古原生代Hotazel Formationの縞状鉄鉱層およびMn堆積物の遷移金属元素分布

The spatial distribution of transitional elements of the BIFs and the manganese rocks in the Paleoproterozoic Hotazel Formation

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The body plan and metabolism of the organisms have evolved in response to the availability of the atmospheric oxygen throughout the earth history (e.g. Cloud, 1968). For example, it is generally thought that the evolution from the prokaryote to the eukaryote have been induced by the increase in the atmospheric oxygen around the Paleoproterozoic. On the other hand, all organisms are also dependent on the specific metals for some biological activities. And, it is well-known that the extent of the utilization for the metals is variable between the organisms with different strains (Willliams and Fraústo da Silva, 2003; Dupont et al., 2006). For example, all the prokaryotes use cobalt (Co) preferentially for the enzyme synthesizing the methionine (one of the essential amino acids). On the other hand, primitive eukaryote (e.g. algae) can use Zn in place of Co. Thus, it might be possible that the availability of specific metal elements in surface environments, as with oxygen, have influenced on the evolution of the organisms belonging to specific strains throughout the earth history (e.g. the evolution from the prokaryote to the eukaryote).
The compositions of chemical sedimentary rocks such as the banded iron formations (BIFs) could be proxies for the paleoseawater chemistry because they adsorbed the dissolved elements of the seawater into their constituent minerals at their depositions. For estimate of the bioavailability of the metal elements in the Paleoproterozoic ocean, we have analyzed the trace-element abundance of the geochemistry of the BIFs and interlayering manganese rocks in the *ca.* 2.4 Ga Hotazel Formation of the Transvaal Supergroup, South Africa.
Whole-rock chemical compositions of the BIFs and the manganese rocks show that Co, Ni and Zn are concentrated in Mn minerals in them, suggesting that those three elements were primarily adsorbed on Mn-oxyhydroxide phases like modern manganiferous deposits. Especially, Ni and Zn contents in them show a positive correlation with Mn contents. However, Co contents show an unclear-positive correlation with Mn contents over 20 wt% of Mn, and Mn-rich rocks (Mn > 20 wt%) have lower Co/Mn ratios than Mn-poor ones. The lower Co/Mn ratios in the manganese rocks suggest that dissolved Co contents in seawater were decreased at their depositions.
Moreover, the distribution mapping of the BIFs without Mn minerals shows that much of Co does not exist in Fe-oxide bands, suggesting that dissolved Co adsorbed on Fe-oxyhydroxide was limited in the Paleoproterozoic seawater. On the other hand, much of Co in the Archean BIFs analyzed for comparison distributes in the Fe-oxide bands.

The low Co/Mn ratios in the manganese rocks and the Co distribution of the BIFs suggest that there was limited Co reservoir in the Paleoproterozoic ocean, possibly due to Co-fixation by Mn oxyhydroxide minerals under oxic conditions.
This study suggest that the Paleoproterozoic ocean proliferated the Co-independent prokaryote, which can use Zn under Co-depleted environments. They became the direct ancestor of the primitive eukaryote, as shown by the molecular phylogenetic study of methionine-synthesizing enzyme (Helliwell et al., 2011).

キーワード：縞状鉄鉱層、Mn堆積物、生命必須元素
Keywords: banded iron formations, manganese deposits, bio-essential elements

