Tracing Earth's Early Oxygenation by Synchrotron Element Mapping of Microbialites

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Introduction:

Oxygenation of surface environments during the Archean-Palaeoproterozoic (the Great Oxidation Event, GOE, around 2400 Ma[1]) was a fundamental prerequisite for all later biological evolution on Earth. This key event in Earth history was possible through the development of cyanobacterial oxygenic photosynthesis[2]. However, exactly when oxygenic photosynthesis evolved, and how it shaped the oxygenation of Earth's surface environments, is an on-going debate[1-3]. This study uses for the first time modern microbial structures (stromatolites) to determine if they record a trace metal (metallomics) signature of oxygenic photosynthesis. Such a modern baseline signature will then allow a test whether it can survive through geological time (Figure 1) and when photosynthesis evolved.

Microbial fabrics in rocks such as stromatolites provide a direct record of microbial consortia, including cyanobacteria, and can potentially trace oxygenation. Carbonate precipitation, which stabilizes and promotes lithification of the microbial mat[4-5], is a typical by-product of photosynthetic processes[6], and of heterotrophic degradation of cyanobacterial biomass[7]. As these consortia respond to changing oxygen levels, they incorporate vital trace elements, such as metals, into the cell structure and extracellular polymeric substances (EPS)[8]. Metals and their degradation potentially provide a tracer of an active photosystem[9-10], and this fingerprint can potentially survive over geological time (Figure 1).

Colleagues at SEES and Stanford University have developed Synchrotron Rapid Scanning X-Ray Fluorescence (SRS-XRF) methods for non-destructive mapping of the chemical composition within biological structures[11]. This allows high-resolution mapping of element concentrations, their oxidation state and coordination with organic carbon and sulfur. Pilots have demonstrated the technical feasibility of analyzing metal enrichment using SRS-XRF on modern mats and Archean stromatolites.

Study Aims:

Using an integrated textural and geochemical approach, the project will determine the geochemical pathways of key metals during formation and lithification of a microbial mat. This allows a test whether modern mats record a distinct photosynthetic signal, and to establish a modern baseline for the metallomic, genomic and proteomic record of oxygenic photosynthesis (Figure 1).

Project Summary:

While key metals do accumulate in a modern culture, no study has yet investigated the fate of metals during the early diagenetic mineralization and lithification of the organic matrix. The investigation therefore needs to characterize both organic and inorganic fractions; the focus will be on calcifying examples. This research requires natural calcifying samples where both a living mat, and partly lithified mats are present. Suitable sites have sufficient background alkalinity to promote calcification, such as continental tufa, karst streams[12], and hydrothermal/geothermal systems (e.g. Yellowstone, Italy[13]). Both are among the few natural systems to allow study of biofilm calcification and modern stromatolite formation[12]. Proteins (proteomics), organic and genetic analyses (genomics) will be added to metallomics to determine if the fingerprint is indeed related to oxygenic photosynthesizers.

The study will characterize the textural makeup of the mat, its microbial constituents and related inorganic minerals, as well as the biochemical processes linking these, via the following tasks:

- Establish the structural make up of the mat and textural relationships between the mat and inorganic minerals via petrographic analysis of standard thin sections, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and integration with hard part microtome sectioning of embedded mat samples, EPS and DNA staining, as well as laser scan microscopy. (Co-I's: Schroeder, Lloyd, Wogelius, Arp, Corella)
- Total organic carbon (TOC), stable isotopes (carbon, oxygen, sulfur) of (in)organic fractions as well as molecular analysis by (Pyrolysis) Gas Chromatography-Mass Spectrometry (Py-GC-MS), Liquid Chromatography Mass Spectrometry (LC-MS), and biomarker analysis will be used to identify microbial communities and biochemical reaction pathways between mats and inorganic minerals. Genome sequencing and amino acid composition analysis will support identification of the photosynthetic communities. (Co-I's: Buckley, van Dongen)
- Analyse pore water chemistry via spectroscopy for total alkalinity, main cations and anions (carbonate, nitrate, sulphate, methane) to assess whether any photosynthetically relevant metals accumulate outside of the mineral-mat framework. (Co-I's: Schroeder, Wogelius, Arp, Corella)
- Inorganic carbonate minerals promoting mat lithification can be related to microbial processes whose identification requires trace element analysis (via electron microprobe, EMPA) and stable isotope analysis. Carbonate $\delta^{13}C$ captures microbial influences on the local pool of dissolved inorganic carbon (DIC). (Co-I's: Schroeder, Arp, Corella)
- Once the textural and geochemical framework established, SRS-XRF, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Fourier Transform Infrared Spectroscopy (FTIR), and nano-Secondary Ion Mass Spectrometry (nano-SIMS) will produce high-resolution maps of chemical compositions. This will resolve the spatial distribution of photosynthetically relevant metals and form the basis for an assessment whether and where such a signal is preserved. (Co-I's: Bergmann, Wogelius)

The project provides training opportunities in a range of standard and innovative geochemical techniques, as well as in field techniques for sample collection. Collaboration between world-class researchers creates a multidisciplinary project with opportunities to work in different laboratories.

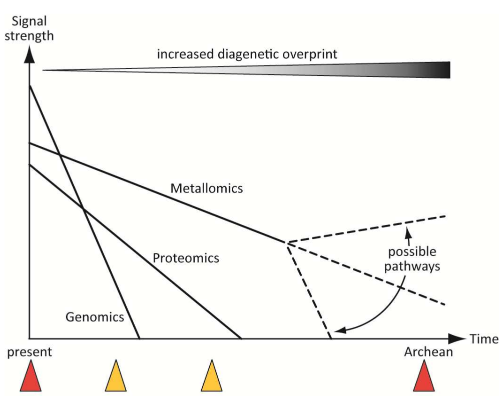

Figure 1: Schematic of the expected degradation of geochemical tracers for oxygenic photosynthesis. The red triangles represent existing pilots; the current study looks at the modern (baseline) signal. Future calibration points (orange) can be evaluated in follow-up studies to trace the degradation of geochemical signals.

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