



	<b>Experiment title:</b> Insights into formation of tin ore deposits: Influence of $fO_2$ on tin speciation in H <sub>2</sub> O-HCl fluids and effect of alkali carbonate solutions on cassiterite solubility	<b>Experiment number:</b> ES1049
<b>Beamline:</b> BM30	<b>Date of experiment:</b> from: 19.01.2022 to: 24.01.2022	<b>Date of report:</b> 28.02.2022
<b>Shifts:</b> 15	<b>Local contact(s):</b> Denis Testemale	<i>Received at ESRF:</i>
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## Report:

The aim of the proposed experiments is to provide new in-situ insight into cassiterite solubility and tin speciation in various hydrous supercritical fluids at pressures and temperatures relevant for formation of hydrothermal tin ore deposits using a hydrothermal autoclave and X-ray absorption spectroscopy.

For a more comprehensive understanding of tin complexation and speciation in supercritical fluids and conclusions on cassiterite precipitating reactions we determined cassiterite solubility in H<sub>2</sub>O-NaCl-HCl solutions and simultaneously established the Sn(II)/Sn(IV) ratio in the fluid as function of oxygen fugacity ( $fO_2$ ) at 400 bar and up to 350°C. Different  $fO_2$  conditions were obtained by adding various solid buffer systems to the experimental load (no buffer, Re/ReO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> or Co/CoO).

## *Preliminary results:*

After setting up the beamline, temperature calibration of the hydrothermal autoclave, and measurements of solid and liquid references, we were able to perform eight cassiterite dissolution experiments with each experiment running at least 4 hours (maximum duration: 14 hours).

Solubility of cassiterite in Cl-bearing fluids buffered with Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> or Co/CoO was below detection limit at least in the timeframe of the experiment (up to 12 hours). This indicates that all free Cl in the fluid is rapidly

consumed by dissolved Fe or Co from the buffer systems (formation of  $\text{FeCl}_2$  or  $\text{CoCl}$  complexes) and suggests that these solid buffer systems are not suitable in this case.

Preliminary results using no buffer or Re-ReO<sub>2</sub> buffer are summarized Figures 1 and 2. Figure 1 shows Sn concentrations in the fluid as function of time elapsed at experimental conditions. Corresponding data on Sn oxidation state is presented in Figure 2. In each successful experiment we observed some kind of oscillation of the Sn oxidation state which is seems to be connected to LN2 refills of the monochromator.

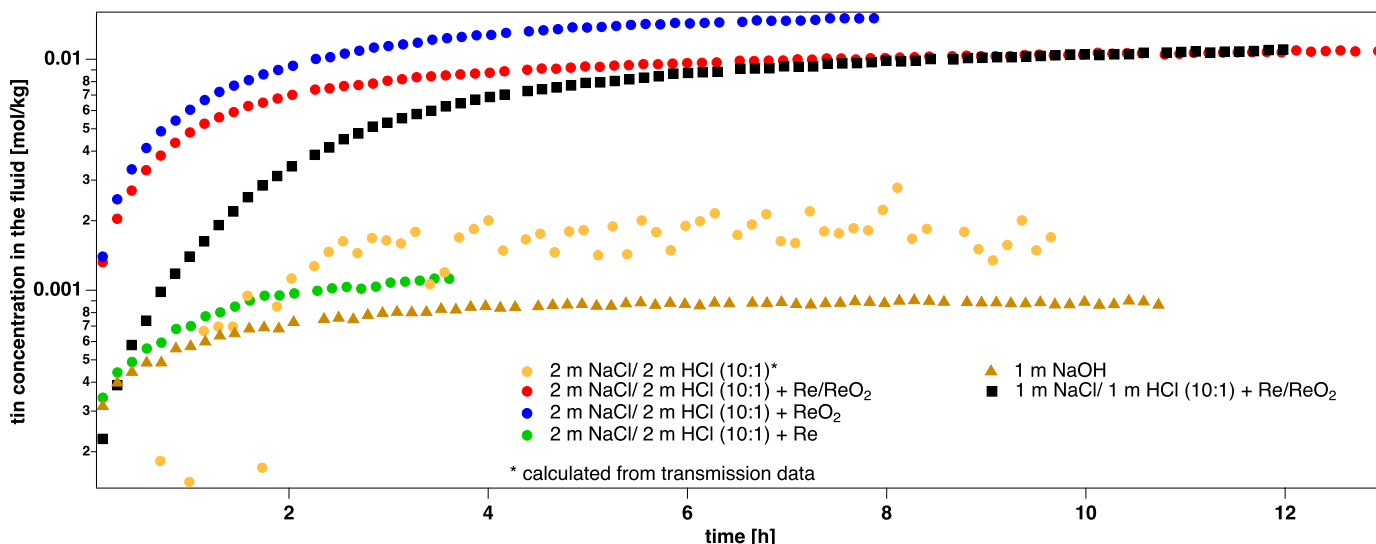


Figure 1: Tin concentration vs. time elapsed at 350 °C and 400 bar. Different colors represent different fluid and/or solid buffer systems.

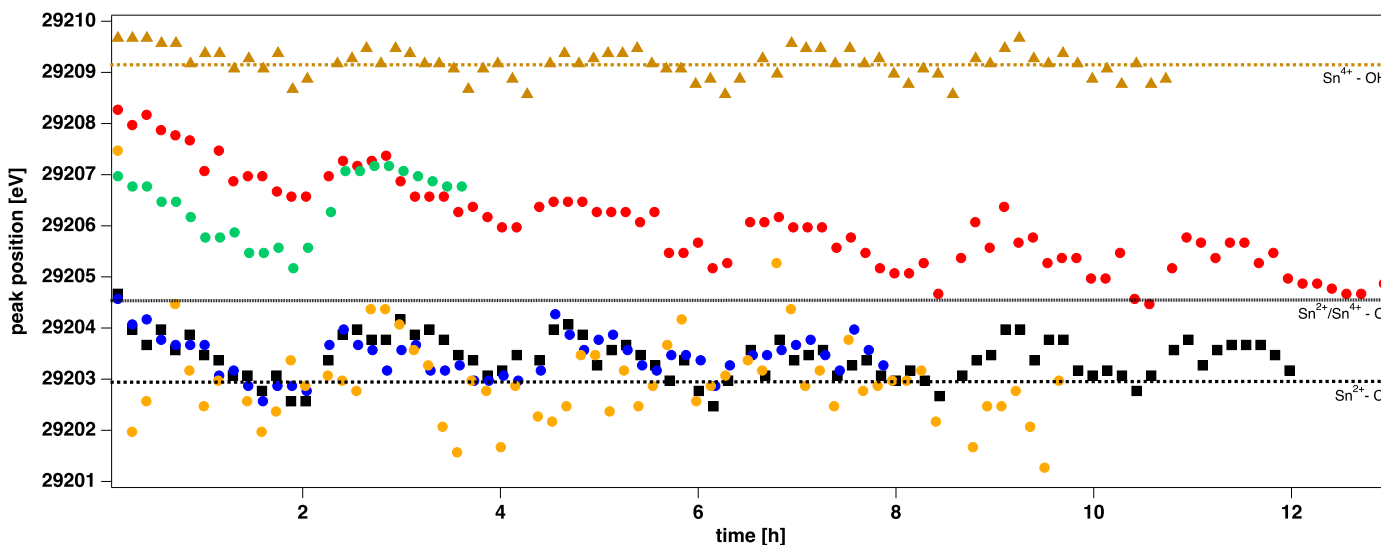


Figure 2: Tin oxidation state in the aqueous fluid vs. time elapsed at 350 °C and 400 bar. Same color code as in Figure 1.

Interpretation of the data is not straight forward and additional Raman experiments will be performed within the near future to understand the potential influence of glass-like carbon cell material on  $f\text{O}_2$  in experiments using Re-ReO<sub>2</sub> as solid buffer.

In general, beamtime was very successful. Results obtained during the experiment are very promising and will enable us to write at least one publication. The overall performance of the beamline was great (only one short beamloss, no problems with the autoclave) and the support by the local contact and the beamline staff is highly appreciated!