

Transitional-element compositions at whole-rock and micro scale of the Banded Iron Formations : Implications for secular variations of bioessential elements in the ocean and their influences on biological evolutions.

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It is generally thought that the surface environments have evolved from anoxic to oxic conditions throughout the earth history. The increase in oxygen of the atmosphere has provoked the evolutions of many genera and metabolic types. Especially, the increase in atmospheric oxygen around the Great Oxidation Event might have provoked the evolutions of the eukaryotic organisms in the Paleoproterozoic, which are more dependent on bioavailable oxygen (Albani et al., 2010; Han and Runnegar, 1992). On the other hand, all organisms are dependent on various transitional elements, which are used mainly for some metabolic coenzymes. The relative dependencies on the elements are different depending on their taxa and their metabolic types (Zerkle et al., 2005; Dupont et al., 2006). For example, prokaryotes are more dependent on Co than eukaryotes for synthesizing methionine, one of the essential amino acids (Dupont et al., 2006). Therefore, secular variations of transitional element compositions in seawater might have been influential on the biological evolutions.

Chemical compositions of the banded iron formations (BIFs) can be proxies for the chemical composition of seawater. In this study, we analyzed the transitional element compositions, especially for Co, of the BIFs from the Eoarchean to Paleoproterozoic at micro to whole-rock scales to estimate the secular variations of the bioavailabilities of those elements.

The Eo- and Mesoarchean BIFs show that whole-rock Co compositions are positively correlated with Fe contents, and not positively correlated with their Al, Ti and HFSE contents. Moreover, the elemental distribution mappings of the Mesoarchean BIFs show that the distribution of Co corresponds to Fe-rich bands. On the other hand, the Paleoproterozoic BIFs in the Hotazel Formation, South Africa, which are interlayered with manganeseiferous sedimentary rocks, show positive correlations of bulk Mn contents with Co contents. The micro-scale distribution mappings of elements in the Mn-poor BIFs, which have lower Co contents than the Eo- to Mesoarchean BIFs, show that the distribution of Co corresponds to not Fe-enriched bands but Al-enriched spots.

Positive correlations of Co with Fe contents in the Eo- and Mesoarchean BIFs at whole-rock and micro scale suggest that much Co in them is derived from adsorbed element on Fe oxyhydroxide in the contemporary seawater. On the other hand, the positive correlations between Mn and Co contents in the Paleoproterozoic BIFs and Mn rocks suggest that much of Co in them exists in Mn-oxide minerals. Moreover, the Co distribution in Mn-poor BIFs corresponding to Al-enriched spots indicates that Co in them is derived not from the seawater, but from the clastic materials. Therefore, bioavailable Co in the Paleoproterozoic ocean might be limited because divalent Co was fixed as insoluble trivalent forms within Mn-oxide minerals.

Cobalt is mainly used for cobalamin (vitamin B12), which is concerned with every metabolic activity in cell. For example, methylated cobalamin (Met H) catalyze the synthesis of methionine, which is an amino acid constituting the terminal domain of all proteins (e.g. Croft et al., 2005). Only prokaryote can

synthesize Met H from dissolved Co in aquatic environment, and depend more heavily on Co than eukaryotes (Dupont et al., 2006). On the other hand, a small group of prokaryotes and eukaryotes can use Zn-bearing enzyme (Met E) in place of Co, and they belong to a monophyletic group (Helliwell et al., 2011).

The decrease in bioavailability of Co during the period from the Mesoproterozoic to the Paleoproterozoic might have encouraged the prosperity of Co-independent prokaryotes, which were the ancestors to the eukaryotes.

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