



Study for Origins of Homochirality and Life: Investigation for the Cosmic Scenario Using Vacuum Ultraviolet Light and Synchrotron Radiation

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Sutudy for Origins of Homochirality and Life: Investigation for the Cosmic Scenario Using
Vacuum Ultraviolet Light and Synchrotron Radiation （ホモカイラリティーおよび生命の起源に関する研究： 真空紫外光，シンクロトロン放射を用いた宇宙起源説の検証）

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論文内容の要旨

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論文題目 (外国語の場合は、その和訳を併記すること。)

Study for Origins of Homochirality and Life: Investigation for the Cosmic Scenario Using Vacuum Ultraviolet Light and Synchrotron Radiation

ホモカイラリティおよび生命の起源に関する研究：真空紫外光、シンクロトロン放射を用いた宇宙起源説の検証

論文要旨

Dominant amino acids, except for glycine, in proteins and dominant sugars in nucleotides on the earth are L-type and D-type, respectively. This important characteristic of life on the earth is called biomolecular homochirality. It is well known that “chiral defects”, random disturbances of homochirality of the primary structure, impede the formation of both the double helix in nucleic acids and α -helices and β -sheets in proteins (Spach and Brack, 1979; Goldanskii *et al.*, 1986). Therefore, it is important to achieve the homochirality in order to produce biomacromolecules and obtain complex 3D conformation, but the origin is not cleared. Following two evidences suggest the homochirality was triggered in space by circularly polarized light (CPL) irradiation and was delivered to the primitive earth (“cosmic scenario”).

- Enrichment of L-type amino acids was detected from Murchison and Murray meteorites (Cronin and Pizzarello, 1997; Pizzarello and Cronin, 2000; Pizzarello *et al.*, 2003)
- Circularly polarized light (CPL) which induces asymmetric photolysis was observed in space (Bailey *et al.*, 1998; Rosenbush *et al.*, 2003; Fukue *et al.*, 2009).

In this thesis, following three experiments are reported as the first step to examine the cosmic scenario.

1. Examination for racemization of aspartic acid during photolysis induced by non-polarized 8.5 eV vacuum ultraviolet (VUV) light irradiation.

In view of cosmic scenario, the enrichment had been kept during space travel. However there are various racemization factors in space. In order to examine whether

(1) aspartic acid (Asp) is racemized by VUV irradiation and (2) the decomposition products have same chirality as Asp, L- or D-Asp sublimated films were irradiated with non-polarized 8.5 eV VUV light.

Sublimated films of L-Asp or D-Asp were irradiated with non-polarized 8.5 eV VUV light in vacuum at room temperature. After irradiation, each film was dissolved with distilled water and analyzed by using HPLC.

Reactions expressed as “L-Asp + $h\nu \rightarrow$ L-Ala + β -Ala (+ other achiral molecules)” and “D-Asp + $h\nu \rightarrow$ D-Ala + β -Ala (+ other achiral molecules)” occurred for L- or D-Asp films irradiated with non-polarized 8.5 eV VUV light. It was concluded that chirality was preserved for photolysis of Asp to Ala. Decomposition quantum efficiency of solid L-Asp was 0.18 ± 0.04 . This means that with probability about 80 %, solid Asp itself was preserved for VUV irradiation. It is reported that in the case of aqueous solutions irradiated with 222 nm UV light (Nakagawa *et al.*, 2000), the decomposition quantum efficiency was 0.48 ± 0.02 . Although the irradiation energy was smaller than this work, Asp in water was easily decomposed. These results suggest that solid Asp was much stable than aqueous. This result suggests that solid Asp is much stable than aqueous solution and supports cosmic scenario.

2. Examination for racemization and dimerization of alanine induced by non-polarized 7.2 eV VUV light irradiation

It is well known that “chiral defects” impede the formation of both double helix in nucleic acids and α -helices and β -sheets in proteins. Therefore, amino acids and nucleosides must polymerize against racemization. In view of origin of life, it is important to examine the ratio of racemization rate to homo-oligomerization rate, namely production rate of oligomers composed only L-type or only D-type molecules. In this experiment, it was verified the decomposition, racemization and dimerization rate of solid L-alanine (Ala) induced by non-polarized 7.2 eV VUV light.

Sublimated films of L-Ala were irradiated with non-polarized 7.2 eV VUV light in vacuum at room temperature. After irradiation, each film was dissolved with distilled water and analyzed by using HPLC.

Reaction expressed as “L-Ala + $h\nu \rightarrow$ L-alanyl-L-alanine (LL) + D-alanyl-L-alanine (DL) + L-alanyl-D-alanine (LD) + D-Ala (+ other achiral molecules)” occurred, namely racemization, homo-dimerization and hetero-dimerization were observed. L-Ala was stable with the probability of 11 % per 7.2 eV absorbed photon. The detail of 11 % was; 0.52 % racemization, namely production D-Ala, 0.13 % homo-dimerization, namely production of LL and 10.35 % the other production of other

(注) 3,000~6,000 字 (1,000~2,000 語) でまとめること。

achiral molecules. The rate of racemization was 4 times as large as the rate of homo-dimerization. In view of chemical evolution in space and achievement of homochirality, this result may be critical problem. Therefore it is necessary to carry out similar experiments at ultra-cold temperature.

3. Examination of the possibility of asymmetric photolysis induced by circularly polarized soft X-ray

Asymmetric photolysis of amino acids induced by circularly polarized ultraviolet has been reported (Flores *et al.* 1977; Nishino *et al.* 2001; Nishino *et al.* 2002; Meierhenrich *et al.* 2005; Takahashi *et al.*, 2009). If the circularly polarized light source is synchrotron radiation, which includes not only UV but also X-ray (e.g. Atoyan and Aharonian, 1996), in space, circularly polarized soft X-ray may also act as an asymmetric energy source. However the effect of circularly polarized X-ray has never examined. In order to examine the possibility of asymmetric photolysis induced by circularly polarized soft X-ray, NCD spectra of Asp, serine (Ser) and Ala, were measured in oxygen K-edge region.

The spectrum curve of L-Asp changed from negative to positive with the increase of photon energy in the energy range of 530-535 eV. In contrast, the spectrum curve of L-Ser changed from positive to negative with the increase of photon energy. In the case of L-Ala, only one negative peak was observed. Difference among three amino acids reflects the difference of chiral environment of the core hole oxygen atom of COO⁻. Since COO⁻ is common part of the biomolecular amino acids, side chain affects NCD of COO⁻. It is interesting in view of application of NCD in soft X-ray region. In order to compare the magnitude of NCD, the ratio *g* of NCD to absorption cross section was obtained. Maximum *g* value of L-Asp was 1.4 %. In the case of L-Ser and L-Ala, Maximum *g* value was 0.055 % and 0.30 %, respectively. Maximum *g* value in soft X-ray region which have reported in the past (Turchini *et al.*, 2004; Tanaka *et al.*, 2005; Nakagawa *et al.*, 2005) besides L-Ser and L-Ala is 10⁻³ orders of magnitude. Thus 1.4 % is quite large value. The reason why L-Asp shows such a large NCD is open question at the present time. It is very interesting in view of both experimental and theoretical soft X-ray NCD studies.

Spectrum shapes and magnitude of NCD among three kinds of amino acids were dramatically different. Therefore, it was concluded that asymmetric photolysis induced by circularly polarized soft X-ray would be occurred in the case of those amino acids. However, in soft X-ray region, achieved enantiomeric excess would be affected by

(注) 3,000~6,000 字 (1,000~2,000 語) でまとめること。

secondary electrons. It is necessary to carry out circularly polarized soft X-ray irradiation experiments.

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(注) 3,000~6,000 字 (1,000~2,000 語) でまとめること。

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論文審査の結果の要旨

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要 旨			
最初の生物の出現に先立つ化学物質としての進化の過程は化学進化と呼ばれ，その解明は生命の起源研究において重要な位置を占めている．1980年代以来多数の隕石からアミノ酸が検出されてきたが，近年それらの隕石のうち2つからはL-体過剰(数%)のアミノ酸が検出された．このことはカイラリティーの偏りが宇宙である程度達成され得ることを示すものであり，どのような物理化学過程がこれに寄与するのかを明らかにすることは，地球上の生命を形づくる生体分子のホモカイラリティーが獲得される過程の第1歩として化学進化研究における焦眉の研究課題である．学位論文提出者 泉雄大の研究は，上述の現状を踏まえ，宇宙においてカイラリティーの偏りを誘起する可能性のある円偏光軟X線の生体分子に対する作用をシンクロトロン放射を用いて調べたものである． 本論文は5章からなる本文および文献・謝辞から構成されている．第1章は序論にあてられ，カイラリティーの偏りを誘起する可能性のある過程を3つあげ，それぞれを検討した．その結果，(1)不斉な表面に吸着したアミノ酸の光学分割に関する研究例からは巨視的な分子数が得られない困難が予想されること，(2)パリティ非保存の弱電相互作用の研究例からはアミノ酸L-体とD-体のエ			

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エネルギー差があまりにも小さく、さらに分子内回転自由度の範囲内でL-体とD-体の安定度の序列が逆転する問題点が予想されること、(3)円偏光による不斉反応の研究例では紫外光で2%程度の偏りが報告されており軟X線領域での実験が期待されることが述べられている。

第2章と第3章では、カイラリティーの偏りをもつアミノ酸が隕石から発見されたという事実を問題の発端とした研究がまとめられている。すなわち、カイラリティーの偏りをひとたび獲得したアミノ酸が地球に飛来する途中にラセミ化因子である非偏光真空紫外線に照射された場合に偏りをどの程度維持できるかという実験が行われた。第2章ではアスパラギン酸それ自体は146nm光によって光ラセミ化せず高い安定性をもつこと、およびアスパラギン酸が光分解してアラニンになる場合にはアスパラギン酸のカイラリティーを保持したままアラニンになることが示された。第3章ではアラニンに対して同様の実験を行った結果がまとめられ、アラニンは光量子効率0.52%でラセミ化し、0.13%でホモダイマーとなり、ヘテロダイマーとなる光量子効率は0.1%以下であることが述べられている。真空紫外線によってアラニンはわずかながらラセミ化するがアスパラギン酸はラセミ化しないというアミノ酸の耐ラセミ化能力の違いがなぜ生じるかについて申請者は側鎖のかさ高さの効果であると説明している。

第4章は本論文の核心部であり、SPring-8において測定された軟X線円二色性スペクトルについてまず記述されている。軟X線は物質との相互作用が大きいため円偏光軟X線はカイラリティーの偏りを導入できる不斉なエネルギー源として注目されてきたが、アミノ酸が円偏光にどの程度応答するかをあらわす円二色性スペクトルを絶対値で測定することは極めて困難である。申請者は数々の困難を克服してこの測定に成功した。その結果、アラニンの酸素 $1s \rightarrow \pi^*$ 遷移は1本の負のピークが、セリンでは正と負の2本のピークが、アスパラギン酸では負と正の2本のピークが観測された。この結果を受けて理論家による計算が活発に行われるようになり、申請者の成果は円二色性科学の発展に明確に寄与している。申請者はさらに得られた円二色性スペクトルをもとにKaganの式を用いて不斉反応の可能性を検討し、アラニンでは初期分子数の90%を分解した場合のエンアンチオ過剰率を0.81%と予測した。この提案の実証実験が待たれるところである。

第5章は全体のまとめに当てられ、第2章から第4章までの成果を簡潔にまとめ、将来の研究の発展を展望している。

本研究は、アミノ酸の分光学的および光化学的研究にシンクロトロン放射とくに円偏光軟X線分光という新しい技術を適用することによってアミノ酸の化学進化を研究したものであり、化学進化研究に重要な知見を得たものとして価値ある集積であると認める。よって、学位申請者の泉 雄大は、博士（理学）の学位を得る資格があると認める。

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