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海外特別研究員としての派遣期間を終了しましたので、下記のとおり報告いたします。
なお、下記及び別紙記載の内容については相違ありません。

記

1. 用務地(派遣先国名) 用務地: ニース (国名: フランス国)

2. 研究課題名(和文) ※研究課題名は申請時のものと違わないように記載すること。
円偏光と彗星内水質変成作用によるアミノ酸・糖の不斉の形成と増幅プロセスの解明

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5. 所期の目的の遂行状況及び成果…書式任意 **書式任意(A4判相当3ページ以上、英語で記入も可)**
(研究・調査実施状況及びその成果の発表・関係学会への参加状況等)
(注)「6. 研究発表」以降については様式10-別紙1~4に記入の上、併せて提出すること。

Cometary organic materials are important to understand the evolution of organic molecules from interstellar molecular clouds to the current solar system as well as the delivery of essential biomolecules to the early Earth. In 2014, the European Space Agency (ESA)'s Rosetta Mission succeeded to land on the nucleolus of the comet 67P/Churyumov-Gerasimenko (Goesmann *et al*., 2015, *Science*). The *in situ* analysis of the cometary volatiles by Rosetta's on-board mass spectrometer ROSINA (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) revealed the existence of various organic molecules. They include a molecule with a mass number of 75 Da, which suggests the presence of amino acid glycine ($C_2H_5NO_2$) (Altwegg *et al*., 2016, *Sci. Adv.*). Amino acids are essential building block of the terrestrial life. The important characteristic of amino acids in the terrestrial life is homochirality. Amino acids have a chiral center in the molecules, thus they have two enantiomers (L-and D-amino acids). The enantiomers are mirror image of each other and there is no difference in the chemical and physical properties between two enantiomers. Therefore, normal chemical reactions produce racemic mixtures of equal amount of each enantiomer. However, living organisms on the Earth almost exclusively use only one enantiomer for the building blocks of their biopolymers. They use L-enantiomer of amino acids for protein. On the contrary, they use D-sugars for nucleic acids (DNA and RNA). Because the existence of both enantiomers would be failed in the proper holding of the proteins, the selection of one enantiomer is an important requirement for living organisms to form their biopolymers. Thus, the selection of one enantiomer must have occurred at an early stage of the evolution of terrestrial life. This fundamental question regarding biomolecular homochirality:

when, how, and why L-amino acids and D-sugars were selected for terrestrial life has been a longstanding question hitherto unanswered.

One of the hypotheses to answer this question is the extraterrestrial origin. Circular polarized light (CPL), which is produced in the massive star-forming region such as the Orion nebula (Fukue *et al.*, 2009, *Astrophys. J.*), has the capability to induce chiral asymmetry into racemic organic molecules. The irradiation of CPL to the presolar environment is considered to have caused the asymmetric synthesis and photolysis of organic molecules in interstellar ice (e.g., Meinert *et al*., 2014, *Angew. Chem.*). In the study, I focus on the symmetry breaking by irradiation of CPL to interstellar ice in the interstellar molecular clouds. The target molecules are amino acids and sugars. Several studies revealed that these molecules could be synthesized by UV-irradiation to simulated interstellar ice analogues by laboratory experiments (Muñoz Caro *et al.*, 2002, *Nature*; Meinert *et al.*, 2016, *Science*). The formation of small enantiomeric excess (~4%) by irradiation of CPL to some amino acids was also reported (Meinert *et al.*, 2014, *Angew. Chem. Int. Ed.*). However, there is no such research conducted about sugars, and the studied wavelengh of CPL for amino acids are also limited.

In order to understand the formation mechanisms of enantiomeric excess in sugars by irradiation of CPL in the interstellar molecular clouds, I joined the CPL-irradiation experiments at Synchrotron SOLEIL in Paris. We obtained the access to the Beamline DESIRS for one week each in May 2017 and June 2018. In these two experiments, we irradiated the CPL in ultraviolet (UV) and vacuum UV spectral range from synchrotron radiation to the racemic mixture of glyceraldehyde ($C_3H_6O_3$). Glyceraldehyde is the simplest sugar molecule with a chiral centre and considered to be a candidate of the chiral precursor of the sugar units of nucleic acids. In the experiments, a commercially available racemic glyceraldehyde (in solid form) was sublimated as a thin film at 110 °C on UV-transparent magnesium fluoride (MgF_2) windows, and placed in the vacuum chamber of the beam line, and then irradiated with left-CPL or right-CPL. The wavelength of the CPL was selected based on the circular dichroism (CD) and anisotropy spectra of individual enantiomers of glyceraldehyde, in which the enantiomeric excess could possibly show the maximum value. The measurement of CD and anisotropy spectra were conducted at the Beamline CD1in the Centre for Storage Ring Facilities Aarhus, ISA (Denmark).

For the analysis of the CPL-irradiated samples, I had planed to develop the analytical methods for the enantioselective analysis of both amino acids and sugars, by using a comprehensive multidimensional gas chromatography couple to time-of-flight mass spectrometry (GC×GC-TOFMS). Although the analytical instrument in the host institution had not been operational for almost whole year due to the severe machine trouble and the time I could access to the instrument was limited, I have developed the analytical method for enantioselective analysis of amino acids. By this method, we can separate the enantiomers of more than 20 amino acids in a mixture. For the sugar analysis, the analytical development is still on going with the colleagues in the host institution. We are continuing collaborating and planning to analyse the samples in the coming year.

Through the experiments at the Synchrotron SOLEIL in Paris and ISA in Aarhus, we discussed the recent advances in biomolecular homochirality research. This discussion, especially focusing on amino acids, was summarised as a review paper (<u>Sugahara, H</u>., Meinert, C., Nahon, L., Jones, N.C., Hoffmann, S.V., Hamase, K., Takano, Y., Meierhenrich U.J., 2018, D-Amino acids in molecular evolution in space – Absolute asymmetric photolysis and synthesis of amino acids by circularly polarized light, *Biochimica et Biophysica Acta (BBA) Proteins and Proteomics*, 1866, 743−758) by collaborating with these European researchers as well as Japanese researchers. In this paper, we discussed the asymmetric photolysis and synthesis of amino acids in the interstellar molecular clouds, and the relationship with the amino acids in meteorites and comets. We also discussed the resent analytical progress in the enantioselective analysis of amino acids. Another perspective of this paper was to make a connection between Japanese and European researchers. It was meaningful that we could discuss and made a consensus about a controversial issue in this research field on the paper. The next paper that had more focus on sugars was also published (Garcia, A.D., Meinert, C., Sugahara H., Jones, N.C., Hoffmann, S.V., Meierhenrich, U.J., The astrophysical formation of asymmetric molecules and the emergence of a chiral bias, 2019, *Life*, *9*, 29).

To conduct the organic chemical analysis of the interstellar ice analogue samples, which I could not perform in the host institution, I visited the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). In JAMSTEC, I developed the analytical methods for the small quantities of amino acids and amines. I applied this method to the interstellar ice analogue samples that was irradiated with UV and then confirmed the formation of eleven amino acids (glycine, α-alanine, β-alanine, sarcosine, serine, α-aminobutyric acid, β-aminobutyric acid, β-aminoisobutyric acid, leucine, aspartic acid, and glutamic acid) and three amines (methylamine, ethylamine, and propylamine) in the samples. In addition, the analyses of the nitrogen isotopic composition of amino acids, as well as that of the bulk samples revealed that there was no nitrogen isotopic fractionation occurred at the formation of the interstellar ice, and thus the nitrogen isotopic ratio of the initial ammonia gas would be inherited to the organic molecules in the interstellar ice. These results were published as a research paper (Sugahara, H., Takano, Y., Tachibana, S., Sugawara, I., Chikaraishi, Y., Ogawa, N.O., Ohkouchi, N., Kouchi, A. and Yurimoto, H., 2019, Molecular and isotopic compositions of nitrogen-containing organic molecules formed during UV-irradiation of simulated interstellar ice, *Geochemical Journal*, 53, 5–20).

I have also involved in the assessment of the organic contamination in the curation facility in the Institute of Space and Astronautical Science/Japan Aerospace Exploration Agency (ISAS/JAXA) that was aimed for Hayabusa2 returned samples. I analysed the amino acid concentrations of the witness coupons exposed in a clean chamber of the curation facilities. The witness coupons, which were made of aluminum foil, were collected at the different time periods that were ranged from 1 day to 1 month to examine the accumulation rate of the contaminants. On the witness coupons, seven common terrestrial amino acids (glycine, alanine, valine, leucine, isoleucine, proline, aspartic acid and glutamic acid) were detected. There was also the increasing trend observed in the concentration from 1 to 7 days. The inter-laboratory evaluation with the OSIRIS-REx team of the National Aeronautics and Space Administration/Johnson Space Center (NASA/JSC) indicated that the quality control against terrestrial contaminants in ISAS/JAXA facility is at the similar quantitative level as in their facility. These results were published in a research paper (Sugahara, H., Takano, Y., Karouji, Y., Kumagai, K., Yada, T., Ohkouchi, N., Abe, M., and Hayabusa2 project team, 2018, Amino acids on witness coupons collected from the ISAS/JAXA curation facility for the assessment and quality control of the Hayabusa2 sampling procedure, *Earth, Planets and Space*, 70, 194).

During my stay at the Université Nice Sophia Antipolis, I had several chances to join the scientific conferences and meetings. I joined the multidisciplinary research group aimed for asymmetry research in the university (University of Côte d'Azur, association of universities and higher education institutions). In the workshop of this asymmetry research group, our research team presented the experimental results (Meinert, C., Sugahara, H., Meierhenrich, U.J., Matter, A., Lopez B., de Souza A.D., 2017, Organic molecules in interstellar space: Detection and symmetry-characterisation, *Second Asymmetry Workshop*, Nice, France). We also organised the “First European Asymmetry Symposium” in March 2018 in Nice, France. This unique multidisciplinary symposium gained attention and was featured in several journals including *Natur*e (https://www.nature.com/articles/d41586-018-03254-w). In addition, I participated in the MOMA (Mars Organic Molecule Analyser) meeting related to ESA's ExoMars Mission that was held in November 2018 in Nice (France). In this meeting, I learned a lot about the gas chromatographic system that will be loaded on a rover and operate on the Martian surface. It is very much meaningful for my future research in the current institution (ISAS/JAXA) that is planning to construct an onboard mass spectroscopy for the future space missions.

In summary, the two years at the Université Nice Sophia Antipolis was very much fruitful and could obtain the good scientific results as well as the various great experiences and the human network. I participated in the CPL-irradiation experiments to the organic molecules in the Synchrotron SOLEIL in Paris (France) and the CD and anisotropy measurements in the Centre for Storage Ring Facilities Aarhus, ISA (Denmark). I also learned the new analytical technique using GC×GC-TOFMS system and developed the analytical method for the enantioselective analysis of amino acids. The analytical development for the enantioselective analysis of sugars is still on going and we are continuing collaborating. During my stay, I published the research results in three papers as the first author and one paper as a co-author. I also participated in several symposium and meetings that helped me to build an extensive network with European researchers. These valuable experiences and the network will be very helpful in my research carrier in the future.