# Toward a better understanding of trace element availability in Paleo-proterozoic seawater

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One of the large gaps between prokaryotic and eukaryotic lives lies in the utilization of trace elements in seawater. Eukaryotes have higher Cu and Zn requirements than prokaryotes; for example all eukaryotes have Cu-Zn-SOD (Superoxide Dismutase), whereas prokaryotes have Fe-Mn-SOD. Phylogenomic reconstruction suggested that above-mentioned protein structures evolved either concurrent with or after the emergence of the Eukaryotic domain. Therefore Cu and Zn would be two of the most likely trace metals to provide a geochemical barrier specific to eukaryotic evolution, and deficits of Cu and Zn in seawater have been hypothesized as one of the explanations for the delayed diversification of eukaryotes.

Previous works have tried to decipher a secular variation of marine Zn inventory based mainly on Zn concentrations in ancient sediments. They suggested that the amount of bio-available Zn remained relatively unchanged through time (Robbins et al., 2013; Scott et al., 2013), but stoichiometric assessment concerning removal process of elements during sedimentation still remains difficult. In order to quantitatively track secular variations of Cu and Zn availabilities in seawater, we adopted Cu and Zn isotopes of carbonate rocks and black shales, because these isotopes are expected to reflect marine inventories of each element.

Francevillian Group in Gabonese Republic was recently established as a typical sedimentary sequence for the Paleoproterozoic, and it contains macroscopic structures interpreted as colonial eukaryotic organisms. We hypothesize that these organisms might have evolved in concert with the oxidation of the atmosphere-ocean system and increases of marine Cu and Zn inventories at that time. Although Chi Fru et al. (2016) recently reported eight Cu isotopic ratios from sediments in the Francevillian Group, sequences round macroscopic structures have never been investigated. We collected some carbonate rocks and black shales from the Francevillian Group, and made thin sections from them. SEM-EDS analysis demonstrated that Cu and Zn are enriched in pyrite grains. Powdery samples were prepared by micro-drilling, and acid digestion was performed with aqua regia at 150 Celsius degrees for 48 hours. For isotopic analysis, Cu and Zn were purified using anion exchange on AG-MP-1M resin column. Bulk Cu and Zn isotopic ratio were obtained with a multi collector inductively coupled plasma mass spectrometry (NEPTUNE) at UC Davis. We will report the preliminary results in this presentation.

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