	Experiment title: Effect of fO2 on tin speciation in H2O-NaCl-HCl fluids – Implication for formation of tin ore deposits.	**Experiment number**: A30-2-1168
Beamline: BM30	**Date of experiment**: from: 30.03.2023 to: 07.04.2023	**Date of report**: 22.05.2023
Shifts: 20	**Local contact(s)**: Denis Testemale	*Received at ESRF:*

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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. This beamtime is a follow-up experimental session to complete the experimental series (previous beamtimes: proposal ES-1049 and an in-house beamtime at P65 at PETRA IV, DESY).

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_2O-NaCl-HCl solutions and simultaneously established the Sn^{4+}/Sn^{2+} ratio in the fluid at fixed oxygen fugacity (fO_2), 500 bar and up to 300°C and as a function of time.

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 four cassiterite dissolution experiments with each experiment running at least 20 hours.
Prelimnary results using Re-ReO_2 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.

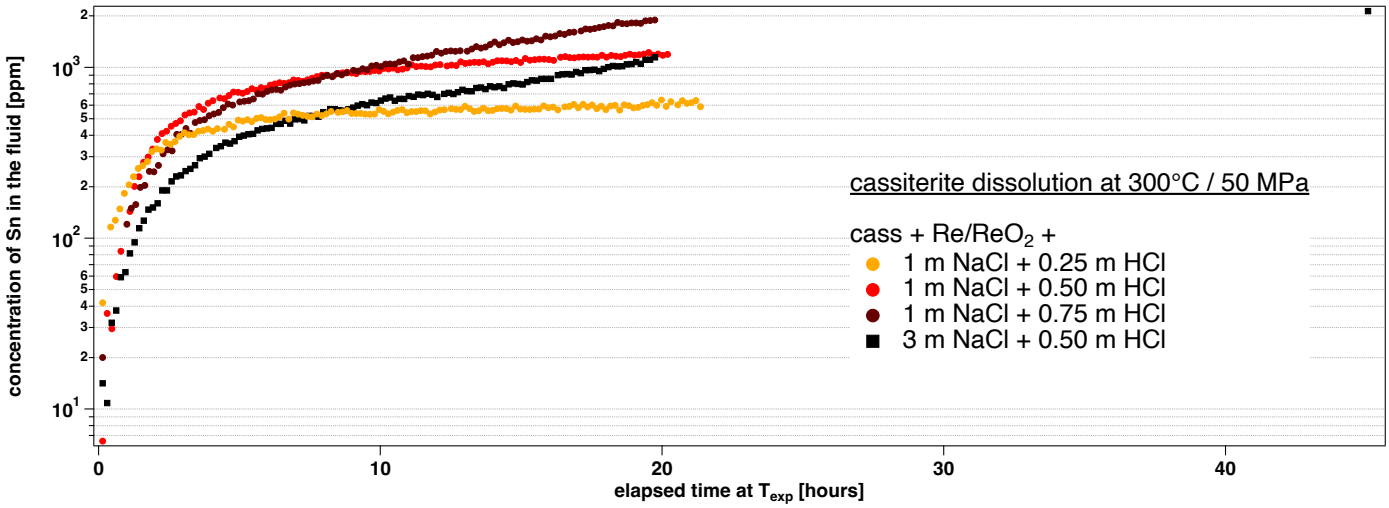

Figure 1: Tin concentration vs. time elapsed at 300 °C and 500 bar. Different colors represent different fluid compositions.

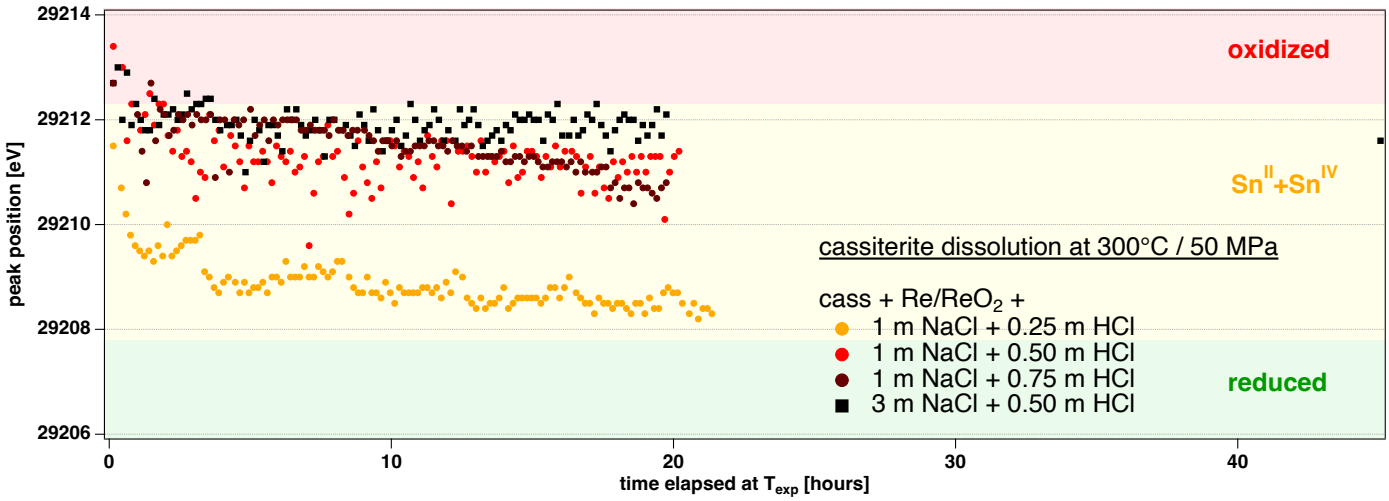

Figure 2: Tin oxidation state in the aqueous fluid vs. time elapsed at 300 °C and 500 bar. Same color code as in Figure 1.

The data clearly show that

a) dissolution of cassiterite is a slow process and depends on the overall Cl content of the fluid. None of the experiments reached equilibrium conditions even after ~45 hours which is a quite nice result as the same is expected for natural systems. So, all obtained cassiterite dissolution values represent minimum values. This is particular true for fluids containing high overall Cl concentrations.
b) Sn^{4+} is present in all experimental runs and the Sn^{4+}/Sn^{2+} ratio decreases with time for some of the experiments. These result will change our picture of formation of hydrothermal tin ore deposits.

In general, beamtime was absolutely sucessful. Results obtained during the experimental session are spectacular and will lead to at least one publication. The overall performance of the beamline was great and the support by the local contact and the beamline staff is highly appreciated!