

## The Archean hydrothermal alteration: Significance of silicification for seawater composition and biological evolution

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The earth is the active planet, where higher forms of life live. Presence of liquid water on surface of planet is necessary to organisms: thus a planet with the liquid water is called a habitable planet. But, enrichment in bioessential elements is also important because they are demanded for their activity. In addition, it is required that they are continuously supplied to biosphere through the elemental cycle. Especially, phosphate is one of the most important nutrients because the DNA and RNA contain large amounts of phosphate contents. Nickel is a bioessential element for methanogen, which was more active in early Earth. However, phosphorus, iron, and nickel are highly depleted in modern seawater because oxic modern seawater causes precipitation of iron oxyhydroxide, which effectively remove the phosphorus and nickel through their adsorption on iron precipitates. The evolution of seawater composition through geologic time accounts for the apparent paradox, namely ancient seawater was enriched in the phosphorus and nickel contents (Planavsky et al., 2010; Konhauser et al., 2009). But, the mechanism of high phosphorus and nickel contents in seawater is still ambiguous. This work presents silicification plays important roles not only on the supply of the phosphorus and nickel into seawater but also on preventing adsorption of the elements on iron hydroxide.

Comparison between major element compositions of modern altered and non-altered MORB (Alt & Honnorez, 1984) indicates present-day hydrothermal alteration increased phosphorus contents relative to titanium contents in the altered basalts because altered MORBs commonly contain over four times higher phosphorus contents than the fresh equivalents (e.g. Alt & Honnorez, 1984, CMP). Therefore, the hydrothermal fluid has relatively low phosphorus content. On the other hand, comparison between Archean altered and non-altered MORB indicates the Archean altered basalts contain relatively lower phosphorus contents than the fresh equivalents (Komiya et al., 2002, IGR, Nakamura & Kato, 2004, GCA). The different behavior of phosphate during the hydrothermal alteration of basalts suggests higher phosphate contents in the Archean hydrothermal fluids. In addition, silicified basalts in the Archean greenstone belts are completely depleted in phosphorus, indicating much amounts of phosphorus were supplied into seawater. Comparison between nickel contents of altered and non-altered basalts and peridotitic komatiites indicates the altered rocks are more enriched in nickel under the moderate hydrothermal alteration condition, contrast to previous hypothesis (Konhauser et al., 2009). However, silicified basalt and peridotitic komatiite are completely depleted in sodium, phosphorus and nickel except for potassium, indicating silicification effectively supplied nickel and others to ocean. It is considered that formation of banded iron formation caused effective removal of nickel and phosphorus from seawater. Especially, recent study of their rare earth element patterns, namely Y/Ho and Sm/Yb ratios, indicate iron oxyhydroxide were precipitated much more from seawater in the Early Archean, suggesting phosphorus and nickel were more efficiently removed from seawater. Higher silica content of seawater in the early Earth accounts for the apparent paradox. The high silica content of ancient seawater had a significant role of the preventing adsorption of phosphorus and nickel on iron oxyhydroxide as well as supplying more phosphorus and nickel to seawater at the hydrothermal alteration.

We propose that high silica contents of ancient seawater resulted in high phosphorus and nickel contents of seawater in the early Earth.

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