



	Experiment title: Impact of sulfur radical ions on platinum transport by hydrothermal fluids and ore deposit formation.	Experiment number: 30-02-1131
Beamline: BM30B	Date of experiment: from: 08 February 2018 to: 13 February 2018	Date of report: 14 February 2018
Shifts: 15	Local contact(s): Jean-Louis Hazemann, BM30B (FAME)	<i>Received at ESRF:</i>
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Report:

Experimental: The solubility and molecular structure of platinum in chloride-bearing and sulfur-bearing aqueous solutions were examined by X-ray absorption spectroscopy (XAS) at Pt L₃-edge (11.57 keV) both in transmission and fluorescence mode with a Si(220) double crystal monochromator, at temperatures (*T*) from 200 to 400°C and pressures (*P*) 600-700 bar, using the FAME high *T-P* autoclave that enables simultaneous measurement of both the total dissolved Pt concentration and its atomic environment in the fluid [1,2]. The internal cell is composed of a glassy-carbon tube with two pistons equipped with Viton seals. The source of Pt in experiments was Pt metal (for both types of system) or K₂PtCl₄ and K₂PtCl₆ (for Cl-systems). The source of chloride was NaCl-HCl and the source of sulfur was elemental S or K₂S₂O₃ whose dissolution in H₂O(±HCl, ±NaOH) at *T* > 200°C yields sulfate (HSO₄⁻ and SO₄²⁻), sulfide (H₂S and HS⁻) and trisulfur ion (S₃⁻) as the major S aqueous forms. Their concentrations may accurately be quantified using the thermodynamic properties of these species and recent in situ Raman spectroscopy measurements in similar systems [3-5]. The choice of the experimental conditions in S-bearing systems was carefully made in order to maximize the concentration of S₃⁻ in the system and to better elucidate its effect of Pt solubility and speciation. To explore more reduced conditions, N₂H₄ was added in some S-bearing experiments to reduce sulfate and S₃⁻ to sulfide. A total of seven experiments have been performed. The concentration of dissolved Pt was estimated either from the absorption edge step in transmission mode (>500 ppm Pt) or, at lower concentrations, from the ratio of fluorescence peaks intensities of Pt and Br, which was added as a spike in each solution (~500 ppm).

Results from the Cl-bearing system: An experiment performed with a K₂PtCl₄-NaCl-HCl solution (2800 ppm Pt) showed the Pt local environment dominated by the PtCl₄²⁻ species to temperatures of 200°C, in good agreement with the literature data [6]. At higher *T*, a fast Pt precipitation was observed, likely due to increasingly reducing conditions generated by partial dissolution of carbon tube. An experiment with Pt metal and a K₂PtCl₆-HCl solution (1500 ppm Pt) yielded spectra consistent with the PtCl₆²⁻ complex at room temperature. With increasing *T*, we observed a fast reduction of PtCl₆²⁻ to PtCl₄²⁻ followed by a precipitation of Pt metal from solution. This result disagrees with the literature data on the Pt⁰-Pt²⁺Cl₄-Pt⁴⁺Cl₆ equilibria studied by UV-Vis spectroscopy and solubility in quartz tubes [7] that demonstrate that both PtCl₄²⁻ and PtCl₆²⁻ in different proportions should be stable in equilibrium with Pt metal. Again, this discrepancy with our observations is likely due to the reducing conditions imposed by our cell material at elevated temperatures.

Results from the S-bearing system: In contrast to the Cl system, experiments in S-bearing solutions at 250-350°C showed progressive Pt dissolution and attainment of a steady state in Pt concentration after a few hours of reaction. The stability of such systems is owing to redox buffering by sulfate-sulfide equilibria which yield reducing conditions close to those originated from carbon dissolution. Unfortunately, we could explore only a quite limited *T*-range (250-350°C) because of carbon-glassy pistons and Viton seals failure at higher temperatures in our solutions. Following this unlucky experience, it is recommended to use alumina pistons and a different type of seals for experiments above 350°C in such systems.

Nonetheless, the results obtained in this narrow *T*-range are of very good quality and are believed to be representative of other temperature conditions. Steady-state total Pt concentrations measured in 1m K₂S₂O₃(±HCl) and 1m S-NaOH(±N₂H₄) solutions at 300°C and 700 bar are within the range 50-200 ppm Pt, which is in quantitative agreement with our recent batch-reactor solubility measurements at the same conditions. Our measured concentrations in S₃⁻ - poor, HS⁻ - dominated solutions (S-NaOH-N₂H₄, pH~6.5, 170 ppm Pt) are comparable within error (±1 log unit) to those predicted using the thermodynamic properties of Pt(HS)₃⁻ from rare scattered literature data [7,8]. In contrast, our measured solubilities in more acidic and oxidizing solutions (K₂S₂O₃ and S, pH<5.0), in which HS⁻ ion is very

minor and S_3^- is abundant, are at least 3 log units higher than the thermodynamic predictions for $Pt(HS)_3^-$, strongly suggesting formation of other, more stable complexes, very likely with the S_3^- ion.

These new findings are supported by both XANES and EXAFS spectra comparisons. Significant differences in both amplitude and energy position of XANES features are apparent in Fig. 1, showing spectra for two most contrasting solution compositions, HS-rich and S_3 -rich, in which $Pt(HS)_3^-$ and a S_3 -bearing complex, respectively, are expected to dominate the Pt speciation. Furthermore, significant phase shifts are also apparent in the EXAFS spectra of these solutions, indicating that the mean Pt-S distances in the Pt- S_3 complexes are ~ 0.04 Å longer than in $Pt(HS)_3^-$, in agreement with what may be expected from coordination chemistry. Work is currently in progress to extract quantitative structural and thermodynamic information from these new data.

Conclusions & perspectives: This experiment yielded the first quantitative in-situ measurement of Pt-S species structure and stability in S-rich solutions typical of PGE and associated (Au, Cu, Mo) deposit geological contexts. Our findings shift the long-standing paradigm that hydrogen sulfide (H_2S/HS^-) is the only carrier of Pt in hydrothermal fluids. The new species discovered in this study will require a revision of both Pt-S speciation and ore-deposit models; also they may potentially have important implications in Pt ore treatment and purification. High-resolution spectroscopy (HERFD-XANES) coupled with molecular dynamics modelling will enable a more robust determination of the exact complex stoichiometry, which is the primary requisite for using these data in modeling of Pt transport and deposition across the Earth's lithosphere conditions.

References cited:

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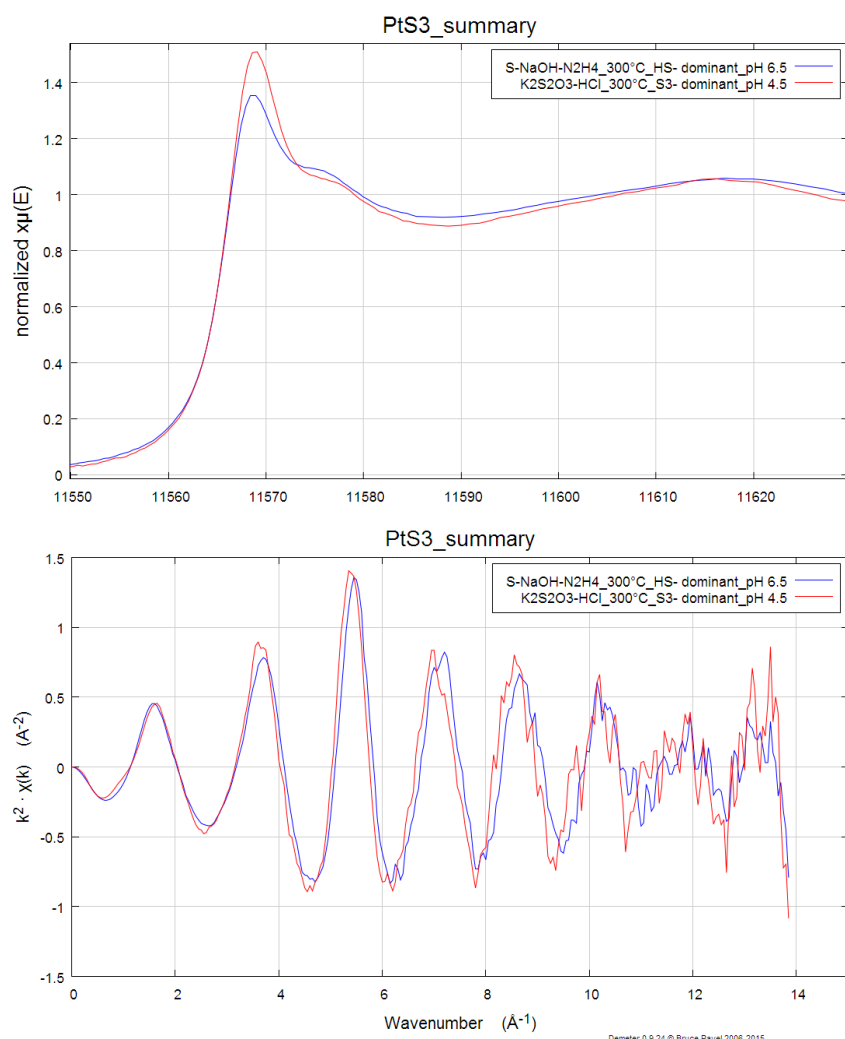


Fig. 1. Pt L_{III} -edge XANES (top) and EXAFS (bottom) spectra at 300°C/700 bar of Pt-S bearing solutions (3 wt% total S) at the indicated composition and pH, in which either the S_3^- (red) or HS^- (blue) ligands predominate. Note significant differences in both XANES feature energy positions and amplitude and EXAFS phase shift (i.e., different Pt-S distances) between the two solutions. The XANES contrast and resolution are expected to be dramatically amplified with the HERFD setup which will be applied in a near-future project, allowing robust identification and quantification of the different Pt complexes with S_3^- and HS^- ligands.