



	<b>Experiment title:</b> Stability and structure of platinum hydrosulfide complexes in geological fluids and their impact on ore deposit formation.	<b>Experiment number:</b> 30-02-1145
<b>Beamline:</b>	<b>Date of experiment:</b> from: 11/02/21 to: 19/02/21	<b>Date of report:</b> 24/04/21
<b>Shifts:</b>	<b>Local contact(s):</b> Jean-Louis Hazemann	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Clement Laskar* (GET, Toulouse); Gleb Pokrovski* (GET, Toulouse); Elena Bazarkina* (Institut Néel, Grenoble); Jean-Louis Hazemann* (Institut Néel, Grenoble).		

## Report:

### **- Objective & expected results -**

Platinum-group elements (PGE) are intimately associated with sulfur in nature, yet our knowledge of the impact of S-bearing fluids on the extraction, transport and deposition of these critical metals is virtually non-existent owing to a lack of robust data on the identity and stability of metal-sulfur chemical entities (i.e. complexes) in the fluid phase. The major sulfur ligand of geological fluids is hydrosulfide ( $\text{H}_2\text{S}/\text{HS}^-$ ), yet our knowledge of its effect on PGE transport is both inconsistent and controversial. In this project, we explored the identity, structure, and stability of Pt complexes with the hydrosulfide ligands in aqueous solutions at controlled redox and acidity conditions at elevated temperature and pressure using in-situ X-ray absorption spectroscopy (XAS) technique.

### **- Results and the conclusions of the study -**

Experiments were performed in  $\text{H}_2\text{S}/\text{HS}^-$ -bearing aqueous solutions in the presence of PtS solid phase at 300°C and 500 bars (5 runs ; thermodynamic equilibrium after ~4h), and 250°C and 500 bars (1 run ; maximum of solubility)). Two types of aqueous solutions were explored: 1)  $\text{H}_2\text{S}$ -saturated NaHS solution (provided by ESRF Chemical Laboratory, H. Muller and L. Bourcet) and 2) thioacetamide  $\text{C}_2\text{H}_5\text{NS}$  aqueous solutions at acidic (5.0 and 5.4), near-neutral (7-8) and alkaline (10) pH. Thioacetamide decomposes at experimental temperatures forming  $\text{H}_2\text{S}$ ,  $\text{CH}_3\text{COOH}$  and  $\text{NH}_3$  [1]. Additional measurements were done in aqueous solutions with known Pt concentration (Pt fluorescence intensity calibration), blanks (solutions with no Pt) and solid standards.

The absorption-edge energy values of the Pt(II)-S (PtS, 11,565.4 eV) and Pt(IV)-S (PtS<sub>2</sub>, 11,566.2 eV) solid references were compared with our Pt solutions at high T-P. This comparison shows that all our experimental solutions have a similar energy position as the Pt(II)-S reference (Fig. 1), implicating the dominant Pt(II) oxidation state in the Pt-S complexes. Thus, a square planar geometry of the 1<sup>st</sup> coordination shell, as for PtS, is most likely [2].

One EXAFS spectra of very good quality could be obtained at low concentrations of Pt in the fluid (~10 ppm) via accumulation of ~20 40-min scans. EXAFS modeling enable to derive the following structural parameters: (i) a mean Pt-S bond length of ~2.30 Å, (ii) a coordination number of ~4 S atoms (Table 1). The EXAFS spectra

of other solutions look rather similar, even though the higher noise, thereby strengthening the the evidence of the same 1<sup>st</sup> shell composed of 4 S in the pH range 5.0<pH<7.8 at 300°C and 500 bars.

Platinum concentrations were determined for each experiment using fluorescence calibration from K<sub>2</sub>PtCl<sub>4</sub> solutions with known Pt concentration (1-15 ppm) and matrix absorption close to experimental solutions. The species Pt(HS)<sub>4</sub><sup>2-</sup> was found to be the main Pt complex in the fluid, Pt concentration measured in the 1M NaHS solution at 300°C and 500 bars (1.3 ppm) is similar to those obtained in previous experiments with sampling autoclave (~1ppm), validating our solubility measurements. In conclusion, we have obtained for the first time two independent evidences (EXAFS + solubility) that Pt(HS)<sub>4</sub><sup>2-</sup> is the main complex in H<sub>2</sub>S/HS<sup>-</sup>-bearing fluids, at least in the temperature range 250-300°C at 500 bars in the pH-range 5.0<pH<7.8.

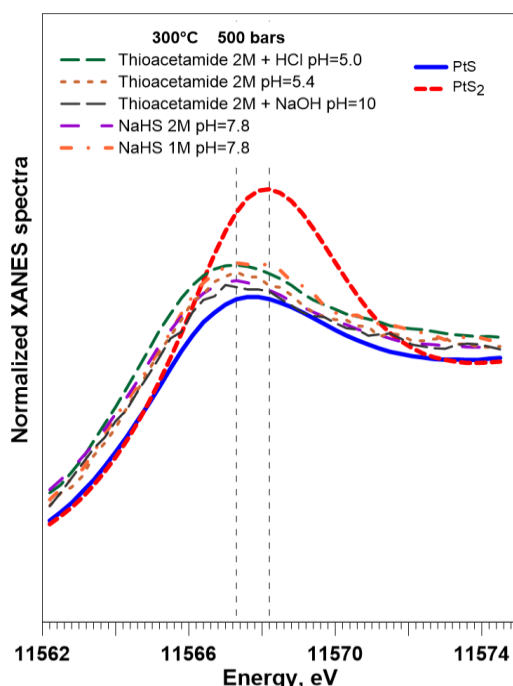
#### **- Justification and comments about the use of beam time -**

FAME has an efficient and fully operational XAS setup enabling in-situ studies of hydrothermal fluids using the FAME autoclave [3]. All 18 shifts were required and fully utilized to examine 6 contrasting solutions pertinent to the contexts of many PGE deposits.

#### **- Publication(s): -**

Laskar C, Pokrovski G, Kokh MA, Hazemann J-L, Bazarkina EF, Desmaele E & Vuilleumier R (2021) EMPG-XVII, 26.

**References:** [1] Pokrovski G.S. et al., 2008. EPSL 266, 345-362 [2] Cotton FA and Wilkinson G, 1988. Advanced Inorganic chemistry [3] Testemale D. et al. 2005. RSI 76, 043905-043909.



**Fig. 1.** Pt L<sub>III</sub>-edge XANES of the two solid reference compounds at 25°C and 1 bar, Pt<sup>II</sup>S and Pt<sup>IV</sup>S<sub>2</sub>, and of our H<sub>2</sub>S/HS<sup>-</sup> solutions at 300 °C and 500 bars at different pH. The white-line energy position of both references is marked by vertical dashed lines to show the clear difference, both in the spectral position and amplitude, between Pt(II) (in PtS and our solutions) and Pt(IV) in PtS<sub>2</sub>(s).

**Table 1.** Platinum(II) local structure in Pt(II)-bearing solutions of the indicated composition (M=molarity), derived from fitting of EXAFS spectra at the Pt L<sub>III</sub>-edge.

T (°C)	P (bar)	Scattering atom	N (atoms)	R (Å)	σ <sup>2</sup> (Å <sup>2</sup> )	Δe (eV)	R-factor
Thioacetamide (2M) (R-range: 1.1-4.5 Å, k-range: 3.0-10.9 Å <sup>-1</sup> )							
250	500	S	4.0±0.4	2.296±0.008	0.003±0.001	7±1	0.028
		S <sub>fwa</sub> <sup>a</sup>	4.0 <sup>a</sup>	4.6 <sup>a</sup>	0.006 <sup>a</sup>		

S<sub>0</sub><sup>2</sup> is set at 0.80.

Multiple scattering paths: forward through absorber (fwa) contribution Pt-S-Pt-S-Pt.

<sup>a</sup> N, R and σ<sup>2</sup> are set to 2×(S)1st shell.