



	<u>Experiment title:</u> Deciphering the impact of sulfur on the transfer of noble metals by hydrothermal fluids using in-situ high-resolution X-ray absorption spectroscopy (HERFD)	Experiment number: ES-788
Beamline: BM16	Date of experiment: from: 06 November 2018 to: 12 November 2018	Date of report: 13 November 2018
Shifts: 18	Local contact(s): Jean-Louis Hazemann, BM30B (FAME)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Clément Laskar (GET, Toulouse), *Elsa Desmaele (ENS, Chimie, Paris), *Gleb Pokrovski (GET, Toulouse); *Elena Bazarkina (Institut Néel, Grenoble), *Jean-Louis Hazemann (Institut Néel, Grenoble)		

Report:

Experimental: The solubility and molecular structure of platinum and gold in sulfur-bearing aqueous solutions were examined by X-ray absorption spectroscopy (XAS) at Pt L₃-edge (~11.6 keV) and Au L₃-edge (~11.9 keV), both in transmission and fluorescence mode with a Si(220) double crystal monochromator and 7 Si(660) or Ge(660) crystals placed in a Roland circle geometry for high energy resolution fluorescence measurements, 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 metal 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 Au and Pt in experiments were Au and Pt metal foils. The 2 sources of sulfur were: i) K₂S₂O₃ whose dissolution in H₂O(±HCl, ±NaOH) at *T* >200°C yields sulfate (HSO₄⁻ and SO₄²⁻), hydrogen sulfide (H₂S and HS⁻) and the trisulfur ion (S₃⁻) as the major S aqueous forms and ii) NaHS yielding only hydrogen sulfide ligands (HS⁻ and H₂S). 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 thiosulfate bearing systems was carefully made in order to maximize the concentration of S₃⁻ in the system and thus to better elucidate its effect of Pt speciation. A total of seven experiments have been performed.

Results from the S-bearing systems with Au : Two experiments could be performed at 350°C and 700 bar on Au-saturated thiosulfate solutions at acidic (4.5) and alkaline (7.5) pH at which Au(HS)S₃⁻ and Au(HS)₂⁻, respectively, are the dominant Au species according to recent work [6]. It was found that measured Au solubility in both experiments is in excellent agreement with the predicted solubility [6]. The high-resolution XANES spectra exhibit detectable differences, which are confirmed by ab-initio simulations of the XANES spectra using the FDMNES code and optimized structures of both complexes obtained by molecular dynamics simulations. Thus the HR-XANES provides the first direct confirmation for the existence of the Au(HS)S₃⁻ complex in acidic and S₃⁻-rich fluids, as was hypothesized in previous studies using less direct methods based on analyses of total gold solubility changes with increasing S₃⁻ concentration.

Results from the S-bearing systems with Pt : Four experiments could be performed at 300°C and 600 bar on Pt-saturated thiosulfate solutions at acidic (4.4) and near-neutral (5.5) pH, and on Pt-saturated hydrogen sulfide solutions at alkaline (8.4) pH. The use of the HR-XANES mode yields both a 2-fold increase of the amplitude of XANES resonances and their energy resolution compared to the spectra in transmission mode (Fig. 1). Thus, the energy of the maximum is precisely defined, making it possible to clearly identify significant differences between the maximum white-line energy values of Pt(II)-S (PtS, 11567.0 eV) and Pt(IV)-S [(NH₄)₂Pt^{IV}(S₅)₃], 11568.0 eV) solid references (Fig. 1). The comparison of these references with our Pt solutions at high *T-P* shows that all solutions have a similar energy position as the Pt(II)-S reference (Fig. 2). Furthermore, the good quality of the EXAFS spectra of a 2 molal thiosulfate solution make it possible to derive two information: (i) a mean Pt-S bond length of ~2.30 Å, close to that in the Pt(II)-S reference PtS, but different from that in the Pt(IV)-S solids which have Pt-S bond lengths longer than 2.34 Å (Fig. 2) ; (ii) a coordination number between 3 and 4. Thus, a square planar geometry of the 1st coordination shell of, as for PtS, is highlighted [7].

Conclusions & perspectives:

First, our exploratory experiments showed that when S₃⁻ has higher concentrations than HS⁻ in the pH range 4.5 < pH < 5.5, the dominant Pt oxidation state in the Pt-S complexes is +II and not +IV. It is an important finding because, while the solid phase Pt^{IV}S₂ is the thermodynamically stable mineral in nature at the redox conditions of the

SO_4^{2-} - H_2S coexistence, in aqueous solution the Pt +II redox state is stable. In hydrogen sulfide dominated solutions (NaHS), $\text{Pt}^{\text{II}}\text{S}(\text{s})$ is the thermodynamically stable mineral in nature, and Pt+II redox state is also found to be stable at alkaline pH. *Second*, the HR-XANES spectra of Pt do not show features that would be clearly indicative of the presence of 2nd shell S atoms, as in the solid reference $[(\text{NH}_4)_2\text{Pt}^{\text{IV}}(\text{S}_5)_3]$ or in Pt-S_3^- complexes. Thus, direct spectroscopic evidence of the existence of Pt-S_3^- complexes is yet lacking. Our near-future experiments will be focused on $\text{H}_2\text{S}/\text{HS}^-$ - bearing fluids, to more accurately measure both Pt solubility (from the accurately calibrated fluorescence signal) and local structure (via acquisition of high-quality EXAFS spectra using the 30-element Canberra detector at FAME beamline).

References cited:

[1] Testemale D. et al. 2005, Rev. Sci. Instrum. 76, 043905-043909; [2] Pokrovski G.S. et al. 2009, Geochim. Cosmochim. Acta 73, 5406-5427; [3] Pokrovski G.S. & Dubrovinsky 2011, Science 331, 1052-1054; [4] Jacquemet N. et al. 2014. Amer. Miner., 99, 1109-1118; [5] Pokrovski G.S. & Dubessy J., 2015. Earth & Planet. Sci. Lett., 411, 298-309; [6] Pokrovski, G.S. et al., 2015. PNAS, 112, 13484–13489; [7] Filimonova O.N. et al., 2019. Econ. Geol. 114, 1649–1663.

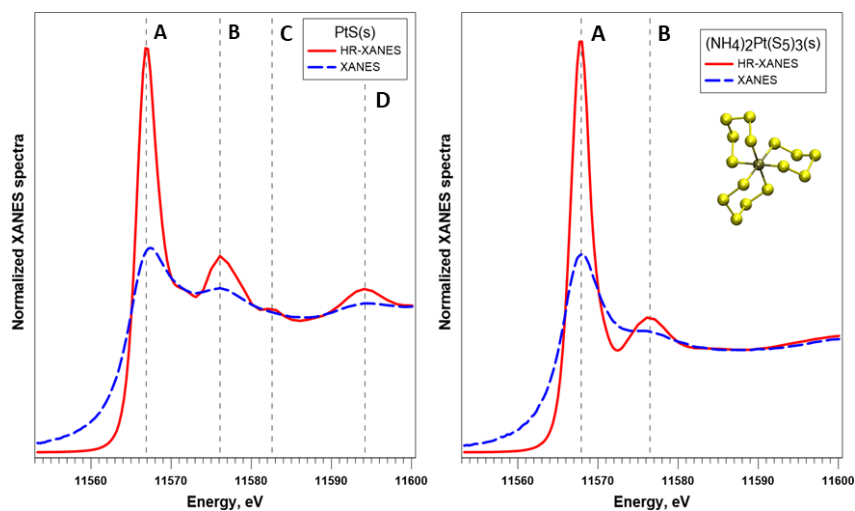


Fig. 1. Pt L_{III} -edge XANES for the two solid reference compounds, $\text{Pt}^{\text{II}}\text{S}$ (left) and $[(\text{NH}_4)_2\text{Pt}^{\text{IV}}(\text{S}_5)_3]$ (right), at 25°C and 1 bar. The spectacular improvement in resolution in HR-XANES mode (red), compared to ‘classical’ XANES spectra (blue), enables precise determination of the white-line maximum energies of the Pt(II)-S (11567.0 eV) and Pt(IV)-S (11568.0 eV) references. The main features present in both references are marked by vertical dashed lines as A and B, and the features marked as C and D are because of the high crystallinity of the PtS reference.

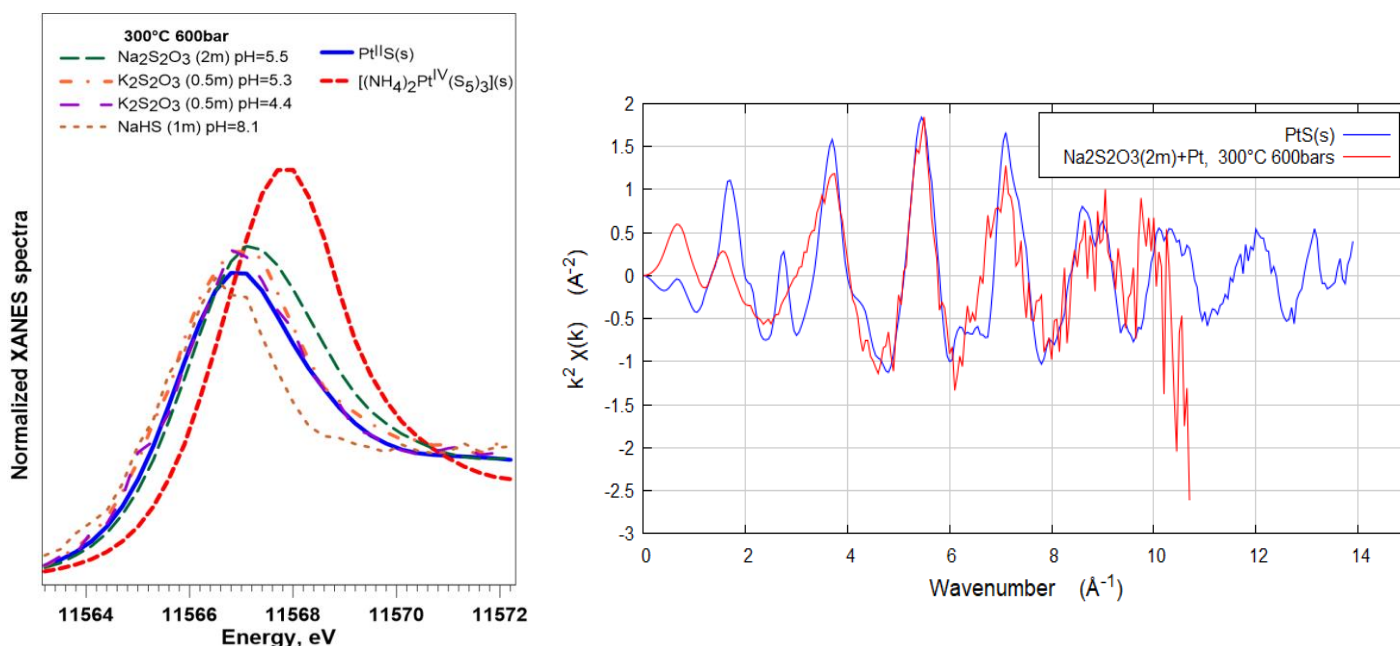


Fig. 2. Pt L_{III} -edge XANES (left) and EXAFS (right) spectra in HR mode at 300°C and 600 bar of Pt-S bearing solutions at the indicated compositions and pH. Note strong similarities both in the white-line energy position and shape, and in the EXAFS oscillations amplitude and phase shift, between our solutions and the Pt(II)-S reference PtS, confirming the same redox state (Pt+II) and square planar coordination of Pt in hydrothermal fluids (as in the PtS solid).