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## 論 文 内 容 要 旨

Paleoproterozoic is considered to be the age of rapid change of oceanic environments in particular for redox state of bottom of oceans. Such change is recognized as a disappearance of BIFs right after 1.9 Ga Gunflint Formation. This is often considered as complete oxidation towards the bottom of the oceans. On the other hand, Paleoproterozoic ecosystem in such ocean and associated elemental cycle has been poorly understood. In order to constrain the microbial ecosystem in Paleoproterozoic oceanic environments, geochemical studies were performed on the ca. 1.9 Ga Gunflint and Rove Formations, Canada.

The major problems for the Paleoproterozoic surface environment are, (1) the chemical composition of the ocean and (2) what is the major part of the microbial community. One of the most famous models for the Paleoproterozoic ocean is stratified ocean that shallow part was oxic and deep part was euxinic. However, there are some opinions that the entire ocean was oxic in this age. Thus, we still do not have the exact answer about the Paleoproterozoic oceanic condition.

In addition, it is not certain if an oxygenic photosynthetic bacteria was the primary producer or two or three primary producers were present in the same oceanic environment. Variety of chemoautotrophs, such as iron-oxidation bacteria and/or methanogen which strongly require the reduced and/or iron-rich environment, were proposed by previous study as a major part of the Gunflint biota. Therefore, in the present thesis, constraining the primary producer in the Gunflint ocean is the major target.

Recently, nitrogen isotope compositions of ancient organic matter are analyzed by many previous investigators because nitrogen is considered to be a useful indicator for detection of the redox condition and microbial activity in the ancient ocean. However, the effect of diagenesis and the heterogeneity of nitrogen in the organic matter are still not well understood.

In chapter 1, the historical background of the evolution of earth's surface environment, previous studies about Paleoproterozoic oceanic environment and microbial activities are reviewed. In chapter 2, stepwise combustion method was performed on Paleoproterozoic kerogen with new technique developed in this study. In chapter 3, the oceanic environment and microbial activity of Paleoproterozoic Gunflint and Rove Formations are discussed based on geological, mineralogical and geochemical analyses.

The major findings of the present thesis study are listed here:

- (1) Heterogeneity of nitrogen isotope compositions of organic matter was found from Paleoproterozoic kerogen by the stepwise combustion method.
- (2) Oxic-anoxic stratified ocean model was suggested for the Gunflint Formation by the mineral occurrences and sulfur isotope compositions of pyrite.
- (3) Microbial ecosystem, which primary producer was cyanobacteria, was revealed based on the carbon and nitrogen isotope composition of kerogen in the Gunflint Formation.
- (4) There was no significant change of ecosystems between the Gunflint and the Rove formations, while there have been a meteoritic impact event during the transition age.

Development of new stepwise combustion analysis is the novel contribution of this thesis to the scientific community. In addition, proposal of intensive nitrogen cycle among Gunflint Biota is also a new aspect in the Precambrian geology.

## 論文審査の結果の要旨

石田章純君は、カナダ・オンタリオ州に分布するガンフリント層およびローブ層の地質学的・地球化学的研究を行った。この二つの層は19～18億年前に形成されており、当時の海洋環境や生物圏の情報を含み、先カンブリア時代の地球環境変動を解明するためには学術的に極めて重要な地層である。特に(1)当時の一次生産者が酸素発生型光合成微生物であったか、独立栄養化学合成微生物であったか、(2)縞状鉄鉱層形成に代表される海洋の環境変動に微生物層がどのように対応したか、(3)酸化還元層状海洋環境でどのような生物圏が存在可能であったか、など未解決の問題が存在していた。石田君はこれら問題を解決するために、現地ですべて4回野外調査を行い、試料を採集した。それら試料に対して、全岩化学分析、鉱物組成分析、軽元素含有量測定、ケロジェン状有機物の抽出、脂肪酸バイオマーカー分析、ケロジェンFT-IR測定、硫黄炭素安定同位体測定などを行った。更に大阪大学の橋爪研究室において段階燃焼法による窒素同位体測定を行った。この手法はケロジェンなどの天然有機物に適用が難しく、既存手法の改良、最適化を博士論文の仕事として手がけた。その成果論文は国際学術誌に受理されている。これらの調査と分析結果から、独立栄養化学合成微生物でなくシアノバクテリアが一次生産者としてふるまい、海洋の環境変動にかかわらず生物の生産性の変化がないことが分かった。また段階燃焼法による窒素同位体組成は、同じケロジェン内でも異なる窒素同位体組成を有する基が存在するという新しい知見が得られた。これら異なる基の窒素同位体不均質性は、当時の海洋酸化還元境界での著しい窒素循環を意味し、この循環は現世では見られない。すなわち「同位体」を「顕微鏡」として活用し19億年前独自の微生物生態系を具体化できた成功例である。これらの成果は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、石田章純提出の博士論文は、博士(理学)の学位論文として合格と認める。