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The Late Archean diversity of organisms: evidence from morphology and in situ iron isotope analyses of pyrites in variou

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The timing of the emergence and flourish of oxygenic photosynthetic organisms is still controversial. However, it is one of the key issues of the biological evolution in early Earth. Reconstruction of redox state of the late Archean seawater is important for understanding the relationship between biological activity and oxygenation.

Ferrous and its compounds were one of the major reduced species in the anoxic Archean seawater. It is widely recognized that the iron isotopic ratio changes largely through redox reactions, especially oxygen limited environment (Beard and Johnson, 2004; Johnson et al., 2004). The iron isotopic ratio of marine sedimentary minerals is useful for understanding the ocean's redox state and iron biogeochemistry in the geological past (e.g., Johnson et al., 2008). Based on the detailed geological survey of the Fortescue Group in Redmont area, we carefully selected 44 samples, which include stromatolitic carbonate rock, sandstone, mudstone, and alternation of calcareous sandstone and mudstone. We analyzed d^{56}Fe value of 225 pyrite grains in these samples, and discovered an extremely large variation of d^{56}Fe value from -4.1 to 3.0 permil.

From the result of microscopic observation, we found the relationship between pyrite grain morphology and iron isotope ratio. Most of pyrite grains with the positive d^{56}Fe values show hexagonal, rectangle, and parallelogram shapes, which are consistent with crystal system of iron-oxides: hematite, magnetite, and goethite, respectively. In contrast, pyrite grains with the negative d^{56}Fe values show pseudo-hexagonal and irregular forms. The pseudo-hexagonal shape corresponds to a monoclinic system that is crystal system of pyrrhotite. The correlation allows the possibility to solve the origin and the formation process of each grain of pyrite. We estimate the d^{56}Fe value of seawater from the positive d^{56}Fe value pyrites in stromatolitic carbonate rock and experimental data of previous studies (Welch et al., 2003; Butler et al., 2005). Based on this estimation, we consider that the d^{56}Fe value of pyrite lower? than ?estimated d^{56}Fe value of sulfide was formed biologically. The quite low carbon isotope ratio of organic carbon with a nadir down to -47 permil indicates the activity of aerobic or anaerobic methanotrophy. On the other hand, the lowest d^{56}Fe value of the pyrite grain, -4.0 permil, indicates the biological iron-reducing: dissimilatory iron-reducing microorganism (DIR) or recently found iron-dependent AOM (AOM/IR). The co-occurrence indicates the oldest evidence for activity of the iron-dependent AOM. On the other hand, the d^{56}Fe values of pyrite grains in the mudstone layer of upper Mingah Member have relatively wide variation from -4 to +2 permil. The positive d^{56}Fe values suggest the partial oxidation of iron in oxygen limited surface environment. The $d^{13}C_{org}$ values are also lower than 40 permil. This suggests the presence of organic carbon from methanotrophs. Iron and carbon isotopes reveal the divergence of microorganisms in Late Archean shallow sea.

Keywords: pyrite, oxygen-producing photosynthetic bacteria, methanotrophy, stromatolite, iron reducing bacteria