



	Experiment title: A XAFS spectroscopy study of antimony speciation and the solubility of Sb-bearing minerals in high-temperature geological fluids: Implications for metal-solvent interactions at critical conditions, and Sb transport in hydrothermal environments	<b>Experiment number:</b> 30-02-644
<b>Beamline:</b> BM30B	<b>Date of experiment:</b> from: 28 October 2004                      to:                      02 November 2004	<b>Date of report:</b> 21 January 2005
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr. Jean-Louis Hazemann, FAME, ESRF	<i>Received at ESRF:</i>
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## Report:

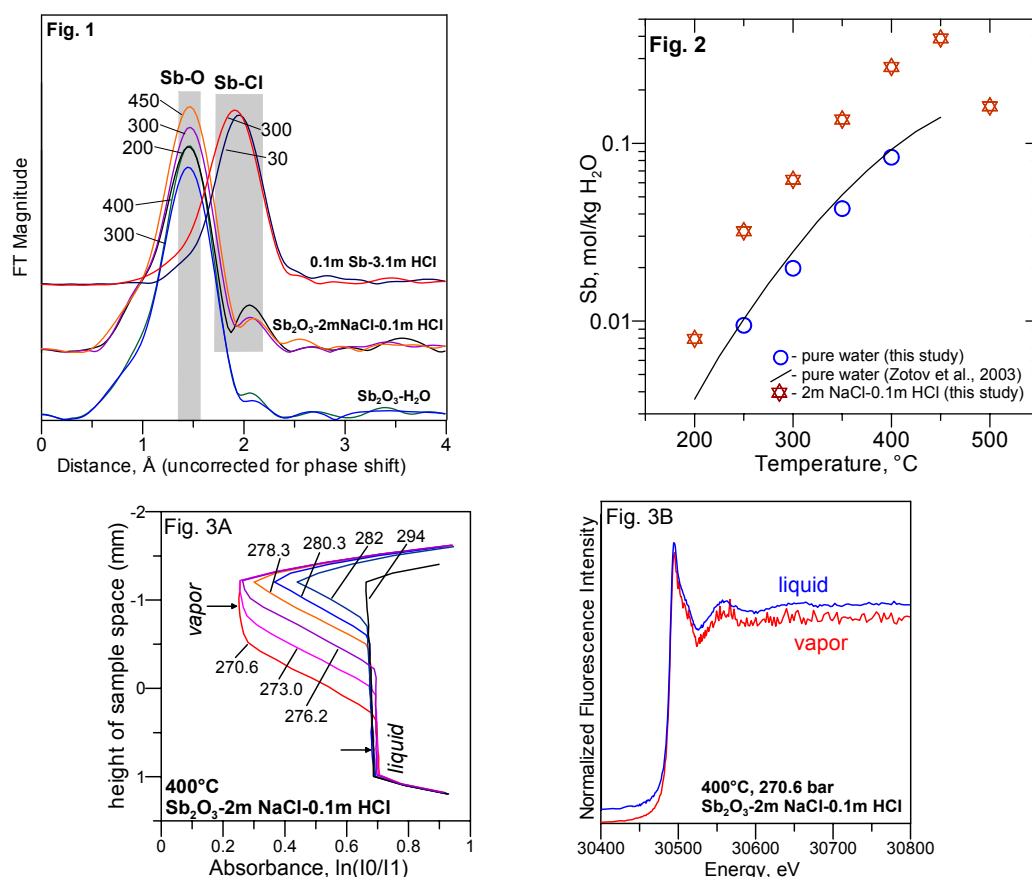
**Experimental:** Dissolution of natural senarmonite ( $\text{Sb}_2\text{O}_3$ , cubic) and local atomic structure around Sb(III) in pure water and NaCl-HCl aqueous solutions were characterized by *in situ* XAFS spectroscopy at Sb K-edge ( $\sim 30.5$  keV) at temperatures to  $500^\circ\text{C}$  and pressures to 600 bar, using a new X-ray cell [1]. This cell allows simultaneous measurement of the absolute concentration of the absorbing element in the fluid (from edge-step height in transmission mode, fluid density and absorption cross-section of the element), and atomic environment around the absorber (from analysis of XANES and EXAFS spectra in fluorescence and transmission modes). Details about the cell operation, spectra analysis and solubility determination can be found elsewhere [2]. The new sample-holder design consists of a vertically oriented glassy-carbon tube with two mobile sapphire pistons inside fitted with Viton seals. This allows controlled changes of the cell internal volume with temperature and pressure. The new construction avoids solute precipitation in the colder parts of the cell and permits acquisition of high-quality spectra on dilute systems because of the low X-ray absorption of the glassy carbon.

**Results on Sb local atomic structure in the fluid:** Four different experiments were performed. Spectra of aqueous Sb in pure water in equilibrium with  $\text{Sb}_2\text{O}_3$  from  $250$  to  $400^\circ\text{C}$  at 600 bar (Experiment 1) exhibit a single-shell contribution from  $3 \pm 0.3$  oxygens at  $1.97 \pm 0.01$  Å, consistent with the  $\text{Sb}(\text{OH})_3$  complex, similar to  $\text{As}(\text{OH})_3$  [3,4]. Spectra of a 0.1m Sb(III) - 3.1m HCl aqueous solution (Experiment 5) show a single Sb-Cl shell with average number of Cl atoms increasing from 2 to 3 and Sb-Cl distances decreasing from 2.43 to 2.38 Å when temperature changes from  $30$  to  $400^\circ\text{C}$  at 600 bar. This is consistent with the formation of Sb chloride complexes, in agreement with previous EXAFS studies [5]. In a 2.0m NaCl - 0.1m HCl solution in equilibrium with senarmonite at 600 bar (Experiment 2), Sb exhibits two nearest-shell contributions arising from  $2.4 \pm 0.3$  O at  $1.97 \pm 0.01$  Å and  $\sim 0.4 \pm 0.2$  Cl at distances decreasing from 2.45 to 2.37 Å when temperature raises from  $200$  to  $450^\circ\text{C}$  (Fig. 1). In addition, a fourth experiment was performed in the same system at the vapor-liquid equilibrium at  $400^\circ\text{C}$  and 320-270 bar (Experiment 3/4, Fig. 3A). Sb atomic environment in the liquid phase is identical to that of Experiment 2, implying same mixed OH-Cl complexes. Although the poor statistics of the vapor-phase spectrum does not allow quantitative treatment, their XANES part is close to that of the liquid-phase spectra, thus suggesting the formation of analogous species (Fig. 3B).

**Results on  $\text{Sb}_2\text{O}_3$  solubility and vapor-liquid partitioning in high-temperature fluids:** Monitoring the amplitude of absorption edge of transmission spectra as a function of time shows that senarmonite-solution equilibrium in Experiments 1, 2 and 3/4 was attained within an hour at temperatures above  $200^\circ\text{C}$ . The derived Sb equilibrium concentrations in pure water (Fig. 2) are in excellent agreement with previous predictions based on batch-reactor measurements which were interpreted by the formation of a neutral hydroxide  $\text{Sb}(\text{OH})_3$  [6]. In the presence of chloride (Experiment 2), senarmonite solubility is  $\sim 3$  times higher in the range  $200$ - $450^\circ\text{C}$ , demonstrating the formation of other Sb complexes (Fig. 1, 2). Combining the measured solubility increase with the average numbers of O and Cl neighbors around Sb derived from the EXAFS analysis above, we conclude that  $\text{Sb}(\text{OH})_3^\circ$ ,  $\text{Sb}(\text{OH})_2^+$  and  $\text{Sb}(\text{OH})_2\text{Cl}^\circ$  contribute almost in equal proportions to the solubility in the NaCl-HCl solution studied. Thus, contrary to previous expectations [6], mixed hydroxide-chloride species may play a major role in Sb transport in acid saline ore-forming fluids. This new finding is also supported by our preliminary batch-reactor measurements (unpublished).

Our X-ray cell allowed the first *in situ* measurement of vapor-brine fractionation in a water-salt-acid system (Experiment 3/4, Fig. 3A,B). The Sb vapor-liquid partition coefficient derived at  $400^\circ\text{C}/270$  bar with  $\sim 0.1$  m HCl,  $K_{\text{Sb}} = 0.092 \pm 0.030$ , is about 2 times higher than that measured using a batch reactor at the same conditions in HCl-poor

system ( $<0.01\text{m HCl}$ ) where Sb vapor- and liquid-phase speciation is dominated by  $\text{Sb}(\text{OH})_3$ ,  $K_{\text{Sb}} \sim 0.045$  [7]. This is the first demonstration that mixed Cl-OH species can significantly contribute to antimony volatility in boiling acid salt-rich natural fluids.



**Fig. 1** Fourier Transforms of EXAFS spectra of 3 different experiments at indicated temperatures. Sb-O and SbCl contributions are indicated by the shaded regions.

**Fig. 2** Senarmontite solubility in water and NaCl-HCl solutions at 600 bar.

**Fig. 3** Demixtion experiment 3/4. (A) Absorbance measured at beam energy 30.57 keV by scanning the height of the cell at indicated pressures. Appearance of the low-density vapor phase is manifested by lower absorbance in the upper part of the cell with decreasing pressure. (B) Normalized XANES spectra of the coexisting phases recorded at 400°C/270.6 bar by subsequently positioning the cell at the beam passage heights indicated by arrows in Fig. 3A. Spectra are shifted along the Y-axis for clarity.

**Conclusion and perspectives:** This experiment demonstrated the capabilities of the XAFS technique for *in situ* measuring of mineral solubilities and, for the first time, vapor-liquid partitioning in high-temperature/pressure near-critical solutions. Our study provides new data about Sb speciation, stability and structure in acid saline fluids typical of natural hydrothermal-magmatic systems. Work is currently in progress to combine these results with batch-reactor solubility data to provide a consistent set of thermodynamic properties of Sb-OH-Cl complexes allowing prediction of Sb transport by crustal fluids. Our near-future projects are intended to better explore by XAFS spectroscopy the role of chloride and sulfide, the major natural ligands, in the transport and vapor-liquid distribution of noble metals, Ag and Au, using this new promising cell design.

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