Pressure-induced reactions in organic materials a new insight for evolution of bio-related molecules

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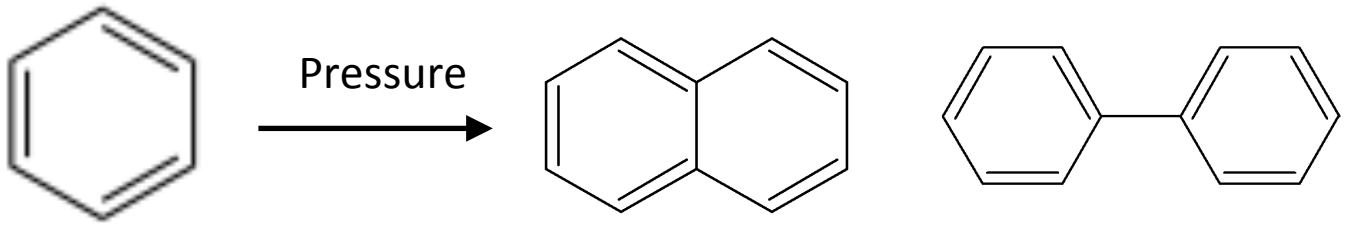
The motivation of our study

To investigate chemical evolution in the interior of icy planets

Recently, we study behaviors of organic molecules under high pressures.

1. Pressure-induced reactions on benzene at room temperature.

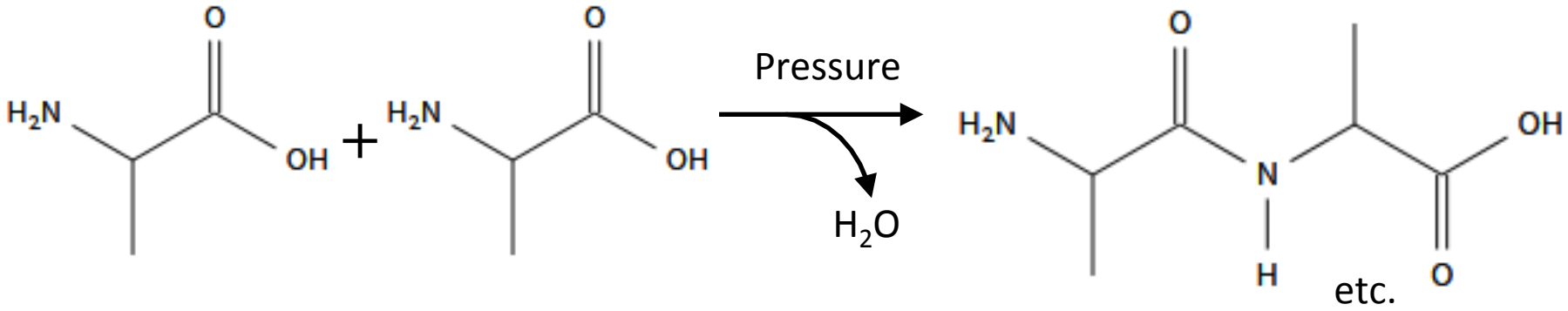
Shinozaki et al. (2014) *J. Chem. Phys.*



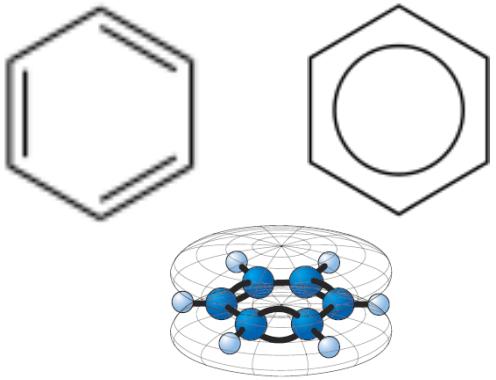
etc.

2. Pressure-induced oligomerization of alanine at room temperature.

Fujimoto et al. (2015) *Chem. Comm.*



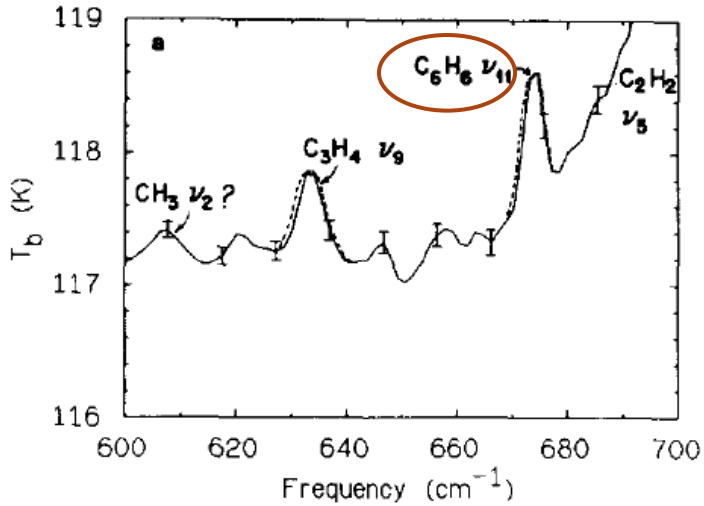
Benzene (C_6H_6)



- Simplest aromatic hydrocarbon
- Delocalized electrons in the π orbital

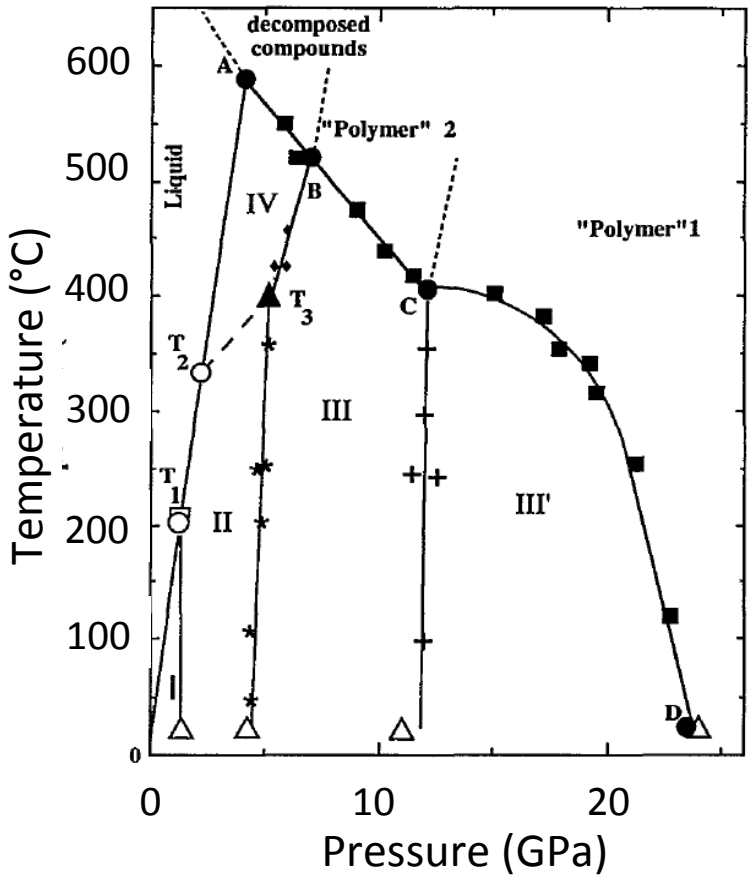
Benzene and/or PAH (polycyclic aromatic hydrocarbons)

- ✓ Martian meteorite
  (e.g. Steele et al. 2012)
- ✓ Atmosphere of Jupiter
  (e.g. Kim et al. 1985)
- ✓ Atmosphere of Titans
  (e.g. Coustenis et al. 2007)

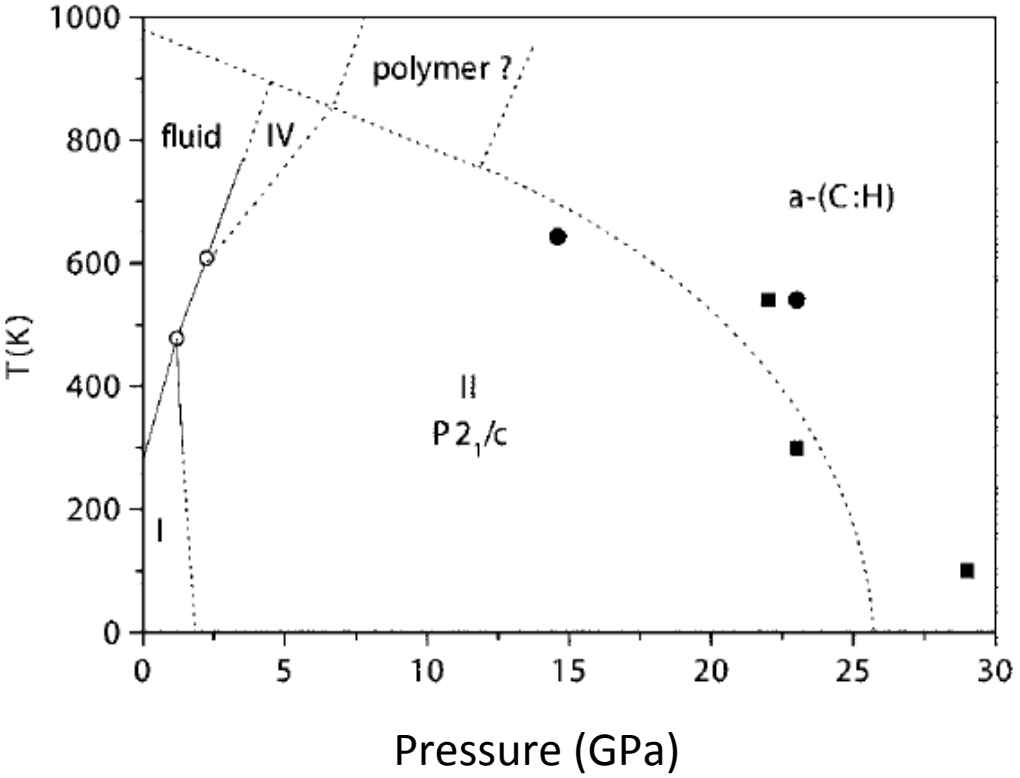


Kim et al. 1985

Phase diagrams of benzene



Cancell et al. 1993



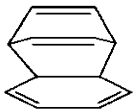
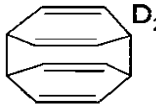
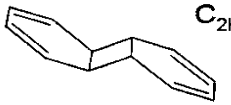
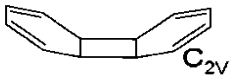
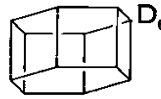
Ciabini et al. 2005

At room temperature, benzene solidifies at ~ 0.1 GPa.
and transforms to the amorphous state at 23 GPa.

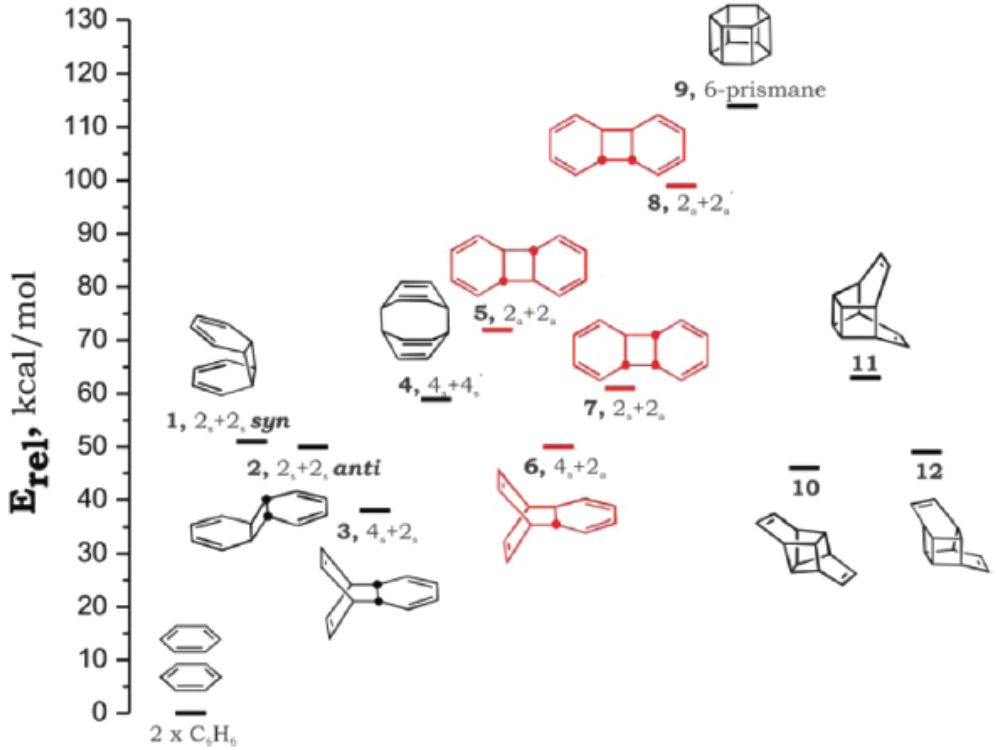
Pressure-induced polymerization of benzene

Theoretical calculation

Approaching the neighbor benzene molecules with compression.

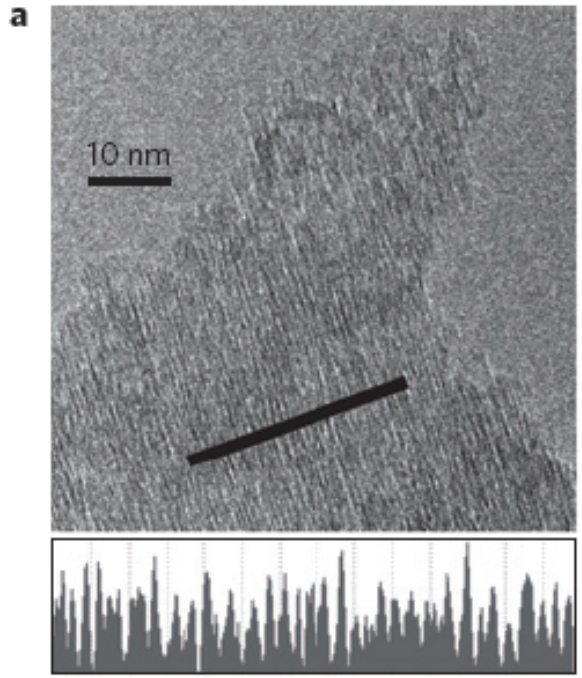
Engelke Dimers Refs. 23-25	 C_S	 D_{2H}	 C_{2H}	 C_{2V}	 D_{6H}
Energy Barrier (eV/pair)	3.8	5.5	6.7	5.5	11.5
Reaction Distance (Å)	2.1	2.75	2.3	2.1	1.75

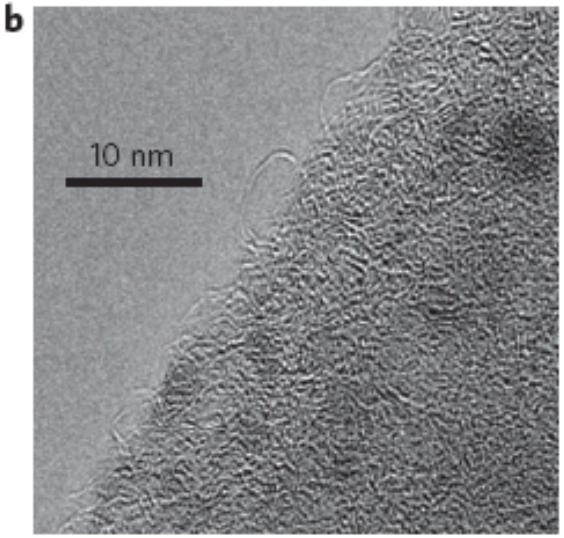
Root and Gupta (2009)

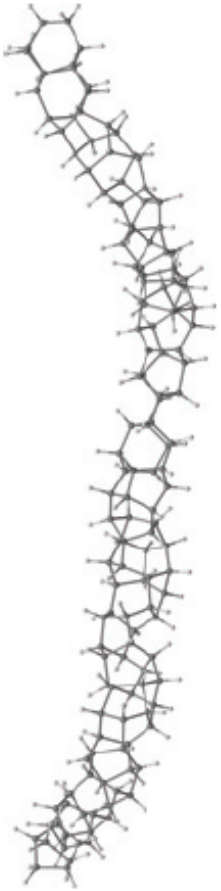


Andrey et al. (2011)

Benzene-derived carbon nanothreads





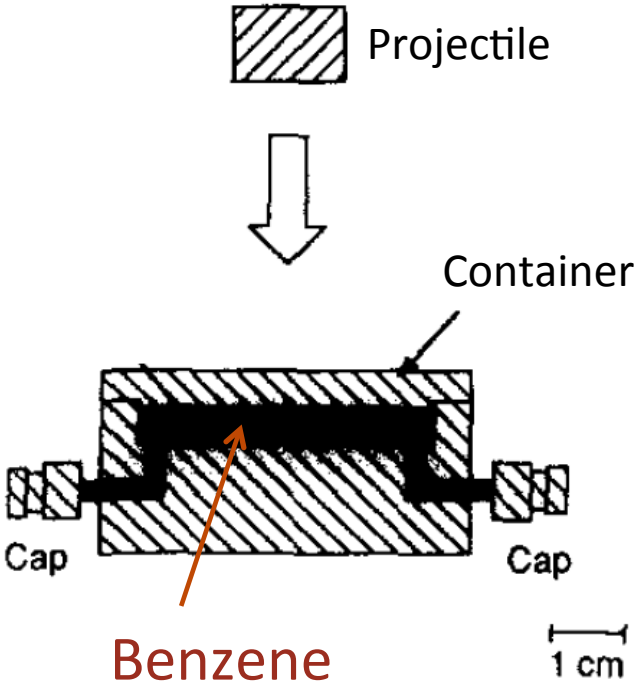


Compression of benzene at 20 GPa and room temperature

Fitzgibbons et al., 2015

Polymerization of benzene by impact shock

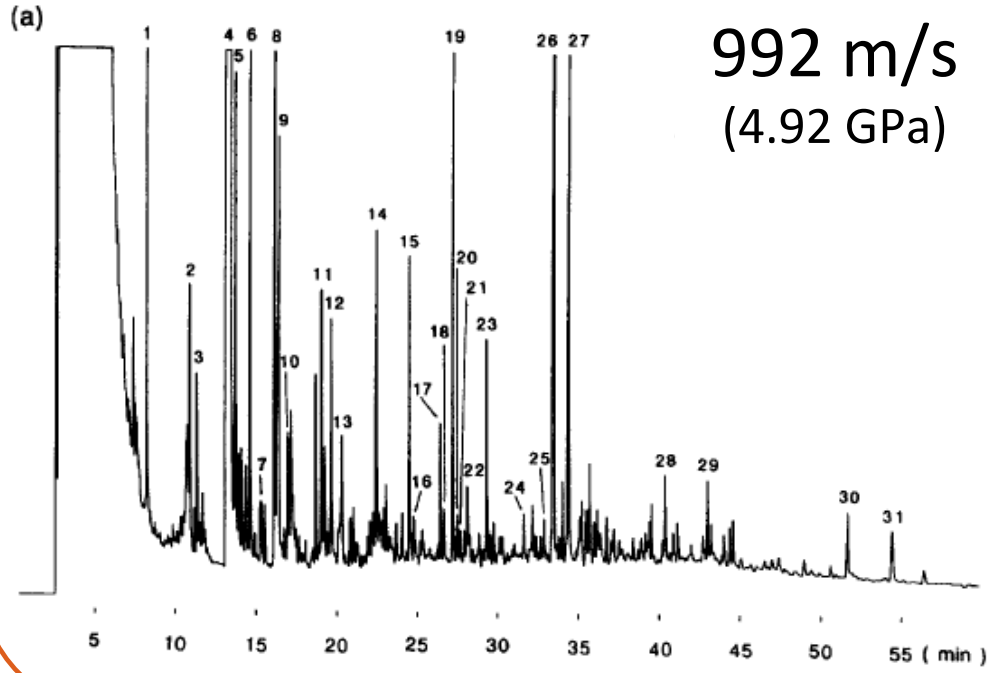
High pressure and
high temperature generated
in short time range



Mimura, 1995

GC-MS analysis on the recovered samples

Gas chromatograph

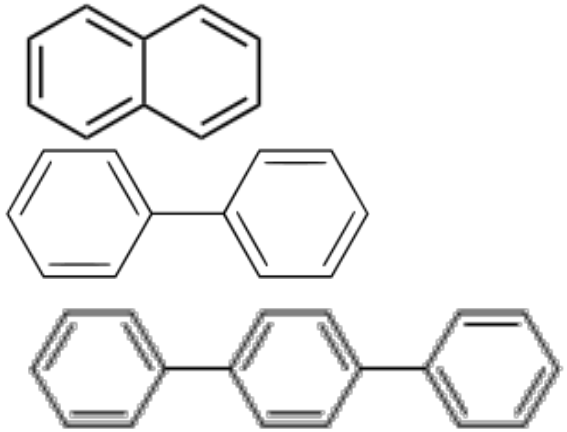


992 m/s
(4.92 GPa)

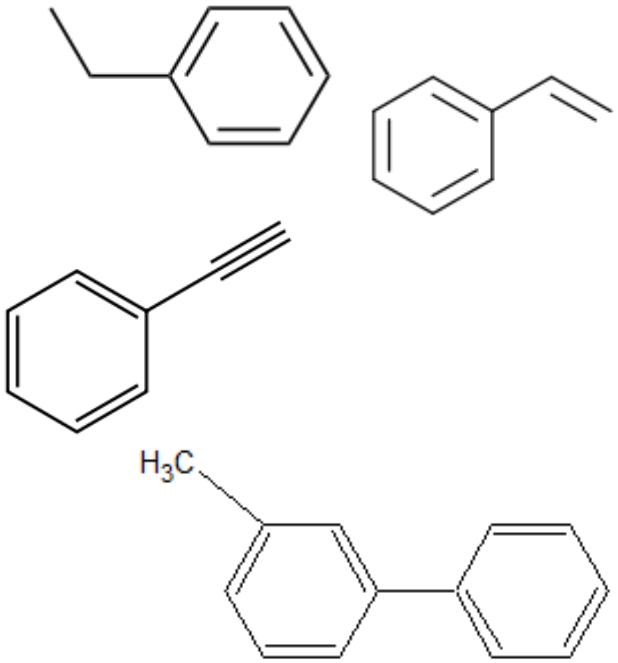
Run products from the shock experiments.

- Naphthalene (C_2H_8)
- Biphenyl ($C_{12}H_{10}$)
- Terphenyl ($C_{18}H_{14}$)

Mimura, 1995



- Ethylbenzene
- Styrene
- Phenylacetylene
- Metylbipheyl
- Methlnaphtalene



etc…

To observe polymerization of benzene under static high-pressure condition behind the phase diagram

We need to detect trace polymerized products

DAC→ double-toroidal anvils

XRD, Raman, IR → GC-MS analysis on recovered samples

High pressure Experiments

Starting material

distilled liquid benzene

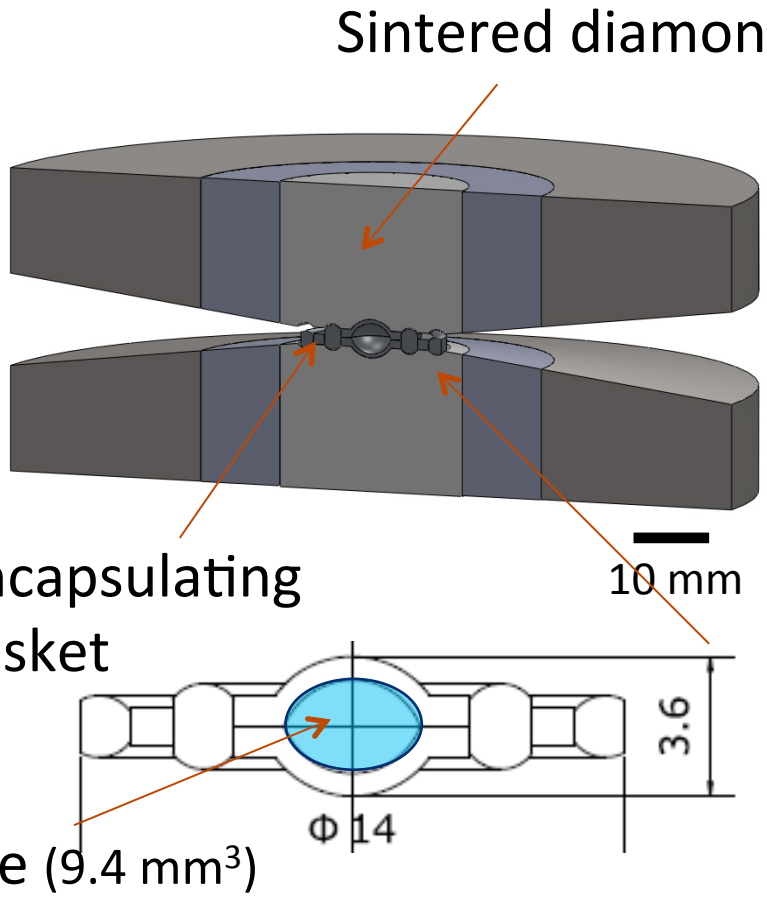
High pressure apparatus

double toroidal anvils, ϕ 4mm

high-pressure experiments at RT

MAX-III (@PF, KEK)

CAPRICON (@ISSP, U Tokyo)



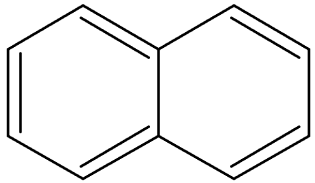
Run list

Run no.	Load (ton)	Pressure (GPa)	preservation time (hour)
1	40	5	1
2	40	5	45
3	80	10	1
4	80	10	45
5	103	13	1
6	130	16	1
7	130	16	45

All experiments were conducted at room temperature.

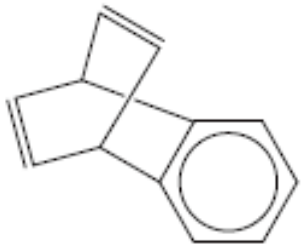
Products recovered from high pressure experiments on benzene at 16 GPa (1 hour)

$C_{10}H_8$ (naphthalene)



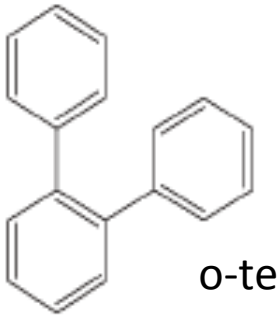
10^{-5}～10^{-4}

$C_{12}H_{10}$

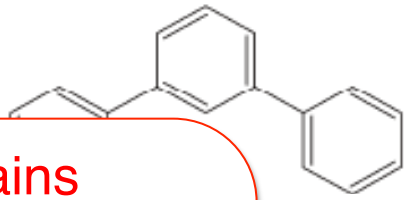


10^{-6}～10^{-5}

$C_{18}H_{14}$ (terphenyl)

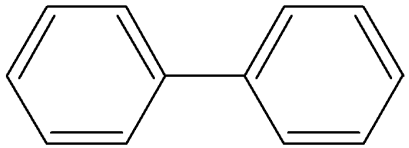


o-terphenyl



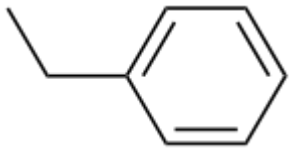
enyl

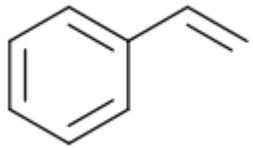
$C_{12}H_{10}$ (biphenyl)



10^{-5}～10^{-4}

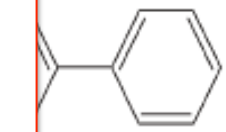
Missing of PAHs with side chains observed from shock-compression.





etc.

Pyrolysis products at high temperature?



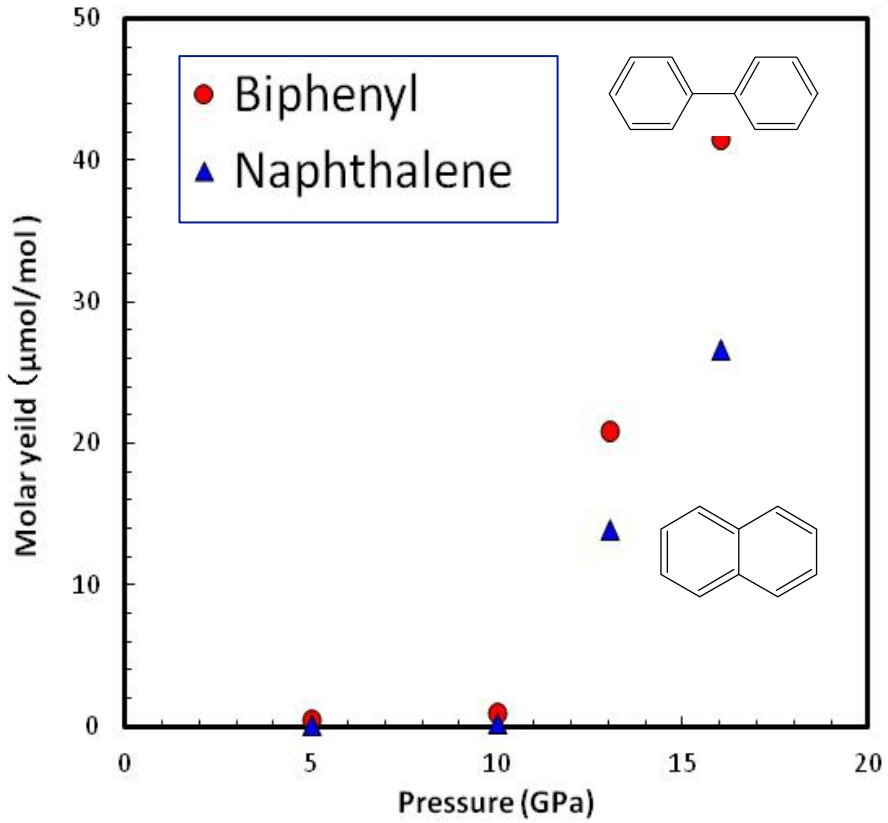
enyl

～10^{-6}

Shinozaki et al., 2014, *J Chem. Phys.*

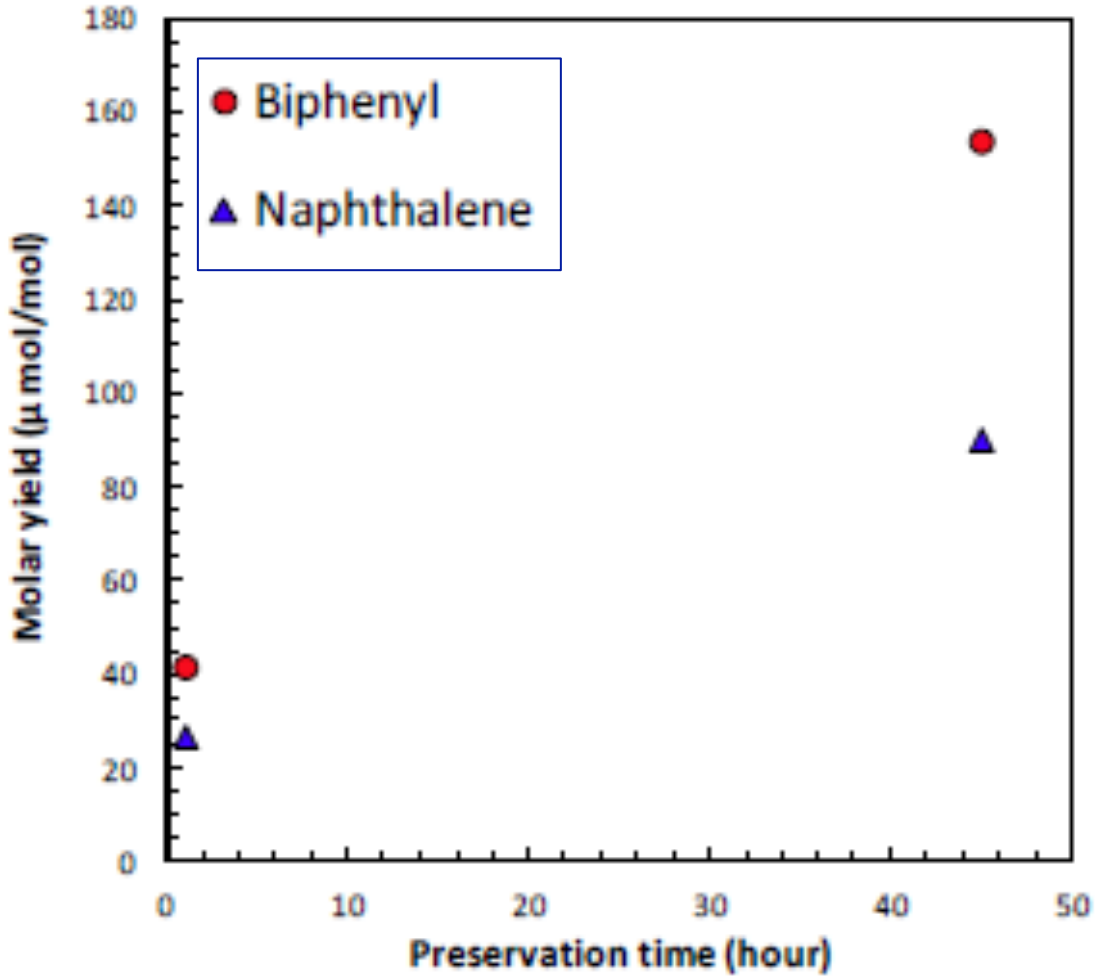
Pressure dependence of amount of the run products

Preservation time: 1hour



The yields of reaction products increase with increasing pressure.

Relation between amount of the run products and preservation time



at 16 GPa

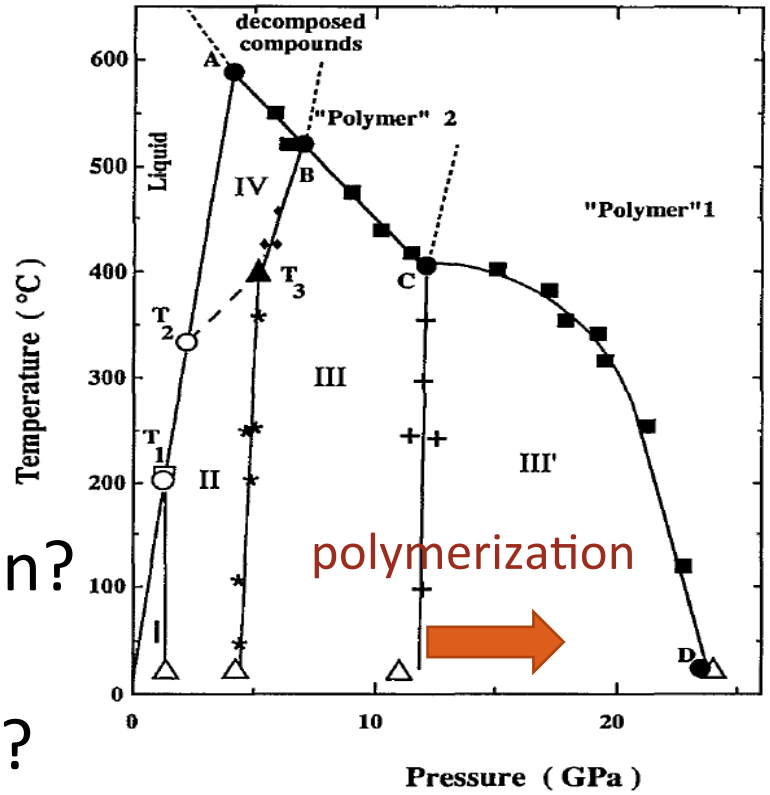
Relation between phase transition of benzene and the polymerization

- Around 11 GPa
  Phase transition of benzene
  (Phase III→Phase III')
- 10～13 GPa
  polymerization of benzene

Phase transition → polymerization?

or

Polymerization→phase transition?

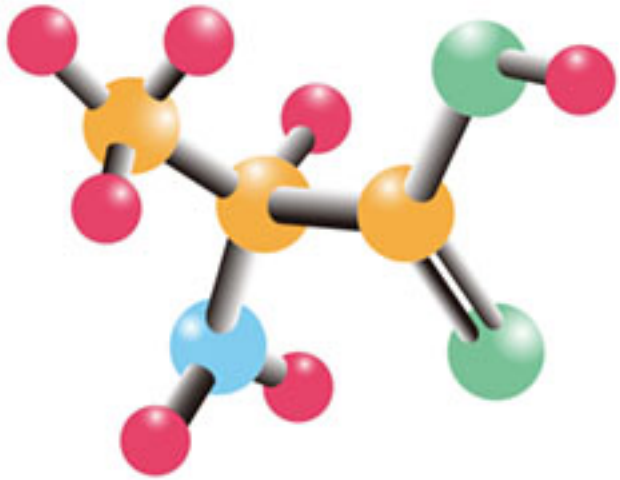


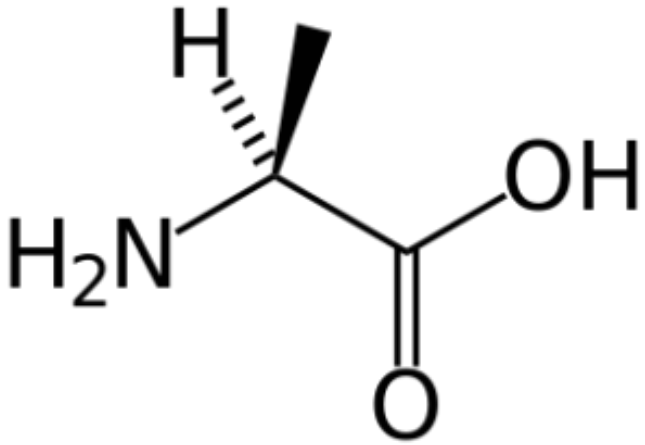
Cancell et al. 1993

Summary 1

- ✓ High-pressure experiments on benzene were conducted up to 16 GPa at room temperature using an opposed-anvil type pressure apparatus.
- ✓ The samples recovered above 13 GPa contained several isomers of benzene dimers, biphenyl, naphthalene, and isomers of terphenyl.
- ✓ Amount of the polymerized products increased with increasing pressure up to 16 GPa, while benzene still remained. The polymerization can be a precursory reaction of the amorphization.
- ✓ Run products from the static compression at room temperature were notably different from those from the shock compression experiments. Pressure-induced polymerization of benzene .

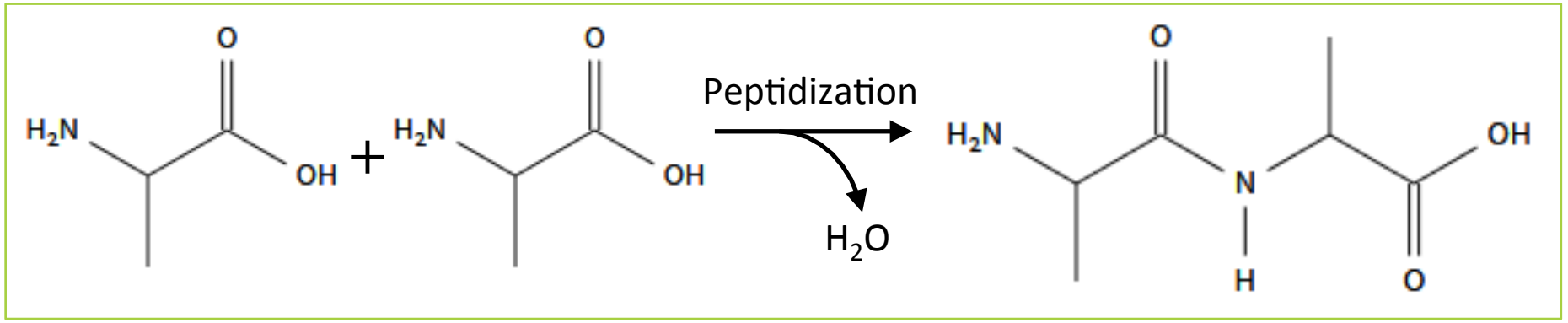
Pressure-induced oligomerization of Alanine at room temperature





Alanine (a kind of amino acid)

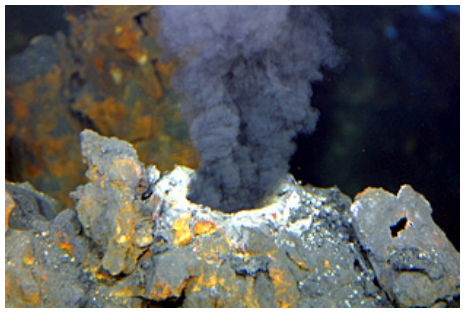
Peptization (condensation) of amino acids: A step to synthesize more complex bio-molecules



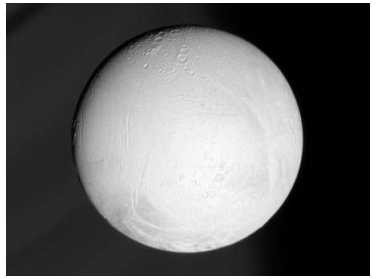
- Amino acids peptidize with dehydration.
- Peptization under prebiotic condition may give a clue to the origin of life.

Peptization under prebiotic condition

- Hydrothermal condition: Formation of glycine trimer (Imai and Honda, 2010)
- High temperature: Formation of dipeptide (Fox and Harada, 1958)
- High energy H^+, Ar^+, N^+ : Formation of dipeptide (Simakov et al., 1997; Wang et al., 2007)



Hydrothermal vent



Enceladus

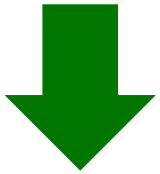
Pressure-induced peptization

- Static Pressure and high temperature (1.0－5.5 GPa, 180－400 ℃): Formation of glycine and alanine pentamer (Otake et al., 2011)
- Shock compression (1.8－26.3 GPa, 200－1170 ℃): Formation of glycine trimer (Sugahara and Mimura, 2014)

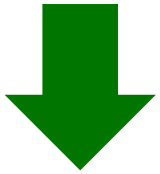
Comet Hale-Bopp

Previous studies on peptidization were conducted at high temperatures, high-energy irradiation, anhydrous conditions

(because the reaction is a dehydration reaction).



Verifying peptide formation
at high pressure and mild temperature

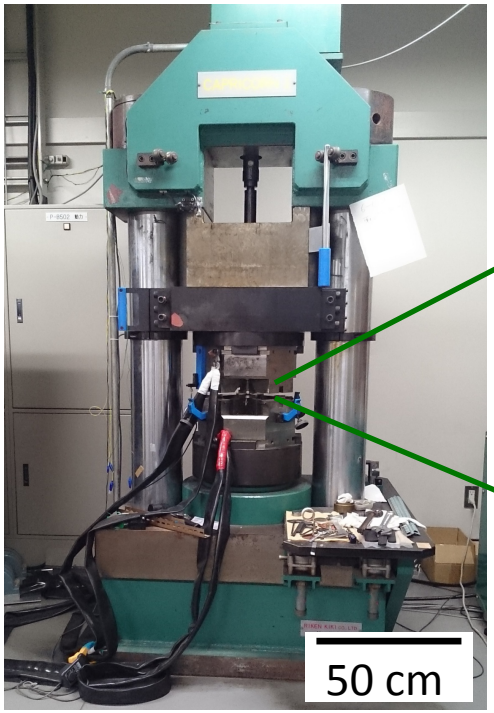


A new possibility for chemical evolution of amino acids and peptides could be proposed.

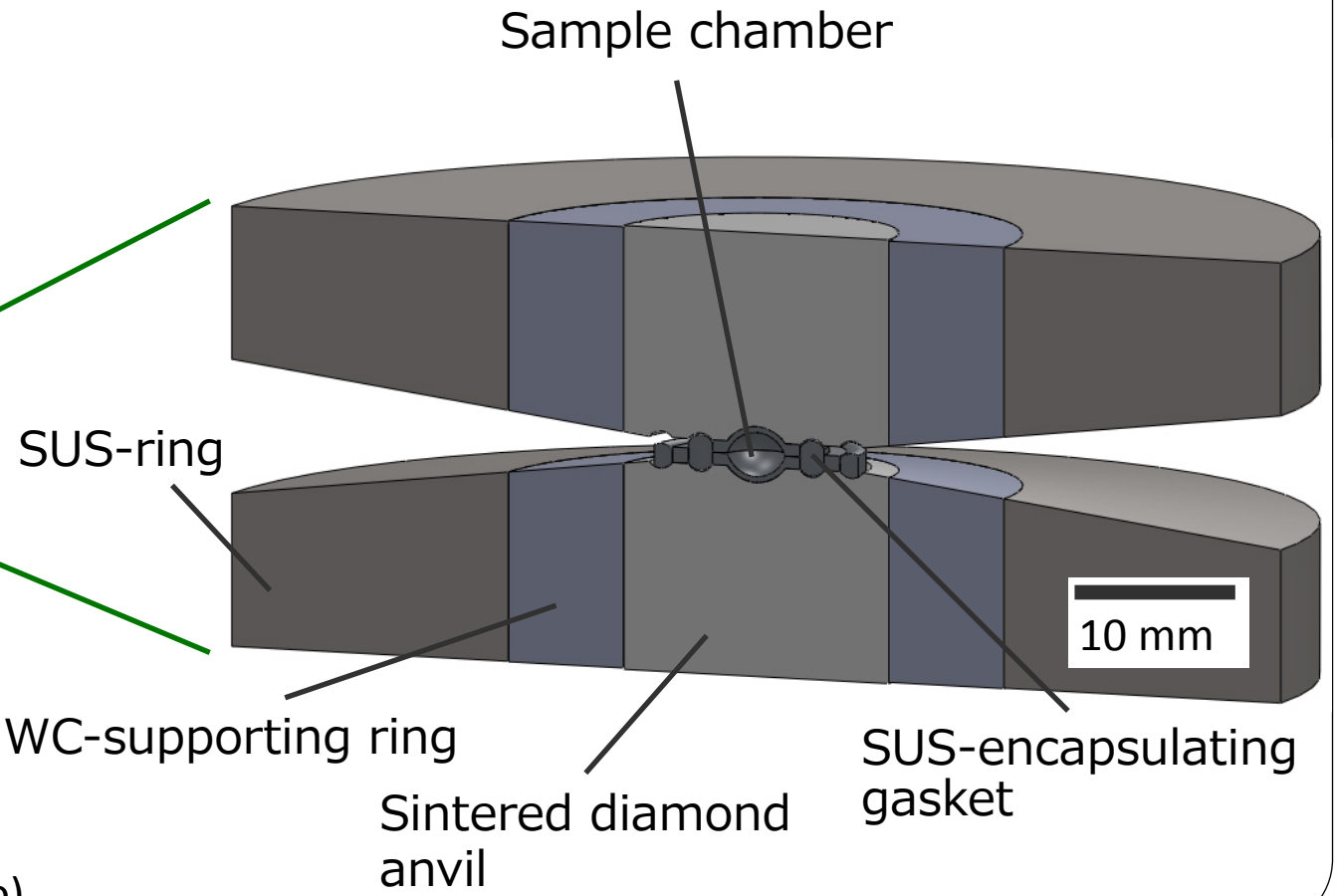
High-Pressure experiments

Starting material: L-Alanine powder (～10 mg)
+Alanine-saturated solution

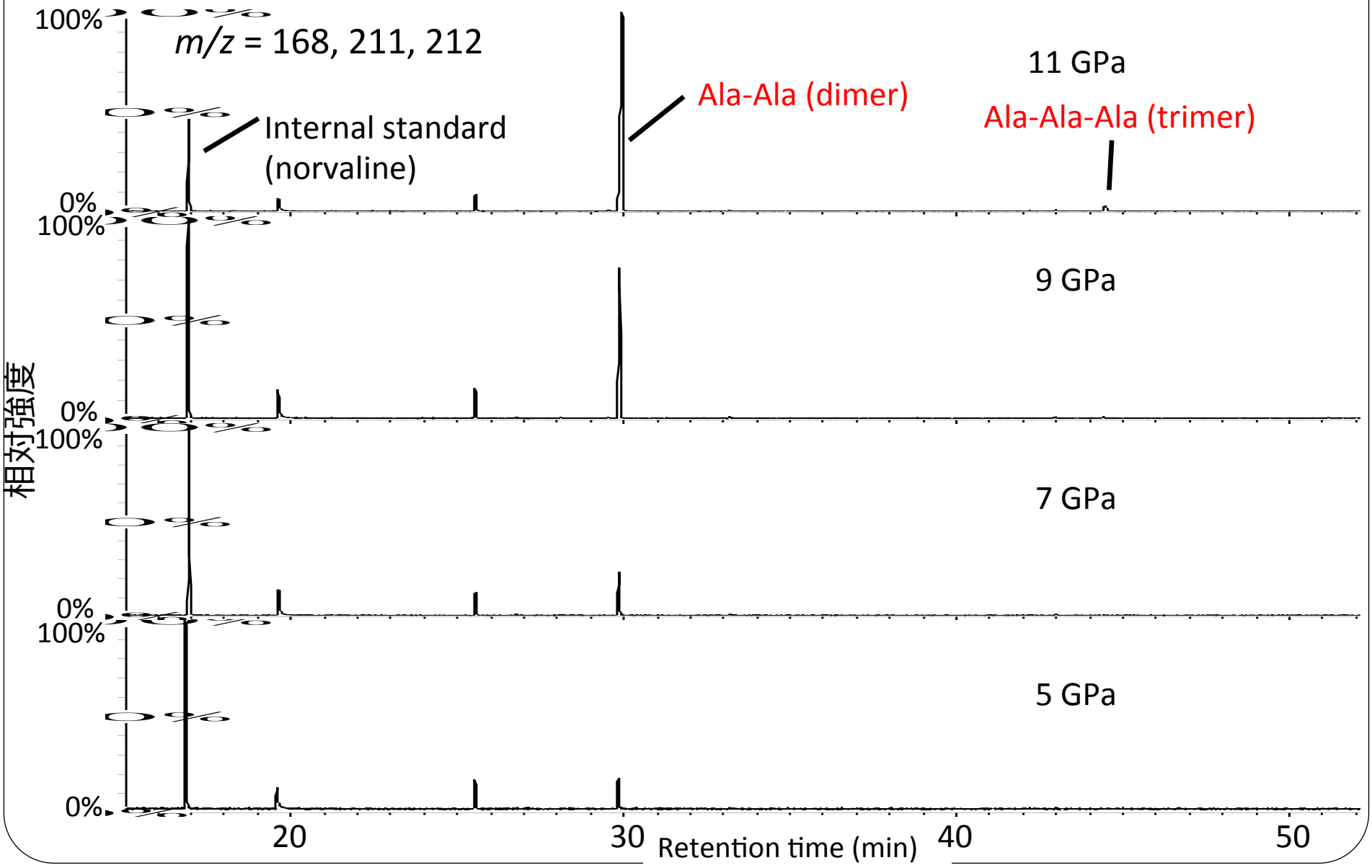
Temperature: 25 ℃
Pressures: 5, 7, 9, 11 GPa
Duration: 1 hour



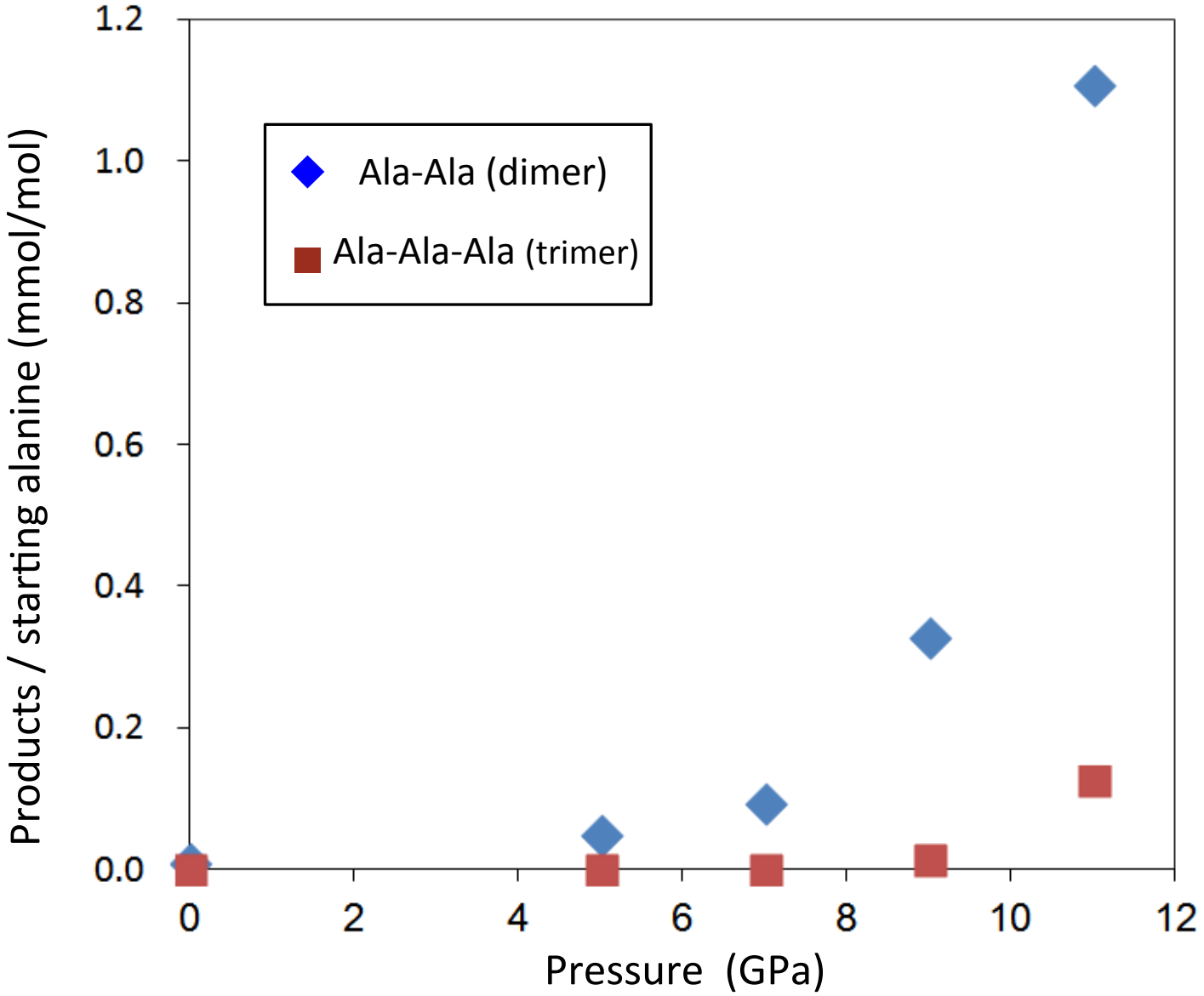
500 ton press
CAPRICORN I (ISSP, U Tokyo)



Chromatograms of the recovered samples

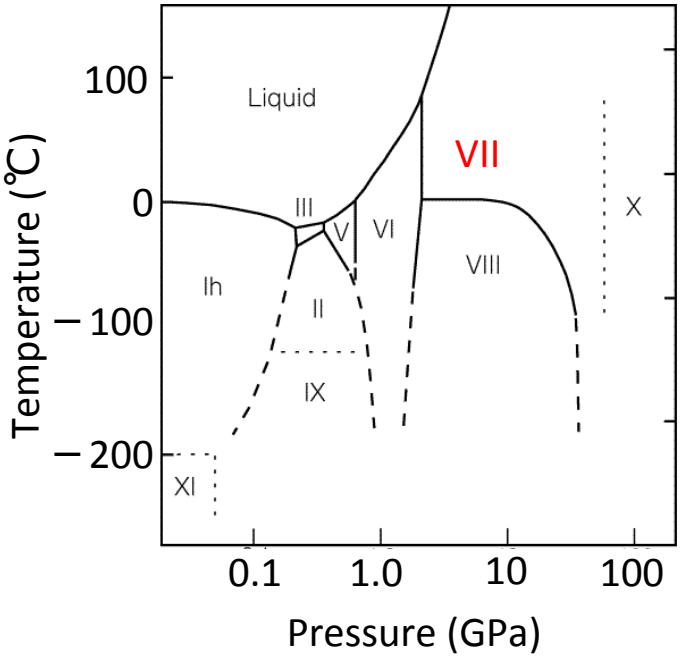


Ala-Ala (dimer), Ala-Ala-Ala (trimer) vs. P



Oligomerization of alanine under the conditions of Coexistence of water, Room temperature, High pressure

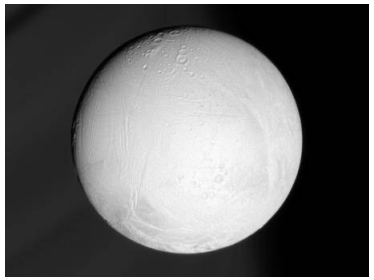
- Starting material = Alanine powder + its saturated aqueous solution (with H_2O)
- Under the *P-T* conditions (5-11 GPa, 25 °C), water exists as ice VII (high-pressure phase of ice).
- Possible existence of Ice VII inside of icy planets (Kubo et al., 2009)



Phase diagram of ice
(Lobban et al., 1998)

Our study propose

Possibility of chemical evolution of acid acids inside of icy planets



Enceladus
(from NASA's web site)

Summary 2

- High-pressure experiments (up to 11 GPa) at room temperature demonstrated the formation of the dimer (Ala-Ala) and trimer (Ala-Ala-Ala) from Alanine powder with its saturated solution.
- The present results suggest a possibility of oligomerization of amino acids in the interior of icy planets.
- The oligomerization mechanism? The pressure-induced oligomerization occurs at anhydrous condition? (Our preliminary results show that the reaction yields in a dry condition are much lower.)
- In future, in-situ observations are required at high pressure, because some of the products might be meta-stable and could not be detected from recovered samples.