
The Role of Complexation by Natural Organic Matter in Transporting Pt and Pd in Surficial Environments

Scott A. Wood

Department of Geological Sciences, University of Idaho, Box 443022, Moscow, ID, 83844-3022, USA
e-mail: swood@iron.mines.uidaho.edu

Recently, the platinum-group elements (PGE) have been found to pose a potential environmental risk. Ironically, the use of these elements in automobile exhaust systems to reduce air pollution (among other uses) has resulted in their becoming contaminants in roadside dust and river sediments (Wei and Morrison, 1994), sewage sludges (Lottermoser, 1994), soils (Jarvis et al., 2001) and the marine environment (Ravizza and Bothner, 1996). The PGE may be both bioavailable and toxic under certain circumstances (Brubaker et al., 1975; Bunger et al., 1996; Gebel et al., 1997). The isotopes ^{107}Pd , ^{103}Ru and ^{106}Rh are fission products of nuclear fuel and the conditions of their potential migration from deeply buried nuclear waste repositories or contaminated surface sites into the biosphere must be understood (Brookins, 1984; McKinley et al., 1988). Knowledge of the stoichiometries and stability constants of potentially important PGE complexes is required to understand the mobility, bioavailability and biogeochemical cycling of these elements in the environment.

It has been suggested that organic ligands might be responsible for the behavior of PGE in surficial environments (Cousins and Kinloch, 1976; Bowles, 1986; Wood and Vlassopoulos, 1990; Bowles et al., 1994; 1995). Acetate and oxalate are important simple carboxylic acid anions that occur naturally in soil solutions, bog waters, sedimentary basinal brines, sediment porewaters and sediment-hosted geothermal systems (Bruckert, 1970; Graustein et al., 1977; Thurman, 1985; MacGowan and Surdam, 1988; Sposito, 1989; Martens, 1990). Perhaps the most important organic material in surficial environments are humic substances (humic and fulvic acid), both with respect to quantity and metal-binding capability. Organic acids and their anions may play a number of roles in governing the behavior of PGE in the environment including (Wood, 1996): 1) increased solubility or decreased sorption owing to the formation of dissolved complexes or a decrease in pH; 2) formation of colloidal particles; 3) reduction; 4) modification of the surface properties of minerals; 5) modification of the rates of various reactions; and 6) modification of bioavailability and/or toxicity. However, thermodynamic data for PGE complexes

with organic ligands likely to be encountered in nature are scarce (Giordano, 1992), which has precluded quantitative assessment of their role in PGE transport. The available evidence, suggests that Pt and Pd form surprisingly strong complexes with organic ligands such as acetate, oxalate, and fulvic and humic acids.

Wood et al. (1994) showed that the presence of acetate increases the solubility of amorphous Pd hydroxide. In the same study, UV-visible and FTIR spectroscopy showed evidence of formation of Pd-acetate and Pd-oxalate complexes. Measurements of the solubility of $\text{Pd}(\text{OH})_2$ (amorph) as a function of acetate concentration, permitted Pickrell (1997) to derive a stability constant for the PdAc_2 complex of $\log \beta_2 = 9.2$. Wood et al. (1994), using the stability constant of $\text{Pd}(\text{ox})\text{aq}$ ($\log \beta_1 = 8.7$) determined by Nabivanets and Kalabina (1972), calculated that this complex may be important at free oxalate concentrations as low as $\sim 10^{-8}$ - 10^{-9} M. Measured acetate and oxalate concentrations in soil solutions and other natural waters are much higher than the concentrations required to form complexes with $\text{Pd}(\text{II})$, but account must be taken of the competition for oxalate by H^+ and metals other than Pd. However, even taking competition into consideration, carboxylate anions (especially oxalate, malonate, citrate) seem likely to play a role in the hydromorphic transport of Pd in soils and some natural waters (see Figure 1). Li and Byrne (1990) showed that amino acids can form sufficiently strong complexes with Pd^{2+} that these complexes may dominate Pd speciation in seawater. It is also expected, based on limited experimental evidence and theoretical considerations, that S-containing ligands would also form strong complexes with the PGE.

Wood (1990) allowed fulvic acid (Armada B horizon) to react with aqueous PtCl_4^{2-} over a wide range of pH (3-11). It was shown that fulvic acid maintained Pt in the aqueous phase to a greater extent than deionized water. In later experiments involving Pd, Wood et al. (1994) demonstrated that fulvic acid inhibited the precipitation of $\text{Pd}(\text{OH})_2$ (amorph) from otherwise

supersaturated solutions over a broad pH range. In the same study it also was demonstrated that simple organic compounds representing simple analogues of fulvic acid, i.e., o-phthalate and salicylate, also form relatively strong complexes with Pd. Bowles et al. (1995) have conducted experiments which suggest that Pt and Pd are taken up by solid HS, and that dissolved HS can result in the solubilization of these metals in aqueous solutions.

Thus, there is much evidence to suggest that simple and complex organic ligands have the capability to mobilize Pt and Pd at geologically relevant concentrations through the formation of aqueous complexes. However, quantitative thermodynamic data, i.e., stability constants for the relevant PGE-organic complexes, are scarce. Moreover, there is essentially no information on the ability of organic ligands to mobilize Os, Ru, Ir or Rh. This lack of data hinders quantitative modeling efforts to assess the precise role of organic ligands in the dispersion of PGE in the surficial environment.

References

- Bowles, J.F.W., 1986, The development of platinum group minerals in laterites: *Economic Geology*, v. 81, p. 1278-1285.
- Bowles, J.F.W., Gize, A.P., and Cowden, A., 1994, The mobility of the platinum-group elements in the soils of the Freetown Peninsula, Sierra Leone: *The Canadian Mineralogist*, v. 32, p. 957-967.
- Bowles, J.F.W., Gize, D.J., Vaughan, D.J., and Norris, S.J., 1995, Organic controls on platinum-group element (PGE) solubility in soils: initial data: *Chroniques de la Recherche Minière*, n. 520, p. 65-73.
- Brookins, D.G., 1984, *Geochemical Aspects of Radioactive Waste Disposal*: Springer-Verlag Inc., New York.
- Brubaker, P.E., Moran, J.P., Bridbord, K., and Hueter, F.G., 1975, Noble metals: A toxicological appraisal of potential new environmental contaminants: *Environmental Health Perspectives*, v. 10, p. 39-56.

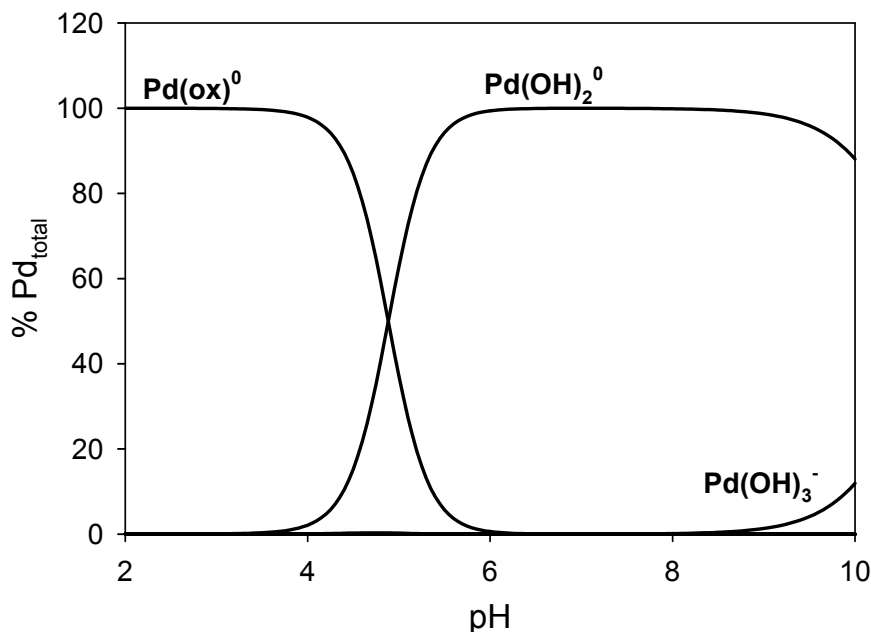


Figure 1. Diagram showing the distribution of Pd(II) species at 25 °C in a model soil solution containing 6×10^{-6} M total chloride, and 10^{-3} M total acetate. Concentrations as high as 10^{-3} M total oxalate are relatively common in soil solutions (Sposito, 1989). Species amounting to less than 1% at all pH values are omitted for clarity. The diagram shows that, at pH less than ~5, oxalate complexes appear to predominate over inorganic species.

- Bruckert, S., 1970, Effect of soluble organic compounds on pedogenesis in an acid environment. I. Field studies: *Annales de Agronomie*, v. 21, p. 421-4521.
- Bunger, J., Stork, J., and Stalder, K., 1996, Cyto- and genotoxic effects of coordination complexes of platinum, palladium and rhodium in vitro: *International Archives of Occupational and Environmental Health*, v. 69, p. 33-38.
- Cousins, C.A., and Kinloch, E.D., 1976, Some observations on textures and inclusions in alluvial platinoids: *Economic Geology*, v. 71, p. 1377-1398.
- Gebel, T., Lantzsich, H., Plessow, K., and Dunkelberg, H., 1997, Genotoxicity of platinum and palladium compounds in human and bacterial cells: *Mutation Research*, v. 389, p. 183-190.
- Giordano, T.M., 1992, Carboxylate complexing of copper, uranium, vanadium, and precious metals in ore fluids of sedimentary origin: *Journal of Geochemical Exploration*, v. 46, p. 237 (abstract).
- Graustein, W.C., Cromack, K., Jr., and Sollins, P., 1977, Calcium oxalate: Occurrence in soils and effect on nutrient and geochemical cycles: *Science*, v. 198, p. 1252.
- Jarvis, K.E., Parry, S.J., and Piper, J.M., 2001, Temporal and spatial studies of autocatalyst-derived platinum, rhodium, and palladium and selected vehicle-derived trace elements in the environment: *Environmental Science and Technology*, v. 35, p. 1031-1036.
- Li, J.-H. and Byrne, R.H., 1990, Amino acid complexation of palladium in seawater: *Environmental Science and Technology*, v. 24, p. 1038-1041.
- Lottermoser, B.G., 1994, Gold and platinoids in sewage sludges: *International Journal of Environmental Studies*, v. 46, p. 167-171.
- MacGowan, D.B., and Surdam, R.C., 1988, Difunctional carboxylic acid anions in oil field waters: *Organic Geochemistry*, v. 12, p. 245-259.
- Martens, C.S., 1990, Generation of short chain organic acid anions in hydrothermally altered sediments of the Guayamas Basin, Gulf of California: *Applied Geochemistry*, v. 5, p. 71-76.
- McKinley, I.G., Bath, A.H., Berner, U., Cave, M., and Neal, C., 1988, Results of the Oman analogue study: *Radiochimica Acta*, v. 44/45, p. 311-316.
- Nabivanets, B.I., and Kalabina, L.V., 1972, Oxalate complexes of palladium and their application in analysis: *Zhurnal Analiticheskoy Khimii*, v. 27, p. 1134-1139 (In Russian; Chem. Abstr. 77: 121855f).
- Pickrell, J., 1997, Stability constants of Pd²⁺ complexes from 25°C to 85°C: M.Sc. Thesis, University of Idaho, 120 p.
- Ravizza, G., and Bothner, M.H., 1996, Osmium isotopes and silver as tracers of anthropogenic metal in sediments from Massachusetts and Cape Cod bays: *Geochimica et Cosmochimica Acta*, v. 60, p. 2753-2763.
- Sposito, G., 1989, *The Chemistry of Soils*: Oxford University Press, New York, 277 p.
- Thurman, E.M., 1985, *Organic Geochemistry of Natural Waters*: Martinus Nijhoff/Dr W. Junk Publishers, Boston, 497 p.
- Wei, C., and Morrison, G.M., 1994, Platinum in road dusts and urban river sediments: *Science of the Total Environment*, v. 146/147, p. 169-174.
- Wood, S.A., 1990, The interaction of dissolved platinum with fulvic acid and simple organic acid analogues in aqueous solutions: *The Canadian Mineralogist*, v. 28, p. 665-673.
- Wood, S.A., 1996, The role of humic substances in the transport and fixation of metals of economic interest (Au, Pt, Pd, U, V): *Ore Geology Reviews*, v. 11, p. 1-31.
- Wood, S.A., and Vlassopoulos, D., 1990, The dispersion of Pt, Pd and Au in surficial media about two PGE-Cu-Ni prospects in Quebec: *The Canadian Mineralogist*, v. 28, p. 649-663.
- Wood, S.A., Tait, C.D., Vlassopoulos, D., and Janecky, D.R., 1994, Solubility and spectroscopic studies of the interaction of Pd with simple carboxylic acids and fulvic acid at low temperature: *Geochimica et Cosmochimica Acta*, v. 58, p. 625-637.