ESRF	Experiment title: **A XAFS spectroscopy study of arsenic complexes in high temperature aqueous fluids: Implications for As transport and the formation of As-bearing minerals in hydrothermal environments**	**Experiment number**: ME-73
Beamline: BM 32	**Date of experiment**: from: 10 May 2000 to: 16 May 2000	**Date of report**: 15 August 2000
Shifts: 18	**Local contact(s)**: J.L. Hazemann, Laboratoire de Crystallographie, Grenoble	*Received at ESRF:*

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Report:

Experimental: Stoichiometry and structure of As(III) and As(V) hydroxide complexes in aqueous solution were caracterised at temperatures from 30 to 500°C and pressures from 1 to 600 bar using high resolution XAFS spectroscopy with a special high T-P optical cell recently designed at the Laboratory of Cristallography in Grenoble and installed at CRG BM32 beamline at the ESRF (Soldo et al., 1998; Testemale, 2000). XANES and EXAFS spectra of the experimental solutions were recorded at the As K-edge (11 keV) in transmission mode. Details on spectra acquisition and treatment procedure were similar to those described by Pokrovski et al. (1999a;2000), and Testemale (2000).

XAFS results for As(III)-bearing solutions: Interpretation of resulting spectra for the As(III) solutions (0.3 mol As) shows that As is surrounded by 3±0.2 oxygens atoms with an averadge As-O distance of 1.79±0.01 A over the entire T-P range studied. No second shell neighbours (O or As) has been detected. This indicates the existence of the monomeric As(OH)3 species, in agreement with previous solubility and Raman spectroscopy studies (Pokrovski et al., 1996; Gout et al., 1997). No changes in spectra were observed in the presence of 10% NaCl (Fig. 1). These results demonstrate that the As(OH)3 complex is the dominant As species in most natural hydrothermal fluids in a wide range of temperatures and pressures.

XAFS results for As(V)-bearing solutions: The spectra of a 0.3 mol As(V) solution below 250°C are consistent with the predominance of arsenic acid H3AsO4 or its anion (H2AsO4-). In these complexes As is found to be tetrahedrally coordinated by oxygens with As-O distances of 1.70 A. No changes in As-O distance were observed from 30 to 300°C, demonstrating, as in the case of As(III), a strong covalent character of As(V)-O bonds, and a weak influence of solvation on the structure of the 1st coordination sphere of As. At temperatures higher than 300°C a precipitation of As(V) in the form of As2O5 solid coupled with reduction of As(V) to As(III) in solution has been observed. The analysis of the XANES part of the spectra recorded as a function of time provides an excellent in situ measure of both oxidation/reduction and precipitation kinetics, and As(III)/As(V) concentrations in solution (Fig. 2). These new data demonstrate that As(V) is not stable in solution with increasing temperature, and allow accurate determination of As(III)/As(V) ratio in solution and absolute As2O5 solubility as a function of temperature. These results permit to estimate, for the first time, the thermodynamic properties of H3AsO4 species and the value of As(III)/As(V) standard oxidation potential at high temperature hydrothermal fluids (Pokrovski et al., in prep.). These calculations are in agreement with the predominance of the As(III) hydroxide species As(OH)3 (Pokrovski et al., 1996) and the scarcity of As(V) in high temperature hydrothermal fluids (Heinrich and Eadington, 1986).

Figure 1

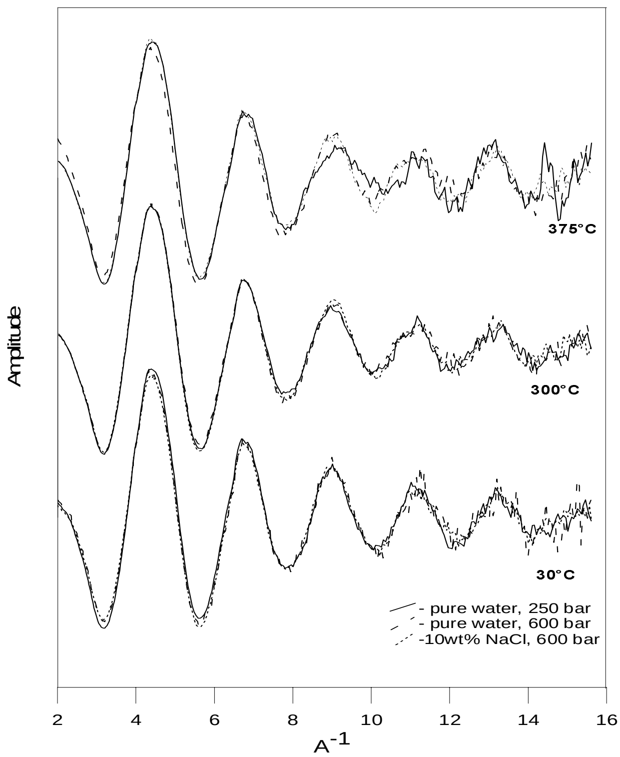

Figure 2

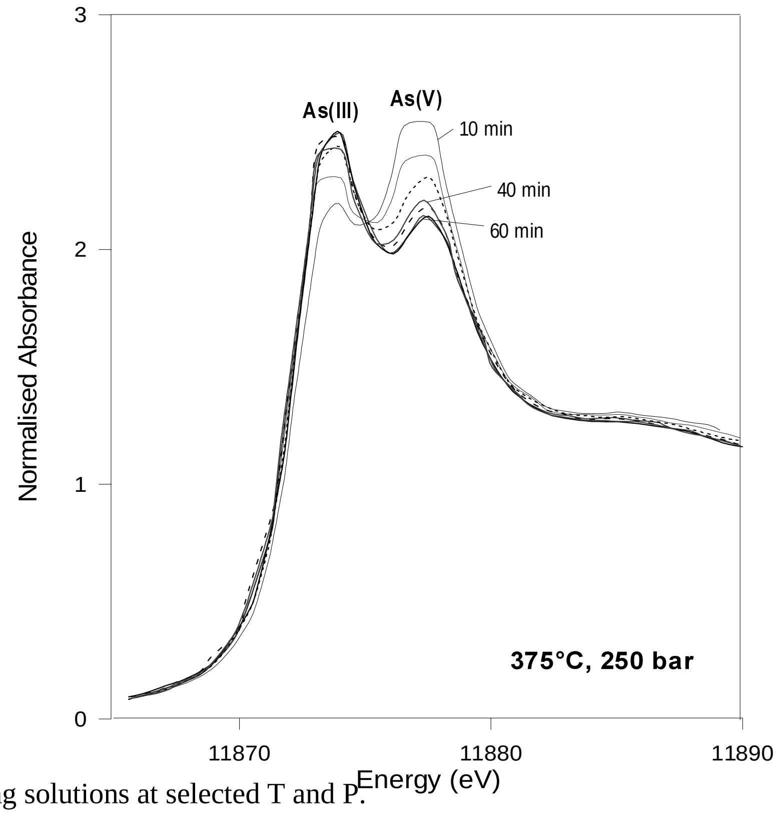

Fig.1 Normalized k2-weighted EXAFS of As(III)-bearing solutions at selected T and P.
Fig.2 Normalised XANES spectra of a 0.3m As solution at 375° and 250 bar, demonstrating the reduction of As(V) to As(III) as a function of time (in minutes) elapsed from the moment of attainment of 375°C.

Conclusion and perspectives: The results obtained in this project demonstrate the capabilities of XAFS technique for not only characterisation of structural atomic environment around the absorbing atom, but also *in situ* monitoring of oxidation/reduction and precipitation kinetics, as well as solubilities of solid phases in high temperature/pressure near- and supercritical solutions. The results obtained during this experiment were partially exposed in a DEA thesis (Testemale, 2000), and are now under preparation for publication in Chemical Geology and Geochimica et Cosmochimica Acta. Also, the work is in progress to combine the results obtained in this study with the available data on As-bearing minerals solubilities and As partition coefficients between vapour and aqueous solution (Pokrovski et al., 1999b) in order to better constrain the thermodynamic properties of As aqueous species and to model arsenic transport and precipitation in high temperature hydrothermal deposits of precious and heavy metals.

In view of the advantages of the XAFS method demonstrated above, studies of both metal atomic environment and solid/liquid and liquid/vapour partition coefficients will be pursued using this technique. These studies will use a new high temperature optical cell recently created in the Laboratory of Crystallography (Grenoble). This cell operates in fluorescence mode and, thus, allows accurate spectra acquisition at metal concentrations as low as 10^{-4}-10^{-5} mol. These concentrations are close to those of many heavy and precious metals (Sb, Au, Pt, TR) found in high temperature hydrothermal fluids. XAFS studies of these and other elements will allow better understanding of their behavior in natural waters and will provide new insights about metal-solvent interactions under near- and supercritical conditions.

References

Gout R., Pokrovski G., Schott J., & Zwick A. (1997) *J. Raman Spect*. 28, 725-730.
Heinrich C.A. & Eadington P.J. (1986) *Econ. Geol.* 81, 511-529.
Pokrovski G., Gout R., Zotov A., Schott J., Harrichoury JC. (1996) *Geochim. Cosm. Acta* 60, 737-749.
Pokrovski G., Schott J., Martin F., Hazemann JL., & Farges F. (1999a) in: *BIOXAS-99*.
Pokrovski G., Roux J., & Zakirov I. (1999b) in: *Proceedings of ICPWS XIII, 12-16 Sept. 1999 (in press).*
Pokrovski G., Martin F., Hazemann J.-L., & Schott J. (2000) *Chem. Geol.* 163, 151-165.
Soldo Y., Hazemann JL., Aberdam D., Inui M., Tamura K., Raoux D., Pernot E;, Jal JF., & Dupuy-Philon J. (1998). *Phys. Rev*. B 57, 258-268.

Testemale D. (2000) Comportement de As et U en milieu aqueux supercritique. Memoire de DEA de l'Université J. Fourier, Grenoble.