ESRF	Experiment title: **A XAFS spectroscopy study of antimony speciation and the solubility of Sb(III) oxides in near- and supercritical aqueous fluids: Implications for metal-solvent interactions at critical conditions, and Sb transport in hydrothermal environments**	**Experiment number**: CH-1190
Beamline: BM 29	**Date of experiment**: from: 14 November 2001 to: 20 November 2001	**Date of report**: 10 February 2002
Shifts: 18	**Local contact(s)**: Dr. Gloria Subias Peruga, BM 29, ESRF	*Received at ESRF:*

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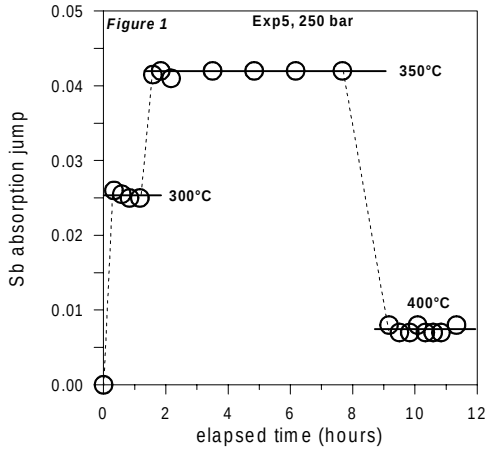
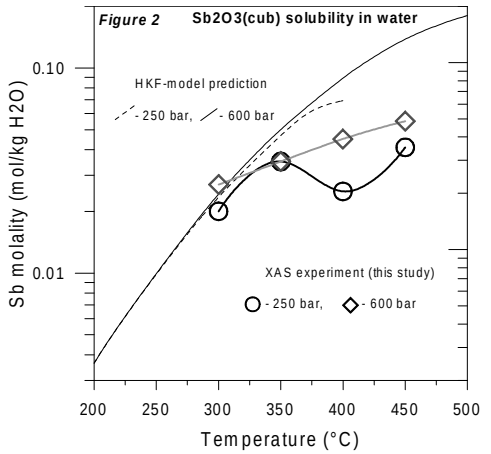
Report:

Experimental: Dissolution of natural senarmontite (Sb_2O_3, cub) and local atomic structure around Sb in aqueous solution were characterized by *in situ* XAFS spectroscopy, at temperatures from 250 to 450°C and pressures 250 and 600 bar, using a special high T-P cell recently designed at the Laboratory of Crystallography (Grenoble). XANES and EXAFS spectra of aqueous solutions in contact with Sb_2O_3 were recorded at the Sb K-edge (~30.5 keV) in both transmission and fluorescence mode at BM29 beamline of ESRF. Details on spectra acquisition and treatment procedure were similar to those described by Pokrovski et al. (2000; 2002a,b) and Testemale (2000).

Results on senarmontite dissolution in high-temperature aqueous fluids: The amplitude of the absorption jump of XAS transmission spectra is proportional to the fluid density (close to that of pure water) times Sb mass concentration in solution. This allows accurate monitoring of Sb dissolution kinetics. First experiments demonstrated a loss of Sb from the hot zone because of its rapid recrystallization in the cold parts of the reaction cell. Consequently, the cell design was essentially modified to avoid this. An example of a successful experiment is shown in Fig. 1. Sb aqueous concentrations were found to attain a steady state with the solid within an hour at temperatures above 300°C. It can be seen in Fig. 2 that at 300 and 350°C Sb_2O_3(cub) solubilities obtained in this study are in good agreement with thermodynamic predictions based on earlier measurements in a close reactor (Zotov et al., 2002 and refs therein). At higher temperatures (≥400°C) however, our solubilities are significantly lower than the predictions, and exhibit a minimum around 400°C at 250 bar, which was not expected from the available thermodynamic models (HKF, Zotov et al., 2002). These new findings imply that important changes in solute-solvent interactions are likely to occur near the critical point of water. Additional experiments are necessary to better constrain Sb solubilities in these low-density supercritical fluids.

Results on Sb local atomic structure in solution: The X-ray flux and fluorescence detection at BM29 were found to be insufficient to obtain good fluorescence spectra for our dilute Sb solutions (<0.05 mol/kg H_2O). Yet, accurate transmission spectra have been obtained, but required very long acquisition time (about 1 to 2 shifts for each T and P). As a result, the local Sb structure could be probed to only 11-12 A^{-1} in the best case (Fig. 3). A preliminary treatment of XANES and EXAFS spectra indicates that antimony has an oxidation state of 3+ in solution and is surrounded by 3±0.5 oxygens with an average Sb-O distance of 1.96±0.01Å from 300 to 450°C. This is in agreement with the $Sb(OH)_3$ complex which is believed to be dominant in these fluids (Zotov et al., 2002). Fine changes in Sb 1st shell structure with temperature and pressure, and the presence of more distant atomic shells could not, however, be detected because of the low signal-to-noise ratio of the transmission spectra.





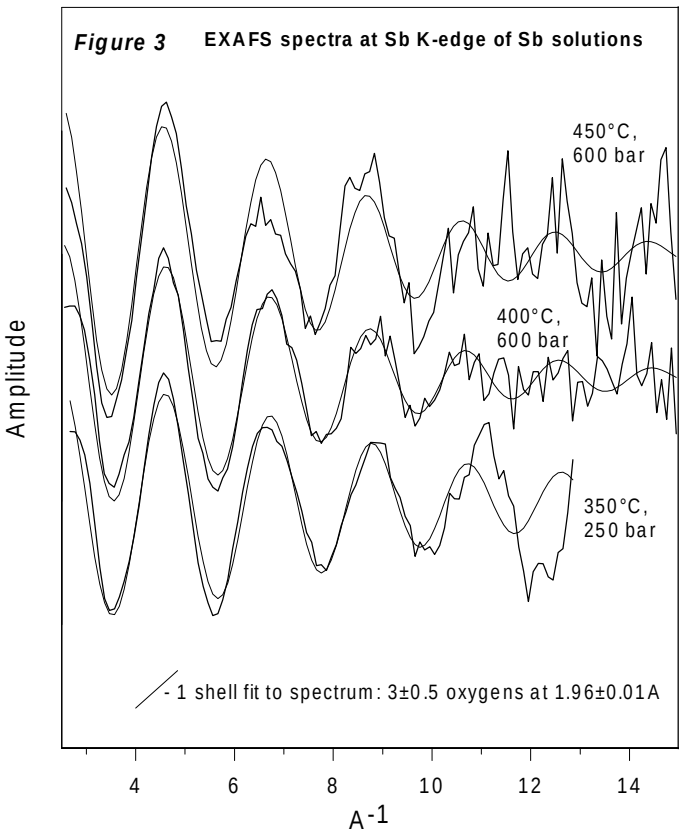


Fig.1 Evolution of the absorption jump of aqueous Sb as a function of time for a successful experiment.
Fig.2 Senarmontite solubility in water as a function of temperature and pressure.
Fig.3 Normalized k^2-weighted EXAFS spectra of Sb(III) solutions in equilibrium with senarmontite at given T and P.

Conclusion and perspectives: This experiment has demonstrated the capabilities of XAFS technique for not only characterization of structural atomic environment around the absorbing atom, but also *in situ* monitoring dissolution/precipitation kinetics, and solubilities of solid phases in high-temperature/pressure near- and supercritical solutions. This study has provided new data about Sb solubilities in crustal fluids, which can help in developing more accurate thermodynamic and structural models of solute-solvent interactions in the vicinity of the fluid critical point. Work is currently in progress to compare the temperature/pressure structural evolution of Sb aqueous complexes with that of analogous As species which have been studied recently (Testemale, 2000; Pokrovski et al., 2002b). It is thus desirable to continue this study using the improved cell design and higher X-ray flux and better detection provided by other ESRF beam lines. The new FAME beam line is likely to be the best suited for such experiments. This would allow to go further in the mysterious domain of supercritical fluids where our current knowledge of the physical chemical and structural behavior of metals is very limited.

References:

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