Using Synchrotron Source FTIR to shed light on High Pressure Organic Chemistry and the Early Earth

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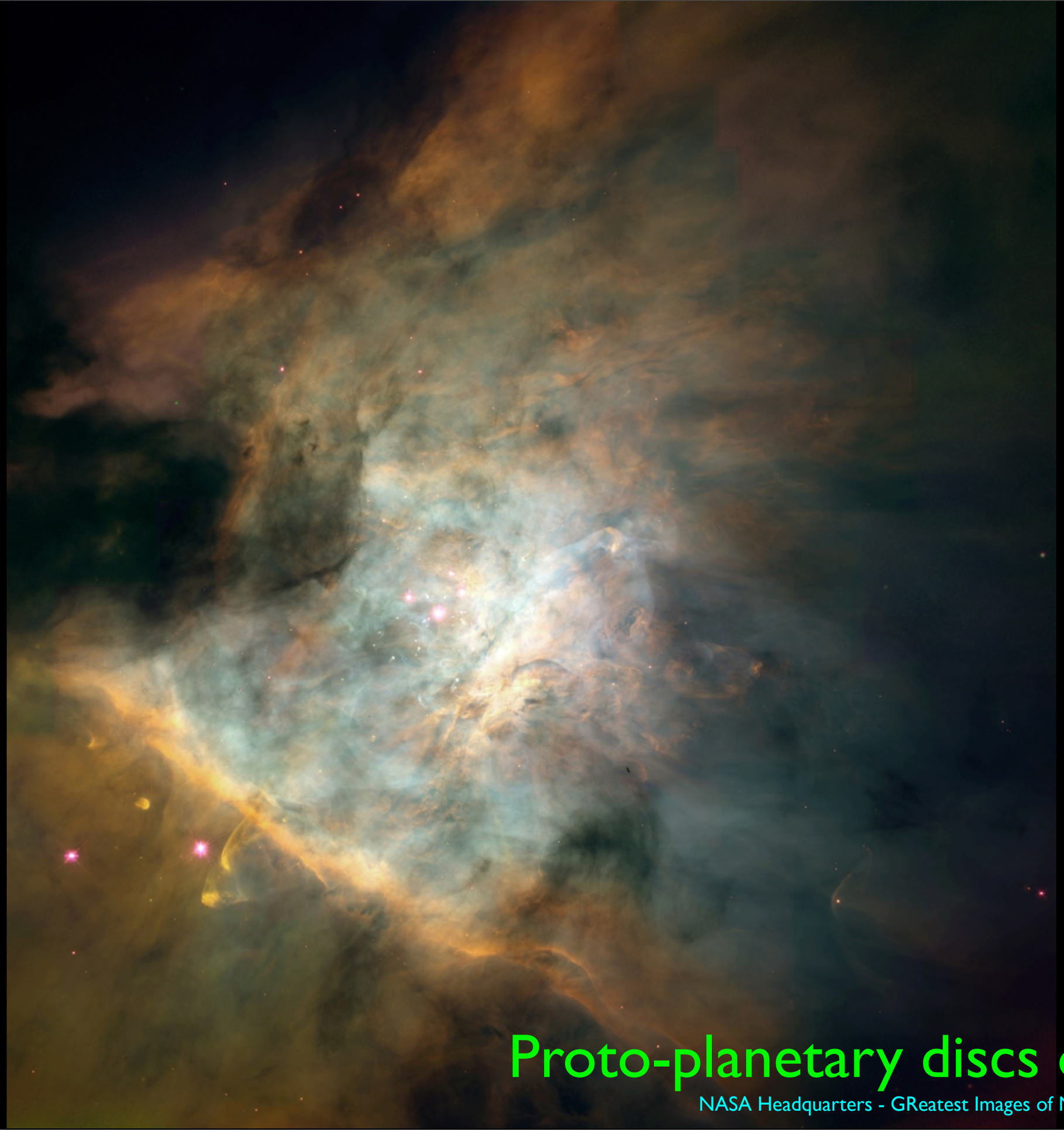
Where did the Earth's organic molecules come from?

Star-forming region W5 Casseiopeia

IRAC Image: NASA/JPL-Caltech/Harvard-Smithsonian CfA/ESA/STScI andVisible Light Image: NASA/JPL-Caltech/Harvard-Smithsonian CfA/DSS



Proto-planetary discs of Orion

NASA Headquarters - GReatest Images of NASA (NASA-HQ-GRIN)

Intrastellar and circumstellar molecules

PN

H_6C_6

CO_2

SiC_4

HCOOH

$HCOOCH_3$

NH_3

aromatic hydrocarbons

$(CH_3)_2CO$

CH_4

HNCO

$CH_2CH(CN)$

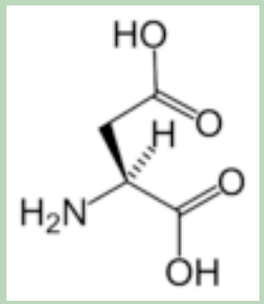
~126 molecules have been identified using infrared, radio and microwave astronomical observations.

National Radio Astronomy Observatory list: http://www.cv.nrao.edu/~awootten/allmols.html
NASA Cosmic Ices Laboratory: http://www-691.gsfc.nasa.gov/cosmic.ice.lab/interstellar.htm

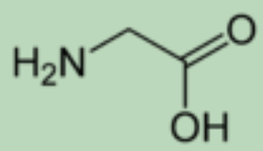
Planetary disc observations (with artist's concept of collision)

NASA/JPL-Caltech/T. Pyle (SSC-Caltech)

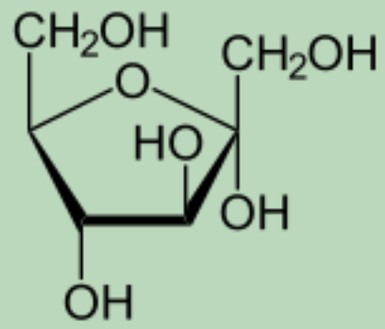
Meteoritic and cometary molecules



amino acids

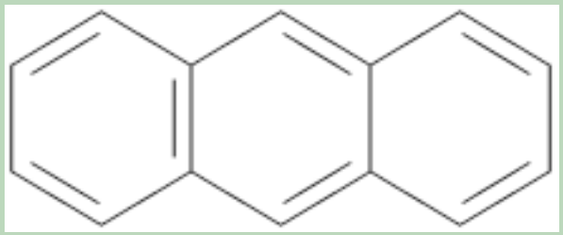


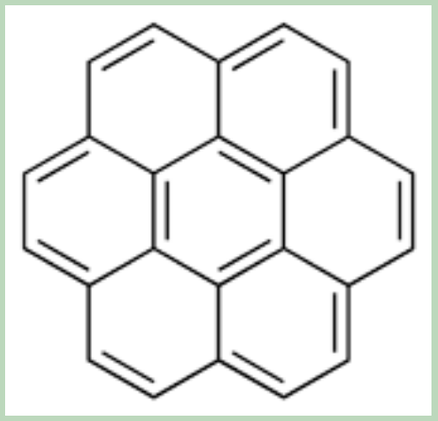
sugars



cyanuric acid

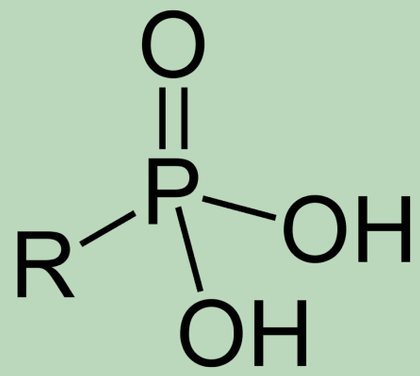
aromatic hydrocarbons



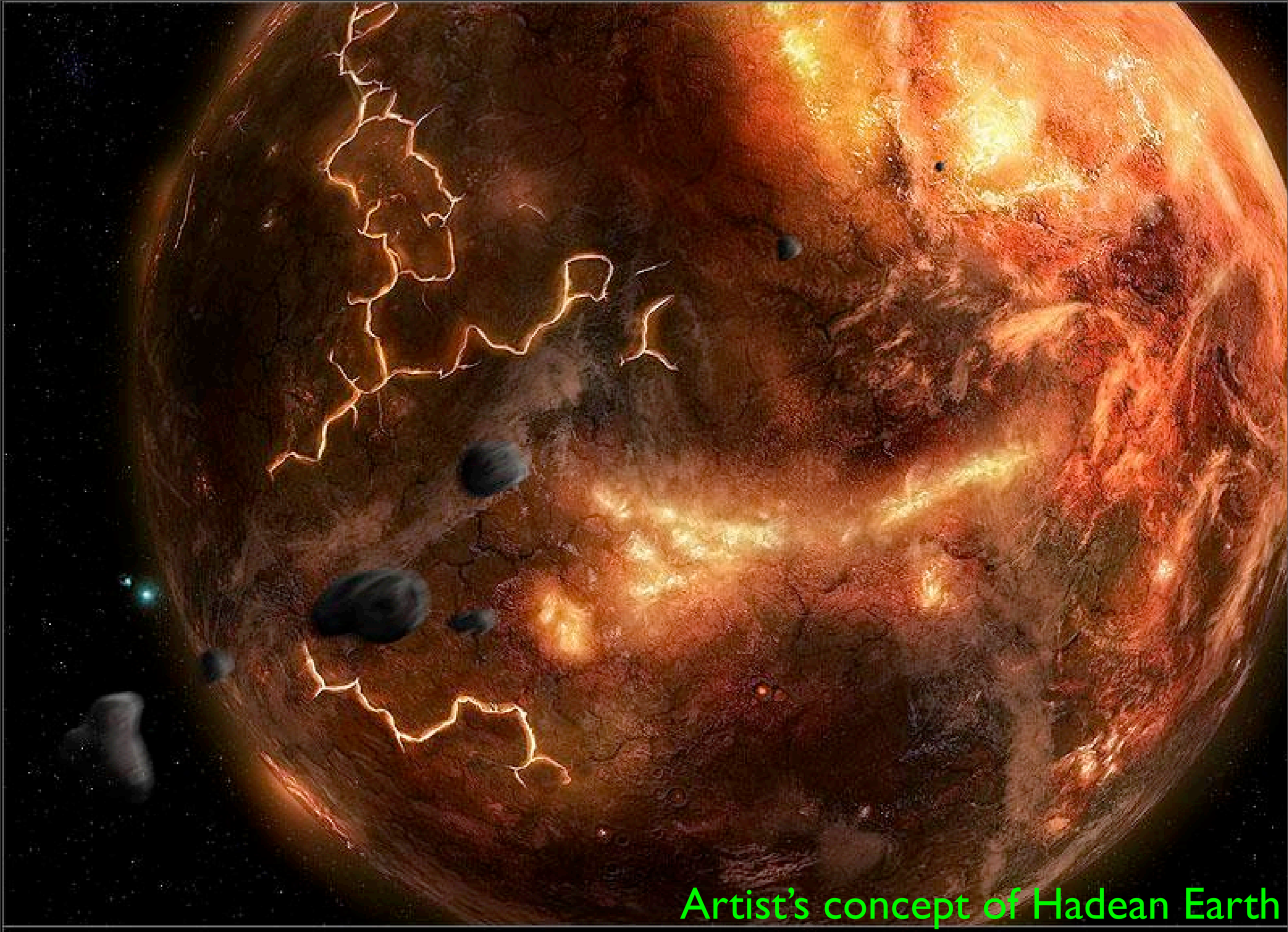


carboxylic acids

phosphonic acids

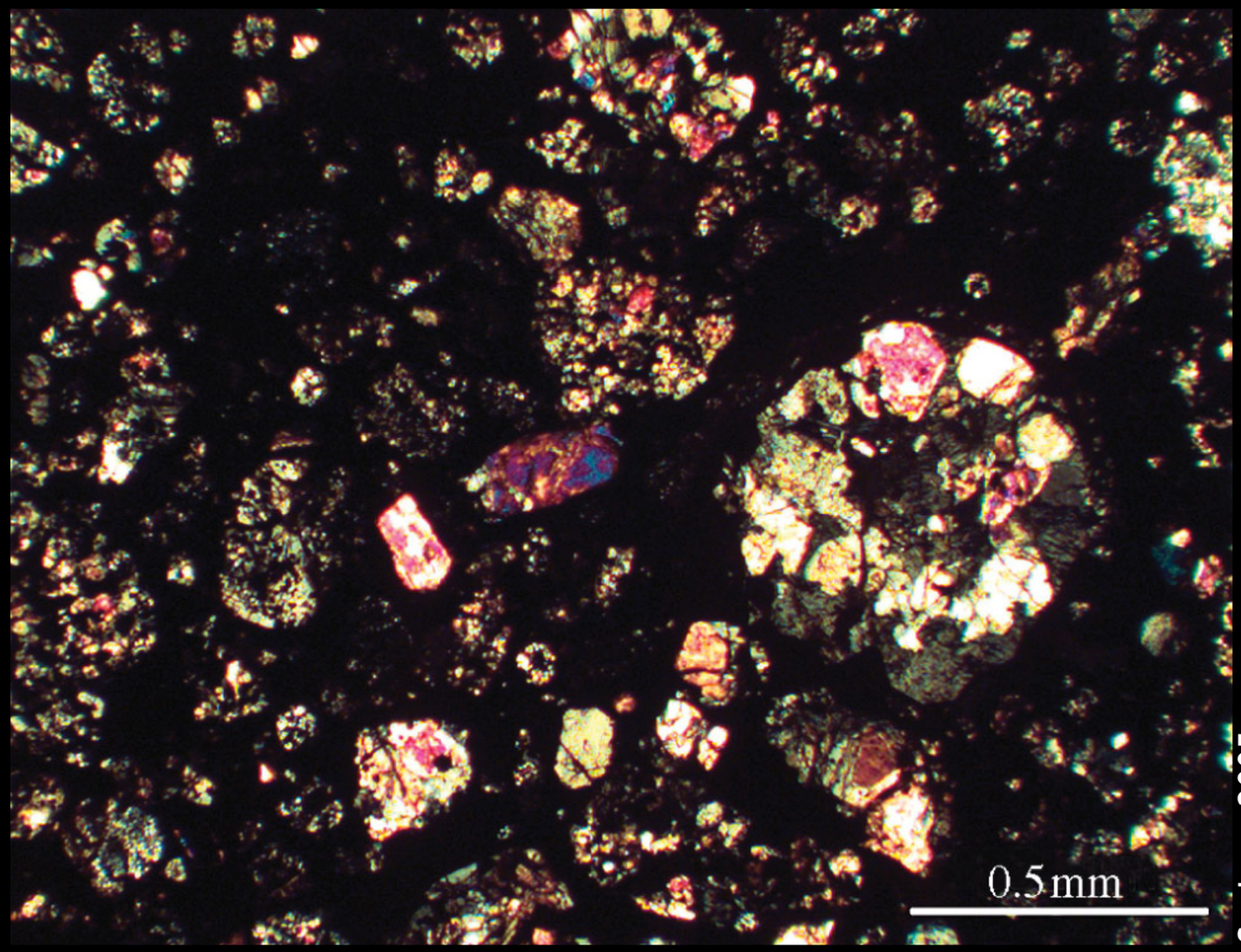


Sephton 2005, Sephton 2006, Sephton 2002, Sanford 2006,



Artist's concept of Hadean Earth

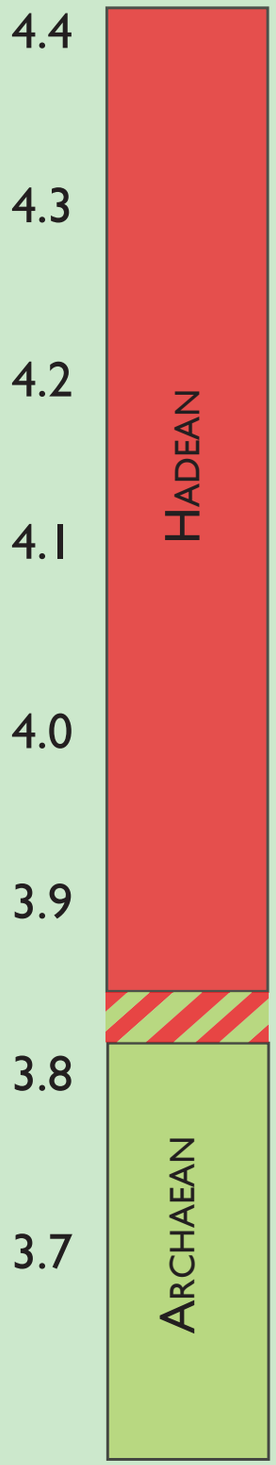
Fahad Sulehria http://www.novacelestia.com



Daar El Gani meteorite containing spherical silicate chondrules surrounded by a matrix composed primarily of clay minerals, oxides and organic matter.

Hadean: Era of Mystery

Mantle Differentiation (appx 4.45 Ga)



Oldest known detrital zircons

During this period, there was a basaltic proto-crust with felsic rocks; water and meteoritic materials were probably present. Continental crust and oceans as we know them were not present.

Claimed oldest surviving crustal material; contains no evidence for life.

End of Late Heavy Bombardment

Tectonism@ 3.8 Ga: Furnes 2007

Starting at 3.8 Ga, there is disputed evidence of life: isotopically light samples, stromatolites, kerogens in various Archaean rocks.

Oceans and tectonism believed to be present.

Undisputed record of life starts at 2.7 Ga.

After Moorbath 2005

From dust to planets: the role of pressure & temperature in the early Earth

- Large impacts are completed by 4.5 Ga. The Hadean and subsequent eras feature smaller impacts and continued delivery of extraterrestrial material.
- Early tectonic processes would lead to burial and subduction of material, including organics.

- Previous work (Ciabini 2006, Katrusiak 1991) has shown the formation of more complex organic materials at elevated pressures and temperatures

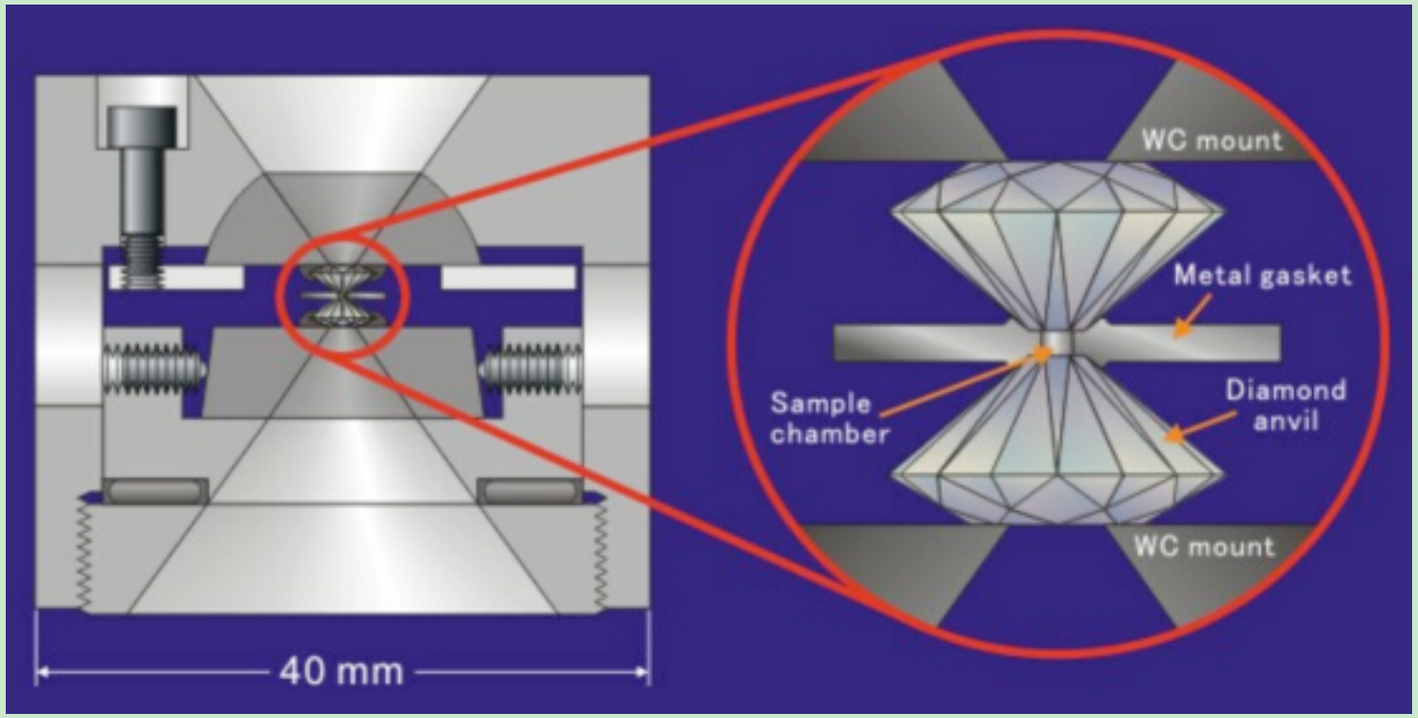
- At 10 GPa, the compression work,

  $P\Delta V$ = approx. 0.1 eV = 10 kJ/mol

  is on the order of many organic activation energies.


1 mm

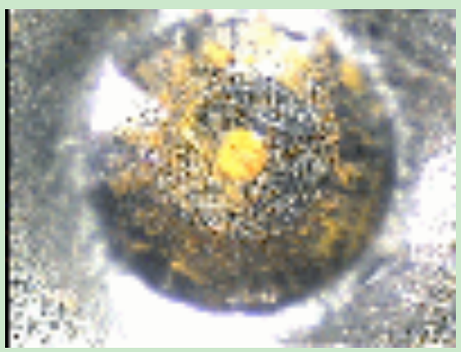
The Diamond Anvil Cell



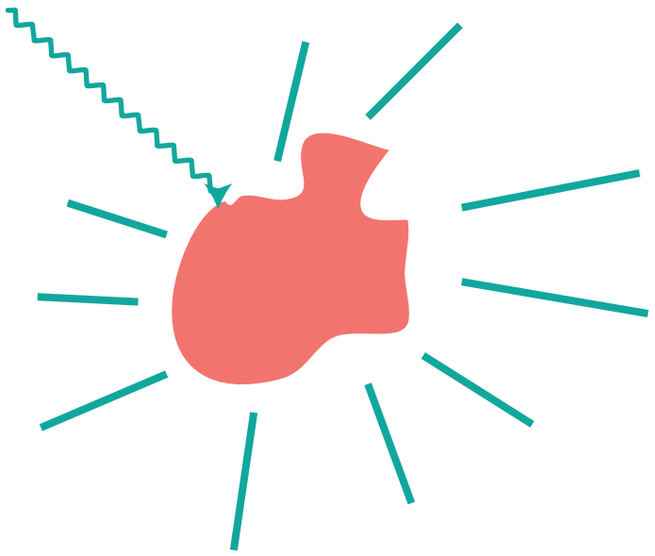
Pressure= Force/Area

The smaller the area, the greater the pressure.

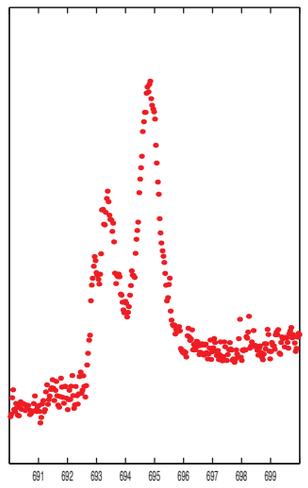
The pressures obtained can exceed >100 GPa (10^6 atm). 10 GPa is comparatively easy.



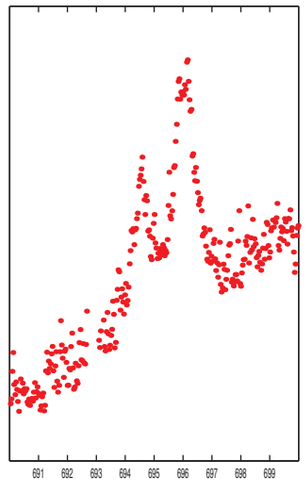
Sample can be heated:
resistively to ~1200 K
laser heating to ~6000 K



$Al_2O_3:Cr^+$



1.68 GPa



8.85 GPa

$$P = \frac{1904}{7.664}\left[\left(\frac{\Delta\lambda}{\lambda_0}+1\right)^{7.664}-1\right]$$

$$\lambda_0 \text{ for } \mathrm{R}_1 = 694.25 \text{ nm}$$

Science at the synchrotron

Swiss Light Source

ruby fluorescence system

IR microscope

ruby readout

IR controls

power supply (temperature controller)

DAC

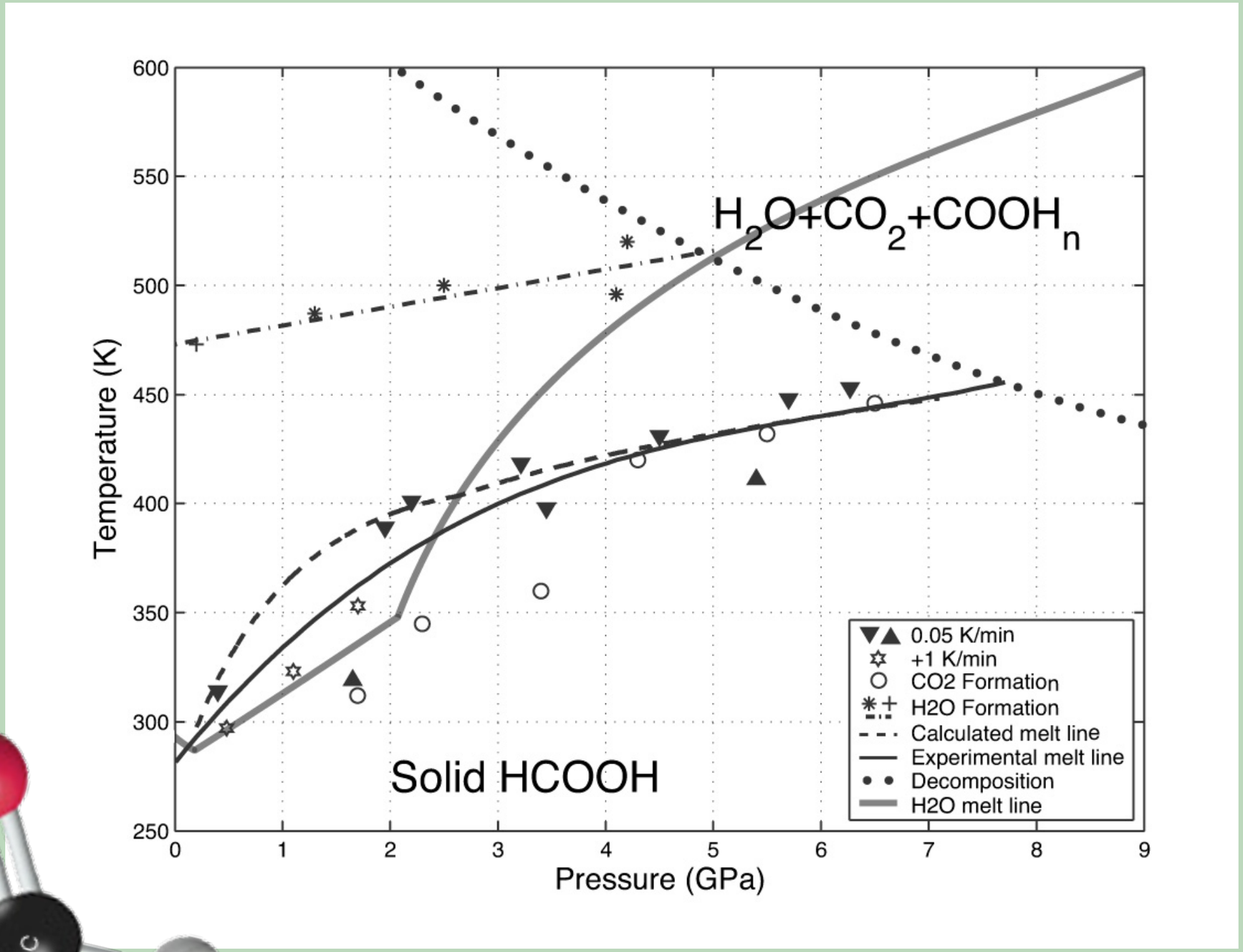
thermocouple reader

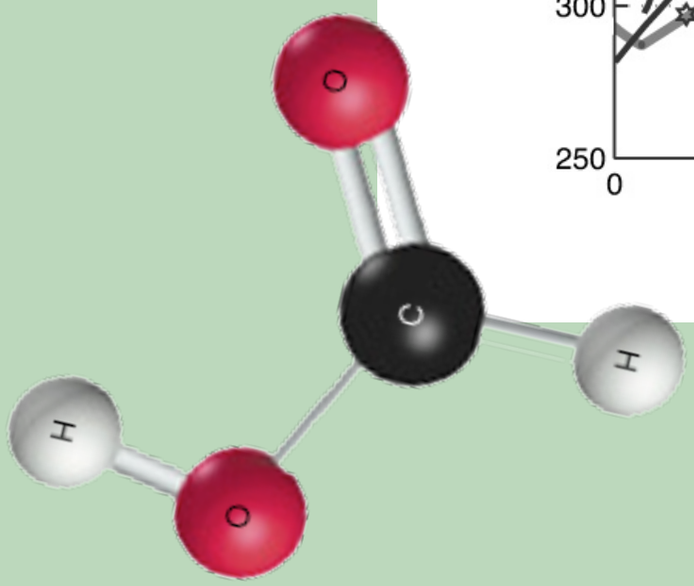
Membrane pressure controller

chiller input/output

Beamline X01DC, Swiss Light Source

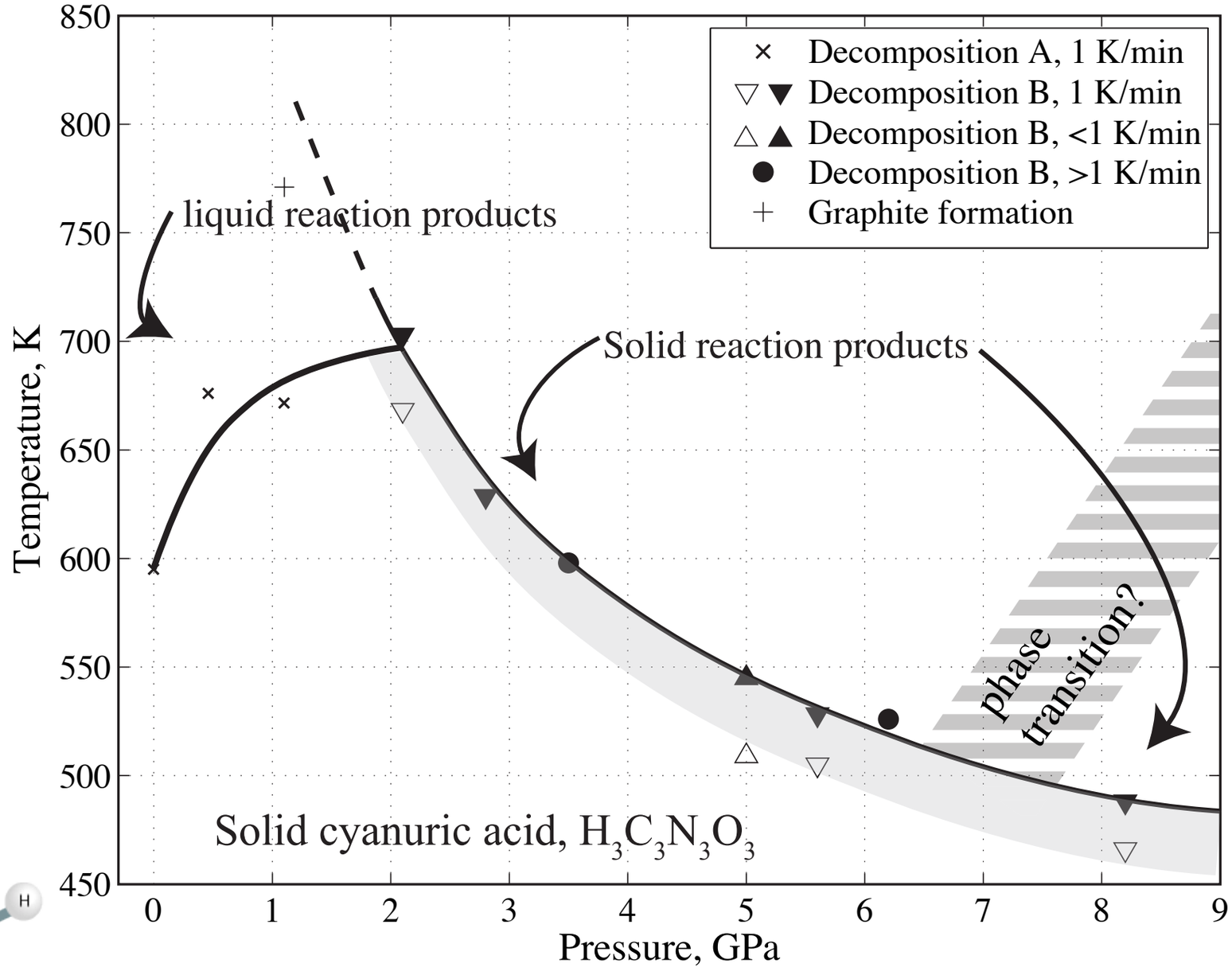
Phase diagram of formic acid, HCOOH

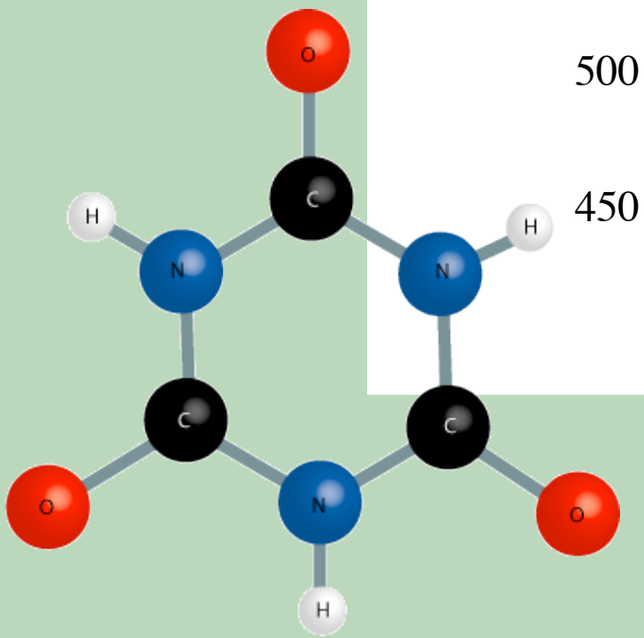




Montgomery, et al., 2005

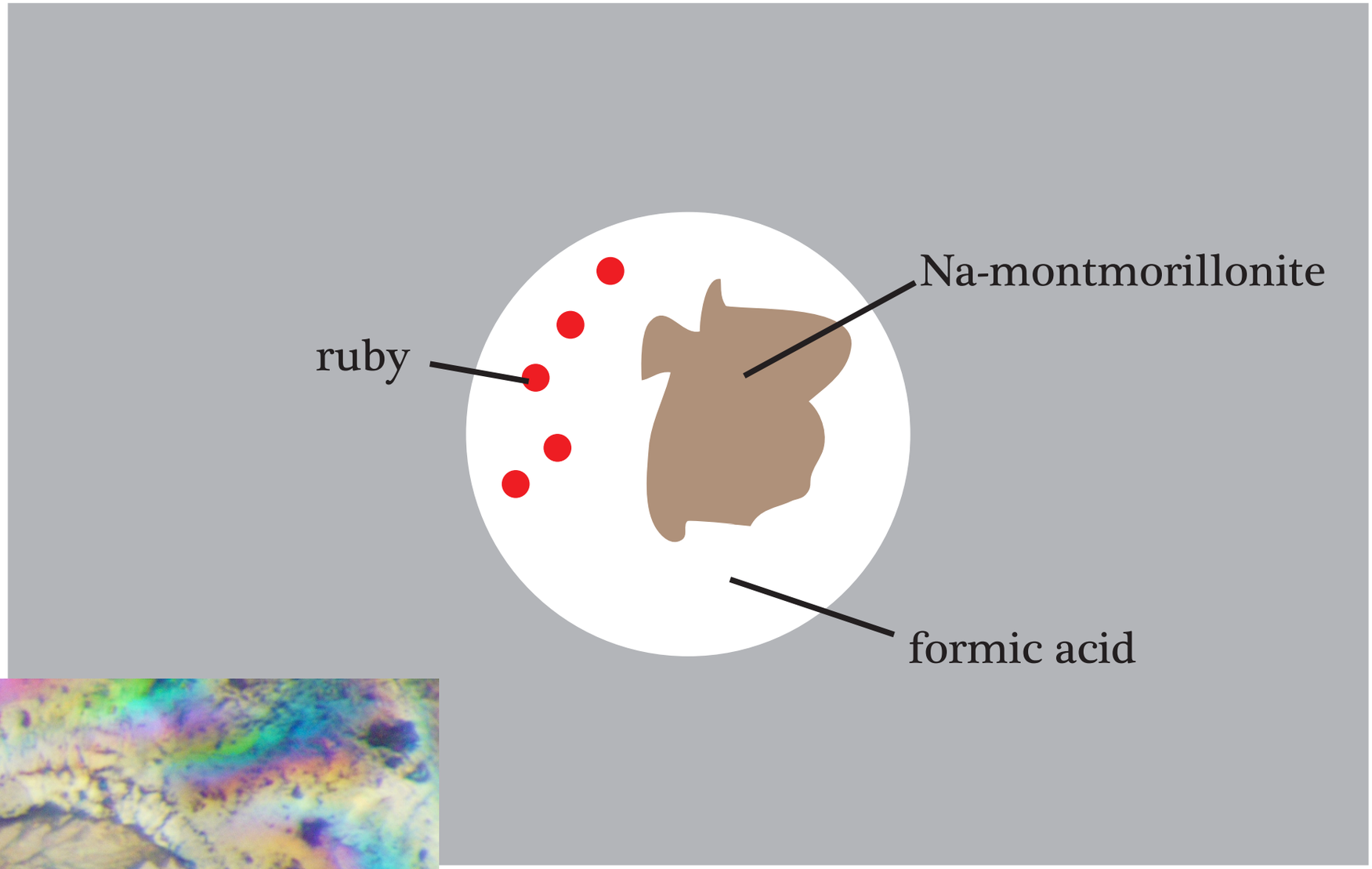
Phase diagram of cyanuric acid, H3C3N3O3

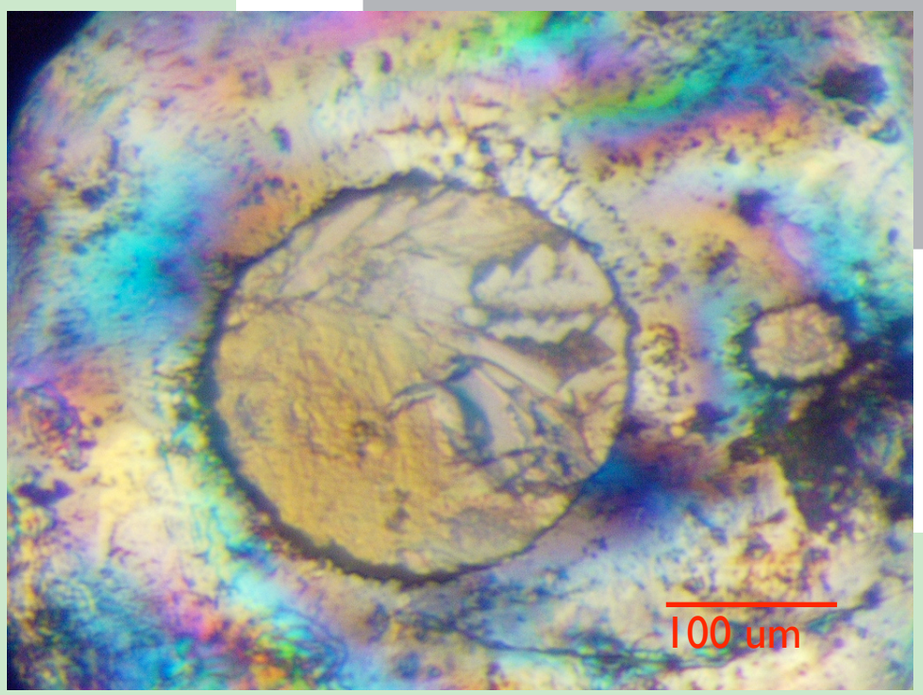




Montgomery, et al., 2008

Formic acid + Montmorillonite



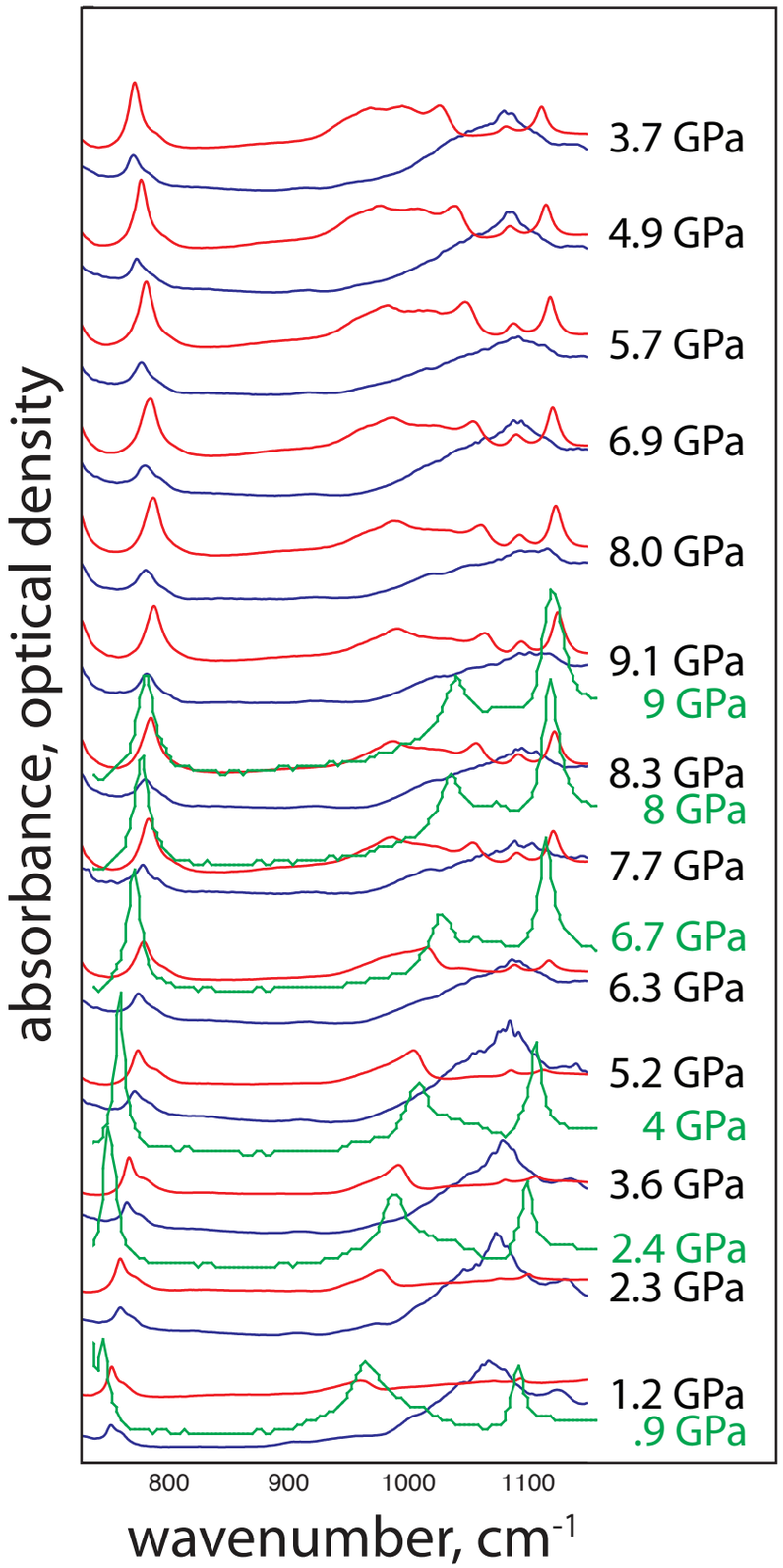


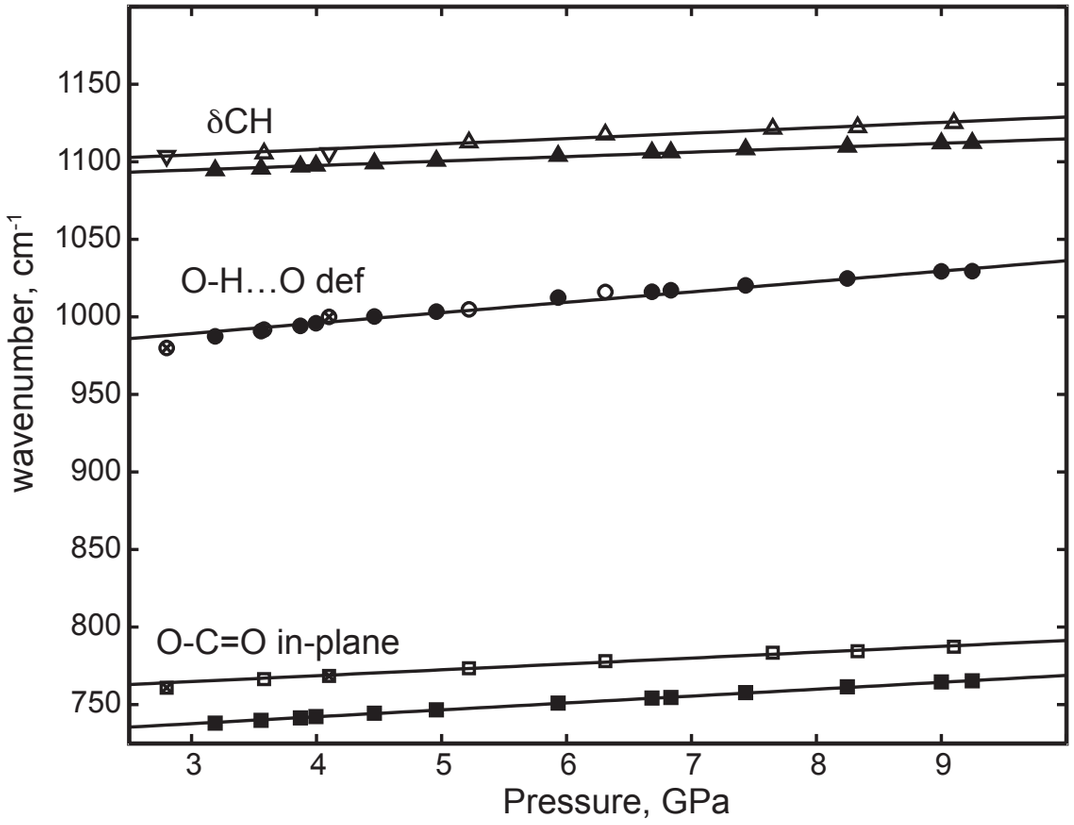
montmorillonite

formic acid

formic acid + montmorillonite

New peaks form at 952, 969 and 1052 cm^{-1}



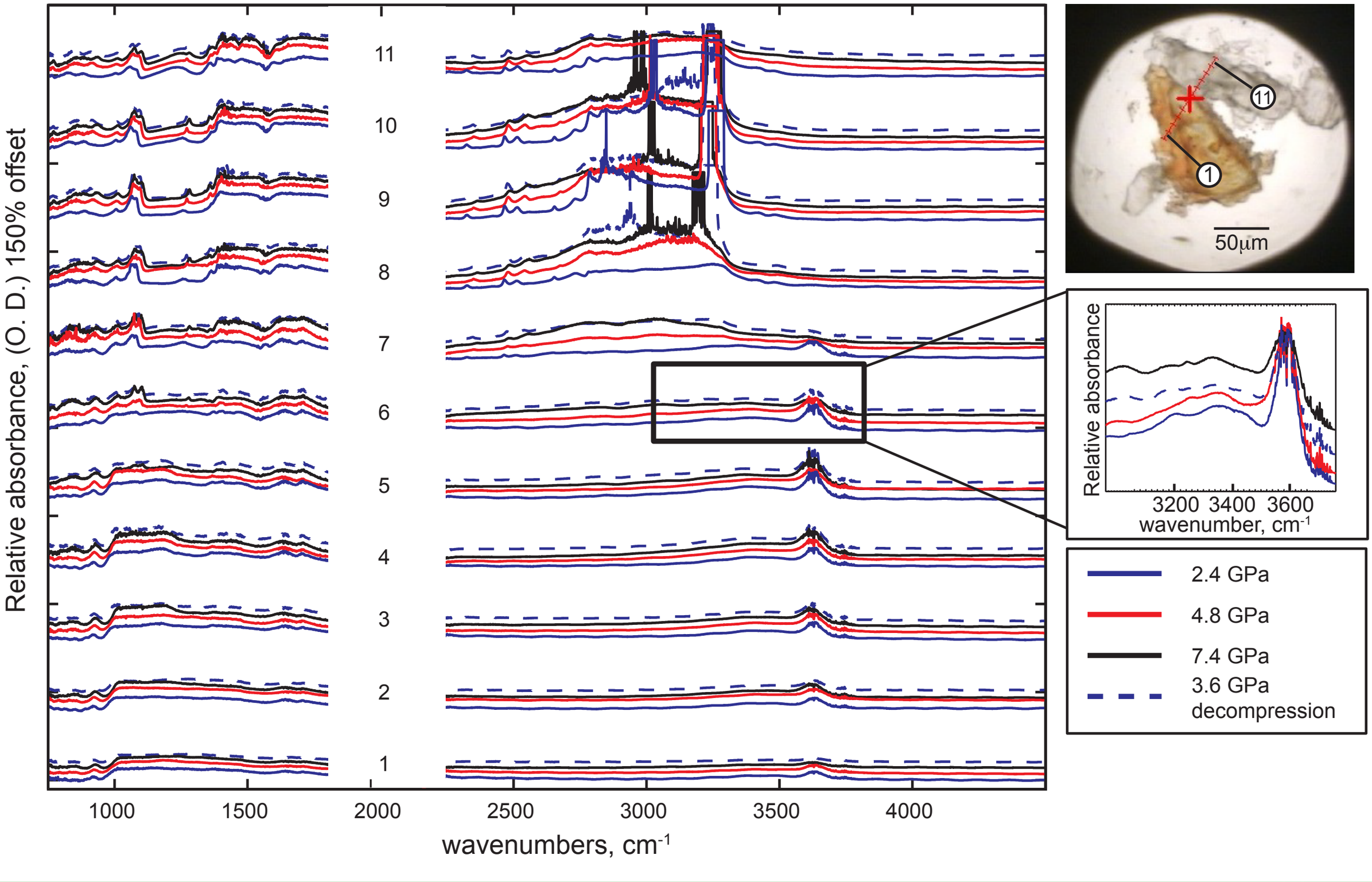


Montgomery, et al., 2011

What is it?

- 952, 969, 996 and 1026 cm^{-1} peaks.
- formates: HCO_2Na or $Mg(HCOO)_2$?
- ring structures – cyclopentane or cyclobutane?
- Si–OH groups or $Si–OCH_2CH_3$
  - Si–O–Si 1082 cm^{-1},
  - CH 1026, 966 cm^{-1}

cyanuric acid + montmorillonite



Montgomery, et al. 2011

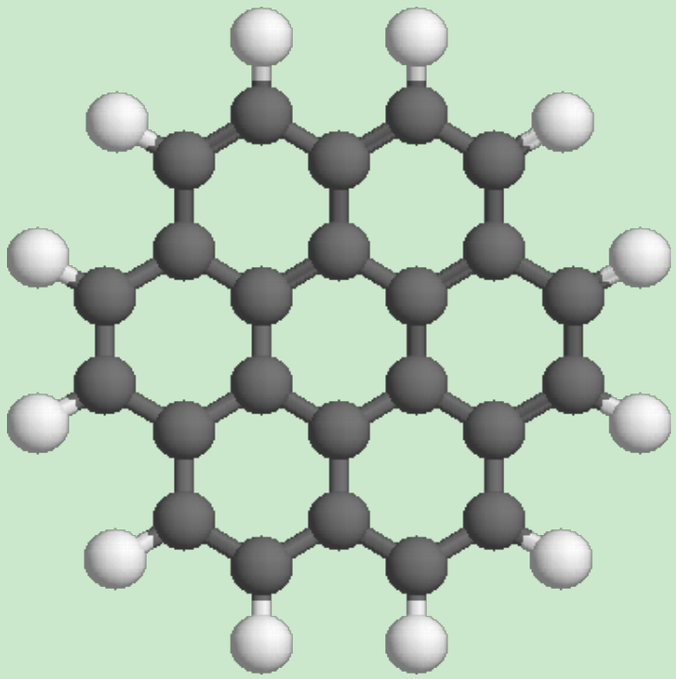
- Silicate-acid interactions under high pressures lead to the formation of new bonds.
  - only a few possible acid-mineral systems have been explored.
- Water can move around the system while under high pressure (and temperatures), so clay may act as a reservoir for water in meteorites and in subducting slabs.

Polycyclic Aromatic Hydrocarbons

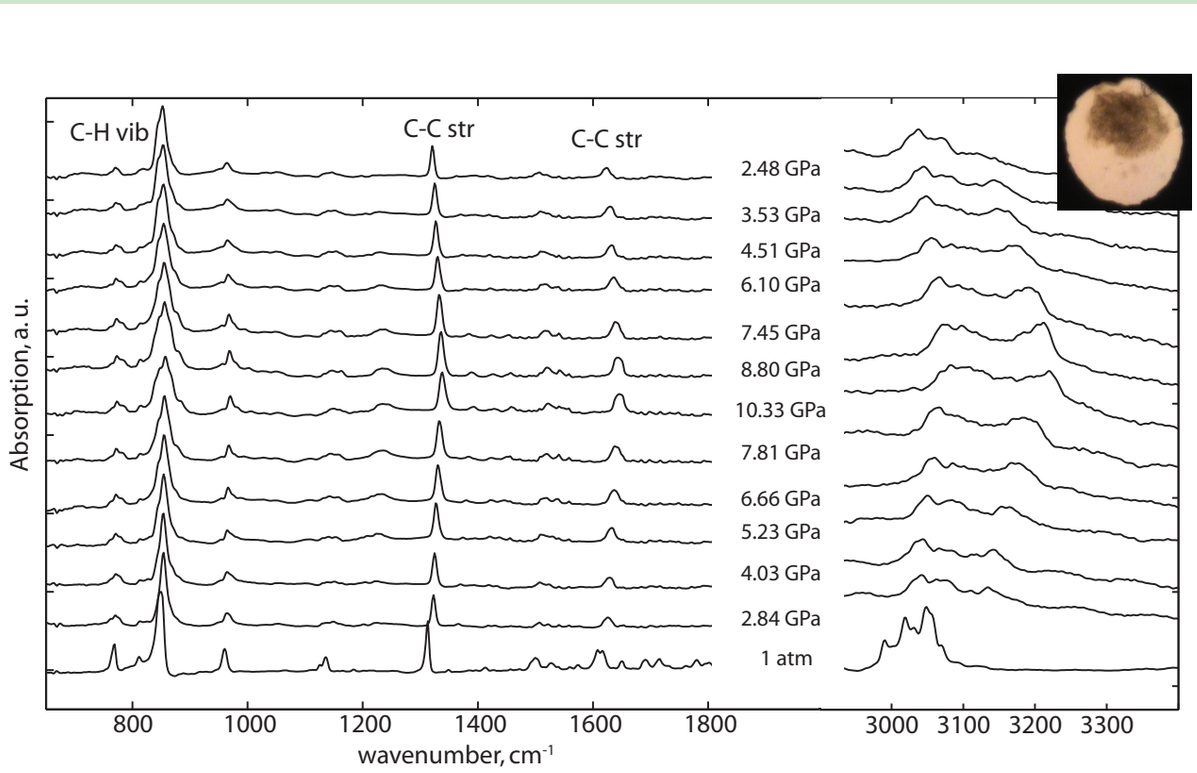
- the interstellar medium is made of PAHs and they are found in meteorites and IDPs
- but PAHs are also found in fresh basalts, volcanic bombs, and other geologic contexts
- regarded as key component for biochemistry: precursor to membranes and informational molecules

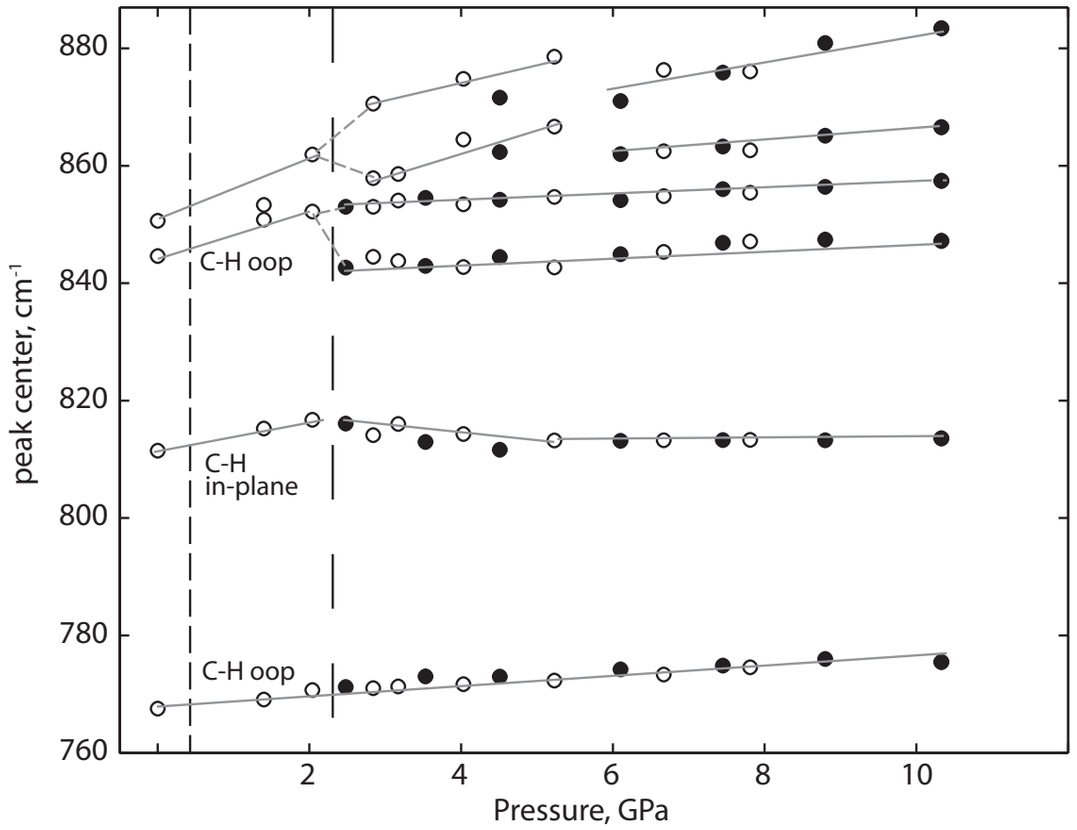
Coronene in earth systems

- Coronene has been recovered from meteorites (Zolotov and Shock 1999), volcanic bombs and volcanic ash (Zubkov 2009).
- It is stable over a range of pressures and temperatures but subtle peak fixing may make it a good barometer and thermometer for geologic processes.



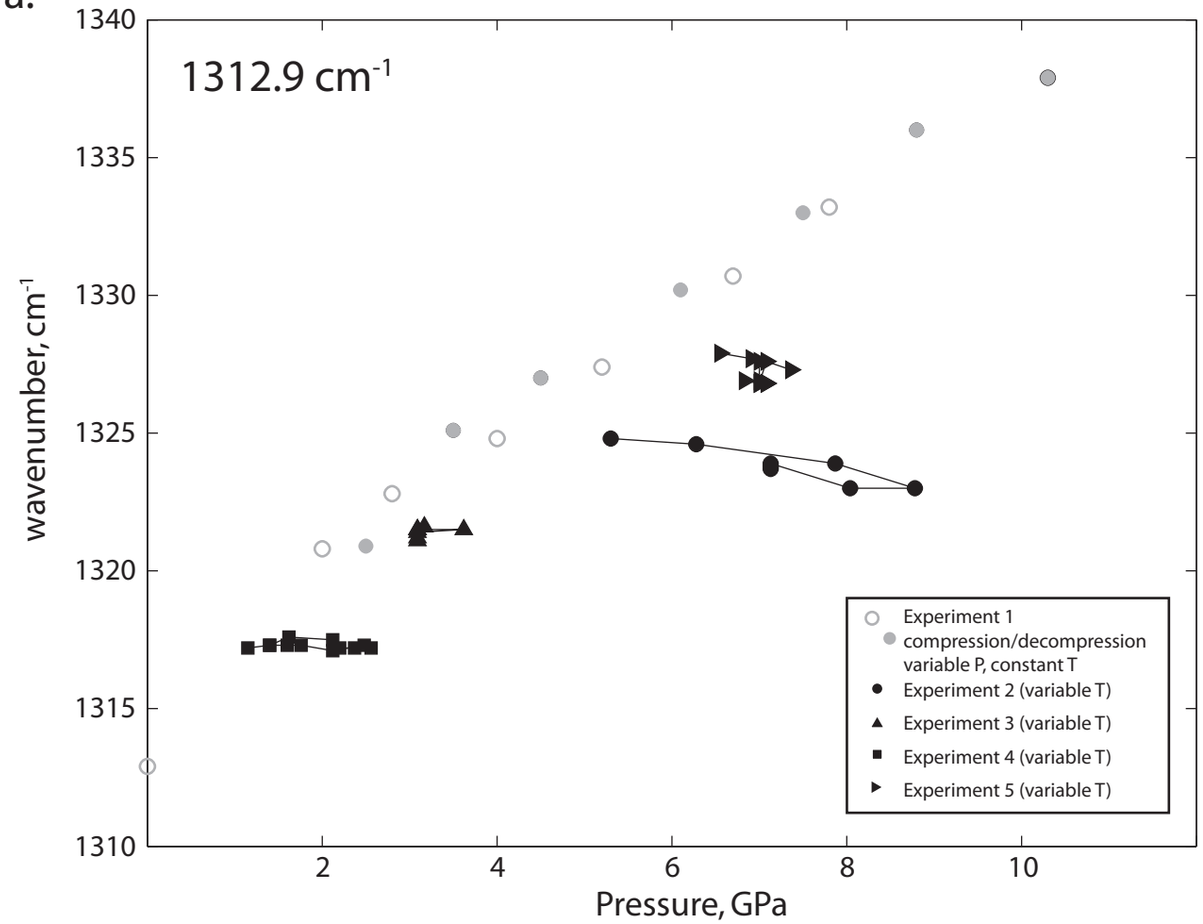
coronene, $C_{24}H_{12}$



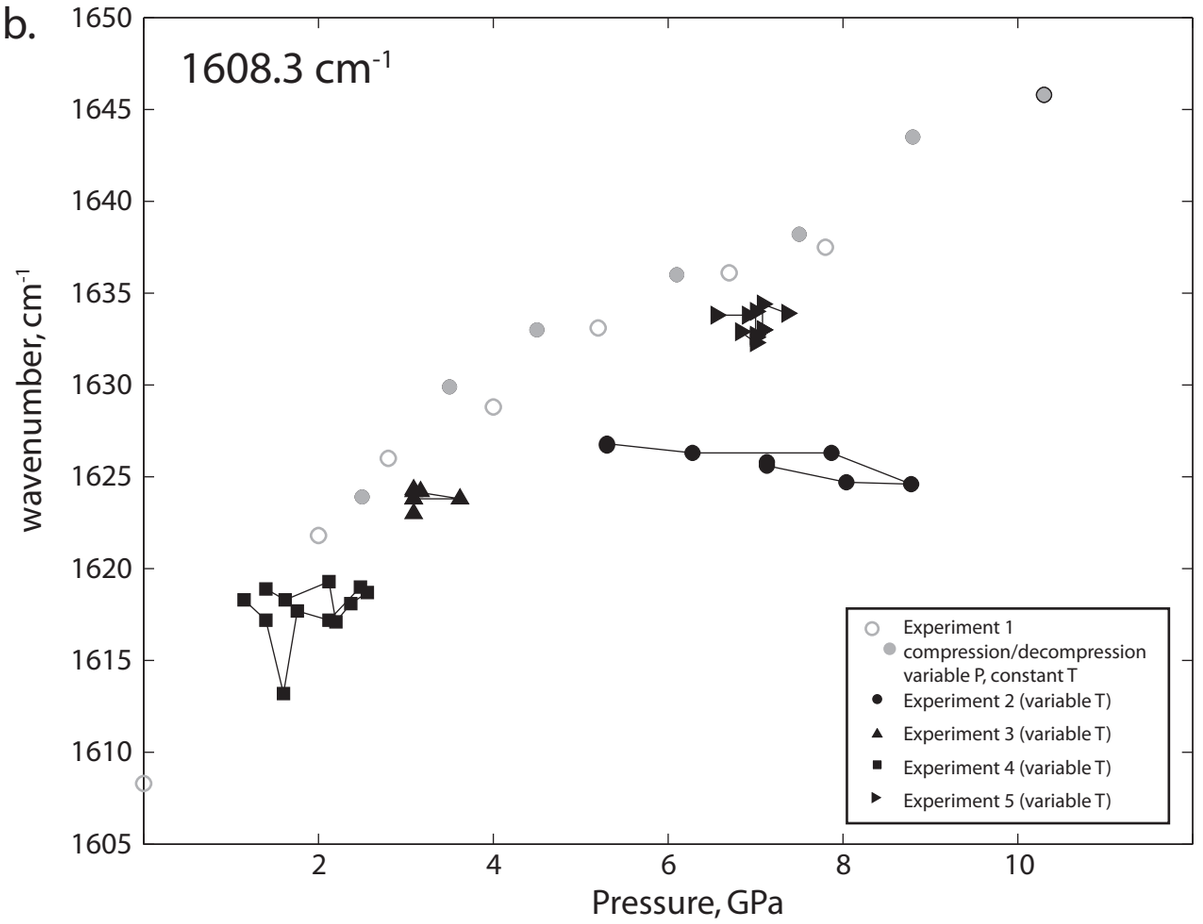


Jennings, et al., 2010

a.


1312.9 cm-1
wavenumber, cm-1
1340
1335
1330
1325
1320
1315
1310
2
4
6
8
10
Pressure, GPa
Experiment 1
compression/decompression
variable P, constant T
Experiment 2 (variable T)
Experiment 3 (variable T)
Experiment 4 (variable T)
Experiment 5 (variable T)

b.


1608.3 cm-1
wavenumber, cm-1
1650
1645
1640
1635
1630
1625
1620
1615
1610
1605
2
4
6
8
10
Pressure, GPa
Experiment 1
compression/decompression
variable P, constant T
Experiment 2 (variable T)
Experiment 3 (variable T)
Experiment 4 (variable T)
Experiment 5 (variable T)

Crystal Predictor

- These molecular crystals are very low symmetry
- CrystalPredictor (Panos Karamertzanis, ICL) was developed to predict polymorphs of pharmaceuticals but also works for high pressures.

Summary

- Organic chemistry occurs under pressures relevant to the early Earth, subduction zones, and planetary formation.
- This chemistry is affected by the presence of silicates.
- Improvements in modelling mean that single component systems can be easily studied.

University of Bristol: James Tuff, (now at Oxford) Simon Kohn, Mike Walter, Ollie Lord (experimental high pressure), Dave Sherman (computational modelling), Ellie Jennings (summer undergraduate researcher)

Imperial College London: Mark Sephton and Richard Court (meteoritics), Panos Karamertzanis (computational modelling)

Advanced Light Source: Mike Martin, Hans Bechtel, Jason Knight

Swiss Light Source: Philippe Lerch