The effect of organic ligands on the mobility of the PGE in soils and natural waters: Implications for exploration and the environment

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The PGE have become a potential environmental concern owing to attrition from catalytic converters and other industrial emissions. There is evidence that the PGE are both bioavailable and toxic. The degree to which the PGE are bioavailable and/or toxic depends to a large extent on their mobility in aqueous media. The degree of mobility of these elements also has implications for the use of geochemistry in the exploration for new PGE resources.

In most natural waters, the predominant inorganic PGE species are hydroxide complexes such as $Pd(OH)_2^0$, yielding relatively low solubilities. Naturally occurring organic ligands such as simple carboxylate anions (e.g., acetate, oxalate, etc.) and humic and fulvic acids have been implicated in PGE mobility in the surface environment in many published field-based studies. We also suggest that siderophores (natural organic ligands secreted by microbes and plants to solubilize nutrient iron) may increase the mobility of PGE, based on published Linear Free Energy Relationships which indicate that siderophores may bind Pd as strongly as Fe. Solubility and spectroscopic investigations show that monocarboxylate anions such as acetate are not likely to increase significantly the mobility of PGE. However, dicarboxylate anions capable of bidentate chelation, such as oxalate, phthalate and salicylate, form much stronger complexes and can increase PGE solubility significantly. Amino acids have been shown to be important Pt species in seawater. Even more important in PGE mass transfer are multidentate ligands such as humic and fulvic acids. Experimental studies show that fulvic acid can increase the solubility of palladium hydroxide by orders of magnitude over a wide range of pH.

We have conducted solubility and spectroscopic studies on the interaction of two siderophores, desferrioxamine B (DFO-B) and ferrichrome, with Pd, Pt, Rh and Ir. These studies confirm strong complexation of PGE by siderophores, and show that there are significant differences in binding between different siderophores. Much more data are required to quantify fully the extent to which siderophores may increase PGE mobility in natural environments. However, they do indicate an important role for siderophores.

Effect of the trihydroxamate siderophores desferrioxamine-B and ferrichrome on the mobility of Pd, Pt, Rh and Ir

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Trihydroxamate siderophores are strong chelators for a variety of metals in near-neutral pH waters. We established that the solubility of amorphous $Pd(OH)_2$ is greatly enhanced by the presence of desferrioxamine-B (DFO-B) at pH 8. Experiments involving the dissolution of metallic Pd, Pt, Rh and Ir in solutions containing DFO-B (106 to 2000 micromolal) or ferrichrome (68, 200 micromolal) at pH 8 and a ionic strength of 0.14 indicate that the dissolution rates of Pd, Pt and Rh increased with increasing DFO-B concentrations up to 300 micromolal, remained independant of DFO-B concentrations between 300 and 1000 micromolal for the first 4500 hours, and then were increased again for a DFO-B concentration of 2000 micromolal. Increased dissolution of Ir only took place in the presence of 2000 micromolal DFO-B. Equilibrium was not achieved even after 6245 hours of reaction. After this time, the Pd concentration in the 2000 micromolal DFO-B solution was 0.62 mg/kg H_2O (Pt 0.29 mg/kg H_2O, Rh 0.02 mg/kg H_2O). This value is 1.5 order of magnitude higher than that for the solubility of amorphous $Pd(OH)_2$ in the absence of the siderophore. By comparison to $Pd(OH)_2$, however, Pd metal dissolves between 2.5 (100 micromolal DFO-B) and 3.5 (1000 micromolal DFO-B) times more slowly. Before 4500 hours, no difference was observed in the rate of dissolution of the individual PGE between the 68 and 200 micromolal ferrichrome solutions. After this time, Pd dissoved slightly faster in the 68 micromolal than in the 200 micromolal ferrichrome solution. Pt and Rh showed similar dissolution rates between DFO-B and ferrichrome solutions, whereas the Pd concentration in the 200 micromolal ferrichrome solution attained a value 3.5 times more elevated than that in the 200 micromolal DFO-B solution after 6245 hours. Ferrichrome is much more effective in dissolving Ir than DFO-B. Whereas the Ir concentration after 3196 hours in the 200 micromolal DFO-B solution was only marginally above that in the solution without siderophore, its concentration was increased by a factor of six in the 200 micromolal ferrichrome solution. These results clearly indicate that siderophores may play an important role in the solution transport of anthropogenic or naturally occurring PGE in the environment.