Co oxidation by Mn oxide produced by a Mn-oxidizing bacterium

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Biogenic Mn oxide has attracted many geochemists and microbiologist in terms of the ability to highly adsorb and oxidize various trace elements. Cobalt 60 is one of the important radionuclides released from radioactive wastes. In this study, therefore, we studied Co oxidation by Mn oxide produced by a Mn-oxidizing bacterium.

A Mn-oxizing bacterium was isolated from stream water using agar plates of HEPES-buffered AY (HAY) medium with 1 mM $MnSO_4$ [1]. The bacterium was identified as *Pseudomonas* sp. by analysis of 16S rDNA. When *Pseudomonas* sp. was cultured in HAY liquid medium containing 1 mM Mn^{2+}, almost all the Mn^{2+} added was removed from the medium after 3 or 4 days due to Mn (II) oxidation. As a result, dark brown precipitates of Mn oxide were formed around cell surfaces.

For sorption experiments of Co, *Pseudomonas* sp. was cultured in HAY liquid medium with and without 1 mM Mn^{2+} to harvest biogenic Mn oxide and bacterial cells, respectively. Sorption experiments of Co on cells and biogenic Mn oxides were made in 10 mM NaCl solution containing 20 µM Co at pH3 and 6. Oxidation states of Co sorbed on the cell surfaces and Mn oxides were determined using XANES [2].

Cobalt K-edge (7.709 keV) XANES spectra showed that Co sorbed on cell surfaces was divalent at pH3 and 6, suggesting that Co oxidation does not occur during sorption process on bacterial cells. On the other hands, XANES spectra of biogenic Mn at pH3 and 6 indicated Co (II) oxidation to Co (III) by biogenic Mn oxides at pH3 and 6. Trivalent Co is highly insoluble relative to Co (II). Consequently, Co oxidation strongly affects the behavior of Co in natural environments. In particular, Co oxidation by biogenic Mn oxide contributes to retardation of migration of radioactive Co (i. e ^{60}Co).

[1] Miyata *et al.* (2006) *Appl. Environ. Microbiol.* **72**, 6467–6473. [2] Takahashi *et al.* (2002) *Chem. Lett.* **31**, 366–367.

Simulating reactive transport of Cobalt-EDTA complexes through large intact sediment cores

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While the predictive capability of empirical models is limited, application of comprehensive geochemical models is constrained by insufficient data, characterization, and understanding of mechanisms. We developed a model with oxidation and sorption reactions to describe transport of Co $(II)EDTA^{2+}$ through eleven large intact Hanford sediment cores under unsaturated conditions [1].

By comparing the results of models with equilibrium and kinetic sorption reactions, we found that the sorption reactions are equilibrium under a variety of saturations and flow rates, and the nonlinear least squares statistics are useful in evaluating whether a reaction is kinetic or equilibrium. The estimated sorption reaction rates suggest little to slight retardation for Co $(III)EDTA^{+}$, and moderate retardation for Co $(II)EDTA^{2+}$. The oxidation reaction rate was estimated to be $10^{5.3}$ $(mol/L)^{-2}$ for four cores with more fine materials, and $10^{6.5}$ $(mol/L)^{-2}$ for the rest. In contrast to [4], where the estimated oxidation rates varies with velocities and initial concentrations, our oxidation rates and the retardation factors are similar to that for an intact saprolite core from TN [2].

The MnO_2 initial concentration was estimated to be much less than the extractable MnO_2 [1], indicating only a small percentage of the MnO_2 is reactive to Co $(II)EDTA^{2+}$ [3]. Because this model is sensitive to intial MnO_2 concentration, which is similar in many geochemical model applications, uncertainty in independent determination of the concentration of initial reactants appear to be one of the major factors limiting the predictability of geochemical models.

[1] Mayes *et al.* (2009) *SSSAJ* **73**, 1938–1946. [2] Gwo *et al.* (2001) *Comp. & Geosci.* **27**, 1231–1242. [3] Jardine & Taylor (1995) *Geochimica et Cosmochimica Acta* **59**(20) 4193–4203. [4] Saiers *et al.* (2000) *WRR* **36**(11) 3151–3165.