

Secular variation of redox condition of seawater and global glaciation, estimated from the composition of carbonate

Tsuyoshi Komiya[1]

[1] Earth & Planet. Sci., Tokyo Inst. Tech.

Redox state of seawater and atmosphere of early Earth is still controversial (e.g. Ohmoto, 1997; Yamaguchi & Ohmoto, 2006). Many previous works suggested that oxygen was free even in the shallow seawater before 2.7 Ga, and then gradually increased because of oxygen-producing lives (e.g. Holland, 1999; Farquhar et al., 2000; Kah et al., 2004; Rouxel et al., 2005). But, the detailed and quantitative estimate of the secular change is still poorly known. It is well known that carbonate minerals are deposited equilibrated with ambient seawater in microbial or abiotic environment. The composition and mineralogy allow us to estimate the physical and chemical properties of paleoseawater (e.g. Hardie, 2003). This work presents in-situ analyses of ME, TE and REE of carbonate minerals with primary sedimentary structures in shallow and deep-sea deposits through time. We estimated the depositional environments from field occurrence of coexisting basaltic lava and sedimentary rocks and fabric of carbonate themselves. The in-situ analyses eliminate secondary carbonate, contamination of detrital materials, diagenesis and alteration. We thermodynamically calculated oxygen content of seawater through the time at the given parameters.

The shallow marine deposits include sedimentary carbonates with stromatolite structure and clastic layers, and amygdaloidal and matrix carbonates of hot-spot basaltic lava since 3.5 Ga. The deep-sea carbonates include those within MORB-type basalts. In addition, we excavated at three localities in South China, and obtained the complete sequence from the Marinoan tillite to early Cambrian rocks. Ce anomaly of carbonate rocks in the sequence is highly fluctuated, concomitant with the carbon isotope. The sequence corresponds to recovery from global anoxic event related to the Marinoan glaciation, and subsequent oxidation of surface environment as well as the Cambrian explosion of life. Deep-sea carbonates have only faint Ce and Eu anomalies between 3.5 and 1.9 Ga. Negative Ce anomaly of shallow carbonates was frequently deviated from those of deep-sea carbonate since 2.78 Ga. It was highly fluctuated, and very high at 2.5 and 2.3 Ga. But, the anomaly decreased during/after the Huronian and Marinoan, probably also Sturtian glaciations. It implies the complicated secular change of redox state in shallow water, whereas deep-sea environment was anoxic until Proterozoic. We calculated oxygen activity of shallow and deep seawater respectively, based on the Ce concentration and anomaly of carbonate minerals at the given parameters of atmospheric carbon dioxide content and Ca ion concentration of seawater. The results show that oxygen content of deep sea was low and constant until at least 1.9 Ga, probably the Mesozoic, whereas that of shallow seawater increased since 2.7 Ga but was quite fluctuated. Especially, it minimized during/after Snowball Earth events. The oxygen activity became quite high at 2.5 and 2.3 Ga, but it eventually increased since the Phanerozoic. In addition, the oxygen content, calculated using different parameters of atmospheric carbon dioxide content, shows that calculation at the condition of high atmospheric carbon dioxide content (e.g. Kasting, 1993) results in higher oxygen content of seawater even in the Archean than at present. The calculation is consistent to relative low atmospheric carbon dioxide content through the geologic time (e.g. Sleep & Zahnle, 2001).

Farquhar et al., 2000, *Science*, 289, 756-758; Hardie, 2003, *Geology*, 31, 785-788; Holland, 1999, *The Geochemical News*, 100, 20-22; Kah et al., 2004, *Nature*, 431, 834-838; Kasting, 1993, *Science*, 259, 920-926; Rouxel et al., 2005, *Science*, 307, 1088-1091; Sleep & Zahnle, 2001, *Journal of Geophysical Research*, 106, 1373-1399; Yamaguchi & Ohmoto, 2006, *Science*, 311, 177a.