

The interaction of Pd- and Pt-bearing chloride solutions with sulfide minerals: XPS, SPM and electrochemical study

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The majority of platinum group element (PGE) deposits are of magmatic origin, and it has generally been assumed that PGEs are unreactive in aqueous media. However, Pt, Pd, and other metals may be mobile in surface environments, so adsorption and precipitation of PGE at sulfide minerals are of particular interest for the mineral processing, PGE analysis, etc. There are only few studies on this matter in the literature, for example, [1].

In the present work, we examined precipitation of Pd and Pt from aqueous PdCl₄²⁻ and PtCl₆²⁻ solutions onto pyrite, pyrrhotite and galena, including those previously reacted under different conditions, applying XPS, AFM, STM/STS, SEM, and cyclic voltammetry. It was found, in particular, that the deposition of Pt is slower than Pd; the quantities of the metals precipitated on pyrrhotite and pyrite are close. Preliminary oxidation of pyrrhotite surface results in an increase in the deposition of Pt, whereas the opposite trend was observed for pyrite. The results were interpreted in terms of the formation of Cl-, O- or S-bearing nanoscale species of Pd and Pt, with their proportion being a function of the reaction time and mineral pre-treatment (Fig. 1). The behaviour of the precipitated Pt and Pd entities was also studied.

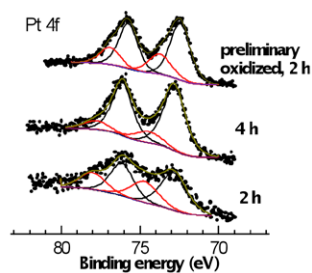


Figure 1: XP spectra from Pt deposited at pyrrhotite under various conditions (room temperature, 1 mM PtCl₆²⁻).

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[1] Hyland *et al.* (1989) *Geochim. Cosmochim. Acta* **54**, 117-130.

PuO_{2+x}·nH₂O nanoparticles formation upon Pu(V,VI) sorption onto hematite

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Plutonium (IV) as well as most of highly hydrolyzable cations forms intrinsic colloids that is demonstrated in many laboratory experiments mostly at relatively low pH values and high Pu concentrations. The gap of knowledge exists on the possibility and mechanisms of intrinsic colloids formation under conditions more relevant to the environment. The purpose of this study was to define the mechanisms of Pu (V, VI) interaction with hematite colloids including redox reactions and formation of intrinsic colloids.

It was previously shown [1] that Pu in high valence states is reduced to Pu (IV) upon sorption onto hematite. In case of Pu (IV) at very low total concentrations, e.g. ~10⁻¹⁴ M, the fast sorption of monomeric species on hematite occur, while in case of Pu (VI), the sorption is kinetically controlled by slow reduction on the surface. For total concentrations of Pu around 10⁻⁶ the reduction of Pu (V, VI) upon sorption onto hematite is confirmed by Pu L_{III} XANES. The reduction is accompanied by the formation of PuO_{2+x} crystalline nanoparticles with average size of 1-2 nm that was independently demonstrated by HR-TEM and Pu L_{III} EXAFS measurements.

The most challenging question is concerning Pu behavior at lower concentrations, i.e. around 10⁻⁹ M and less. Due to the increase of concentration near the surface, Pu (IV) could polymerize even at this relatively concentration that strongly effect both kinetics of sorption and leaching behavior. For the first time it was demonstrated by HRTEM that Pu (V, VI) reduction upon sorption result in the formation of low-crystallinity PuO_{2+x} nanoparticles.

[1] Romanchuk *et al.* (2011) *Radiochim. Acta* **99**, 137-144.