ESRF	**Experiment title:** Hydrothermal transport of palladium in near- and supercritical fluids	**Experiment number**: 30-02-1010
Beamline: BM30B	**Date of experiment**: from: 06 April 2011 to: 12 April 2011	**Date of report**: 22 February 2012
Shifts: 18	**Local contact(s):** Dr. Jean-Louis Hazemann (hazemann@grenoble.cnrs.fr)	*Received at ESRF:*

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Report:

Experimental. The local atomic structure around Pd in aqueous solutions was studied by XAFS spectroscopy at the Pd K-edge (24.35 keV) at 30 – 450°C and 600 bar using an X-ray cell developed at the Institut Néel [1]. Two types of experiments were performed: experiments on Pd-bearing solutions with or without Cl and solubility experiments of PdO and PdS in equilibrium with Cl-rich solutions. Spectra were collected in both transmission and fluorescence mode at BM30B beamline (FAME).

Results from the Pd-bearing Cl-free solutions. Two Cl-free solutions were examined: 0.010m Pd – 0.49m HNO_3 and 0.008m Pd – 3.66m $HClO_4$ (where m denotes the number of moles of each solute per kg of water) at T = 30-350°C and P = 600 bar. XANES and EXAFS spectra for both solutions at 30-100°C are very close. EXAFS spectra show that at 30-100°C Pd in the first atomic shell is coordinated by 4 oxygen atoms at 2.00±0.01 Å. These structural data are consistent with the planar square $Pd(H_2O)_4^{2+}$ cation in solution. At $T \geq 100$°C this species is unstable. In the ClO_4^- solution at 150°C Pd metal precipitation is observed on the cell windows. In the NO_3^- solution at 200-250°C 2.0±1.0 nitrogen atoms are detected at 2.82±0.06 Å. In similar experiments with Cd such changes in the Cd atomic environment at 200-250°C were not observed [2]. This difference may be explained by the Pd complexing with NO_3^- or rather with NH_4^+ appeared due to strong catalytic properties of Pd favoring reduction of NO_3^- in the glassy carbon cell. At 350°C all Pd precipitated from the solution.

Results from the Pd-bearing Cl-rich solutions. Five chloride solutions were studied at 30-500°C in the system $Pd/PdCl_2$-HCl-$HClO_4$-LiCl-H_2O with 0.01, 0.032, 0.24, 2.55, and 9.08m of total Cl concentration. At 30°C the evolution of XANES spectra with increasing Cl concentration is shown in Fig. 1a. These changes are in line with EXAFS modeling. At 30°C with increasing mCl oxygen atoms in Pd coordination shell are replace quickly by chlorine (Fig. 1b) and interatomic distances increase (Pd-O at 2.00±0.01 Å in Cl-free solutions, 2.08±0.01 Å in 0.032m Cl; Pd-Cl at 2.25±0.01 Å in 0.011m Cl, 2.31±0.01 Å in 0.032-9.08m Cl solution). The spectra of solutions with 0.24-9.08m of Cl show identical XANES and EXAFS shapes. Thus at 30°C with addition of Cl, the $Pd(H_2O)_4^{2+}$ cation transforms to the $PdCl_4^{2-}$ complex. This complex is also square planar and is the dominant Pd aqueous species in a wide Cl concentration range (0.24-9.08m). The fraction of intermediate species with 1-3 chloride atoms is too weak to be detected in our spectra at 30°C.

The effect of temperature is rather weak for both XANES and EXAFS spectra indicating that the structure of Pd aqueous species remains planar square at all temperatures. An example of XANES spectra at 200°C as a function of Cl concentration is given in Fig 2a. The average number of Cl and O atoms found from EXAFS modeling are given in Fig. 2b. With increasing T in all solutions, except 9.08m, the average number of Cl around Pd slightly decreases (Fig. 3). It is interesting to note that this slight decrease of Cl atoms seems to have an important effect on Pd precipitation from the solutions (see stars in Fig. 3). Pd-Cl and Pd-O distances were found to be 2.31±0.01 and 2.08±0.02 Å for all Cl-bearing solutions at all T above ambient.

Results from solubility experiments. Three PdO solubility experiments (0.02, 0.05 and 1.14m of total Cl) and two PdS solubility experiments (2.24 and 3.56m of total Cl) have been performed. PdO solubility in 0.02m HCl solution was measured at 30°C (0.001m) but during heating the precipitation of Pd metal was observed on the cell windows. The temperature dependence of PdO solubility in 0.05m HCl solution is presented in Fig. 4. It can be seen in this figure that the equilibrium is likely to be reached at 300 and 350°C. Both XANES and EXAFS shapes for this solution equilibrated with PdO at 300-400°C do not change with T and are identical to those of 0.032m Cl Pd-bearing solution. The structural data are consistent with the $PdCl_2(H_2O)^0_{(aq)}$ species. The PdO solubility measured in 0.05m HCl-1.09m NaCl (1.14m of total Cl) reached 0.022 m at 300°C. At 450°C most Pd precipitated from the solution.

The solubility of PdS in both experiments is very low and only demi-quantitive determinations can be done. The low concentration of Pd (about 10^{-5} m) in these experiments do not allow the quantitative EXAFS modeling for these solutions even for fluorescence spectra. The high solubility of PdO and low solubility of PdS contradict to their thermodynamic properties. To resolve this discrepacy a more detailed thermodynamic analysis is required.

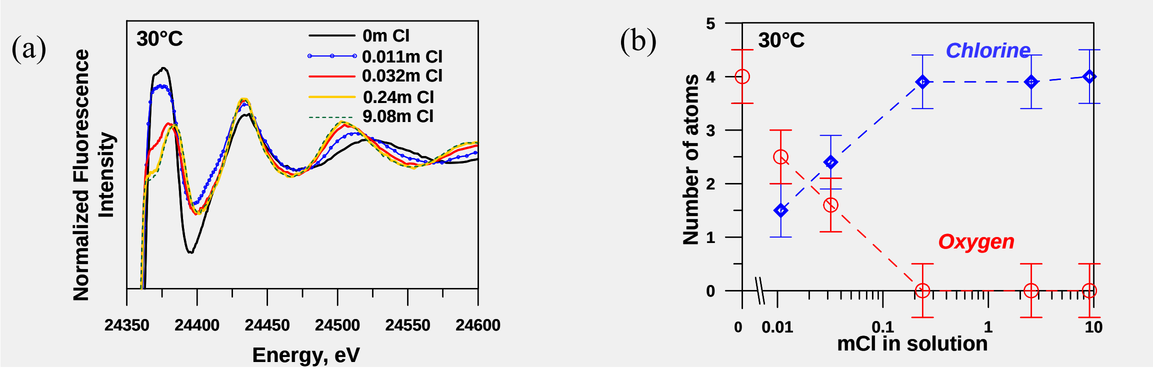

Fig 1. Evolution of XAFS spectra (a) and average number of Cl and O around Pd found from EXAFS modeling (b) as a function of Cl concentration in solution at 30°C.

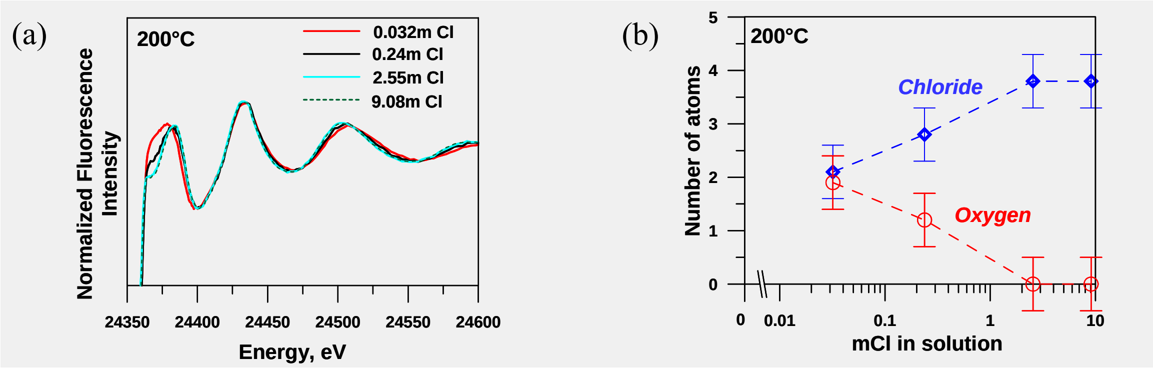

Fig 2. Evolution of XAFS spectra (a) and average number of Cl and O around Pd found from EXAFS modeling (b) as a function of Cl concentration in solution at 200°C.

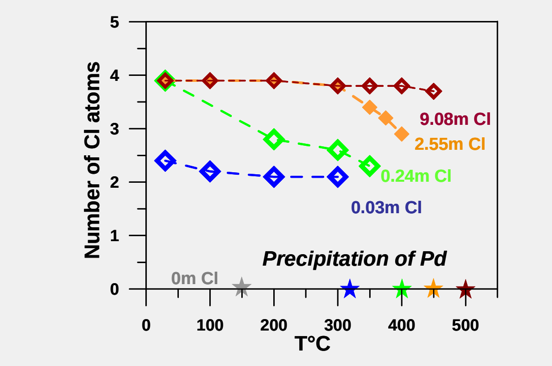

Fig 3. The number of Cl around Pd as a function of T. Stars indicate the T of Pd precipitation.

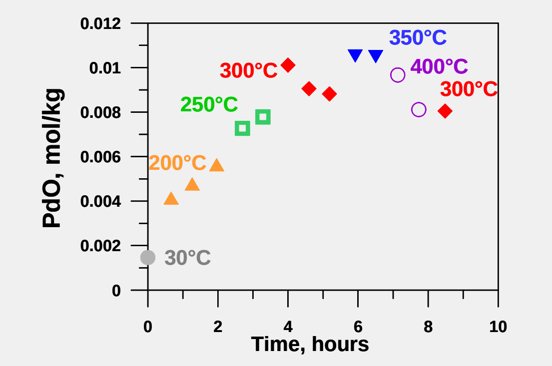

Fig 4. Solubility of PdO in 0.05m HCl – H_2O solution as a function ot time and temperature.

<u>Conclusions and perspectives.</u> Our data show that the coordination number of Pd in the first coordination shell remains 4 at all studied T and mCl. Our found Pd-Cl and Pd-O distances are close to those reported earlier at ambient T-P [3]. Our measured slight decrease of the Cl atoms number around Pd with T is much weaker than that from thermodynamic predictions [4], indicating that the fraction of $PdCl_4^{2-}$ at T ≥ 100°C is higher than previously thought. All observed spectra can be described as a sum of $Pd(H_2O)_4^{2+}$, $PdCl_2(H_2O)^0_{(aq)}$ and $PdCl_4^{2-}$. To estimate the possible role of the $PdCl_3(H_2O)^-$ species at high T and to interpret our measured PdO and PdS solubility data an accurate thermodynamic analysis of all data including those available in the literature will be performed. Our new data demonstrate the strong complexing of Pd with Cl at high T-P. This means that hydrothermal fluids may play an important role in Pd and others Pt group metals (Pt, Ir, Rh, Ru) transport and ore deposition.

<u>References.</u>

[1] Testemale D. et al. (2005) *Rev. Sci. Instrum.* **76**, 43905 [2] Bazarkina et al. (2010) *Chem.Geol.* **276**, 1. [3] Boily&Seward (2005) *GCA* **69**, 3773. [4] Sassani&Shock (1998) *GCA* **62**, 2643.