Theoretical Investigation of a Mechanism of Chirality Induction for Amino Acids in the Early Solar System

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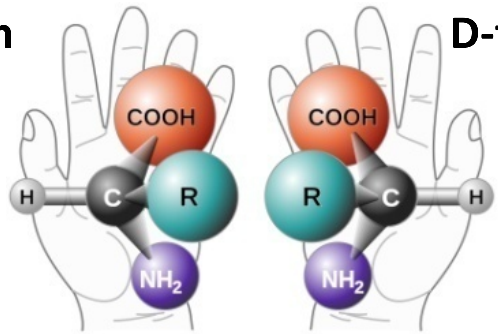
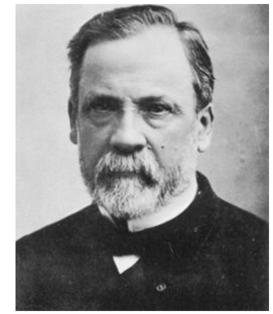
Introduction: What is L-form amino acid excess?

Enantiomer

Amino acid has two different conformations called enantiomer.

L-form **D-form**

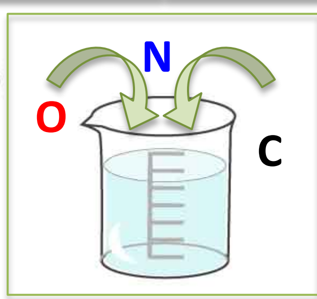


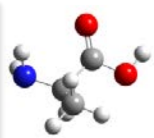


Louis Pasteur（1822-1895）

Proportions created in Laboratory

L-form	D-form
50%	50%





In vitro

Proportions generated in living organisms

L-form	D-form
over 99%	

In vivo

e.g. D-glutamic acid is tasteless.

The origin of chirality for amino acids has not been revealed yet and remains as one of the big mysteries in the study of the origin of life.

Discovery of Amino acids and Enantiomeric Excess in Meteorites

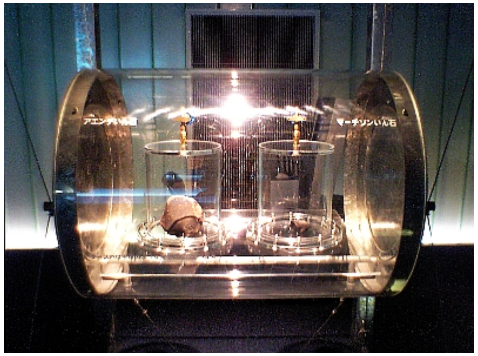
<u>Murchison meteorite</u>

Australia in 1969

Engel & Macko, Nature 1997, 389, 265

Pizzarello & Cronin , 2000, Geochimica et Cosmochimica Acta, 64, 329

Amino acids like glycine, alanine, valine, and isovaline, which forms proteins, are detected in the Murchison meteorite. Also, the excess of L –form amino acids (enantiomeric excess) was found. The isotope ratio is different from that on the earth.

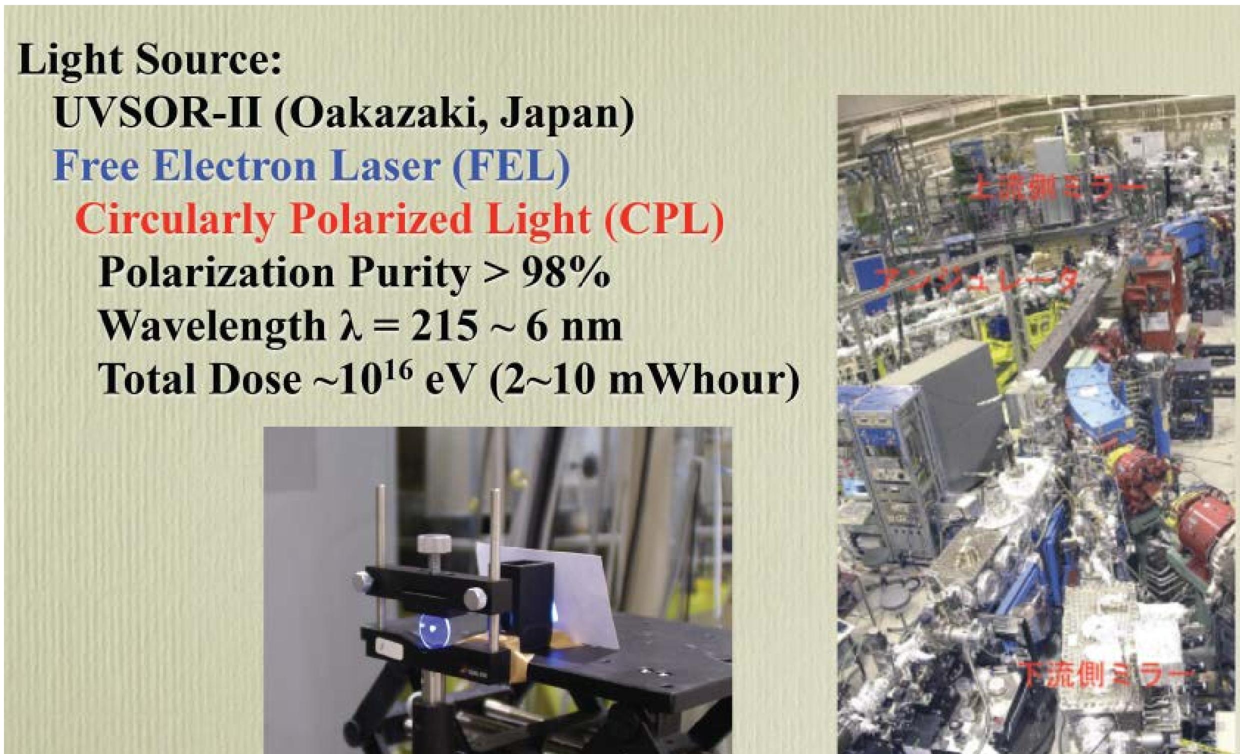


Experiments

Asymmetric photoreaction of Amino Acids

Meierhenrich et al. 2010, Angrew. Chem. Int. Ed, 49, 7799

The irradiation of circularly-polarized light causes the enantiomeric excess of amino acids.



Irradiation of circular-polarized light on amino acids (J. Takahashi et al.)

Discovery of Circularly-Polarized Light In Star-forming Regions

Bailey et al., 1998, Science, 281, 672

3.9-m Anglo-Australian Telescope

Intensive circularly-polarized infrared light was detected in Orion-molecular cloud -1.

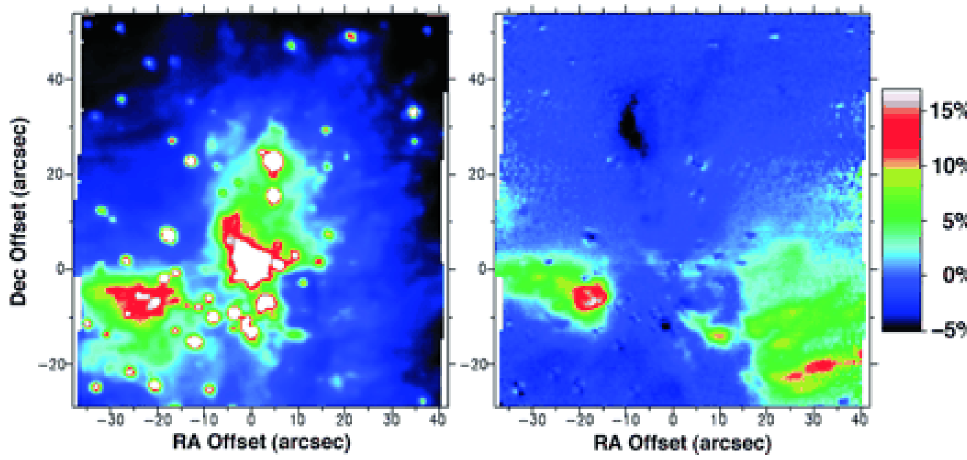
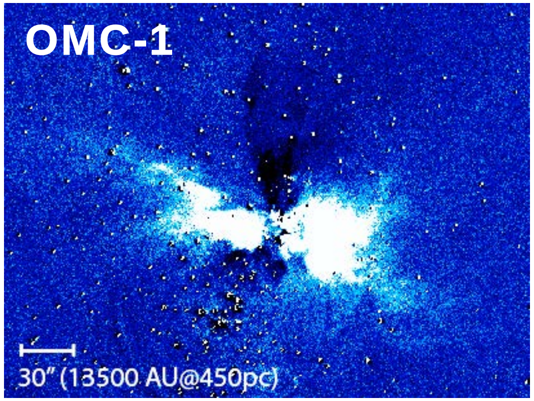
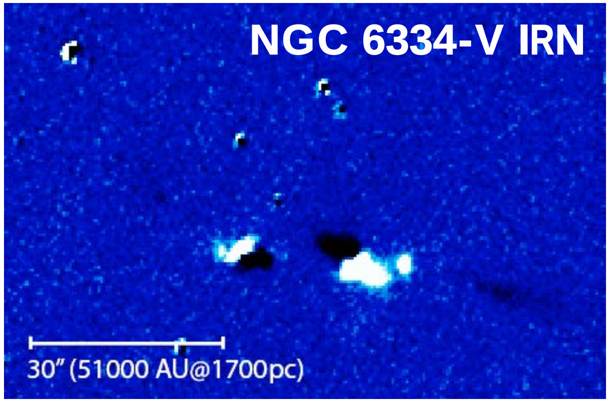


Fig. 1. Circular polarization image of the OMC-1 star-formation region in Orion at 2.2 μm (K_n band). (Right) Percentage circular polarization ranging from −5% (black) to +17% (white). Polarization accuracy ranges from about 0.1% in the brighter regions to 1% in the fainter regions. By convention, positive polarization means that the electric vector is seen to rotate counterclockwise in a fixed plane by an observer looking at the source. (Left) The total IR intensity. The bright source at coordinates (0, 0) is the Becklin-Neugebauer object. The size of a typical protostellar disk (~100 astronomical units) is less than 1 arc sec at the 450 pc distance of OMC-1 and therefore much smaller than the observed polarization structure.

Tamura et al. 2014

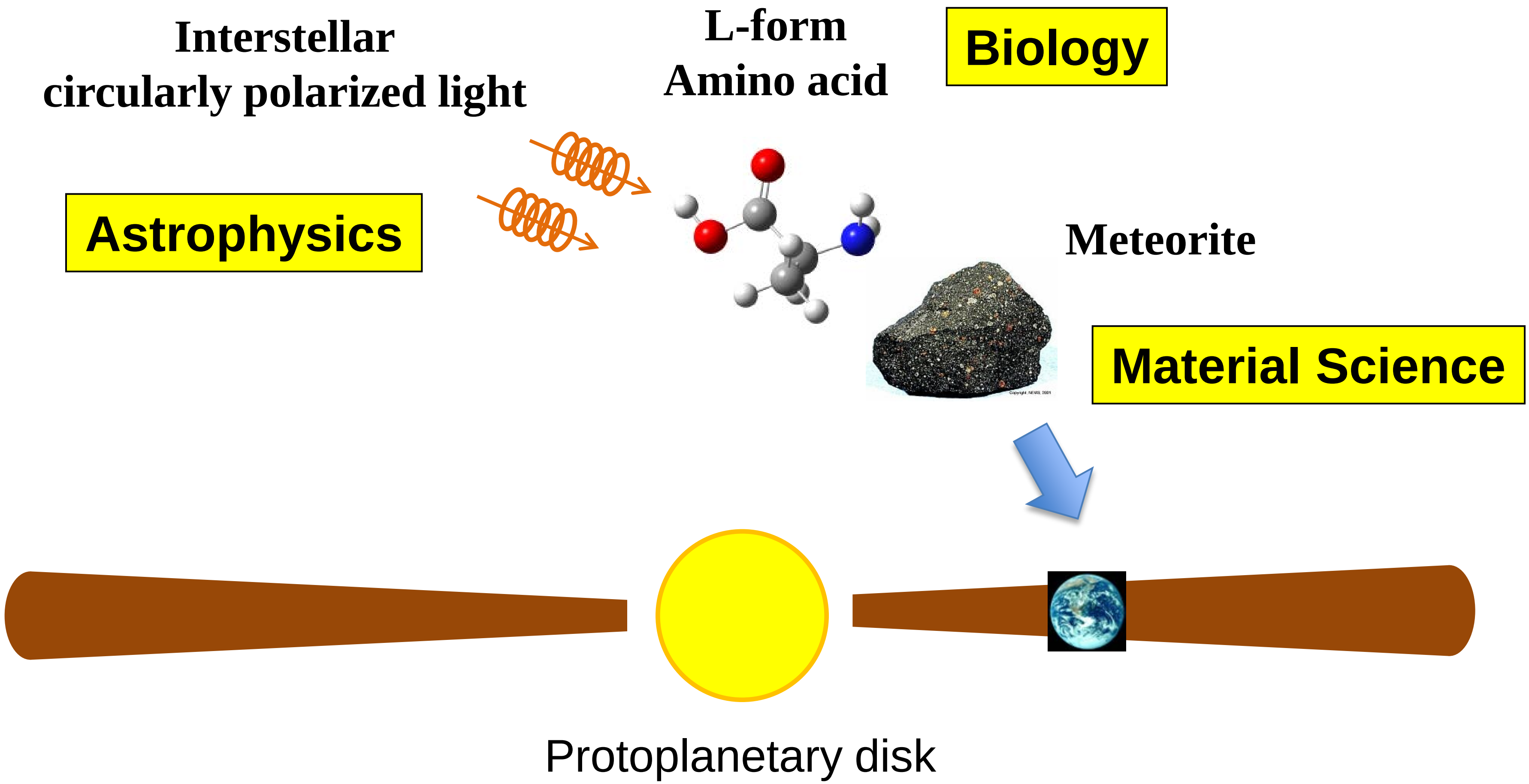
Higher and more **extensive** circular polarizations with **quadrupolar** patterns in other star forming regions





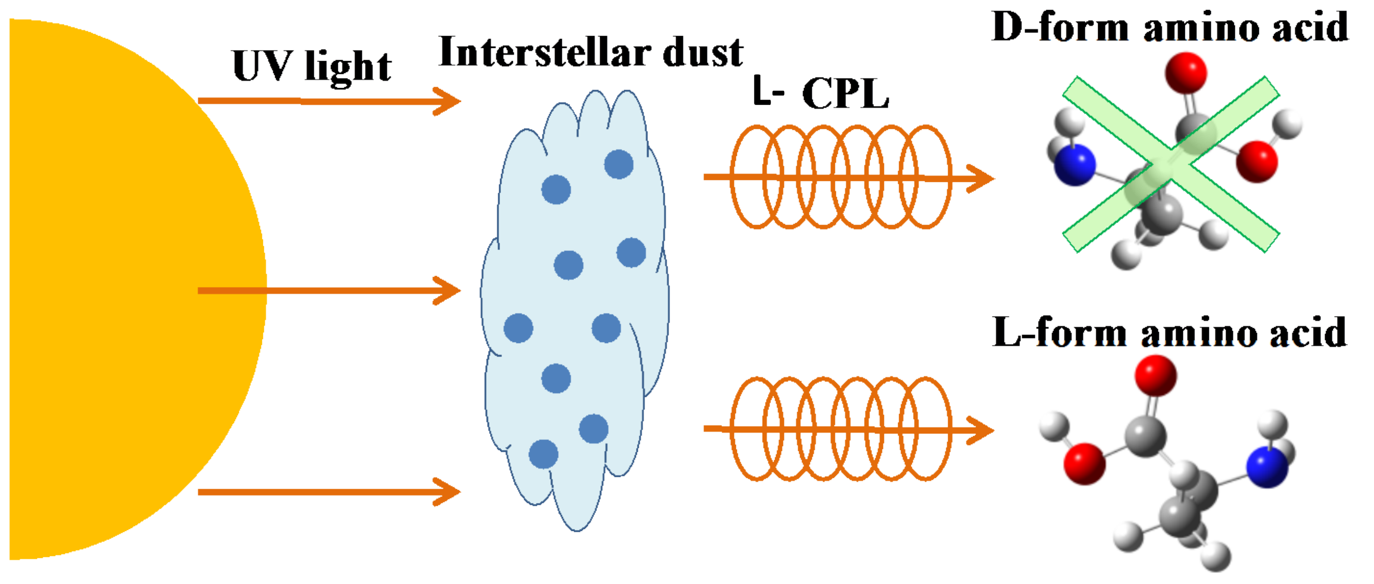
Cross-cutting research

Approach by three different fields



Purpose

- To reveal properties and wavelength of light which would induce the asymmetric decomposition for amino acids.



By experiment, it's hard to clarify the process of molecular decomposition.

Computational Method is effective!!

Potential energy surfaces (PESs) are obtained by ab-initio calculation which is the method to solve Schrödinger equation without any assumption or approximation.

Computational Method

Time-dependent Kohn-Sham equation is solved

$$\left[-\frac{1}{2}\Delta + v_{eff}(r,t)\right]\phi_i(r,t) \quad = \quad i\frac{\partial \phi_i(r,t)}{\partial t}$$

effective potential: $$v_{eff} \quad = \quad v(r,t) + \int \frac{\rho(r',t)}{|r-r'|}dr' + \mu_{XC}(r,t)$$

exchange-correlation term: $$\mu_{XC}(r,t) \quad \equiv \quad \frac{\delta A_{XC}[\rho(r,t)]}{\delta\rho(r,t)}$$

Electron density: $$\rho(r,t) \quad = \quad \sum_i |\phi_i(r,t)|^2$$

Oscillator Strength

$$f_{(g\to n)} = \frac{2}{m\hbar\omega_{(g\to n)}}[\langle\Psi_g|\mu_{ele}|\Psi_n\rangle\langle\Psi_n|\mu_{ele}|\Psi_g\rangle]$$

$$\mu_{ele} = -\sum_i r_i + \sum_M Z_M R_M$$

$$\mu_{mag} = -\frac{1}{2}\sum_i r_i \times p_i + \sum_M \left(\frac{Z_M}{2M_M}\right) R_M \times P_M$$

ignored by Born-Oppenheimer approx.

r_i, p_i : position and momentum of electron i

Z_M, M_M, R_M, P_M : charge, mass, position, and momentum of atom M

m, ω : mass and frequency of electron

Circular Dichroism (CD) Spectra

CD shows the difference of absorption intensity between L-CPL and R-CPL. It depends on both molecule structure and wavelength of light.

$$R_{(g\to n)} = Im[\langle\Psi_g|\mu_{ele}|\Psi_n\rangle\langle\Psi_n|\mu_{mag}|\Psi_g\rangle]$$

CD is also expressed as below.

$$\Delta A = (\Delta\varepsilon)cl$$

$$\Delta\varepsilon = \varepsilon_{left} - \varepsilon_{right}$$

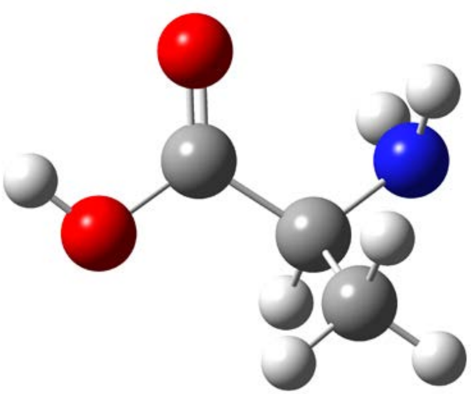
ε [cm^2/mol] : molar absorptivity

Choice of amino acids

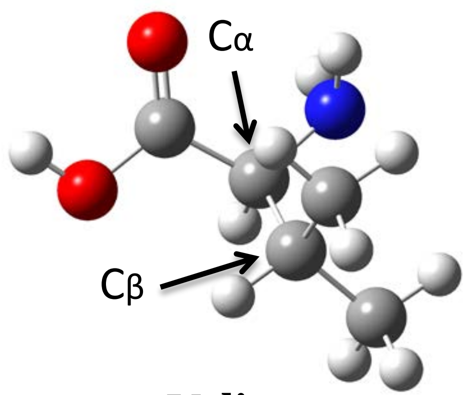
	molar weight [g/mol]	In Murchison meteorite [nmol/g]	Living body	Number of chiral carbon
Alanine	**89.09**	**10.4**	○	**1**
Valine	**117.15**	**8.0**	○	**1**
Isovaline	**117.15**		×	**1**

[M. H. Engel *et. al.*, *Nature* **389**, 265 (1997)]

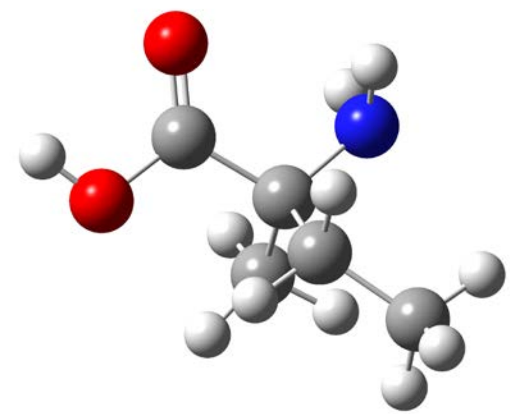
Stable structures of the amino acids in ISM



Alanine



Valine



Isovaline

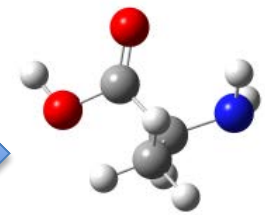
Conclusions

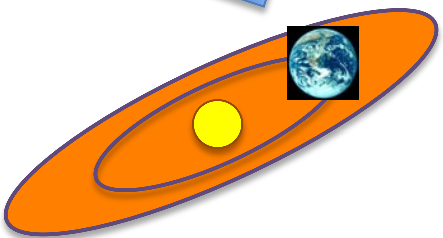
enantiomeric excess

Vacuum Ultraviolet Circularly Polarized Light (VUV-CPL)

Ly α wavelength

L-form





solar system

By L-CPL irradiation

D- absorbed UV. → D- is excited. → D- is decomposed. → L-form excess

A new field of “Quantum Astrophysics”