Comet Impacts as a Driving Force of Glycine Oligomerization

Koichi Mimura and Haruna Sugahara
Graduate School of Environmental Studies, Nagoya University

Image Credit: NASA/JPL-Caltec

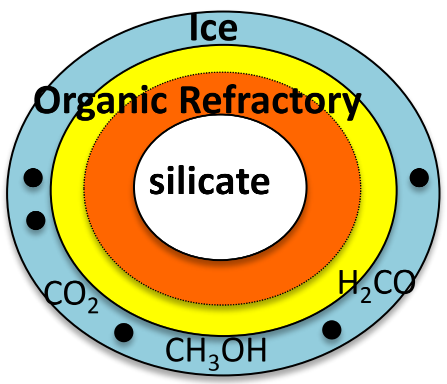
1-1. Introduction - Comets

- formed by the coalescence of dusts in interstellar medium (ISM)

  → one of the most primitive bodies in the solar system

- consist of water ice, silicates, and organic materials

  (water ice : silicates : organic materials = 1 : 1 : 1,wt)



a model of dust in comet
(Greenberg and Mendoza-Gomez, 1992)

C_2H_2, C_2H_6, CH_3OH, H_2CO, HCOOH, $HCOOCH_3$, NH_3, HCN, HNCO, HNC, CH_3CN, HC_3N, NH_2CHO, H_2S, OCS, SO, CS_2, SO_2, H_2CS

Crovisier *et al*. (2004)

Concentration of organic materials is over 10 times higher than that in carbonaceous chondrites.

Did comets deliver organic materials to the early Earth?

1-2. Introduction - Amino acids in extraterrestrial materials

focus on amino acids (A.A.)

1. Essential materials for origins of life
2. Biologically interesting materials (e.g., homochirality: Life uses only L-A.A.)

the Murchison meteorite

Over 70 species of A.A.
Protein A.A.
Slightly L–excess (8.4 % for isovaline)

(Cronin *et al.*,1995; Pizzarello and Cronin, 2000)

Micrometeorites (IDPs)

Aminoisobutyric acid

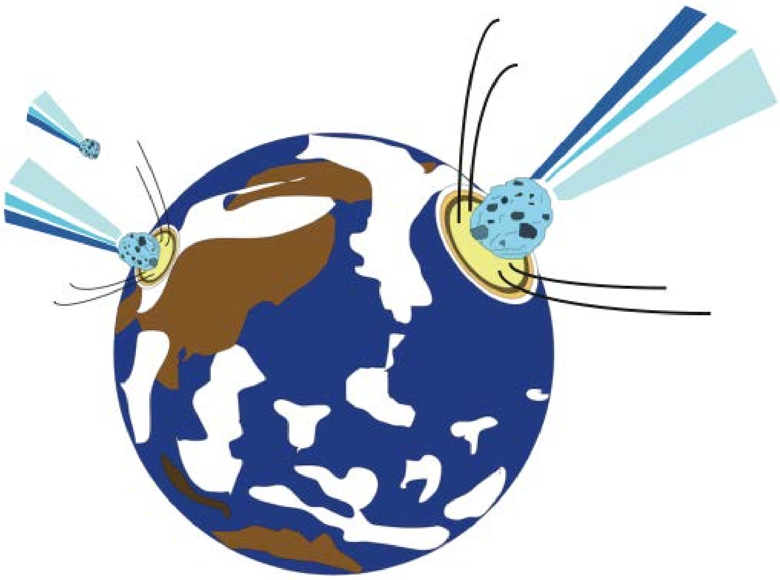
(Glavin *et al.*, 2004)

Comet (comet 81P/Wild 2)

Glycine (Elsila *et al.*, 2009)

Considering these reports, comets probably contain a lot of A.A.

2. Study's Purpose



Comets impact the Earth.

↓

A.A. in the comets experience high pressure and high temperature conditions.

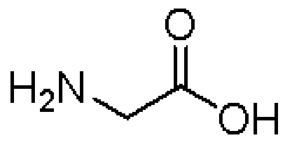
↓ What happens to the A.A.?

Decomposition or oligomerization?

Shock experiments simulating comet impacts to reveal the behavior of A.A. at the impacts.

3-1. Methods - Starting material

A frozen mixture of



Glycine (**GLY**)

+ Forsterite powder (Synthetic forsterite Mg_2SiO_4: 1μm) **+** H_2O

〈Glycine〉

most simple A.A.

found in cometary dusts

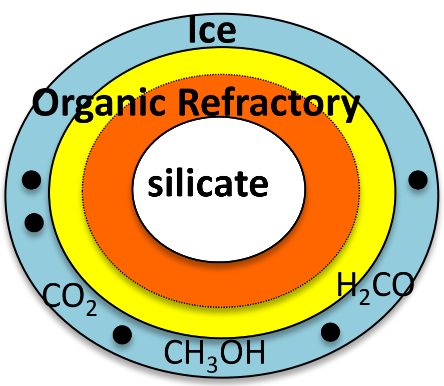
〈Mixing ratio〉

Glycine/Forsterite powder/Water

1/10/8 (wt./wt./wt.)

Based on

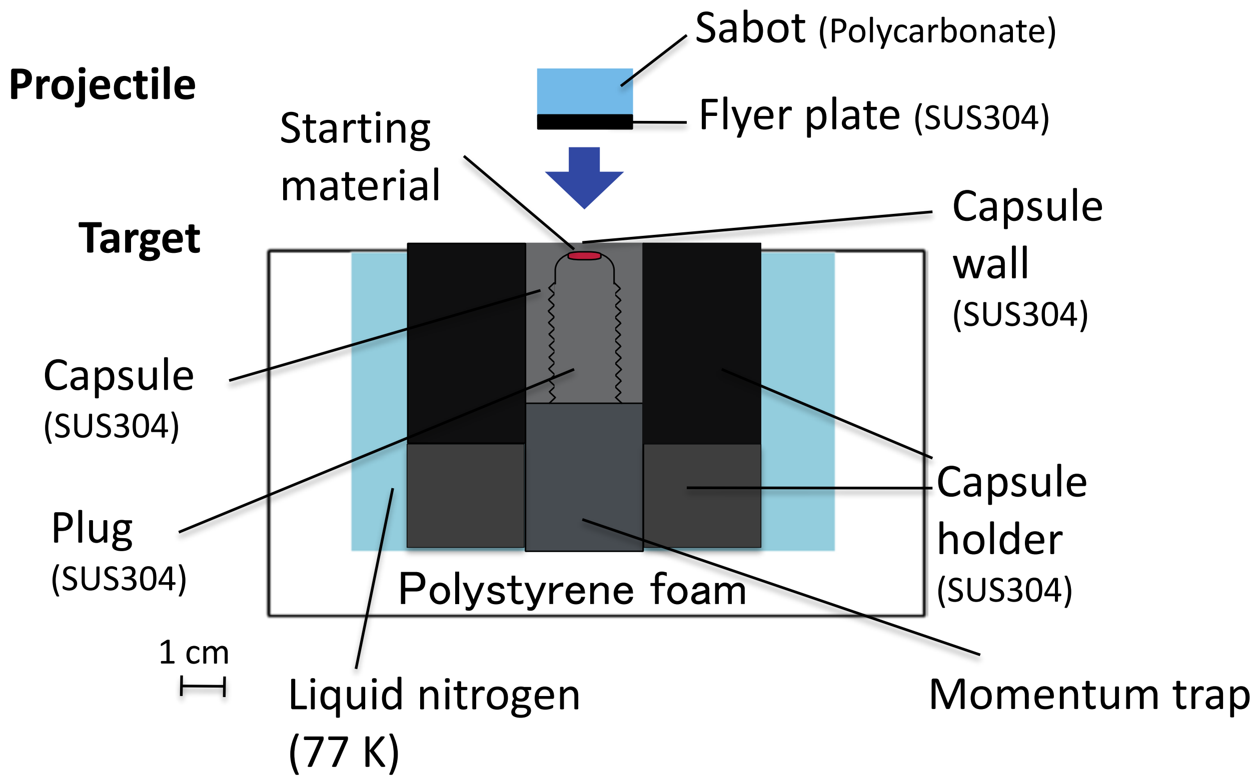
1. the composition of cometary dusts
   Organic materials / Silicates / Water＝1/1/1
2. an assumption that A.A. are about 10% of the organic fraction



(Greenberg and Mendoza-Gomez, 1992)

3-2. Methods - Shock experiments at cryogenic condition (77 K)

A vertical propellant gun



the projectile velocity that was measured just before reaching to the capsule.

➡ Calculation of shock pressure and shock temperature

3-3. Methods – Run conditions of the shock experiments

Several parameters were calculated based on the property of the materials used and the projectile velocity.

Run Name	Projectile velocity (m/s)	Shock pressure (GPa)	Shock temperature (K)	Shock pulse duration (μs)
GLY-1	284	4.8	460	0.81
GLY-2	521	9.2	550	0.78
GLY-3	806	14.6	650	0.73
GLY-9	1020	17.2	720	0.70
GLY-10	1170	20.6	780	0.68
GLY-7	1430	26.3	900	0.65

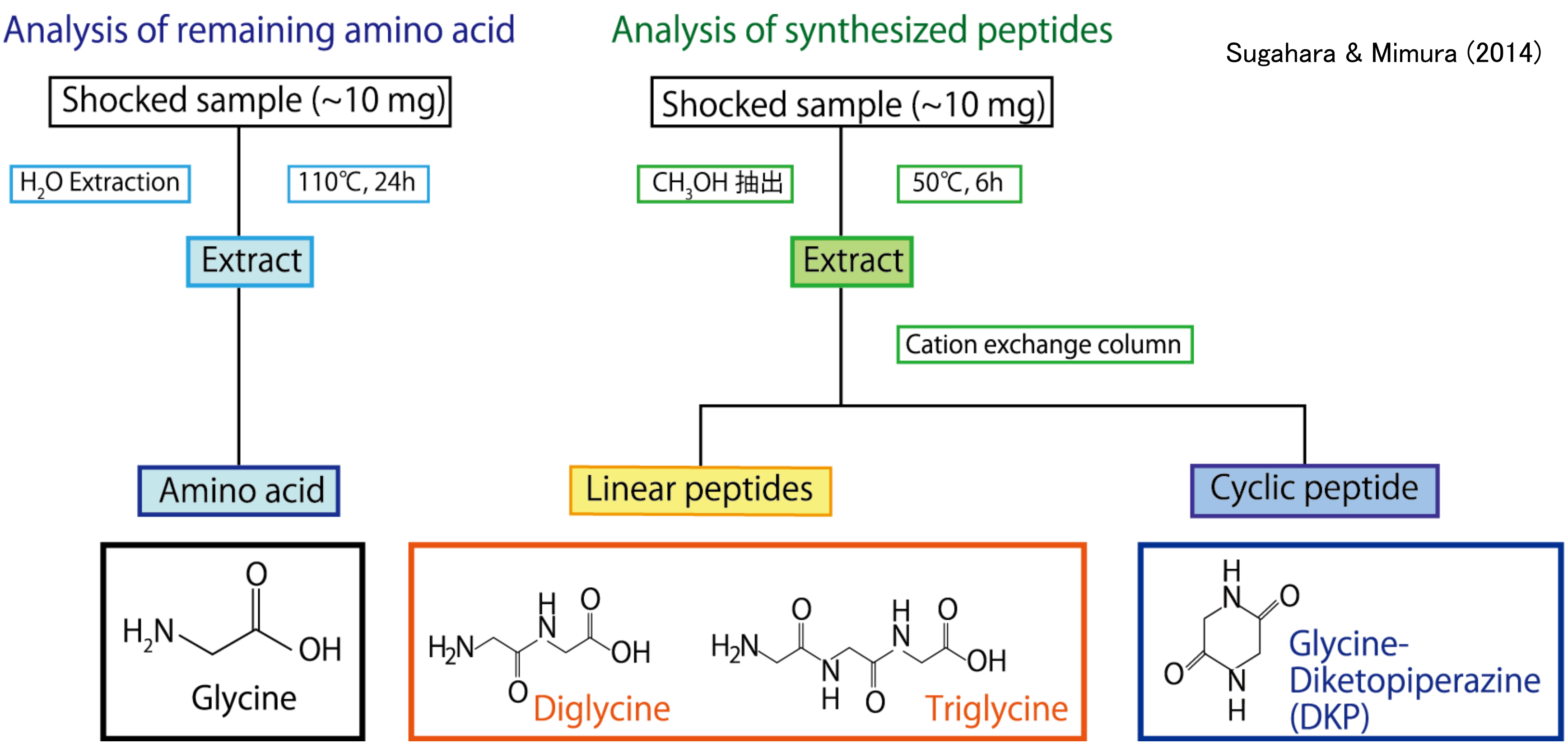
Shock pressure : 4.8 – 26.3 GPa

Shock temperature : 460 – 900 K

Shock pulse duration : 0.65 – 0.81 μs

the period of time during which the shock wave propagates the sample.

3-4. Methods – Chemical analyses



Derivatization: A.A. → 1.25 M HCl-isopropanol (110℃, 1h) & TFAA

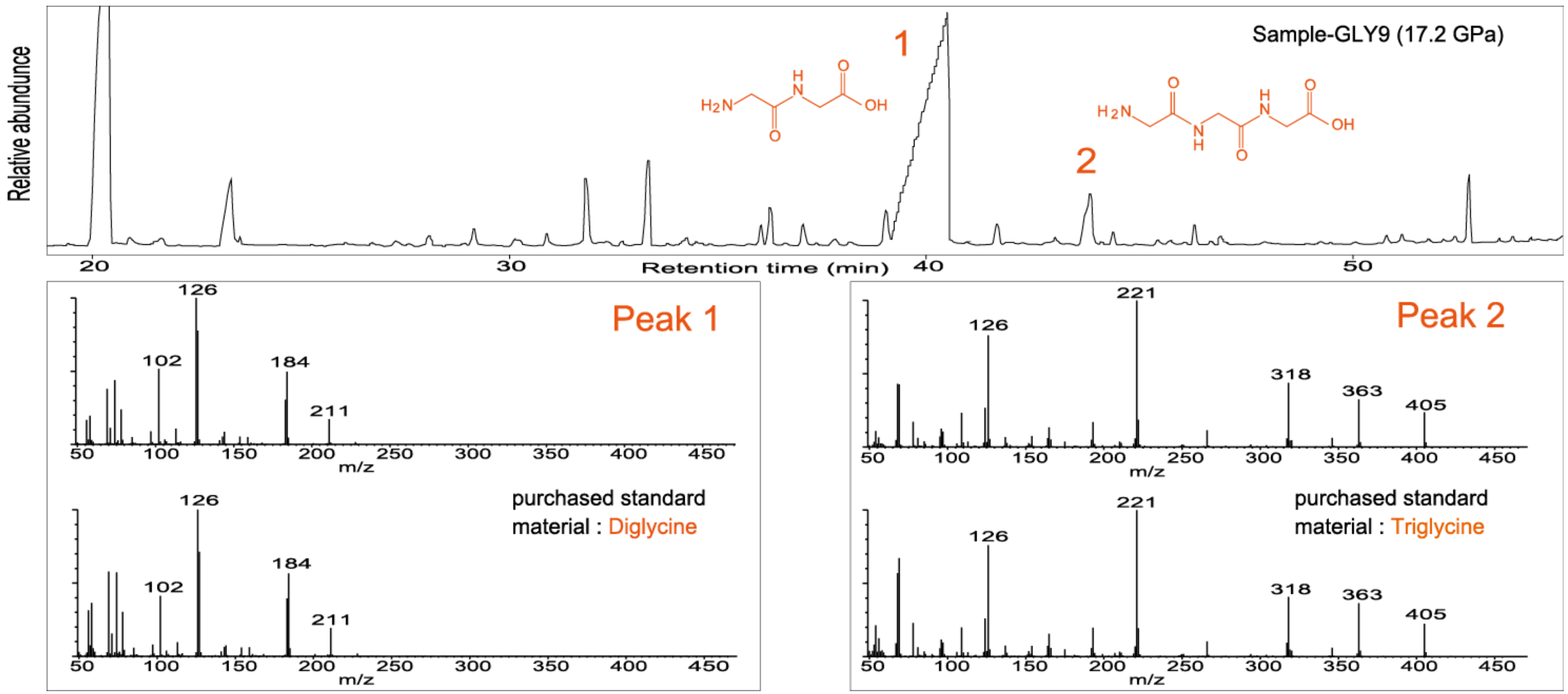
Peptides → 1.25 M HCl-isopropanol (40℃, 12h) & TFAA

DKP → MTBSTFA

Determination : GC-FID & GC-MS (Internal Standard: Norvaline)

4-1. Results- Identification of linear peptides (by GC/MS)

Linear peptide fraction

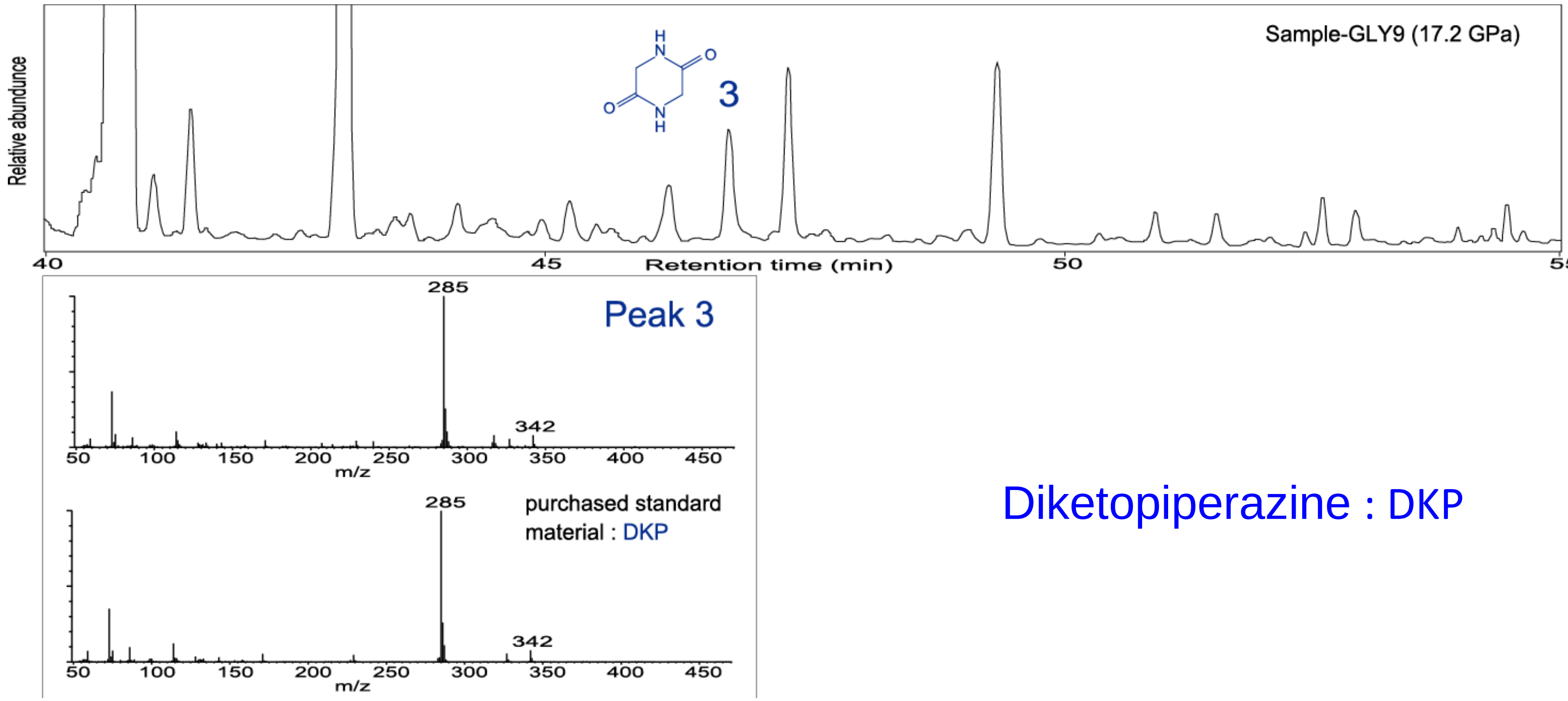


1. Diglycine and triglycine were identified by comparison of their retention times and mass fragmental patterns of purchased standard materials.
2. These peptides were not detected in samples below 9 GPa.
   → the detected peptides were not contaminants

Diglycine and triglycine were formed by impact shock.

4-2. Results - Identification of <u>cyclic peptide</u> (by GC/MS)

Cyclic peptide fraction

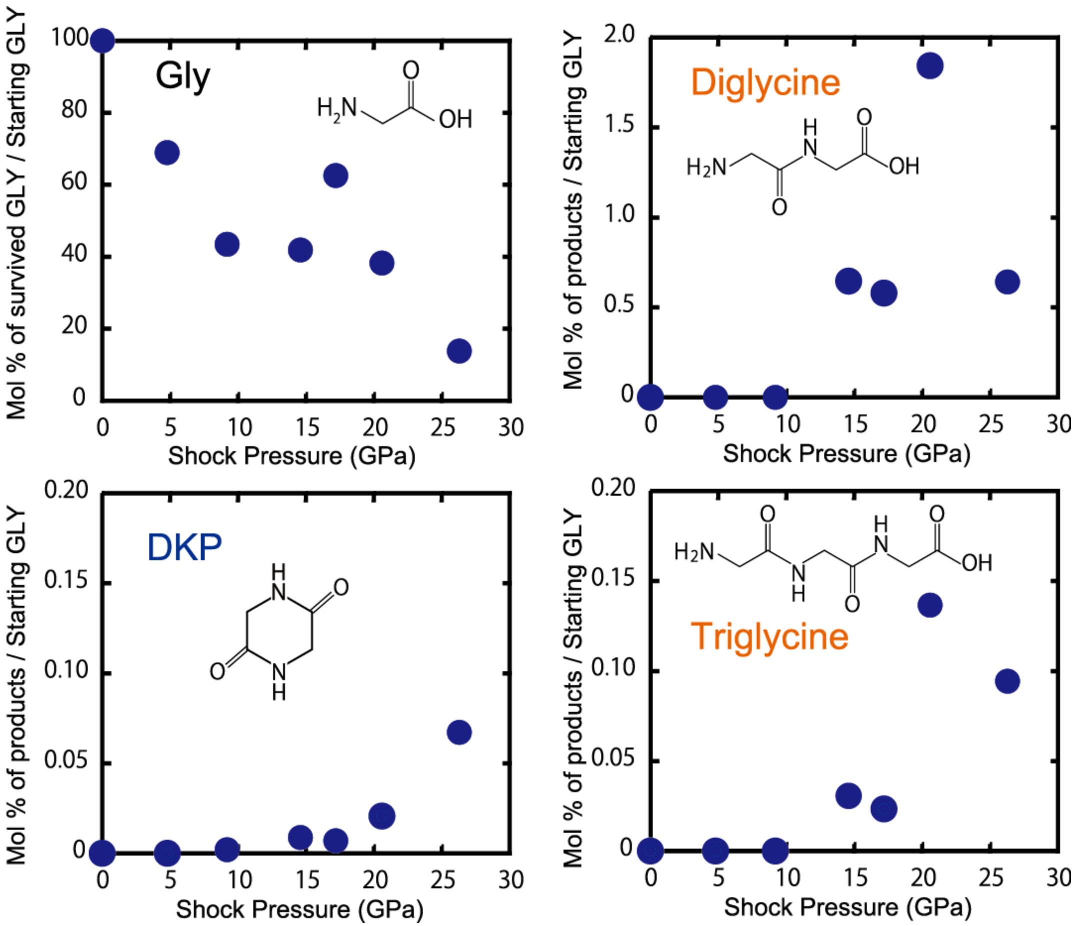


Diketopiperazine : DKP

1. In the same way of linear peptides, DKP was identified.
2. DKP was not detected in samples below 9 GPa.
   → the detected DKP is not a contaminant

DKP was formed by impact shock.

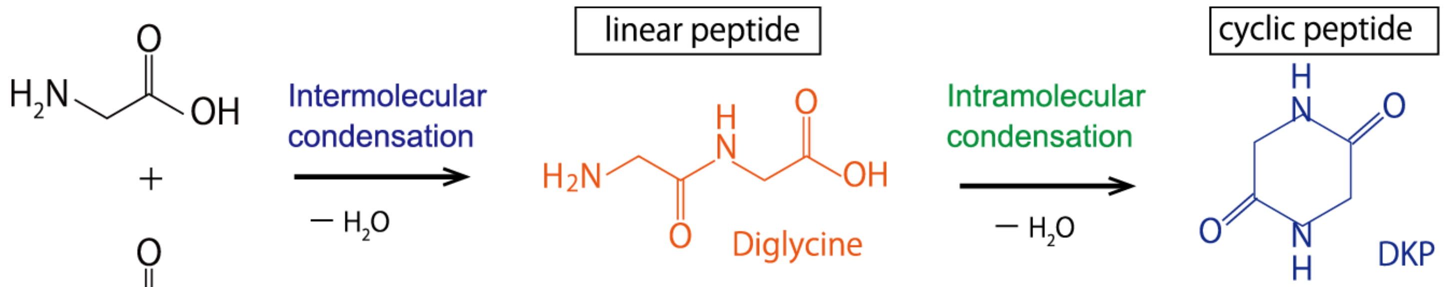
4-3. Results - Survivability of glycine and yields of peptides

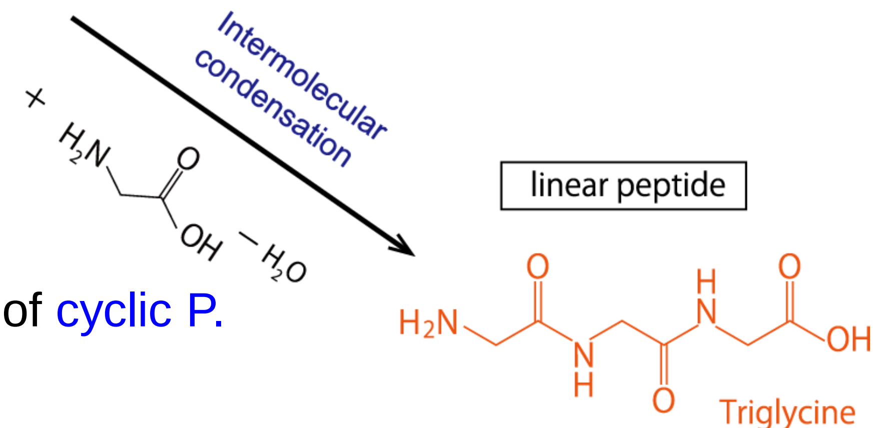


1. Survival ratio decreases to 15 mol% at 26 GPa.
2. Yields of diglycine and triglycine increase to 1.8 and 0.15 mol% at 21 GPa, and then decrease to 0.65 and 0.1 mol% at 26 GPa.
3. Yield of DKP increases to 0.07 mol% at 26 GPa.

Linear peptides were formed more easily than cyclic peptide under the pressure range of this study.

5-1. Discussion – A process of peptide formation from glycine





At heating (Harada and Fox, 1958)

Formation of linear P. < Formation of cyclic P.

At impact shock (our study)

Formation of linear P. > Formation of cyclic P.

Linear peptides can combine to form more complex organic compounds.

Shock reactions lead to the preferential synthesis of linear peptides compared with heating .

The difference of products may be due to the extremely short heating time and the high pressure of impact shock.

5-3. Discussion—Comparison with Blank et al. (2001)

Blank et al. (2001)

shock experiment on aqueous A.A. at room temp.

Yield (dipeptide) / Yield (cyclic) = 1

not detect tripeptide

Our study

shock experiment on frozen A.A. at 77K

Yield (dipeptide) / Yield (cyclic) > 10

detected tripeptide

	amino acid concentration (g / mL)	shock pressure (GPa)	shock temperature (K)	phase of water	composition of stating material
Our study	0.088	14.6 – 26.3	650 - 900	solid	water + amino acid + forsterite
Blank et al. (2001)	0.057 – 0.12	16.5 -21.0	740 - 870	liquid	water + amino acid

Phase of water

influences the chemical reaction caused by accelerated particles at shock front.

(shock front : a transitional region of the shocked material after the wave propagates)

(Velikodnyi and Kurochkin, 2002)

Existence of forsterite

affects the formation of peptides or not?

5-4. Discussion – Supply of synthesized peptides to the early Earth

Average impact velocity of the short-period comets : 24 km/s
⟶ over 200 GPa when impacting the Earth's ocean vertically

Such pressures are beyond the application of our results.

We need scenarios that can reduce the shock pressure of comet impacts.

1. Aerodynamic drag and airburst in the thick early Earth's atmosphere
(Bland and Artemieva, 2006)

2. Oblique impacts
the relation between impact angle(θ) and shock pressure (P) : $P_{\theta} = P_{vertical} \times \sin\theta$
(Pierazzo and Melosh, 2000)

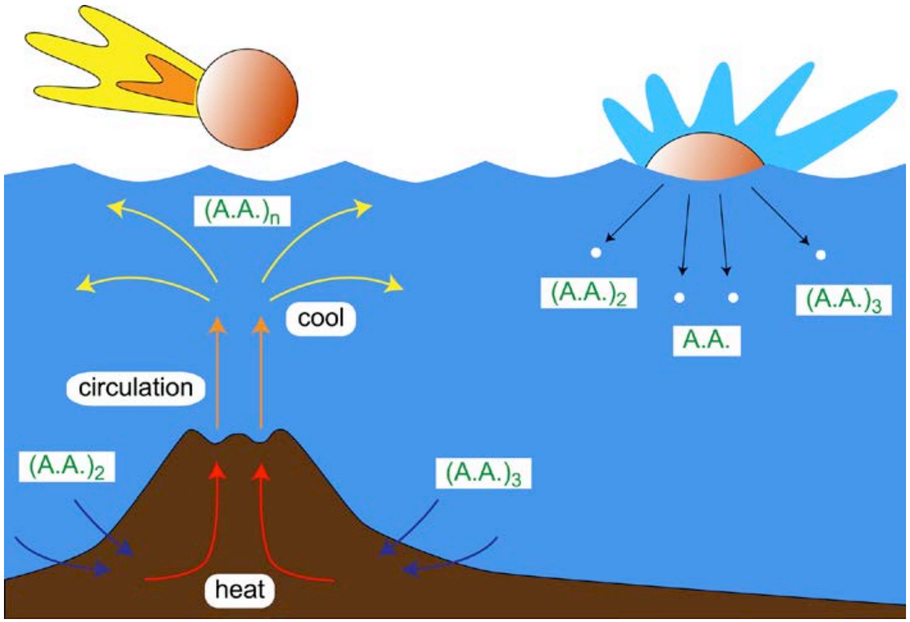
3. Heterogeneity of shock pressure in an impacting body
There are very lower-pressure areas inside the body than the pressure at the point of impact. (Pierazzo and Melosh, 2000)

Taking account of these scenarios, a significant amount of shock synthesized peptides can be supplied to the early Earth.

5-5. Discussion - Elongation of peptides on the early Earth

Peptides synthesized by impacts would have spread over the early Earth.

important seeds for further chemical evolution



One suitable place for the evolution

→ Submarine hydrothermal vents

The peptides can be elongated by heating and the circulation of water from hot to cold regions.

The elongation by the addition of peptides occurs more easily than the peptide formation from single A.A. molecules.

→

the formation of an initial peptide

||

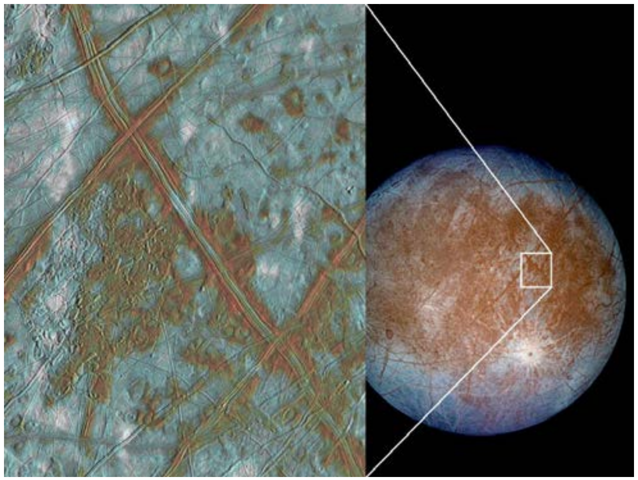
a type of nucleation process

Comet impacts might have been an important process in the first step of peptide synthesis on the early Earth.

5-6. Discussion - Shock synthesized peptides in icy satellites

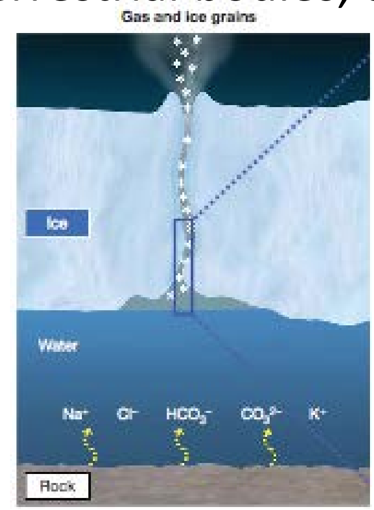
Comet impacts are ubiquitous phenomena in the solar system.

→ Peptide syntheses must have occurred on the extraterrestrial bodies, too.



Europa (Icy satellite of Jupiter)

Enceladus (Icy satellite of Saturn)



Postberg *et al.* (2009)

<u>Icy satellites</u>

formed by the accumulation of comet-like bodies.
contain considerable amounts of peptides synthesized by comet impacts.
have subsurface oceans with potential energy sources. (Sohl *et al.*, 2010; Hussmann *et al.*, 2010)

In the subsurface oceans,
the peptides become more complex materials with the energy.

> Icy satellite environments are suitable for the subsequent chemical evolution of the peptides.

6. Summary

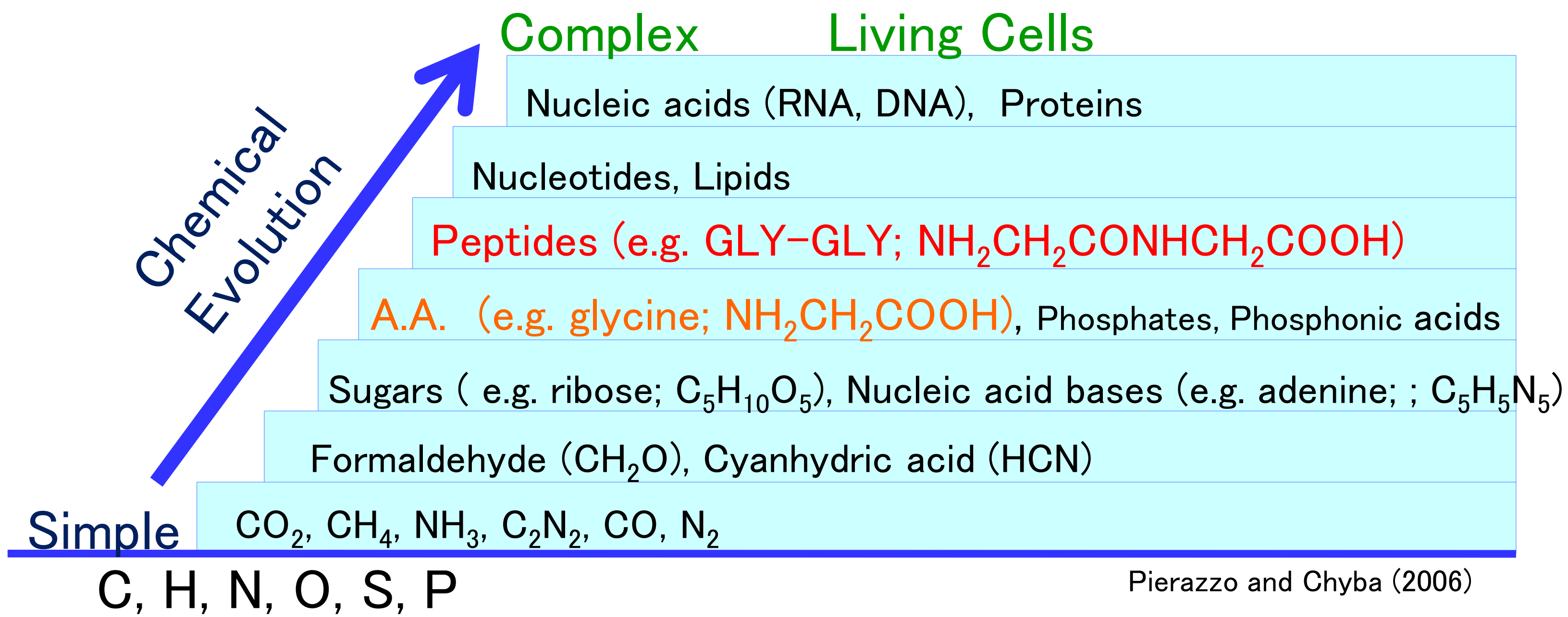
<Experiments>

Shock experiments on a mixture of glycine, forsterite, and water ice at cryogenic conditions to simulate comet impacts.

<Results>

Impact shock synthesized peptides up to triglycine and favored the formation of linear peptides.

Comet impacts can account for the oligomerization of A.A. and played an important role in chemical evolution on the Earth and the icy satellites.



Pierazzo and Chyba (2006)