

Iron isotope evidence for the emergence of dissimilatory iron-reducing bacteria in the early history of the Earth

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Evolution of the Archean biosphere remains a first-order problem in studies on the evolution of the Earth. Evidence from molecular phylogeny suggests that photosynthesis evolved quite early in Earth's history. Biomarker evidence also suggests that organisms related to cyanobacteria, (oxygenic photosynthesizers) evolved by at least 2.7 billion years (Gyr) ago. It has also been proposed that, on the basis of molecular phylogeny, dissimilatory Fe(III) reduction (DIR) may have been one of the earliest forms of respiration on Earth, preceding other important respiratory processes, such as sulfate reduction, nitrate reduction, and oxygen reduction. Although such a view is consistent with known phylogenies of extant organisms, it is impossible to prove without corroborating geochemical evidence that provides a time line for the process. The possibility that DIR occurred early in Earth's history is particularly important because of its implications for the chemical and redox evolution of the early Earth. If little Fe(III) existed on the early Earth, an Fe(III)-reductase would not have functioned because there would be no advantage in assimilatory and dissimilatory metabolism of Fe (or other metals) to sustain life. Specific metabolisms can sometimes produce unique isotopic fractionations of essential elements, such as C, H, N, and S, that may be detected in the rock record. The main objective of this study, therefore, is to examine if the evidence for early emergence of DIR can be found in Fe isotope ratios of Archean sedimentary rocks.

We report the finding of very low $^{56}\text{Fe}/^{54}\text{Fe}$ ratios ($d^{56}\text{Fe} = -2.5$ to $+1.0$ per mil) in organic carbon- and magnetite-rich shales of 2.9 - 2.6 Gyr age, which suggests that the significant fractions of Fe $^{2+}$ -bearing minerals (siderite, magnetite, and pyrite) in these rocks formed by reduction of Fe $^{3+}$ -(hydr)oxides (goethite and hematite). Dissimilatory Fe $^{3+}$ reduction is the most likely explanation for such low $d^{56}\text{Fe}$ values, suggesting it was a significant form of respiration since at least 3 Gyr ago. Important implications emerging from our discovery include that Fe(III), the oxidized form of Fe, was readily available for the activity of dissimilatory Fe(III)-reducing bacteria since at least 3 Gyr ago. However, the processes that produced Fe(III) in the surface environments of the Earth 3 Gyr ago are currently unconstrained.

This study is a collaborative work with Clark Johnson (Univ. Wisconsin - Madison), Brian Beard (Univ. Wisconsin - Madison), Kenneth Nealson (Univ. Southern California), and Hiroshi Ohmoto (Penn State Univ.).