### 4.2.14

# Effect of the siderophore Desferrioxamine-B on the mobility of Pd

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Use of the platinum-group elements (PGE) has increased considerably in the last few decades. Whereas the PGE used in the automotive industry in catalytic converters (Pt, Pd, Rh and Ir) have benefited the environment in reducing polluting gas emissions, a significant increase in the particulate matter concentration of PGE in roadside and urban dusts due to attrition from catalytic converters is causing a growing environmental concern. Whereas the mobility of the PGE in the environment remains poorly understood, there are indications that they are bio-available and toxic. The solubility of palladium is low under ambient conditions in dilute, organic ligand-free waters of pH values typically encountered in soils (4 to 9). However, PGE mobility in the environment may be increased by the presence of strong chelators, such as siderophores. Desferrioxamine-B (DFO-B), one of more than 200 identified naturally-occurring siderophore compounds, is a common trihydroxamate siderophore secreted by some aerobic micro-organisms. Estimates in the literature based on linear free energy relationships suggest that DFO-B could form very strong complexes with Pd. For this study, we conducted two series of experiments aimed at determining the potential for palladium transport in the environment by DFO-B. In the first series of experiments, amorphous Pd(OH)<sub>2</sub> was reacted with DFO-B solutions ranging in concentration from 0 to 1000 micromole/kg H<sub>2</sub>O at a pH of 8 and an ionic strength of 0.1. In the second series of experiments, equilibrium was approached from supersaturation by titration of a Pd solution in solutions containing 500 micromolal DFO-B at pH values of 5, 6, 7 and 8. Our experiments show that there is a substantial increase in the solubility of Pd in aqueous solutions in the presence of DFO-B relative to the system Pd-O-H-Cl-P-(Na, K). During dissolution of Pd(OH)<sub>2</sub>(am), the Pd concentration in a 1000 micromolal DFO-B solution at pH 8 and I=0.1 increases to > 240 times the value for a solution without DFO-B after 5000 hours. The initial rate of dissolution of Pd(OH)<sub>2</sub>(am) also increases systematically with increasing DFO-B concentration. In the second set of experiments, the molar ratio Pd/DFO-B=0.7 at saturation and pH 7, indicating strong complexing. Our results show that the effect of siderophores may need to be taken into account in models of the behavior of the PGE in the near-surface environment. This has important implications for both exploration and environmental geochemistry.

### 4.2.15

## Adsorption of heavy elements by *Pseudomonas fluorescens* cells in the presence of desferrioxamine siderophore

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#### Introduction

Siderophores, produced by microorganisms to access insoluble Fe(III) for iron uptake, are known to form complexes with heavy elements, such as rare earth elements (REEs) and actinides, and then change their solubility. We conducted adsorption experiments of heavy elements using *Pseudomonas fluorescens* cells in the presence of trihydroxamate siderophore, desferrioxamine B (DFO) in order to elucidate the influence of siderophores on the migration of heavy elements in the environment.

#### Experimental

In the first experiment, twenty micromolar Eu(III)-, Hf(IV)-, Pu(IV)-, and Fe(III)-DFO complexes were incubated with *P. fluorescens* cells at pH 7.1. In the second one, adsorption of 1.0 mg/L REE each (La, Ce, Pr, Nd, Sm Eu, Gd, Tb, Dy, Ho and Er) by *P. fluorescens* cells in the presence of 0.5 mM DFO was also examined at pH 7.1. In both experiments, concentrations of metal ions in supernatants were measured after separating the cells by centrifugation. **Results and discussion** 

In the first experiment, Eu(III) was adsorbed on *P*. *fluorescens* cells. On the other hand, adsorption of Fe(III), Hf(IV), and Pu(IV) on *P*. *fluorescens* cells was negligible. Adsorption of DFO was not commonly obserbed.

In the second experiment, the amount of REEs adsorbed on *P. fluorescens* cells decreased with an increase of the atomic number of REEs except Ce.

From these experiments, it was elucidated that the adsorption of heavy metals on *P. fluorescens* cells in the presence of DFO increases in the order Fe(III) = Hf(IV) = Pu(IV) < Eu(III) < La(III), which is in accordance with the order of the stability constants of the metal-DFO complexes. No adsorption of DFO indicates that the adsorption of metals from DFO. X-ray absorption near edge structure (XANES) analysis showed that the Ce in DFO complex was in tetravalent state, resulting in the lower Ce adsorption on *P. fluorescens* cells, compared to that of the neighboring trivalent REEs.