

Fe isotope fractionation during Fe(II) oxidation by cyanobacteria

TIMM BAYER¹, WENFANG WU¹, ANDREAS KAPPLER¹,
RONNY SCHOENBERG¹ AND ELIZABETH D. SWANNER¹

¹Department of Geoscience, University of Tuebingen
timm.bayer@student.uni-tuebingen.de

In Precambrian times, the chemistry of the Earth's oceans was characterized by anoxic and Fe(II)-rich conditions. Cyanobacteria, who inhabited these oceans, produced oxygen through oxygenic photosynthesis. Fe(II) rapidly reacts with oxygen at neutral pH to form poorly soluble Fe(III) iron (oxyhydr)oxides. Chemical Fe(II) oxidation by O₂ produced by oxygenic photosynthesis is one possible process that led to the production and deposition of Fe(III) minerals from Precambrian oceans, the so-called banded iron formations (BIFs). Fe isotopes in BIFs can be used to track Fe redox processes during deposition and diagenesis. However, there is currently no constraint on the Fe isotope fractionation imposed during Fe(II) oxidation by cyanobacteria. We therefore investigated the Fe isotope fractionation during growth in experiments with anoxic, Fe(II)-rich medium and the marine cyanobacterium *Synechococcus* PCC 7002.

We determined the Fe(II)/Fe(total) ratios and the Fe isotope compositions of different aqueous or solid fractions: 1) aqueous Fe(II) or Fe(III), 2) precipitated Fe(II) or Fe(III) minerals, and 3) Fe(II) or Fe(III) adsorbed to the minerals, organic phases, or in colloidal forms. Preliminary measurements showed a significant proportion of Fe(III) in the aqueous phase. Confocal laser scanning microscopy (CLSM) indicates that this dissolved Fe(III) could be stabilized via an association with exopolysaccharides (EPS). Fe isotope measurements indicate that this organically-bound Fe-fraction is isotopically lighter than precipitated Fe minerals.

Mössbauer spectroscopy indicates that the Fe(III) mineral precipitates are poorly crystalline. Synchrotron-based extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray total scattering are consistent with the presence of Fe(III)-organic species or colloidal Fe(III) oxyhydroxides. These results also show that Fe(III) is present in colloidal forms, possibly associated with extracellular polymeric substances (EPS), which can serve as a way to avoid cell encrustation by complexation. These data indicate a role for organically-complexed Fe in producing distinct Fe isotope fractionations during Fe(II) oxidation. These results may be useful in discerning the role of cyanobacteria in Precambrian Fe(II) oxidation and BIF formation.