

Isotopic evidence for internal oxidation of the Earth's mantle during accretion

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The Earth's mantle is currently oxidised and out of chemical equilibrium with the core. Why this should be the case, and why the Earth's mantle should be oxidised relative to other terrestrial planets is poorly understood. It has been proposed that the oxidised nature and high ferric iron (Fe³⁺) content of Earth's mantle was produced internally by disproportionation of ferrous iron (Fe²⁺) into Fe³⁺ and metallic iron by perovskite crystallisation during accretion [1]. Here we show that there is a substantial Fe isotope fractionation between experimentally equilibrated metal and perovskite, which can account for the heavy Fe isotope compositions of terrestrial basalts relative to equivalent samples derived from Mars and Vesta [2,3] as the latter are too small to stabilise perovskite. Mass balance calculations indicate that all of the mantle's Fe³⁺ could have been generated from a single disproportionation event, which is consistent with complete dissolution of perovskite in the lower mantle during the Moon-forming giant impact. The similar Fe isotope compositions of terrestrial and lunar basalts [2,3] is consistent with equilibration between the mantles of the Earth and Moon in the aftermath of the giant impact [4] and suggests that the heavy Fe isotope composition of the Earth's mantle was established prior to, or during the giant impact. The oxidation state and ferric iron content of the Earth's mantle was therefore plausibly set by the end of accretion, and is decoupled from later volatile additions [5], tectonic plate recycling and the rise of oxygen in the Earth's atmosphere at 2.45 Ga [6].

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Characterization of elemental sulfur reducing bacteria using transmission electron microscopy and their impact on sulfur isotope fractionation

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The process of elemental sulfur (S⁰) reduction by a microorganism isolated from an acetate-stimulated aquifer at the Department of Energy's Rifle Integrated Field Research Challenge (IFRC) site in Rifle, Colorado (USA) was studied using a combination of transmission electron microscopy (TEM) and isotopic techniques. Results were compared to those obtained using the well-characterized S⁰ reducer *Geobacter sulfurreducens*. The site isolate was obtained from Rifle groundwater using acetate and S⁰ flowers as the electron donor and acceptor, respectively. Based on 16S rRNA analysis, the isolate was most closely related to the β -proteobacterium *Azospira orzyae* (syn *Dechlorosoma suillum*). TEM revealed the isolate to be a curved rod with a single polar flagellum. Finely particulate S⁰ granules (<5nm) were observed along the outer membrane as aqueous sulfide concentrations reached peak values of ca. 1200 μ M. Prolonged growth resulted in an abundance of aggregated filaments bound within a sulfur-rich matrix; their biogenesis and relation to cell growth remains unknown. Microbial reduction of S⁰ coupled to oxidation of acetate may lead to significant deviations in the $\delta^{34}\text{S}$ values of sulfide relative to $\delta^{34}\text{S}$ values of S⁰.

Such studies are critical for understanding the process of sulfur reduction in reduced environments, hypothesized to enable prolonged U(VI) immobilization at the Rifle IFRC site. Research at the site has identified significant accumulation of S⁰ accompanying oxidation of aqueous sulfide by Fe(III)-oxide minerals, with the process generating an abundant electron acceptor capable of supporting the activity strains implicated in enzymatic U(VI) reduction (e.g. *Geobacter*) following exhaustion of reactive Fe(III) minerals. These results will enable incorporation of rates of microbial S⁰ reduction and $\delta^{34}\text{S}$ fractionation within reactive transport models describing biogeochemical processes at the Rifle site and provide additional insights into sulfur cycling pathways.