Effects of microbial iron oxide reduction on pH and alkalinity in anaerobic bicarbonate-buffered media: implications for metal mobility

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The iron cycle in aquatic environments involves the reduction of ferric iron (Fe(III)) followed by the oxidation of ferrous iron (Fe(II)). Under natural conditions these reactions are microbially catalyzed. The reduction of Fe(III) is thought to be one of the most important microbially mediated processes in aquatic systems. Fe(II) tends to be soluble and mobile in water, while Fe(III) tends to form insoluble oxyhydroxides and remain immobile. Iron oxides have high surface areas and adsorption capacities and are therefore effective scavengers of trace metals. However, the adsorbed trace metals can be released upon reduction of Fe(III) phases (Chapelle, 1993), which may be catalyzed due to the action of dissimilatory Fe(III)-reducing bacteria and dissimilatory-sulphate reducing bacteria present in anaerobic sediments (Lovley, 1991). Much of the Fe(II) and trace metals that are released upon reduction do not enter the aqueous phase, but are instead sequestered as metal oxides, carbonates, and iron bearing sulphides.

Another interesting aspect of microbially mediated Fe(III) reduction is its possible affect in the carbonate cycle. The reduction of Fe(III) by microorganisms via organic matter oxidation can potentially increase the alkalinity of the system through the production of HCO^{-}_3 and OH^- . The increase in alkalinity can cause authigenic carbonate mineral precipitation by increasing the degree of water saturation with respect to carbonate phases (Coleman *et al.*, 1993). Roden and Lovley (1993) showed the precipitation of $FeCO_3$ during growth of Fe(III)-reducing bacteria in a bicarbonate-buffered medium.

Recent studies have shown that precipitation of carbonate mineral phases can directly contribute to the immobilization of dissolved trace metals and radionuclides present in subsurface and groundwater systems (Thompson and Ferris, 1990). The potential exploitation of this immobilization concept has relevance to development of new clean-up technologies to be used at contaminated sites where Fe(III)-oxide phases are abundant. To better understand geochemical processes operating in such an environment, the exact nature of pH, alkalinity, and dissolved inorganic carbon (DIC) changes due to Fe(III) reduction must be thoroughly quantified.

The objectives of this study were to (1) determine how quickly and to what extent microbial reduction of Fe(III)-oxides change pH, alkalinity, and DIC in both natural and synthetic Fe(III)-oxide media, and (2) to compare the effects of carbonate precipitation induced by microbial Fe(III)-oxide reduction on the distribution and speciation of two metals (Ca^{2+}, Sr^{2+}).

Methods

Media Preparation. Media for Fe(III)-oxide reduction experiments consisted of NH_4Cl, KH_2PO_4, and a mixture of vitamins and minerals (described by Lovley and Philips, 1998) in a dilute 2–10mM HCO_3^- buffer adjusted to an initial pH of 6.8. Synthetic amorphous ferrihydrite (HFO), produced in the laboratory, and natural Fe(III)-oxide sediments, obtained from a freshwater riparian wetland, were used as experimental substrates. Media was spiked with Sr^{2+}as $SrCl_2$ and, in some cases, Ca^{2+}as $CaCl_2$. Incubation experiments were initialized by inoculating media with pure cultures of the anaerobic and facultative dissimilatory iron-reducing bacteria *Geobacture metallireducens* and *Shewanella alga.* In two separate incubations involving *S. alga*, 50mM HEPES buffer was added to the media. All incubation experiments were performed in duplicate.

Sampling and Analysis. Samples for pH, whole vs.

porewater DIC, $Fe(II)_{(aq)}$, and 0.5N HCl-extractable Fe(II) were taken over time during incubations. All sampling procedures and measurements were conducted inside a Coy products anaerobic chamber. Aqueous concentrations of Ca^{2+}, Sr^{2+}, and Fe^{2+} were determined by inductively coupled plasma emission spectroscopy, while solid-phase metal concentrations were determined from 0.5 N HCl extractions using the Ferrozine technique. X-ray diffraction and scanning electron microscopy were used to determine major and minor mineral phases present in experimental products. Solute speciation and mineral saturation indices were calculated using MINTEQA2.

Results and discussion

Significant reduction of both natural and synthetic Fe(III)-oxides occurred in each of the incubations involving *G. metallireducens*. Approximately 15–35% and 95.6% of the total Fe was reduced in HFO and natural Fe(III)-oxide sediments, respectively. Even higher Fe(III) reduction levels were accomplished by *S. alga*, which reduced roughly 64% and 98%, respectively, of the total Fe present in HFO and the natural Fe(III)-oxide sediment. Significant pH increases were observed in all *G. metallireducens* incubations, providing a strong positive correlation (r^2 = 0.93–0.95) between the amount of $Fe(II)_{total}$ produced and the resulting/observed pH increase. There were significant increases in DIC throughout the course of each incubation. Incubations involving the reduction of HFO by *S. alga* showed variations in the amount of whole vs. porewater DIC on the order of 5–8mM in the HCO_3^- and HEPES+HCO_3^- buffered systems. Minor (0.5–1 mM) differences were observed between whole and porewater DIC concentrations in incubations involving reduction of natural Fe(III)-oxide sediment by *S. alga*.

Calculated log IAP values indicated that the observed increases in DIC and $Fe(II)_{(aq)}$, together with increases in pH, were sufficient to cause the aqueous phase to become supersaturated with respect to $FeCO_3$, $CaCO_3$, and $SrCO_3$ in incubations spiked with 0.5–1 mM Sr^{2+} and 1–10mM Ca^{2+}. The lack of major declines in DIC and aqueous metal concentrations argued against significant metal-carbonate formation despite the saturation index values obtained. SEM coupled with EDX analysis of solid-phase material provided evidence for the presence of $FeCO_3$ in incubation experiments involving reduction of HFO by *S. alga*. However, no SEM or XRD evidence was obtained for the presence of solid-phase carbonates in natural Fe(III)-oxide sediment experiments.

The fate of the Fe(II) produced during Fe(III) reduction may play a significant role in controlling solution alkalinity, pH shifts, and subsequent carbonate mineral formation. In all incubations < 20% of the total Fe(II) produced was accounted for by $Fe(II)_{(aq)}$, indicating that the majority of the Fe(II) was partitioned as some type(s) of solid-phase. Formation of Fe(II) surface complexes and/or surface precipitates on Fe(III)-oxides may have attenuated pH increases by consuming OH^- alkalinity during microbial reduction. Another effect of Fe(II) surface complex/precipitate formation would be to remove much of the Fe(II) from solution, thereby preventing the formation of $FeCO_3$. Due to high SiO_2 concentrations in the media, it is likely that the formation of Fe(II,III)-silicate phases occurred during the incubations.

Finally, the amount and rate of Fe(II) production may be a very important factor in determining the extent of, or potential for, $FeCO_3$ formation. An extremely high rate of microbial Fe(III) reduction, producing large quantities of soluble Fe(II), may be required to force the experimental system to produce carbonate solid-phase material at a detectable level. The rate of Fe(III) reduction in the above incubations may simply have been too slow for the formation of large quantities of carbonate phases. Over a much longer time frame (years) and under the appropriate conditions, significant microbial reduction of Fe(III)-oxides could be an important factor in the generation of carbonate minerals. However, these experimental incubations have provided evidence for the formation of carbonate solid-phase minerals, over a short time span (months), as the direct result of organic matter oxidation via microbial Fe(III)-oxide reduction.

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