

# Geochemical study of Mn and P in modern and Archean hydrothermal systems: its importance to activities of primitive microorganisms

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博士論文

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its importance to activities of primitive microorganisms

(現世・太古代熱水系におけるマンガン・リンの地球化学的研究：  
原始的な微生物活動の重要性について)

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## Abstract

Biological activities have greatly altered compositions of atmosphere, hydrosphere, and lithosphere on the Earth since the rise of first life around 3.8 Ga. Early biological activities have been studied intensively using bio-essential elements, such as carbon, nitrogen, oxygen and sulfur, which are majorly present in atmosphere and hydrosphere. However, biological activities are also essentially sustained by bio-essential elements whose major reservoirs are lithosphere, such as metals in enzymes and P (phosphorus). Consequently, their supply process from lithosphere, hydrosphere to biosphere have likely controlled biological activities through time. For example, Mn (manganese) and P are essential for cyanobacteria's activities, because "Mn cluster ( $Mn_4CaO_5$ )" is essentially used to split water into oxygen during photosystem II and P is an essential component of RNA and DNA. Yet, their transportations from lithosphere, hydrosphere to biosphere have not been certain in modern and Archean environments.

In modern ocean, continental weathering is known to be major process to transport P from lithosphere to hydrosphere. In addition, the following process from hydrosphere to biosphere have been well understood. On the other hands, large uncertainties exist for Mn leaching from lithosphere, and its mobility in hydrosphere and then to biosphere.

The Archean surface redox conditions were considered as different compared to those in modern Earth. The generally reducing surface environments might have caused different geochemical cycle of Mn. Many researchers consider that deficiencies of continental crusts also had limited P availabilities in the Archean oceans, and thus, limited biological productivities. On the other hands, P and Mn leaching from lithosphere to hydrosphere through submarine hydrothermal activities have not been studied.

In chapter 1, geochemical and mineralogical studies were conducted on Mn ores, which were formed by 12 Ma submarine hydrothermal activities in felsic volcanisms in

the Hokuroku district, Akita prefecture, Japan. The mobilization of Mn from submarine volcanic rocks during rock/water interaction and evolution of Mn species in hydrothermal fluids were understood. Non-biological and biological processes to precipitate Mn oxide and Mn carbonates were also evaluated. These results clarified Mn leaching from lithosphere, and its mobility from hydrosphere to biosphere in modern environments.

In chapter 2, metagenomic, geochemical and mineralogical studies were conducted for chemical precipitates and microbial mats at modern Mn-rich samples at Hachikuro or Mizusawa hot springs in Akita prefecture, Japan. Evidence of oxidation of soluble  $Mn^{2+}$  by Mn-oxidizing bacteria was obtained. Further, enzyme and Mn-oxidizing genes associated with Mn oxidation were specified. A series of metagenomic analyses robustly proved biologically mediated process oxidized Mn. It is also demonstrated that supply of elements from lithosphere stimulate activities of Mn-oxidizing bacteria.

In chapter 3, Mn and P mobilizations from early Archean oceanic basalts were examined. Investigations on Archean oceanic basalts revealed that it could be an important P sources through submarine hydrothermal activities, and P flux from the basalt into ocean sustained contemporary biosphere. Mn was also confirmed to be significantly leached from the basalt.

Combining these results revealed that supply process of Mn and P from lithosphere, hydrosphere to biosphere in modern and Archean environments. In particular, leaching elements from lithosphere has likely stimulate biological activities. Consequently, their elemental fluxes have played significant roles of biological evolution through time.