

## Using conductivity to measure Iron reduction rates from flask to field

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Researchers at several field sites have noticed anomalous electrical conductivity signatures associated with organic contaminant plumes. It has been hypothesized that signals at these sites are at least in part being generated by bacterial dissimilatory metal reduction. The waters in and around organic contaminant plumes have been shown to quickly become anoxic due to bacterial activity. This creates an ideal situation for the use of metal oxides as terminal electron acceptors in biogeochemical redox processes. Since iron oxides are one of the most abundant and readily utilized metal oxides we have focused our work on dissimilatory iron reduction. We present laboratory data that demonstrates the possibility of quantifiably monitoring iron reduction reactions via changes in fluid conductivity. We conducted three separate lab experiments increasing in complexity from abiotic iron reduction with ascorbic acid to in vitro iron reduction using total membrane fractions (TM) from *Shewanella oneidensis* MR-1 and ending with in vivo iron reduction using whole cells. We varied the concentration of electron donor in order to vary the reaction rate. Abiotic reduction of goethite with 0.01M ascorbic acid produced a 26% increase in conductivity (53  $\mu$ S/cm) and 69  $\mu$ M Fe(II) over the course of a five hour experiment. *In vitro* experiments with TM and 0.01M sodium formate produced a 70  $\mu$ S/cm increase in just one hour and much larger concentrations of Fe(II) (647  $\mu$ M). However, much of this iron adsorbed onto the TM and goethite surfaces and did not contribute to changes in conductivity. Whole cell experiments exhibit similar increases in conductivity from background to 50  $\mu$ S/cm in the first hour. We use stoichiometrically balanced master equations to model concentrations of conductive and non-conductive species as indicated by conductivity measurements. Furthermore, the rates of conductivity increase in each system are used to obtain model reaction rates. The use of conductivity to quantify reaction rate in flask experiments is then applied to reactions occurring in the Cape Cod aquifer system.

## Thallium isotope constraints on early Cenozoic climate change

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The thallium (Tl) isotope composition of seawater, as inferred from Fe-Mn crusts, exhibits a sharp 6  $\epsilon$ -unit increase between 60 and 40 Ma and has subsequently remained relatively constant [1]. This record is remarkably similar to the seawater sulphur isotope curve for the same period [2]. Possible causes for the observed 5‰ increase in the S isotope composition of seawater include the termination of North Atlantic volcanism in the early Eocene and a substantial increase in the burial of marine pyrite [2, 3].

Thallium is a highly volatile element, such that up to 45% of dissolved Tl in the oceans may be derived from subaerial volcanism [4]. If volcanic Tl furthermore were to be isotopically lighter than other source fluxes, declining volcanic inputs could account for the observed change in the seawater Tl isotope curve at 60 to 40 Ma and provide new constraints on the effect of volcanism on the sulphur isotope composition of seawater. To explore this hypothesis, we have analysed the Tl isotope compositions of volcanic aerosols from six volcanoes.

Quiescent volcanic emissions are highly enriched in Tl but the Tl isotope compositions are generally similar to the mantle, continental crust, and other marine input fluxes [5, 6]. When incorporated into a model that tracks the evolution of oceanic Tl, changes in volcanic activity therefore cannot explain the observed variations in the Tl isotope composition of seawater. A decrease in the overall input of Tl from 60 to 40 Ma can reproduce the isotopic shift but this also requires a large reduction in the proportion of Tl that is deposited in oxic pelagic sediments relative to mass fraction that is removed by low-temperature alteration of ocean crust, which dominates Tl removal from the modern ocean.

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