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| ESRF | **Experiment title:** Unraveling the formation of economic tungsten deposits in the Earth's crust in hydrous fluids: Solubility of scheelite (CaWO4) in supercritical fluids in the system H-O-Cl-F | **Experiment number**: ES 621 |
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## Report:

Within the beamtime allocated for proposal ES-621, we performed a very successful and detailed study on the solubility and dissolution of $CaWO_4$ (scheelite) in supercritical hydrous liquids. The experiments reveal that tungsten (W), a so-called "strategic technology metal" [1], is indeed very mobile in hydrous supercritical fluids. We conducted *in-situ* EXAFS experiments at the L3-edge of W (10.207 KeV) to study scheelite solubility at a constant pressure of 600 bars at temperatures between 30°C to 500 $^{o}$C, using the hydrothermal autoclave at ESRF [2-3]. In order to assess possible chemical effects on the solubility and the complexation of W in high-P and high-T fluids, we ran experiments in pure $H_2O$, but also with diluted acids (e.g., HF (0.01, 0.1, 2 molar) and HCl (0.01, 0.1, 1 and 5 molar)). Figure 1 shows isobaric absorption spectra that clearly show that scheelite solubility increases with increasing T, only at T=500°C, the solubility decreases as precipitation of $CaWO_4$ or other tungstates occurs. Figures 2 and 3 show EXAFS data on $CaWO_4$ equilibrated with an HCl-solution at different T and $NaWO_3$ dissolved in $H_2O$ at different T.

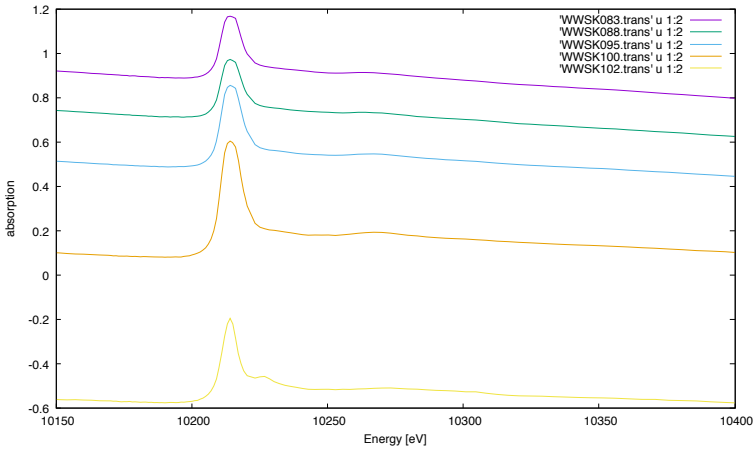


Fig. 1: Absorption spectra measured in transmission on 0.1 m HCl-solution equilibrated with crystalline $CaWO_4$ at 600 bar and temperatures indicated (°C).

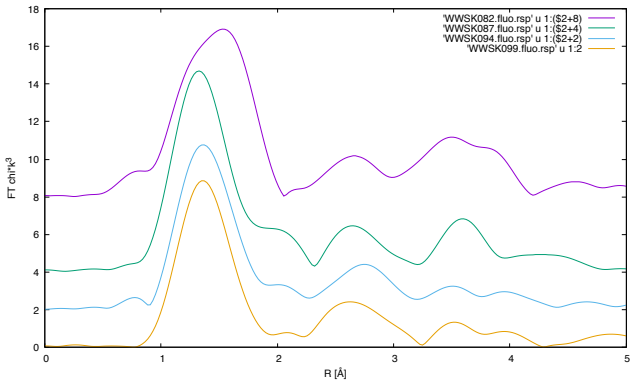


Fig. 2: Fourier transform of EXAFS-spectra for the same system as shown in Fig. 1. Difference between upper spectrum (100°C) and all other spectra indicates exchange of ligands with temperature. Colour coding as in Fig. 1.

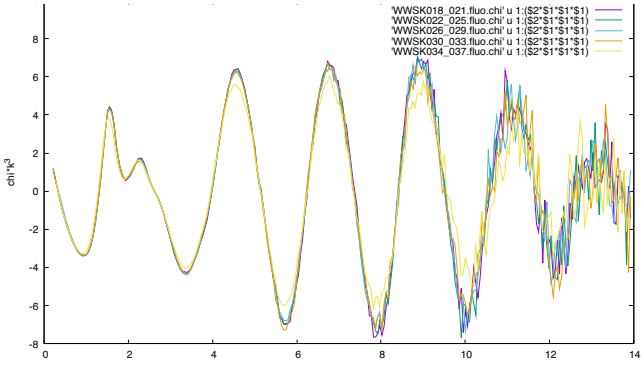


Fig. 3: W L-edge EXAFS-spectra of $H_2O$ with 0.03 m $NaWO_3$ dissolved, between 30 and 400°C at 600 bar. Spectra show no indication for changes in speciation, other than temperature effects.

Clearly, our new data from ES-621 provide new insights into W-mineral solubility and speciation of W in hydrous supercritical fluids and our data will prove important to assess earlier results from quench experiments [4,5] that claimed that scheelite solubility increases with increasing Cl of the fluid. As we have not fully reduced our data set, we cannot fully constrain the nature of the W-complexes in the different fluids, yet, but out data will certainly prove helpful in testing previous hypotheses that claimed that W is transported in fluids as $H_2WO_4$ and that Cl-complex formation was not relevant in hydrothermal fluids [6,7].

**References:**

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