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研究課題名（和文）Electrocatalytic Reductive Functionalization of Carbon Dioxide

研究課題名（英文）Electrocatalytic Reductive Functionalization of Carbon Dioxide

研究代表者
Ｌｉ　Ｙａｍｅｉ（Li, Yamei）

東京工業大学・地球生命研究所・特任准教授

研究者番号：１０７４５１２８

交付決定額（研究期間全体）：（直接経費）　　2,500,000円

研究成果の概要（和文）：炭素質コンドライトの有機進化は、初期の太陽系天体で起こった進化の歴史に関する重要な手がかりを与えます。 我々は以下のことを明らかにしました: 1)水性変化によるタンパク質構成アミノ酸の分解影響。2)各種炭素質コンドライト母体のアミノ酸分布の不均一性の起源。
これらの結果は、生命の起源に対する隕石の貢献と、宇宙での生命の構成要素の探索を導く上で重要な意味を持っています。 この結果は、査読済みの 2 つの論文 (Nat. Comm.、2022 年および Sci. Adv.、2023 年) に掲載され、いくつかの国内および国際会議で報告されました。

研究成果の学術的意義や社会的意義
Origin of life's building blocks is key to understand the origin of life (OOL). This research proposed a new model based on the non-equilibrium thermodynamics, which brings new insights into the organic chemical evolution on the Solar System small bodies and meteorites' contribution to OOL.

研究成果の概要（英文）：Organic evolution on carbonaceous chondrites gives important clues on the evolutionary history occured on the early Solar System bodies. We have clarified the following: 1) the degradation effect of aqueous alteration on proteinogenic amino acids. The alfa-amino acids tend to decompose electrochemically via deamination and decarboxylation pathways; 2)the origin of heterogenity of amino acid distribution on various types of carbonaceous chondrite parent bodies. We proposed that the difference in the core and mantle within a water/rock differentiated parent planetesimal is the origin for such heterogenity.
These results have important implications on meteorites' contribution to life's origin and guiding the search for life's building blocks in space. The results were published on two peer-reviewed papers (Nat. Comm., 2022 and Sci. Adv., 2023) and reported in several domestic and international conferences.

研究分野：Organic cosmochemistry; Astrobiology

キーワード：Asteroid Ryugu　Carbonaceous chondrite　Amino acid　Electrochemistry　Mineral catalysis　Aqueous alteration

１．研究開始当初の背景

This project aims at achieving reductive functionalization of CO_2, for expanding the product spectrum of CO_2 utilization. During this project, several additives were introduced to facilitate the reaction, such as amino acid compounds. However, it was found that amino acids were decomposed under electrochemical conditions. Specifically, aliphatic α-amino acids were decomposed to aliphatic amines and α-hydroxy acids. These compounds were reported to coexist with amino acids in carbonaceous chondrites; thus, these results inspire me to consider the relevance between geo-electrochemistry and meteoritic observations. Based on extensive literature survey, the research target has been shifted to clarify the reaction mechanism of amino acid decomposition and its implications to the chemical evolution on the parent bodies of carbonaceous chondrites (CCs), which are the most primitive bodies in our Solar System.

Amino acids on CCs were formed in multiple continuous evolutionary processes, including intersteller medium, protosolar nebula, and the parent body processes. Therefore, the chemical characteristics and distribution carry the most primitive record of solar system evolution. It has been a research frontier in cosmochemistry field to constrain the chemical evolutionary history based on the distribution patterns [1]. Besides, CCs are the only extraterrestrial material that carry more than 30 types of life's building blocks; thus, the formation and coexisting mechanisms and their contributions to origin of life (OOL) has become one of the important research topics in astrobiology[2]. These scientific values of CCs have directly promoted the sample return missions of JAXA's Hayabusa 2 and NASA's OSIRIS-Rex to obtain pristine samples from asteroid Ryugu and Bennu.

There has been a long-standing gap between the reaction models and laboratory results and meteoritic observations in terms of organic distribution and variation tendencies. This has caused great challenges on rationalizing the observational data. Specifically, previous studies have shown that CCs' amino acids were strongly affected by the type of metamorphism (thermal and aqueous alteration)[3, 4, 5]. Amino acid abundances greatly decrease upon increase in the aqueous alteration degree, which is contradictive to the experimental studies showing that amino acids can be efficiently synthesized via multiple pathways (e.g., formose-type reaction, Strecker reaction, reductive amination).

２．研究の目的

The research aims at elucidating the effect of aqueous alteration on the amino acid distribution on carbonaceous planetesimals, which are the parent bodies of carbonaceous chondrites and asteroids.

３．研究の方法

Here in this project, I proposed a new geochemical model, namely geo-electrochemical driven alteration of amino acids, to account for the mechanism of amino acid decomposition under relatively low temperature (e.g., 25 ^{o}C). The following experiments were conducted:

1) Electrolysis of aliphatic amino acids. Three model amino acids (glycine, alanine, and valine) were used as the substrates. Freshly precipitated FeS and NiS were used as the model catalyst.

The electrolysis was conducted at a wide potential range of -0.5 to -1.0V vs. SHE, simulating the range of redox potential of H^+/H_2 couple in the rocky core.

2) Electrolysis of dicarboxylic amino acids. Two dicarboxylic amino acids (aspartic acid and glutamic acid) were used as the substrates. Similar experimental conditions as described in 1) were applied.
3) Product analyses. After reaction for one-week and two-week durations, samples were analyzed for the amino acids, amines, carboxylic acids using combined analytical methods (NMR, fluorescence HPLC with post-column derivatization and ion chromatography). Chirality of resulted amino acids after reaction was analyzed by GCMS with a chiral column.
4) Compare the product distribution with meteoritic data. More than 20 carbonaceous meteorites with a wide range of aqueous alteration (with petrological type of 1 to 3) were investigated in terms of their amino acid, amine, and α-hydroxy acids abundances.
5) Mechanism study. Isotope labeled reagent was used to trace the bond breaking and forming pathways involving carbon and nitrogen atoms.

４．研究成果

Two peer-reviewed papers were published related to this project. In the first paper6, the following research achievement was obtained: 1) Clarified the effect of aqueous alteration on the amino acid abundances in CR chondrites with a wide range of aqueous alteration degree (CR2.0-2.8).2)Proposed a new cosmo-electrochemical model to explain the organic evolution under low temperature regime. In the second paper[7], the following research achievement was obtained: 1) Verified the generality of geo-electrochemical mode on explaining the amino acid distributions in diverse groups of carbonaceous chondrites; 2) Proposed a new evolutionary model of parent bodies of carbonaceous chondrites and asteroids, which can explain the origin of chemical heterogeneity in the soluble organic matter; 3) The newly proposed model can also explain the amino acid distribution in the return sample from asteroid Ryugu, providing molecular-level evidence of the evolutionary linkage between CI chondrite and asteroid Ryugu.

This research has been highlighted in the media of Earth-Life Science Institute of Tokyo Institute of Technology, and a recent JSPS interview.

The research results were reported in several academic conferences, including JpGU meeting, AbSciCon meeting, and Hayabusa 2 Symposium.

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7. Li Y, *et al.* Aqueous breakdown of aspartate and glutamate to n-ω-amino acids on the parent bodies of carbonaceous chondrites and asteroid Ryugu. *Sci Adv* **9**, eadh7845 (2023).

５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　1件／うちオープンアクセス　3件）

１．著者名 Li Yamei、Kitadai Norio、Sekine Yasuhito、Kurokawa Hiroyuki、Nakano Yuko、Johnson-Finn Kristin	４．巻 13
２．論文標題 Geoelectrochemistry-driven alteration of amino acids to derivative organics in carbonaceous chondrite parent bodies	５．発行年 2022年
３．雑誌名 Nature Communications	６．最初と最後の頁 1-14
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41467-022-32596-3	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Li Y.	４．巻 -
２．論文標題 Minerals as Prebiotic Catalysts for Chemical Evolution towards the Origin of Life	５．発行年 2022年
３．雑誌名 Intechopen	６．最初と最後の頁 1-18
掲載論文のDOI（デジタルオブジェクト識別子） 10.5772/intechopen.102389	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Kurokawa H.、Laneuville M.、Li Y.、Zhang N.、Fujii Y.、Sakuraba H.、Houser C.、Cleaves H. J.	４．巻 -
２．論文標題 The origin of Earth’s mantle nitrogen: primordial or early biogeochemical cycling?	５．発行年 2022年
３．雑誌名 Geochemistry, Geophysics, Geosystems	６．最初と最後の頁 -
掲載論文のDOI（デジタルオブジェクト識別子） 10.1029/2021GC010295	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

〔学会発表〕　計8件（うち招待講演　3件／うち国際学会　3件）

１．発表者名 Yamei LI
２．発表標題 Geo-electrochemistry drove chemical evolution in water/rock interacted environments on Earth and icy planetesimals
３．学会等名 21st International Sedimentological Congress（国際学会）
４．発表年 2022年

１．発表者名
Yamei LI

２．発表標題
Geoelectrochemistry-driven alteration of amino acids to derivative organics in carbonaceous chondrite parent bodies

３．学会等名
AbSciCon meeting（国際学会）

４．発表年
2022年

１．発表者名
Yamei LI

２．発表標題
Geo-electrochemistry drove chemical evolution in water/rock interacted environments on Earth and icy planetesimals

３．学会等名
The 45th Annual Meeting of the Molecular Biology Society of Japan（招待講演）

４．発表年
2022年

１．発表者名
Yamei LI

２．発表標題
molecular descriptors of aqueous alteration-induced organic decomposition in parent body of carbonaceous chondrites and Ryugu asteroid

３．学会等名
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４．発表年
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１．発表者名
Li Yamei

２．発表標題
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３．学会等名
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４．発表年
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１．発表者名
Li Yamei

２．発表標題
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３．学会等名
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４．発表年
2021年

１．発表者名
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Geo-electrochemical Alteration of Amino Acids Reproduces Soluble Organics in Carbonaceous Chondrites

３．学会等名
JpGU Meeting 2021

４．発表年
2021年

１．発表者名
Yamei LI

２．発表標題
Thiazolidine-facilitated CO2 fixation

３．学会等名
JpGU-AGU Joint Meeting 2020

４．発表年
2020年

〔図書〕　計1件

１．著者名	４．発行年
Yamei LI	2022年
２．出版社	５．総ページ数
Intech Open	266
３．書名	
Mineralogy	

〔産業財産権〕

〔その他〕

Research highlight
https://www.elsi.jp/en/news_events/highlights/2022/chemical_evolution_early_solar_system/

6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考
研究協力者	中野　裕子 (Yuko Nakano)		
研究協力者	藤森　言 (Fujimori Gen)		
研究協力者	伊佐　純子 (Isa Junko)		
連携研究者	関根　康人 (Sekine Yasuhito) (60431897)	東京工業大学・地球生命研究所・professor (12608)	
連携研究者	黒川　宏之 (Kurokawa Hiroyuki) (80713643)	東京大学・大学院総合文化研究科・准教授 (12601)	

6．研究組織（つづき）

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考
連携研究者	北台　紀夫 (Norio Kitadai) (80625723)	国立研究開発法人海洋研究開発機構・超先鋭研究開発部門(超先鋭研究開発プログラム)・主任研究員 (82706)	
連携研究者	上野　雄一郎 (Ueno Yuichiro) (90422542)	東京工業大学・理学院・教授 (12608)	
連携研究者	癸生川　陽子 (Kebukawa Yoko) (70725374)	東京工業大学・理学院・准教授 (12608)	
連携研究者	中村　龍平 (Nakamura Ryuhei) (10447419)	東京工業大学・地球生命研究所・教授 (12608)	
連携研究者	藤島　皓介 (Fujishima Kosuke) (00776411)	東京工業大学・地球生命研究所・准教授 (12608)	

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関