Identifying and quantifying the intermediate processes during nitrate dependent Fe(II) oxidation

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Anaerobic nitrate-dependent Fe oxidizing (NDFO) bacteria are thought to play a role in the generation of Fe minerals in systems low in other oxidants such as Mn(IV) and nitrite. However, the details of the processes involved in NDFO remain controversial as contradictory results in the literature have failed to resolve whether NDFO bacteria utilize an unknown enzymatic process or reactive intermediaries abiotically oxidize Fe(II). Therefore, this study was aimed at deciphering the relative contributions of NDFO-driven and abiotic processes to the oxidation of Fe(II). Three separate Fe mineral transformation pathways were investigated along with the fate of metal(loids).

First, literature data from growth experiments using the NDFO bacteria *Acidovorax* strain BoFeN1 were used to develop and constrain numerical models and to assess the plausibility of different conceptual models. Dedicated column experiments were then performed with sand or Fe(III)-oxide coated sand inoculated with pure or cocultures of BoFeN1 and/or other bacteria. Each column was designed to understand Fe mineral transformation pathways driven by (i) dissimilatory nitrate reduction, (ii) dissimilatory Fe reduction, and (iii) NDFO using groundwater amended with aqeuos Fe(II) and nitrate. Dissolved arsenic (As) and zinc (Zn) were introduced into the columns, and the evolution of effluent composition was determined to understand the fate of contaminants.

All sand columns produced goethite and ferrihydrite irrespective of bacteria used for inoculation, while only BoFeN1 columns produced minor amounts of green rust. Fe(III)-oxide coated sand colums differed in mineralogy, with magnetite forming in both the pure BoFeN1 culture and coculture with an Fe reducer. In all cases As and Zn were effectively removed from solution through adsorption and/or coprecipitation.

Reactive transport modelling was used to quantify the biogeochemical processes responsible for the Fe mineral formation and metal(loid) immobilization on the basis of initial conceptual and numerical models where development was guided by literature data.