

## **Metal Availability and the Evolution of Metabolism in the Archean Eon**

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Changes in redox conditions over the course of Earth's history, particularly due to global oxygenation, has influenced the availability of different metals and substrates that are central in biology. As a result, the coevolution of novel metabolisms unfolded, which incorporated different transition metals over geologic time. Oxidoreductase proteins are molecular nanomachines responsible for all biological electron transfer processes across the tree of life. The majority of these enzymes contain transition metals in their active sites, and such metals are critical for catalytic function. In this study we examine the geologic record for preserved biosignatures and redox changes with the goal of dating the approximate time of origin for specific metabolic pathways and their redox metal utilization in the Archean oceans.

We trace biosignatures for sulfur reduction, sulfate reduction, methanogenesis and anoxygenic photosynthesis at approximately 3.8 to 3.4 Ga. Hydrogen metabolism is assumed to be central among these pathways. Readily available metals in the Archean ocean were employed in the oxidoreductases driving these metabolisms, including iron sulfur clusters and hemes. Linked with expanded use of transition metals, reliable biosignatures of nitrogen fixation, oxygenic photosynthesis, methane oxidation and nitrification/denitrification appear between 3.2 to 2.5 Ga. Of specific interest, the exploitation of copper preceding the Great Oxidation Event (GOE), allowed access to higher redox potentials and greater substrate specificity.

Big data mineralogy and protein structure network analysis are being pursued to find further links between the coevolution of the geosphere and biosphere. The distribution of oxidoreductase metal ligands shifted among metabolically representative microbial taxa through deep time, indicating that Earth surface redox state and metal incorporation influenced the evolution of metabolism, biological electron transfer and microbial ecology.