

## Appendix A

### Effects of pH and salinity on the hydrothermal transport of tungsten: Insights from *in situ* Raman spectroscopic characterization of K<sub>2</sub>WO<sub>4</sub>-NaCl-HCl-CO<sub>2</sub> solutions at temperatures up to 400 °C

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## **Thermodynamic modeling of the stability of aluminosilicate phases at varying fluid pH**

The thermodynamic modeling was carried out to confirm the speciation of aluminosilicates (including K-feldspar, muscovite, topaz and kaolinite) as a function of environment's acidity in hydrothermal systems. The basis and detailed technics used for the Gibbs free energy minimization simulation can be found in [Zhong et al., \(2015\)](#), and the supplemental materials of [Wang et al. \(2019\)](#). The simulation was conducted in the K-Na-Al-Si-O-H-Cl system at 300, 350, 400 and 420 °C and 500 bar. A fluid-predominated system (with high fluid/rock ratio) was used to simulate the hydrothermal ore-forming system, with 1 kg of fluid containing 1.7 *m* of dissolved NaCl and 0.17 *m* of KCl. Varying amounts of HCl was added to the fluid to control the fluid pH. To monitor the speciation of aluminosilicates with changing fluid pH, small amount of silicate mineral (0.1 mol of muscovite) and excess quartz (1 mol) were added as the starting material. In general, muscovite will covert to K-feldspar in alkaline fluids (with high K<sup>+</sup>/H<sup>+</sup> ratios), and topaz (at high temperatures) or kaolinite (at lower temperatures) in acidic fluids, and this simulation investigates at which pH points these transitions takes place. The modeling results are shown in [Fig. S1](#). For comparison, the neutral pH values (those of pure water) are 5.43 at 300 °C, 5.57 at 350 °C, 5.94 at 400 °C and 6.22 at 420 °C (*P*=500 bar).

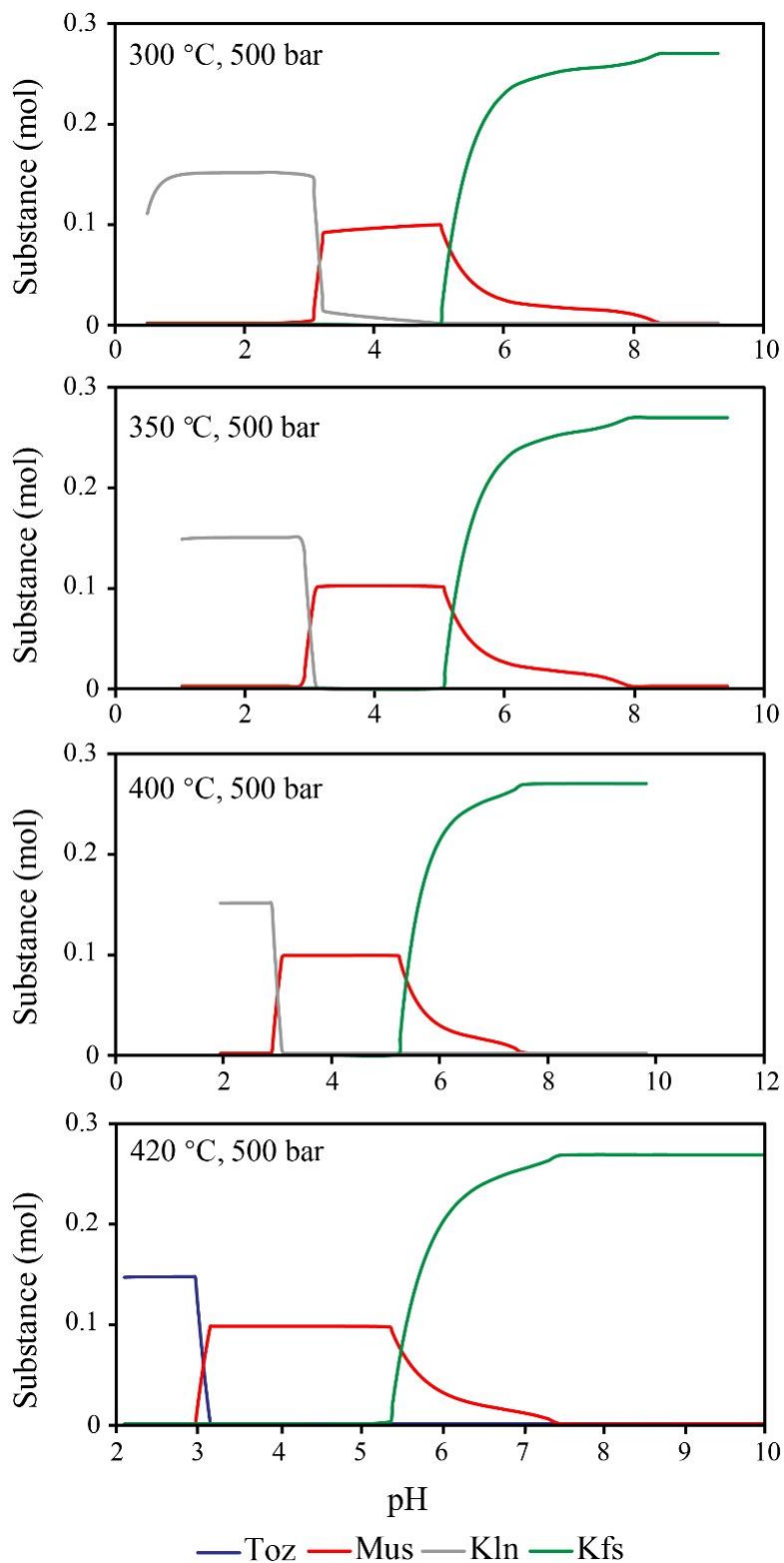


Fig. S1. The speciation of aluminosilicates at varying fluid pH. Quartz is in excess and not shown. Abbreviations: Toz=topaz, Mus=muscovite, Kln=kaolinite, Kfs=K-feldspar.

## References

- Zhong, R.C., Brugger, J., Chen, Y.J., and Li, W.B., 2015. Contrasting regimes of Cu, Zn and Pb transport in ore-forming hydrothermal fluids. *Chemical Geology* 395, 154–164.
- Wang X., Qiu Y., Lu J., Chou I-M., Zhang W., Li G., Hu W., Li Z., Zhong R. (2020) *In situ* Raman spectroscopic investigation of the hydrothermal speciation of tungsten: Implications for the ore-forming process. *Chem. Geol.* 532, article no. 119299, p1 – 14.