Williams Bridgman**  
(1882 – 1961, NP in Physics 1946)

# Diamond Anvil Cell

## Diamond anvil cell

$$p = F/A$$

$$p = 40 \text{ GPa}$$

$$A_{\text{table}} / A_{\text{culet}} = 10 : 1$$

$$A_{\text{culet}} = 100\text{-}200 \mu\text{m}$$

laser heating  $T > 2500 \text{ }^\circ\text{C}$

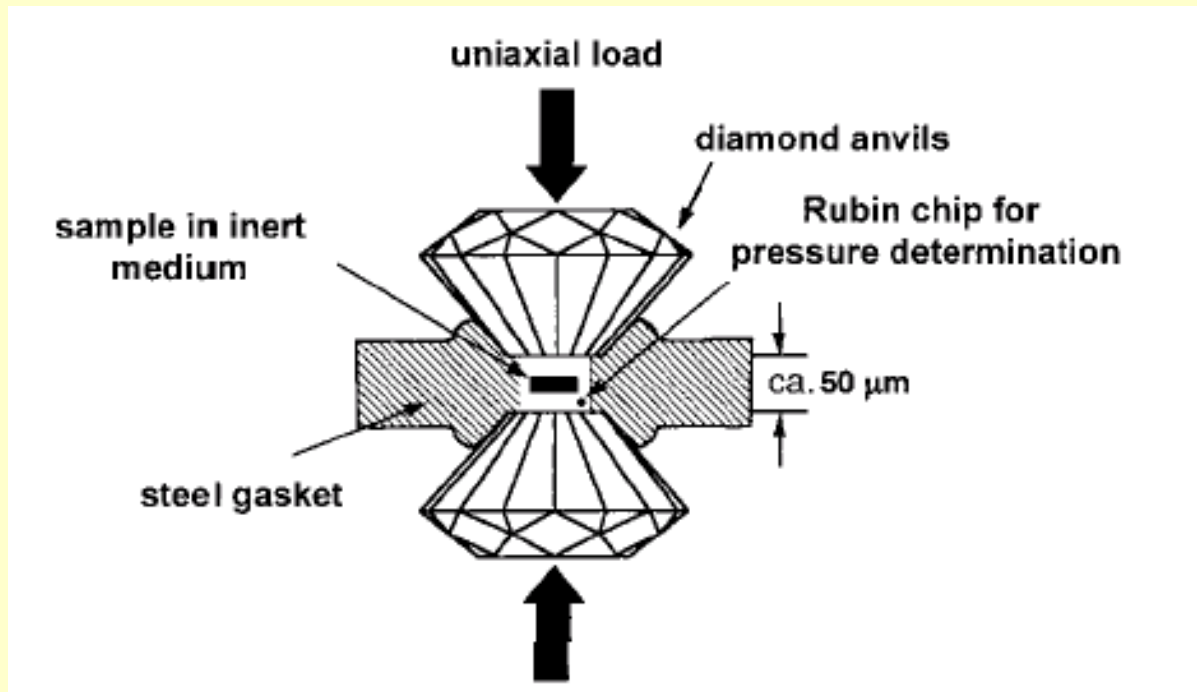
Re, steel gasket

Diamond transparent

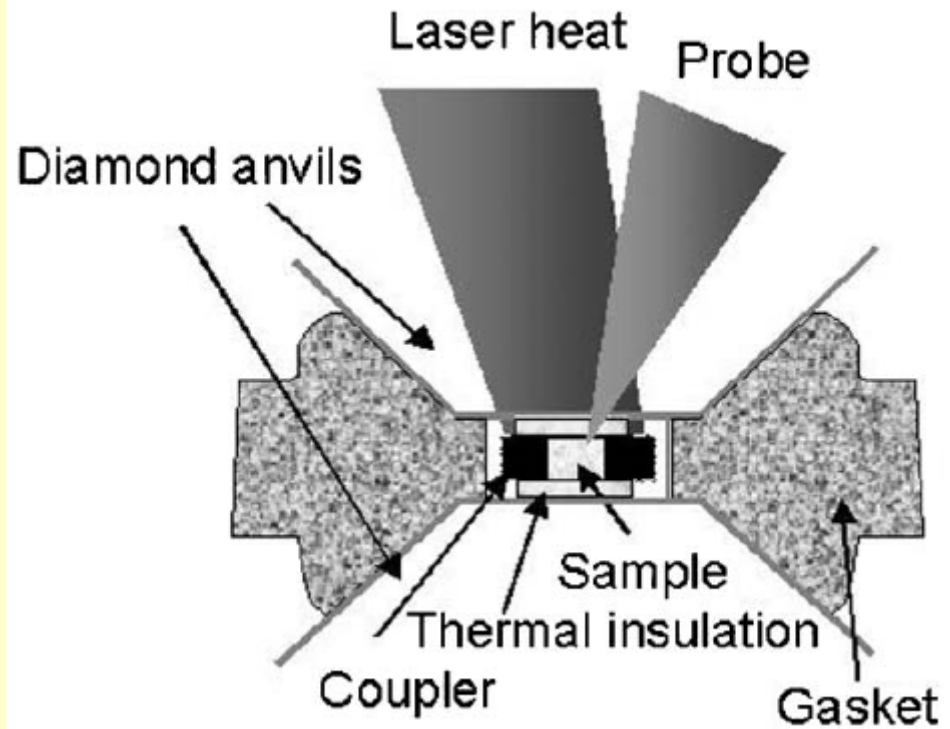
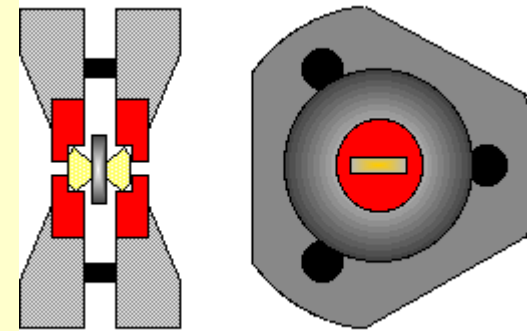
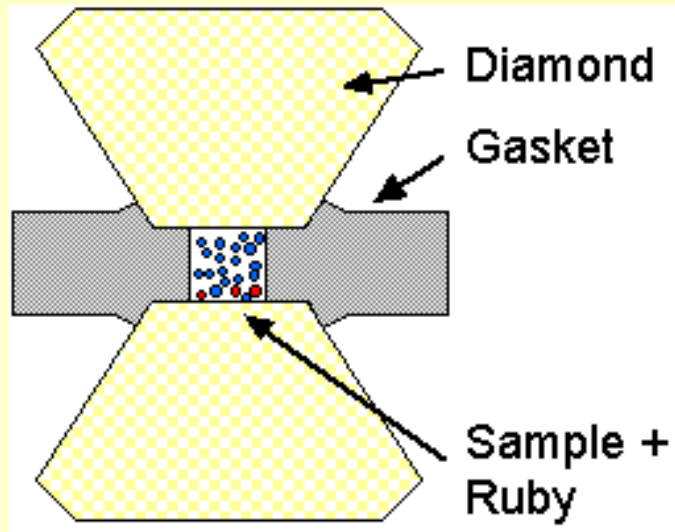
to radiation from IR to X-ray

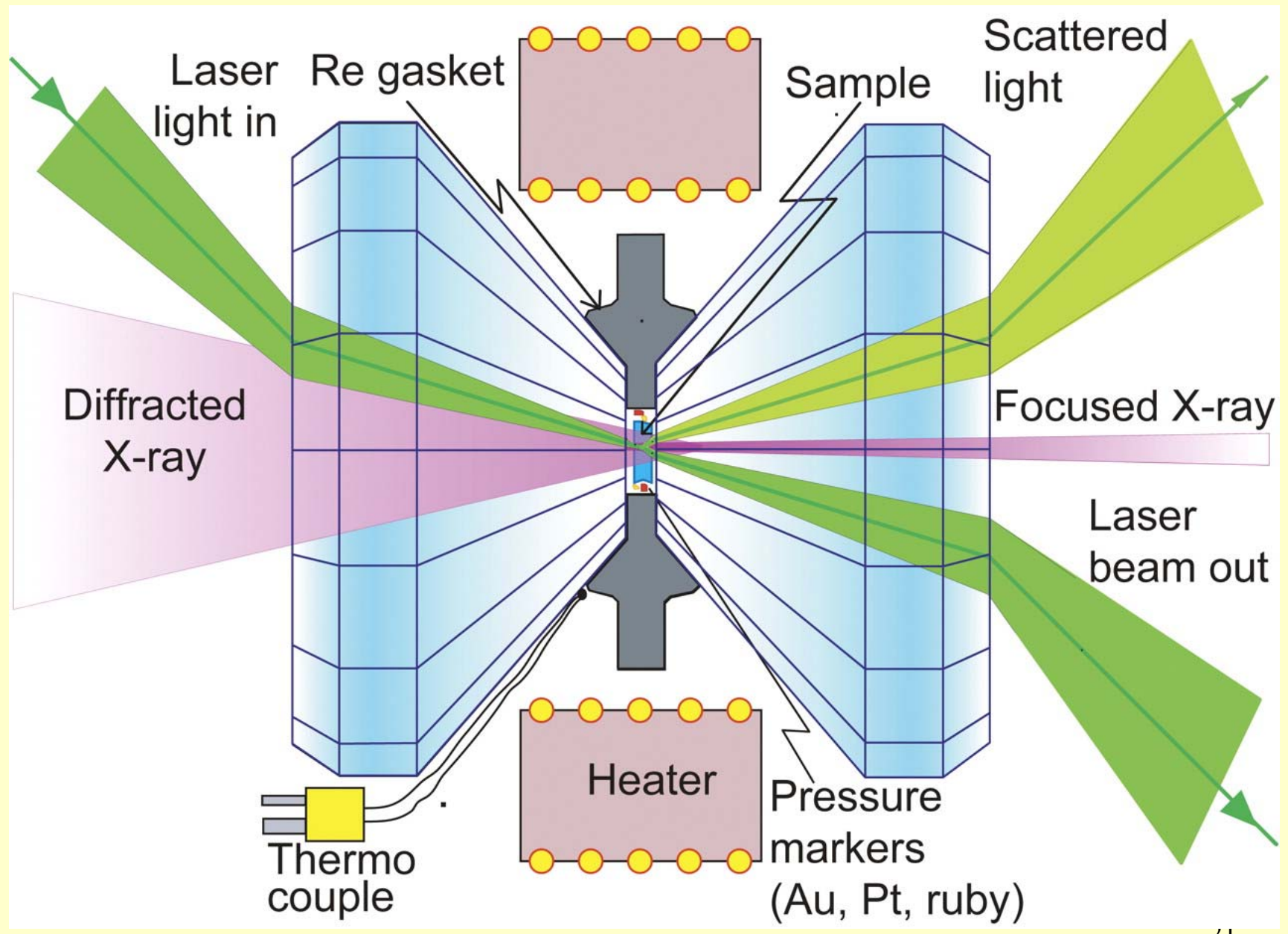
pressure transmitting medium:

solid Ar, N<sub>2</sub>, O<sub>2</sub>,



# Diamond Anvil Cell



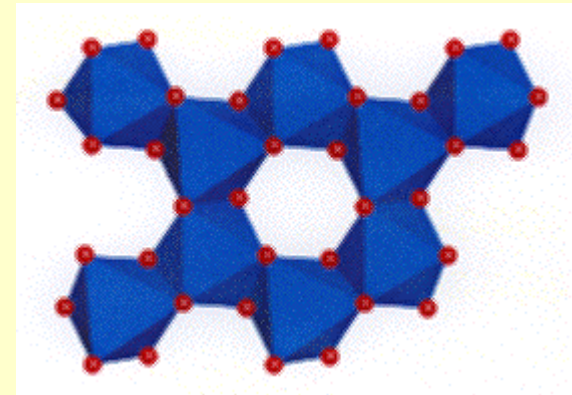


# Dry High-Pressure Methods

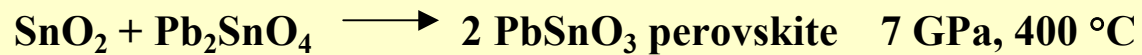
**Calibrating a high pressure diamond anvil**

- **Ruby - fluorescence transition**
- **Bi, Tl, Ba pressure induced phase transition**

**Ruby = Cr doped corundum**

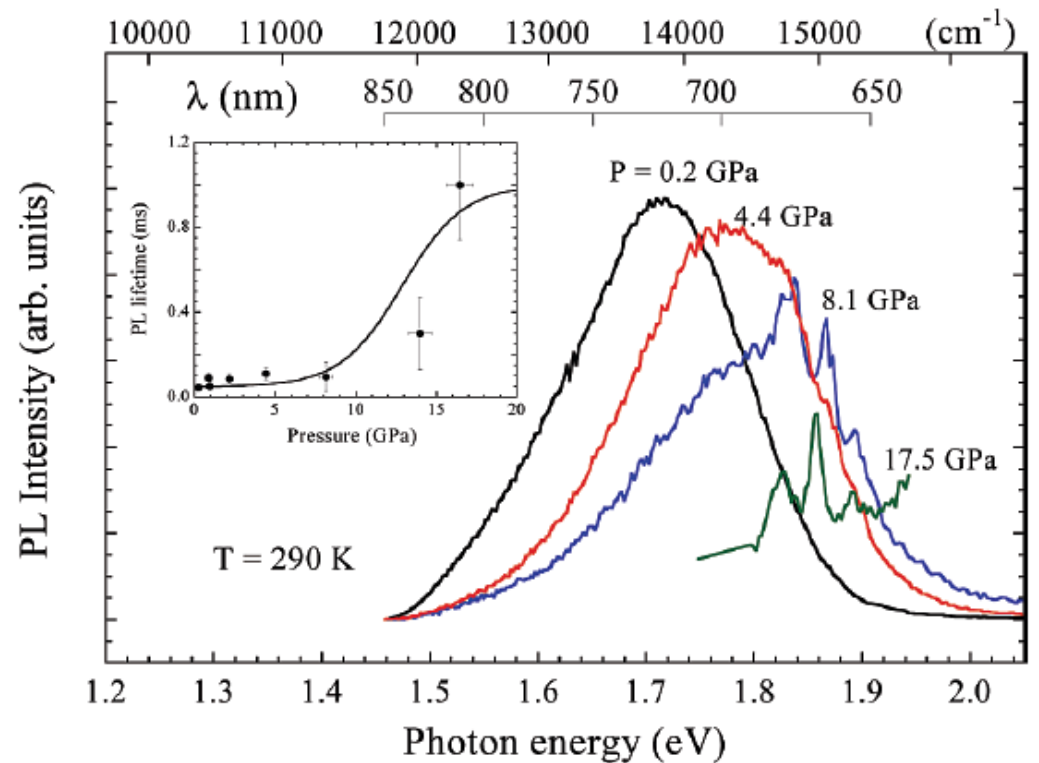
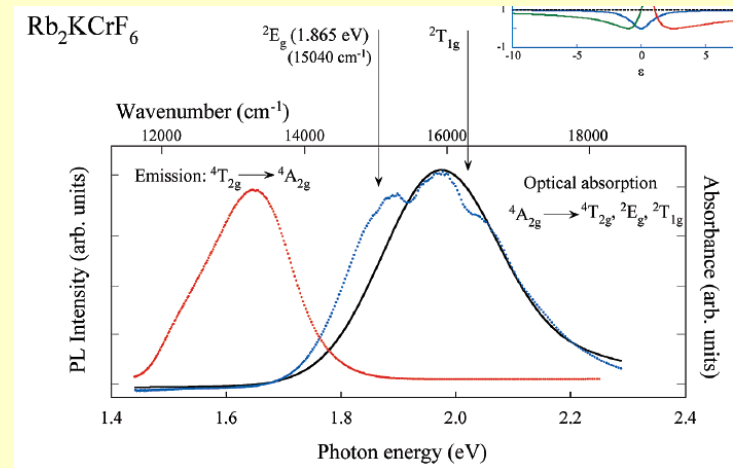
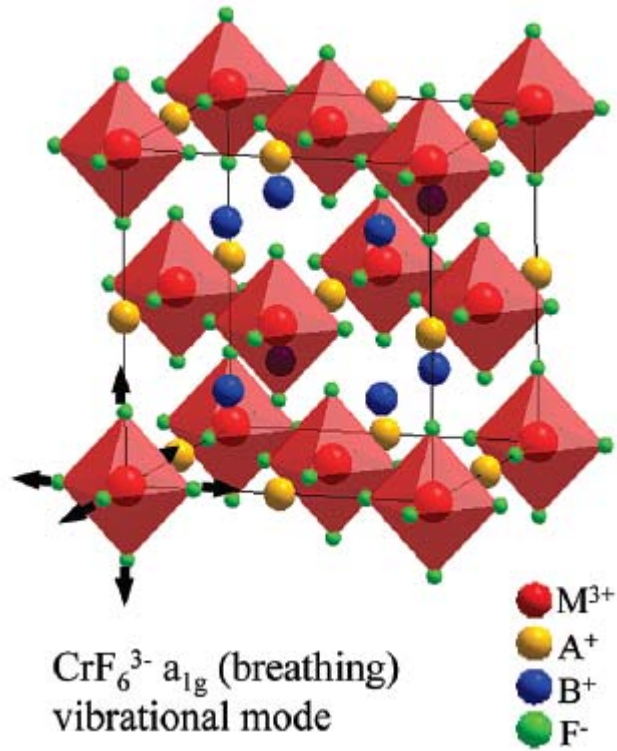


**High pressure synthesis**

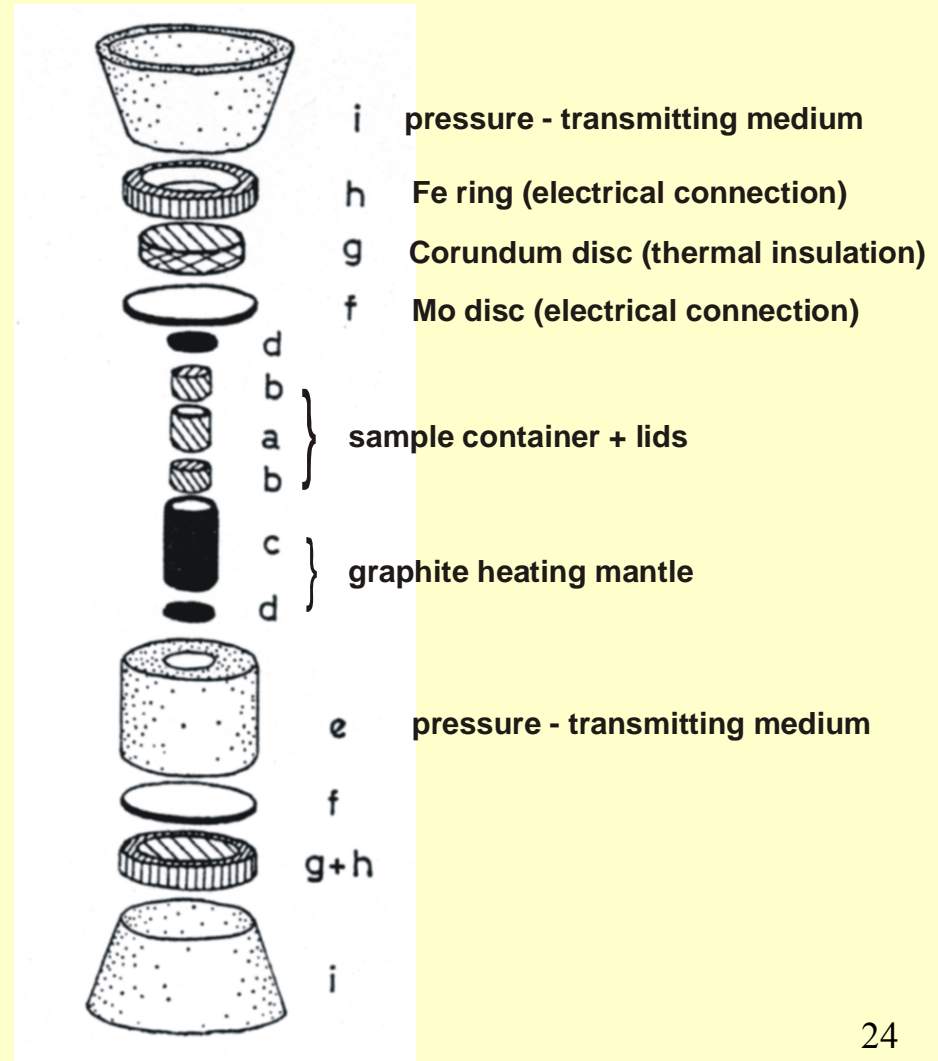
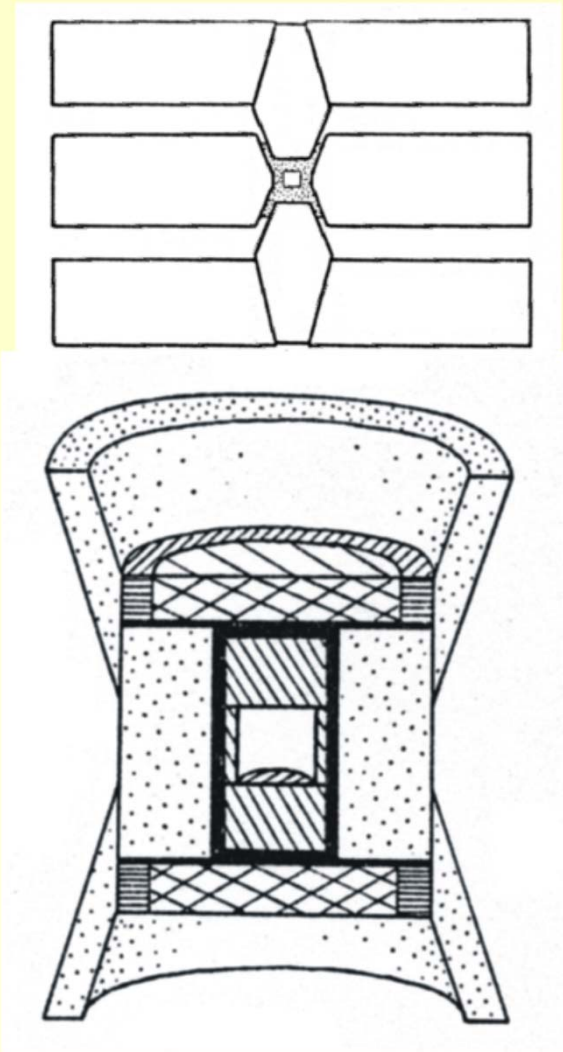


**At ambient pressure only SnO<sub>2</sub> and PbO products**

# Rb<sub>2</sub>KCrF<sub>6</sub>



# High Pressure Two-Die Belt-Type Apparatus





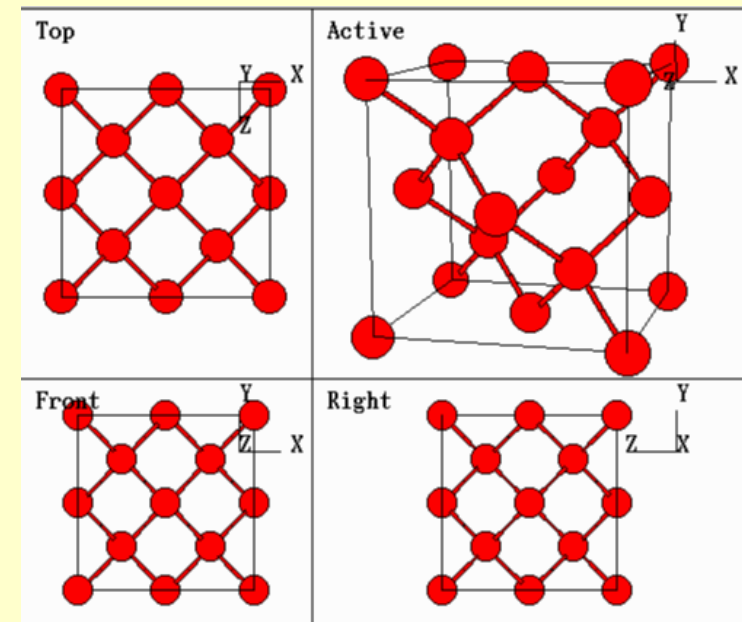
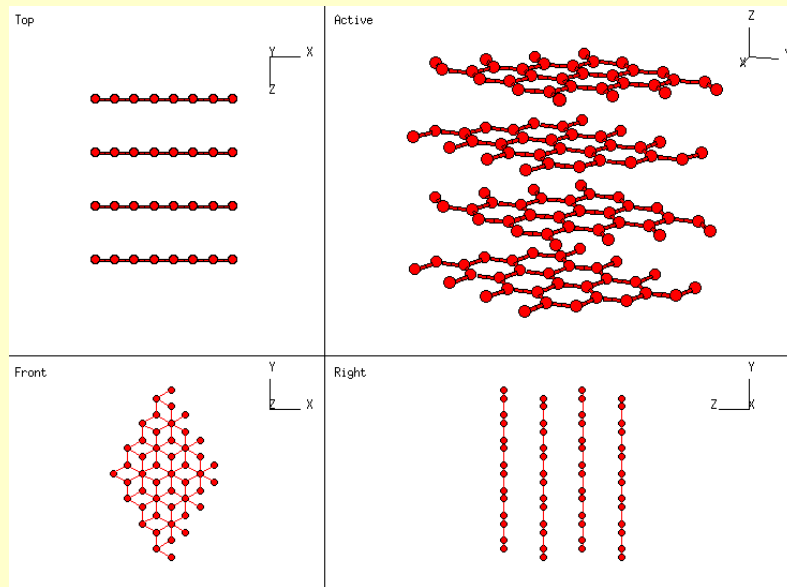
# Synthesis of Diamonds



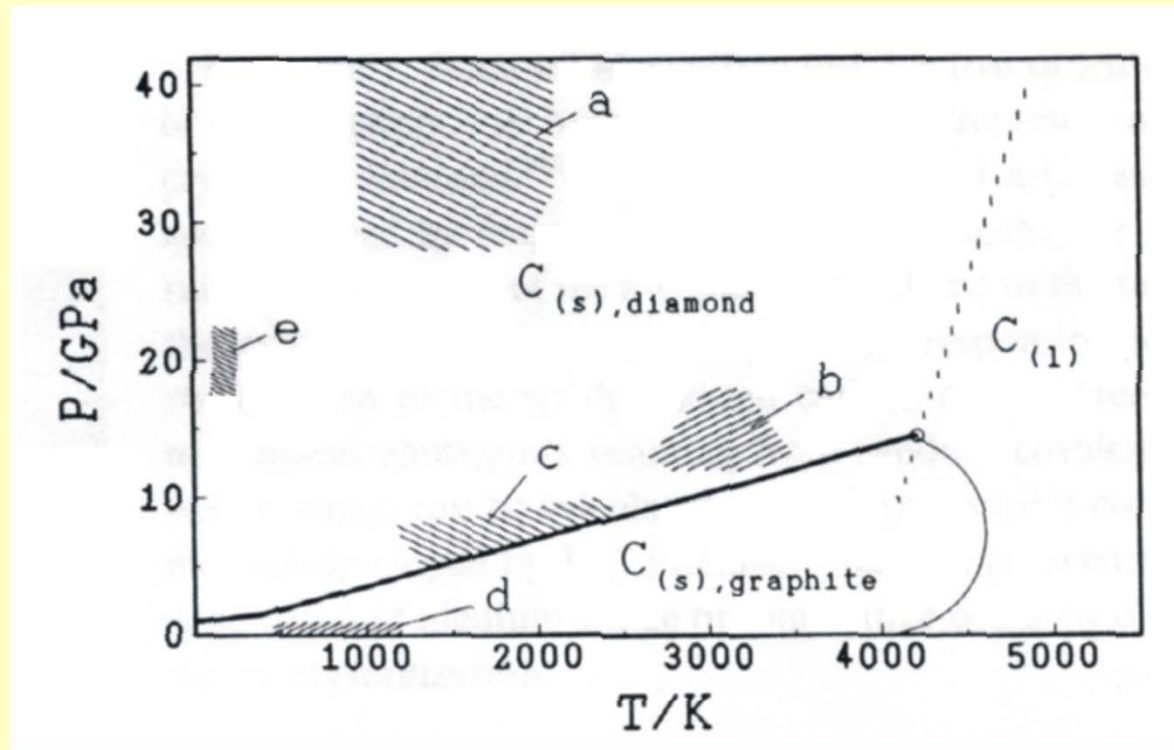
The hardest known substance, the highest thermal conductivity

Difficult to transform graphite into diamond

Industrial diamonds (GE) made from graphite around 3000 °C and 13 GPa



## p, T Diagram of Carbon



- a – shock wave production of diamond
- b – high-temperature, high-pressure synthesis of diamond
- c – catalytic region for diamond formation
- d – CVD diamond
- e – transformation of  $C_{60}$  into diamond

# Synthesis of Diamonds

The activation energy required for a  $sp^2$  3-coordinate to a  $sp^3$  4-coordinate structural transformation is very high, so requires extreme conditions

Ways of getting round the difficulty

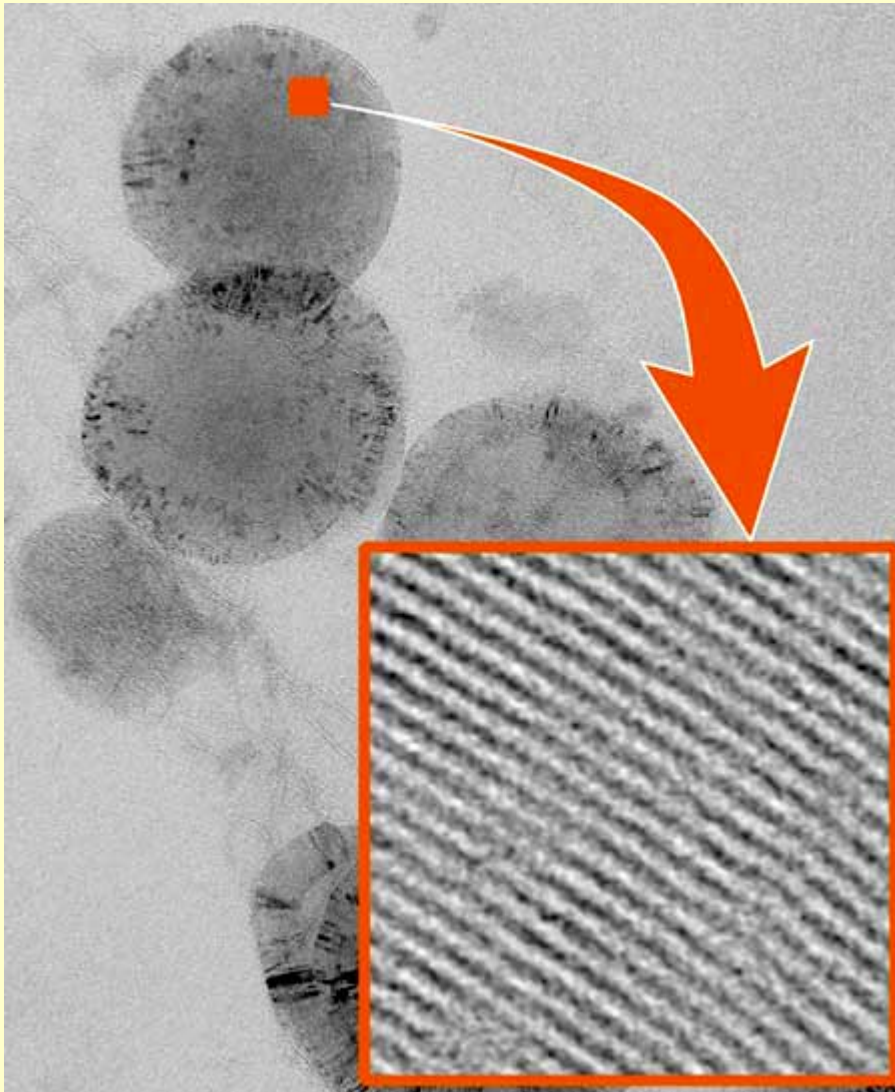
◆ Catalyst: transition metals (graphite is dissolved in molten metal: Fe, Ni, Co, 6 GPa, 1000 °C), alloys (Nb-Cu),  $CaCO_3$ , hydroxides, sulfates, P (7.7 GPa, 2200 °C, 10 min)

◆ Squeezing (uniaxial not hydrostatic pressure), no heating, buckyball carbons are already intermediate between  $sp^{2-3}$

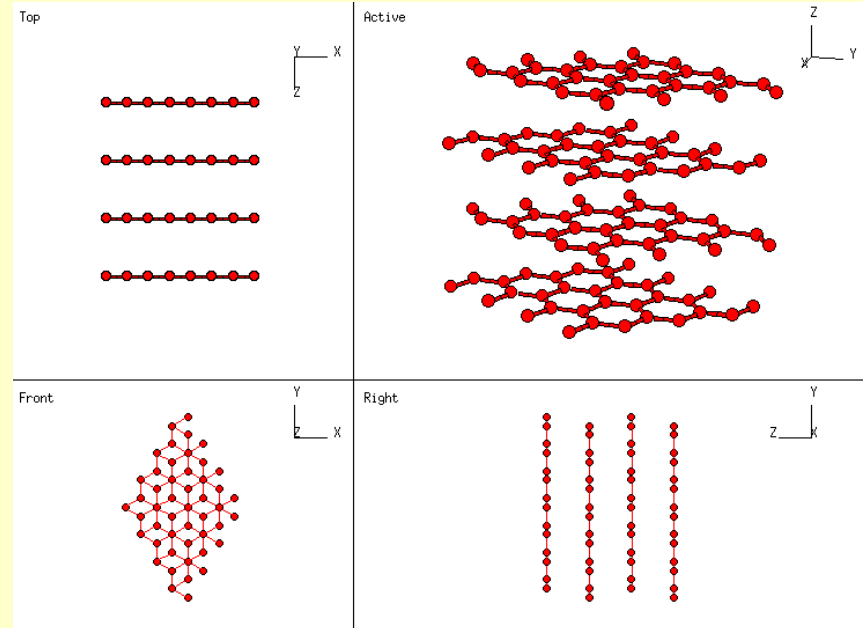
$C_{60}$ , diamond anvil, 25 GPa instantaneous transformation to bulk crystalline diamond, highly efficient process, fast kinetics

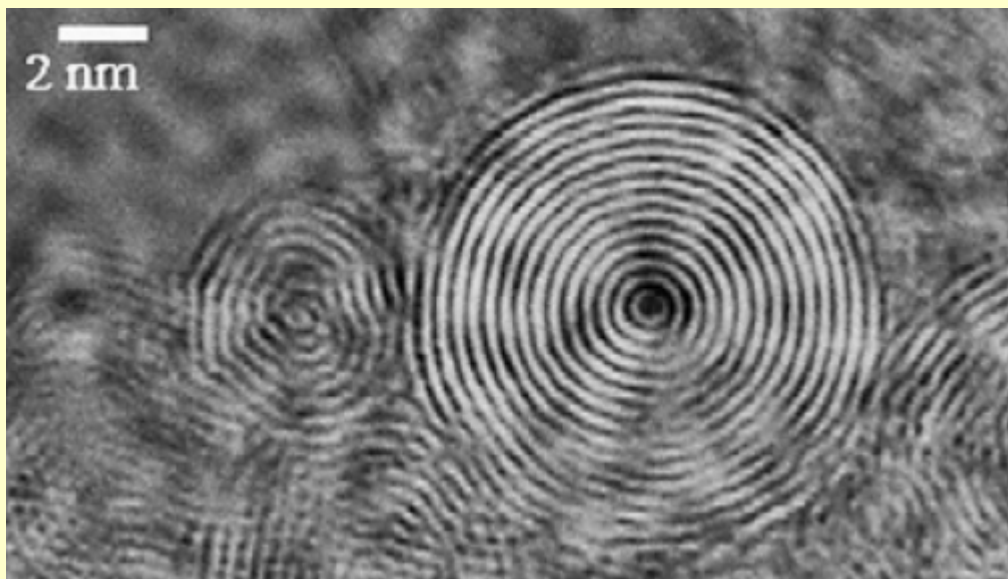
◆ Carbon onions, electron irradiation of graphite, concentric spherical graphite layers, spacing decreases from 3.4 Å to 2.2 Å in the onion center, 100 GPa, 200 keV beam, in several hours, pressureless conversion to diamond

◆ Using  $CH_4/H_2$  microwave discharges to create reactive atomic carbon whose valencies are more-or-less free to form  $sp^3$  diamond, atomic hydrogen saturates the dangling bonds, dissolves soot faster than diamond, a route for making diamond films, 50 μm

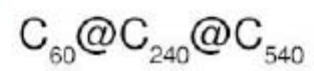
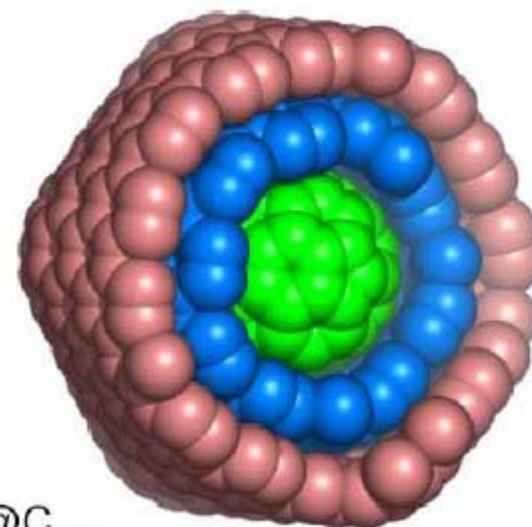
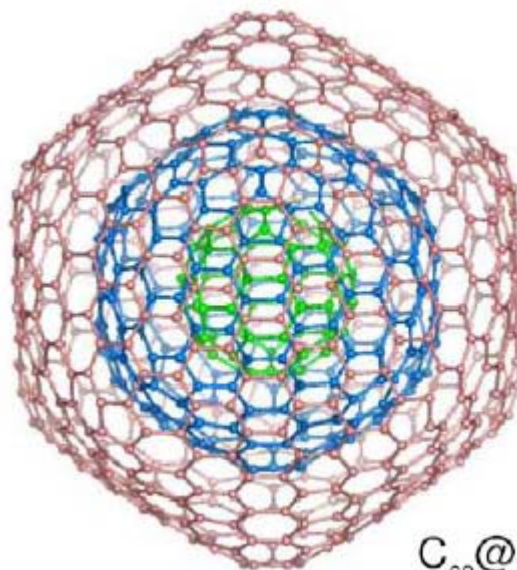


# Graphite

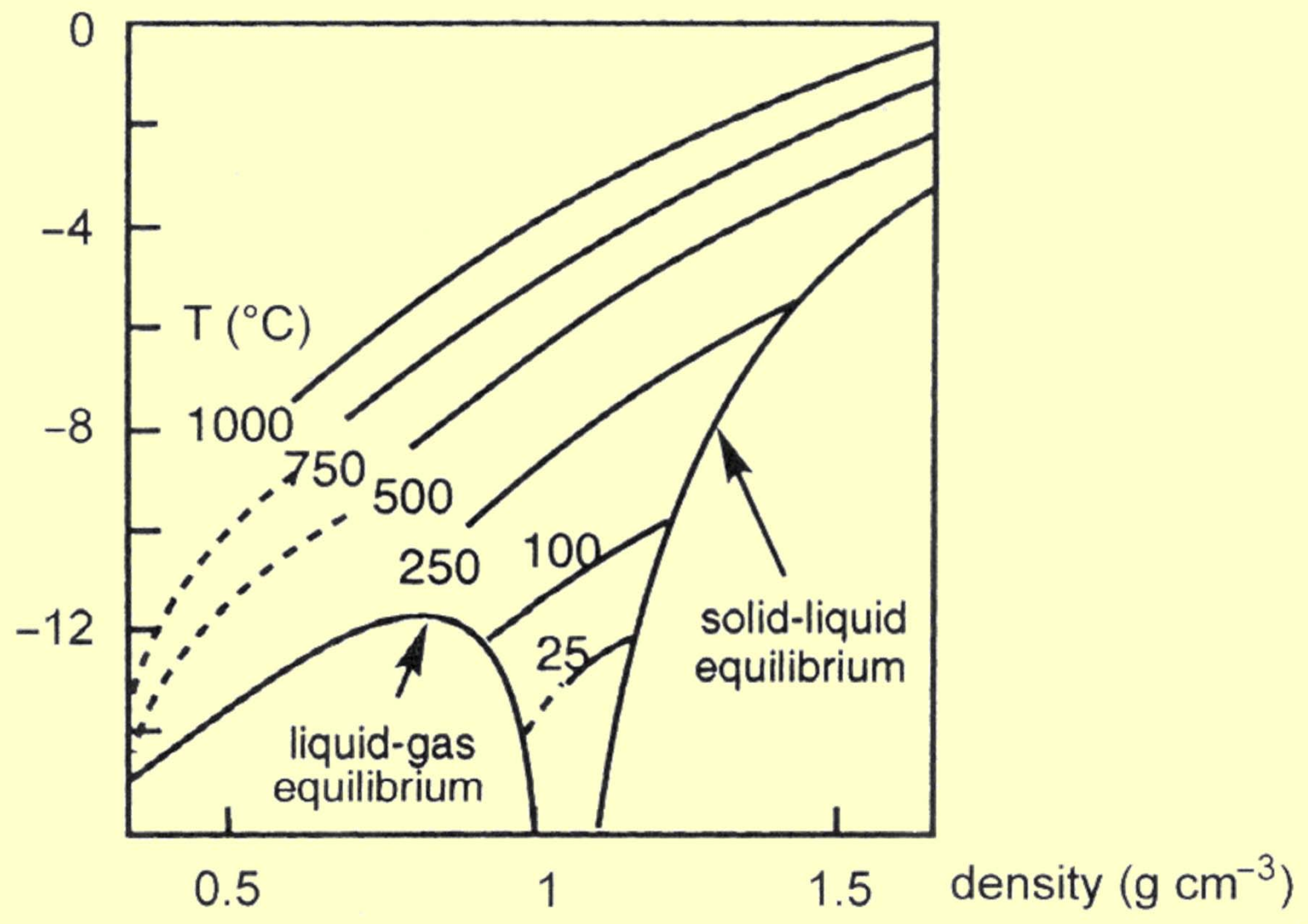




## Carbon onions



$\log K_e$



## **Organic molecule theory of diamond cleavage**

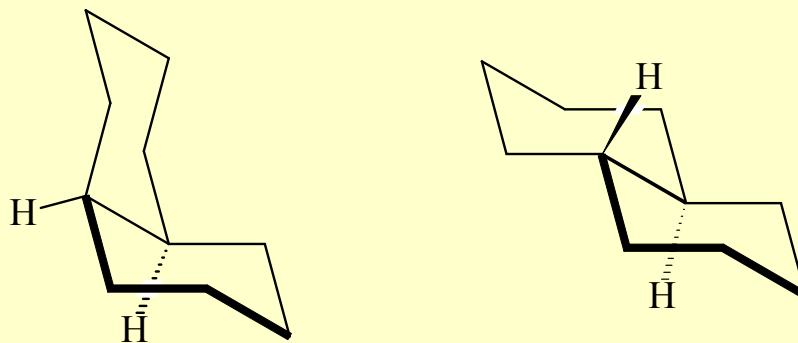
**The jeweler's chisel if placed correctly on a diamond, with a well oriented blow, always cause cleavage along {111} greater than 90% of the time, imagine the cost of a mistake with a large crystal**

**The number of bonds broken per unit area (that is, surface energies) for different planes does not explain the observations of preferential {111} cleavage!!!**

**Diamond viewed in terms of layers of polycondensed cyclohexane rings with axial bonds between layers and equatorial bonds within layers**

**Unfavorable axial-axial C-C bond interactions at 2.51 Å versus equatorial-equatorial at 2.96 Å**

**Model compounds like cis-decalin versus trans-decaline comprised of two fused cyclohexane rings trans-decalin is 11-12 kJmol<sup>-1</sup> more stable because cis-strain cannot be relieved by bond rotation as in cyclohexane itself, cis can only isomerize to trans by bond cleavage followed by recombination, hence origin of the high activation energy for the cis-to-trans isomerization of decalin.**



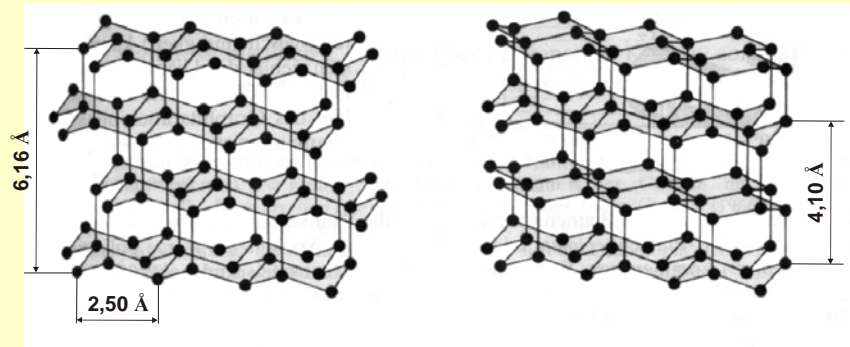
**A breaking molecule theory: axial-axial unfavorable interactions cause the mechanical energy of the jeweler's chisel to be funneled into preferential breakage of an axial C-C bond  
This then induces a kind of domino effect whereby the adjacent axial C-C bonds break and C-C bonds throughout the entire {111} plane are severed**



# Lonsdaleite - hexagonal diamond

**Discovered in the Canyon Diablo meteorite  
(AZ, 50 ky, 30 t)  
Found also in some rocks**

**May be stronger and stiffer than diamond**

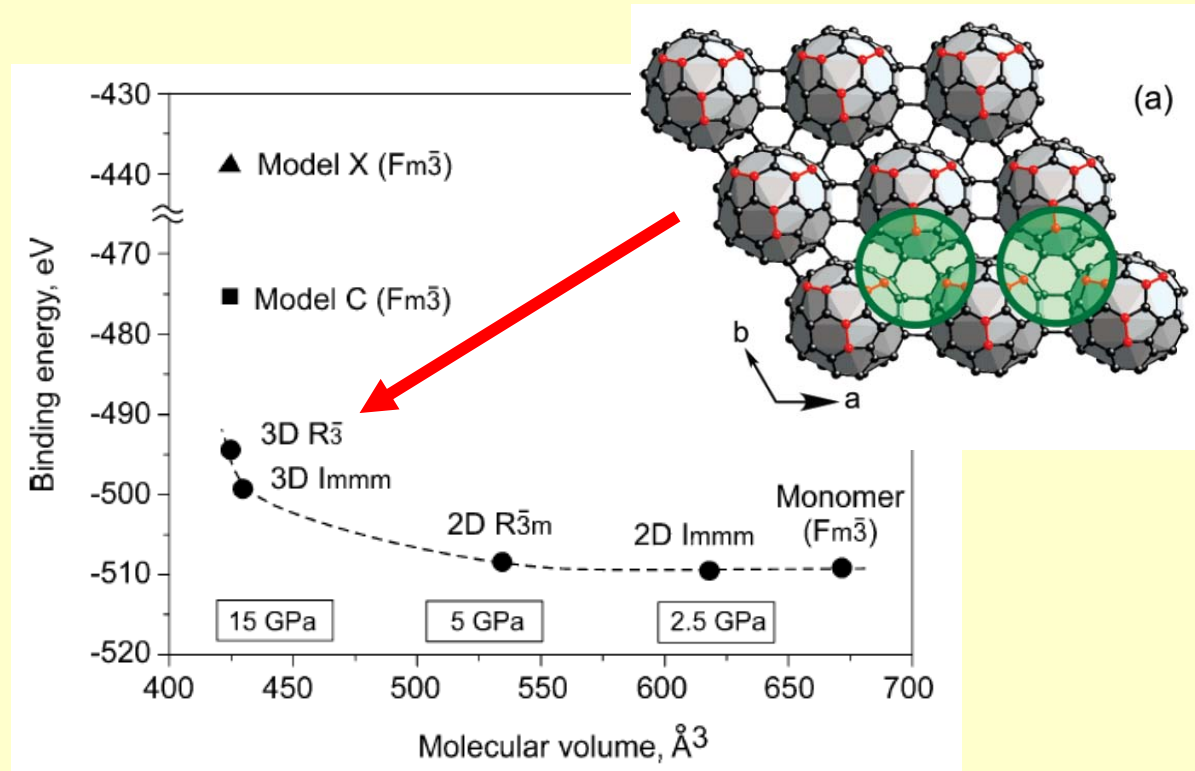
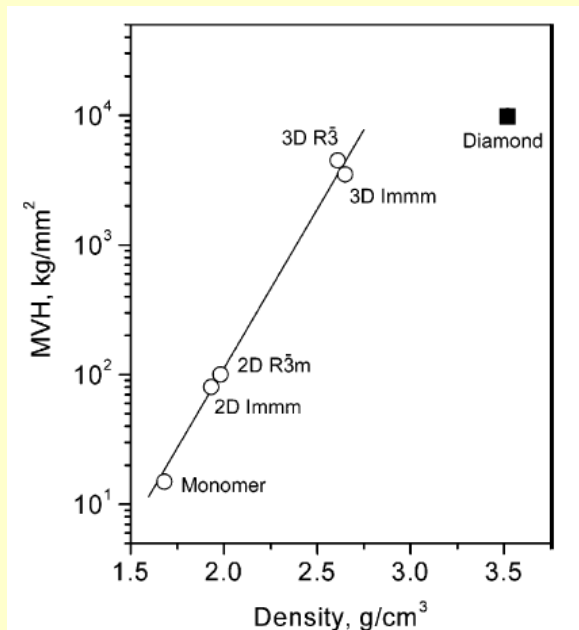


**Synthesized in the laboratory at static pressure of 130 kbar and temperature over 1000°C from well-crystallized graphite in which the c axes of the crystallites are parallel to each other and to the direction of compression**

**The crystal structure is hexagonal with  $a = 2.52 \text{ \AA}$  and  $c = 4.12 \text{ \AA}$ .  
density is  $3.51 \text{ g/cm}^3$ , same as cubic diamond**

**Prepared also from crystalline graphite by a method involving intense shock compression and strong thermal quenching**

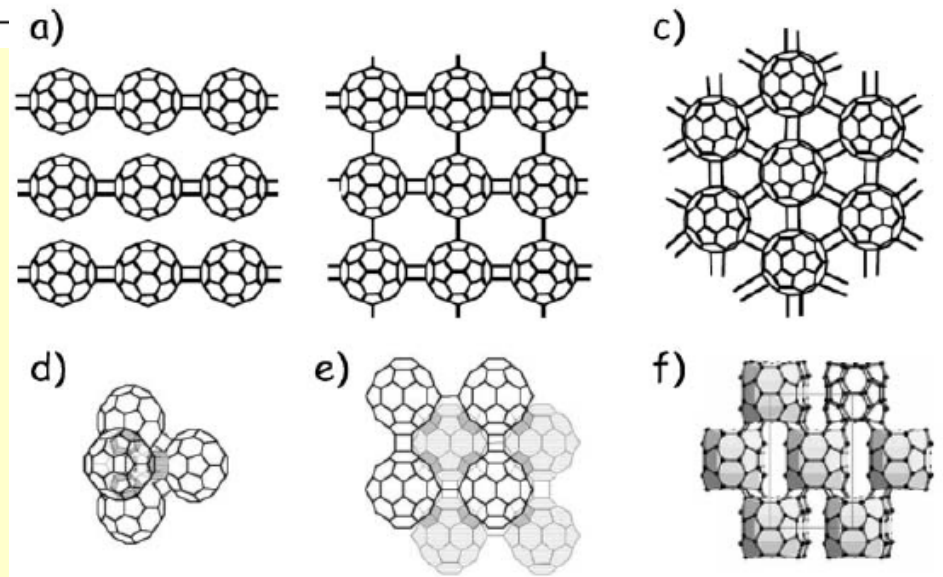
# Topochemical 3D Polymerization of C<sub>60</sub> under High P and T



Micro-Vickers hardness (MVH)

# Polymerization of C<sub>60</sub>

C <sub>60</sub> phase	no. of covalently bonded neighbors	MVH, kg/mm <sup>2</sup>	$d_{\text{calcd}}$ g/cm <sup>3</sup>	$d_{\text{obs}}$ g/cm <sup>3</sup>
monomer	0	15	1.684	1.68
2D <i>Immm</i>	4	80	1.936	1.93
2D $R\bar{3}m$	6	100	2.004	1.98
3D <i>Immm</i>	8	3,500	2.78	2.65
3D $R\bar{3}$	12	4,500	2.81	2.61
Diamond <sup>a</sup>		10,000	3.52	
c-BN <sup>a</sup>		5,000		



- **Electrical conductivity of semiconductors increases with T. The change of conductivity with T is one way of measuring the band gap.**
- **Conductivity also increases with P, because atoms are pushed closer together.**
- **All elements eventually adopt metallic structures at high P.**
- **The interior of Jupiter is **thought** to contain metallic hydrogen!**