



Experiment title: High-energy resolution XAS/XES study of the valence state and ligation of Au and Pt in hydrothermal fluids and ore minerals

Experiment number:
20-01-782

| | | |
|---------------------------------|---|--------------------------------------|
| Beamline: BM20 | Date of experiment: from: 07.12.2016 to: 16.12.2016 | Date of report: 21.03.2017 |
| Shifts: 26 | Local contact(s): Kristina Kvashnina, BM20, ESRF | <i>Received at ESRF:</i> |

Names and affiliations of applicants (* indicates experimentalists):

***Kristina Kvashnina**, ESRF, Grenoble

***Alexander Trigub**, NRC “Kurchatov Institute”, Moscow, Russia

***Maximilian Nickolsky**, ***Olga Filimonova**, ***Boris Tagirov**, Institute of Geology of Ore Deposits RAS, Moscow, Russia

Report:

The experiment was designed in order to elucidate some important problems of hydrothermal chemistry of Au and Pt, including the chemical state of Pt in sulfide ores, and the chemistry of these metals in chloride hydrothermal fluids and melts. The experiment consisted of two parts. The first part was performed at RCH-II experimental station. This part included record of ambient temperature Pt L_3 -edge high energy resolution fluorescence detected (HERFD) XANES spectra and resonant inelastic X-ray scattering (RIXS) maps for synthetic Pt phases. The HERFD XANES spectra were recorded for all possible crystalline compounds of Pt with chalcogens, semimetals, and for some intermetallic compounds which were synthesized in our laboratory:

- PtS, PtS₂, PtSe₂, PtTe, PtTe₂, PtAs₂, PtSb₂, PtBi₂, PtGa, PtGa₂, PtGa₆, Pt₂Ga₃, Pt₃Ga₇, Pt₅Ga₃, PtIn, Pt₂In₃, PtSn, PtSn₂, PtSn₄, Pt₂Sn₃, PtPb, PtPb₄, Pt₃Pb, PtHg, PtBiTe, and Pt₂HgSe₃. The Resonant inelastic X-ray scattering (RIXS) maps were recorded at the Pt L_3 -edge for Pt, PtS, and PtS₂. In addition, we recorded HERFD XANES spectra for Pt-Cl compounds – aqueous solution of H₂PtCl₆ and K₂PtCl_{4(cr)} where Pt exists in different oxidation states. Collected data will be used to evaluate the unoccupied DOS for 5d orbitals of Pt, and to reveal the regular changes of atomic charges which take place with the changes of the compositions of Pt compounds.

The second part of the experiment was performed at RCH-I station and consisted of the record of TFY XAS (XANES and EXAFS) spectra. The experimental systems included:

1) Au-Cl and Pt-Cl aqueous fluids. For this experiment we prepared a series of silica glass capillaries (250µm ID, 600 µm OD, 13 mm length) filled with experimental solution and a small piece of Au or Pt. Experimental solutions were 7.2m HCl/4.2m CsCl (+Na₂SO₃/H₂SO₄ oxygen buffer), and two solutions of 3.8m HCl + KCl/K₂S₂O₈ (potassium persulfate served as a source of oxygen which is necessary for the metal dissolution). The capillaries were heated to desired temperature using Microtomography furnace available at ESRF. At high temperature the metals dissolved in aqueous fluids, and, after the signal stabilization, the Au and Pt L_3 -edge spectra were recorded. The spectra collected during this part of the experiment are shown in Fig. 1. These spectra will be used to reveal the nature of Au-Cl and Pt-Cl interaction in high temperature geological fluids, and to calculate stability of Au and Pt chloride complexes.

2) Au and Pt in dry chloride melts. These experiments were performed by heating of silica glass capillaries which contained RbCl/KCl mixture of eutectic composition + K₂S₂O₈ as an oxygen source. The spectra collected at 650 °C demonstrated strong Au- and Pt-Cl complexing even in the absence of water. Interpretation of EXAFS spectra showed the presence of Cs atom in the second coordination shell of Au and Pt in dry melts, whereas Cs was not detected in distant coordination shells of Au and Pt aqueous chloride complexes.

3) Pt admixture in pyrite FeS_2 and pyrrhotite Fe_{1-x}S . The Pt L_3 -edge spectra of several samples of synthetic crystals of Pt-bearing pyrites with $C(\text{Pt})$ 0.2–4 wt.% Pt, and one sample of pyrrhotite with 0.1 wt.% Pt were recorded. One sample of Pt-bearing pyrite was heated in silica glass capillary to the synthesis temperature of 650 °C. The spectra for Pt-bearing pyrite with 4 wt.% Pt collected at ambient and high temperature is shown in Fig. 2 together with the fitting results. This experiment demonstrated, for the first time, that Pt in Fe-S minerals can present in the chemically bound nonmetallic state in the form of isomorphous solid solution or nanosized Pt-Fe-S particles.

4) In in sphalerite $(\text{Zn}, \text{Fe})\text{S}$. The aim of this experiment was to determine the chemical state of In in sphalerite - the main source of this strategic metal. To date this task has not been solved, mainly due to low concentration (ppm level) of In in natural sphalerites. Besides, previously we found that the concentration of Au disseminated in the matrix of sphalerite is correlated with the concentration of In. We recorded In K -edge spectra for several samples of synthetic pure and Fe-sphalerites which contain up to 0.1 wt.% of In, together with the spectra of reference compounds – In sulfides and oxides. These data will contribute to understanding of the local atomic environment and oxidation state of In in sphalerite and, we expect, will be useful for the In ore processing.

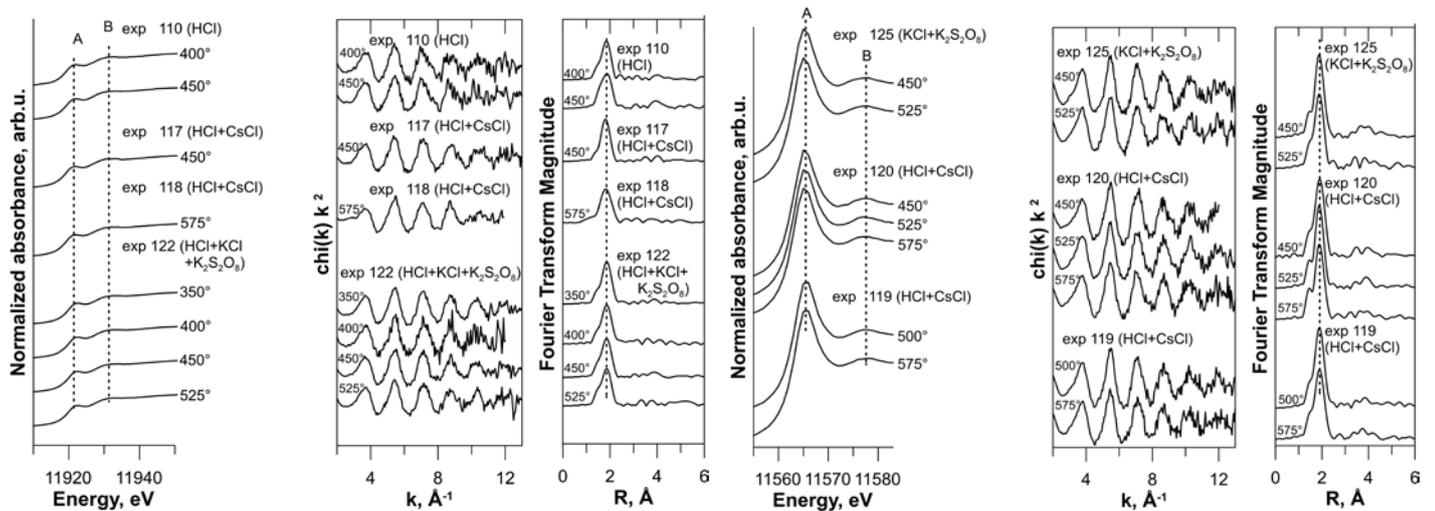


Fig. 1. Gold (*left*) and platinum (*right*) L_3 -edge XANES spectra, background subtracted EXAFS spectra, and Fourier transforms of the EXAFS spectra (uncorrected for phase shift) of acidic chloride fluids. Pressure range 0.5 – 2.5 kbar. Vertical dotted lines indicate positions of two main spectral features of XANES spectra, and position of the first peak of the Fourier transform of EXAFS function which corresponds to Me-Cl pair correlation.

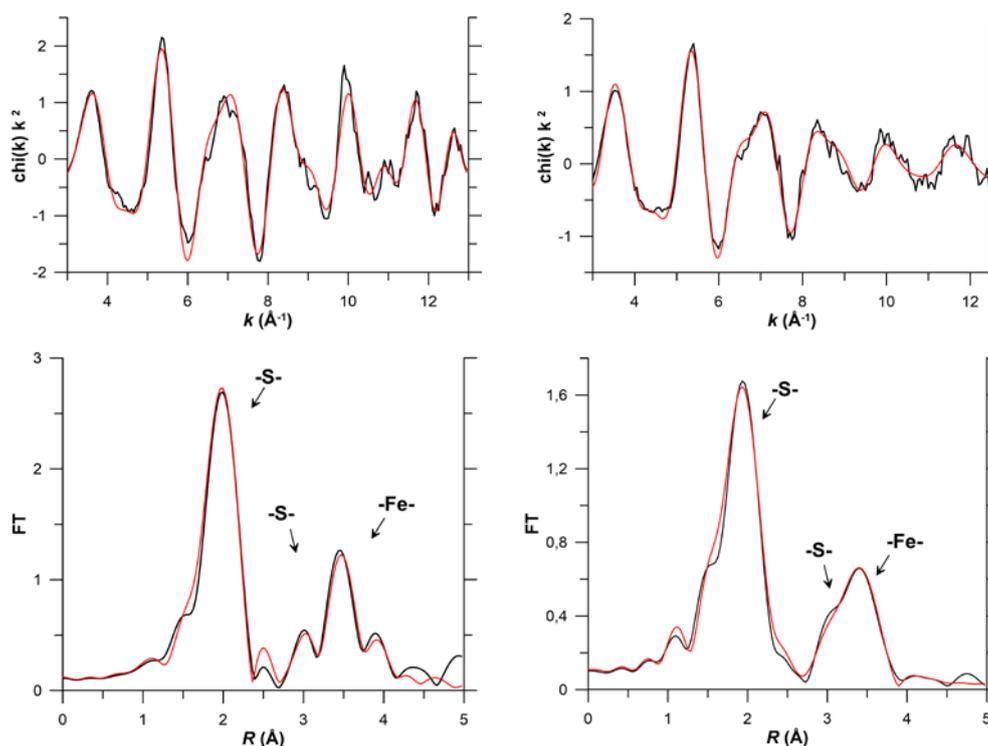


Fig. 2. The k^2 -weighted Pt L_3 -edge EXAFS spectra recorded for synthetic Pt-bearing pyrite FeS_2 (synthesis in $\text{RbCl}/\text{NaCl}/\text{KBr}$ eutectic mixture at 650 °C), and their Fourier transforms. The pyrite sample contains 4 wt.% Pt. *Left* – ambient temperature, *right* – heated to $t = 650$ °C. Black lines show the experimental spectra, red curves – their preliminary fit. The feature labels show scattering paths from different atoms. Six S atoms present in the first coordination shell of Pt at 2.37 ± 0.02 Å, the distant shells are fitted using modified pyrite atomic structure.