

Abstract

Recognition of fossils in the Archean sedimentary rocks is essential to constraining when and how life evolved, and the nature of the microbial metabolisms present on early Earth. Unfortunately, preservation of microorganisms is very limited in the Archean rock record. Direct observations of Archean microfossils are not convincing, yet, indirect traces of metabolic activity are described as early as ~3.5 Ga in form of stromatolites. Stromatolites are laminated organo-sedimentary benthic structures formed by the activity of microbial communities. They represent the oldest archives of life on Earth. However, laminated structures have also been reproduced by abiotic experiments, undermining the biological origin of the ancient stromatolite specimens. This thesis work focuses on refining geochemical and isotope proxies that can be used to assess the stromatolite biogenicity. I investigated pyrite, a mineral that is ubiquitous in the stromatolite record. It is well demonstrated that in modern sediments specific microorganisms produce Fe^{2+} and H_2S that ultimately lead to the formation of micrometric pyrite. Over the course of microbial activity and mineral precipitation, both sulfur and iron exhibit large isotope fractionations. Iron is transformed to pyrite through various aqueous and mineral species in the environment through redox-sensitive processes. Therefore Fe isotopes are used in reconstructing paleoredox conditions, diagenetic processes and/or metabolic signatures. Consequently, this thesis (1) tests if iron isotope compositions of micrometric pyrite can be used as a biosignature and (2) assesses sensitivity of Fe isotopes in pyrite with respect to global redox changes. I used a spatially resolved secondary ion mass spectrometry technique (SIMS) to develop a new analytical protocol to investigate the Fe isotope variability in pyrite smaller than 10 μm . In this thesis, samples of different age (modern, Mesozoic and Archean) have been selected to reconstruct the iron isotope variations through time and to differentiate the global versus local environmental influences on the pyrite isotope compositions. Modern samples are two microbialites collected from two different environments. Spatially resolved S isotope analyses is employed via nanoscale secondary ion mass spectrometry (NanoSIMS) to document the large isotope ranges and its relationship to the pyrite morphology and the activity of sulfate-reducing bacteria. As one of the main findings of the thesis, Fe isotope compositions (from -3.5 to +3.5‰) measured on a micrometer scale are consistent with a microbially-mediated Fe-oxide reduction by Fe-reducing organisms. The studied here Mesozoic samples were deposited during the Smithian-Spathian boundary (SSB, ~251 Ma), an interval post-dating the end-Permian mass extinction event. According to multiple lines of evidence, the oceans experienced abrupt swings in redox state and temperature, all of which leading to a major biotic diversity crisis. During this period of major ecological stresses, microbial communities flourished leading to deposition of a rich stromatolite record. I measured eight samples deposited along a ramp system which revealed a wide Fe isotope range (i.e. ~7‰). The $\delta_{56}\text{Fe}$ values show a clear influence of the depositional environment and the nature of deposit, i.e. the presence of microbialite. The Fe 14 isotope compositions collected on the Archean Tumbiana stromatolites, displayed the widest range of $\delta_{56}\text{Fe}$ values measured in the entire Archean sedimentary pyrite record (i.e. -2.2 to +4.4‰). This exceptionally large isotope range is interpreted as the result of an intense local iron cycling within the microbial mat, including repeated cycles of partial oxidation and microbially-mediated reduction processes, related to biogeochemical carbon and sulfur cycles. All together, Fe isotope compositions of micrometric pyrite grains are likely to record synsedimentary and early diagenetic processes that occur within the sediment or in the biofilm. Importantly, the seawater column has a limited influence on the final $\delta_{56}\text{Fe}$ values of pyrite. The $\delta_{56}\text{Fe}$ values measured in pyrite highlight the intimate interaction between the local pools of Fe, O, C and S. The speciation and isotope compositions of these elements are affected by the microbially mediated cycling as well as the redox gradients created abiotically. Therefore, to better

understand the conditions of microbialite formation through geological time, it is critical to couple the Fe- and S-isotope measurements with detailed sedimentological and petrological studies.