

TITLE

The Archean origin of assimilatory sulfate metabolisms provides novel insight into redox conditions and early Earth environments

ABSTRACT

Dissimilatory sulfur metabolisms recording differing biological isotopic fractionation are well studied, important components of sulfur cycling (Mateos et al., 2023). Assimilatory sulfur metabolisms and genes across life provide a complementary window into sulfur biogeochemistry with individual pathways having specific isotopic fractionations acting on distinct redox states (e.g. sulfate, sulfide, sulfite) for anabolism (Liu et al., 2012). An assimilation pathway exists, which starts with sulfate adenylyltransferase (sat/ATP sulfurylase) catalyzing a reaction of adenosine triphosphate (ATP) and sulfate (SO_4^{2-}) resulting in adenosine 5'-phosphosulfate (APS), and incorporation of more reduced sulfur into biomolecules. This sat/ATP sulfurylase enzyme represents the first step required by life to incorporate sulfur and informs our understanding of biological processes performing this fundamental chemical reaction. A phylogenetic and molecular clock analysis of the sat/ATP sulfurylase gene family (E.C. 2.7.7.4) was performed to determine the age of sulfate assimilation. Extant diversity of sat proteins was estimated to have a last common ancestor ~ 3.6 Ga (95 % CI 3.9-3.5 Ga) using relaxed molecular clocks calibrated with eukaryotic and microbial groups with previously determined fossil calibrated age ranges. These results suggest sulfate cycling in Archean environments, despite extensive evidence of low marine sulfate concentrations (Crowe et al 2014). Archean sulfate biogeochemical cycling could result from microbial sulfur oxidation and sources could include abiotic oxidation of volcanic sulfur, hydrothermal processes or pyrite (Canfield 2001, Lyons et al 2024). This phylogenomic evidence of sulfate during Archean times provides an independent complement to geochemical records and allows insight into environmental niches and redox potentials.