Tungsten (VI) speciation in hydrothermal solutions up to 400°C

E. CAROCCI[1], L. TRUCHE[2], M. CATHELINEAU[3], M.C. CAUMON[4], E. BAZARKINA[5]

1Univ. Lorraine, CNRS, Georessources, Nancy, France

2Univ. Grenoble Alpes, CNRS, ISTerre, Grenoble, France

*eleonora.carocci@univ-lorraine.fr

The knowledge of tungsten (W) speciation in hydrothermal solutions is of primary importance to develop geochemical models for the genesis of W ore deposits. Currently, W mobility in deep and hot geological fluids is poorly constrained. W in aqueous solution mainly exists under the form of $(WO_4)^{2-}$ and its protonated forms[1] depending on pH. Chloride does not form stable complexes with W[2]. However, polymeric W species such as the hexamer $(H_nW_6O_{21})^{n-6}$ or alkali metal complexes such as $NaWO_4$ or KWO_4, may also exist, but there is currently no thermodynamic data to predict their abundance[3]. Here, we evaluate the effect of pH, chloride and carbonate ligands on W speciation under hydrothermal condition. We use Raman spectroscopy coupled to the fused silica glass capillary technic to define the stability of the undocumented tungsten-polymers at T up to 400°C. In alkaline solutions, the only existing species is $(WO_4)^{2-}$, while in acidic solutions W speciation is far more complicated with the coexistence of $(HWO)^{4-}$ together with several polymeric species like $(W_6O_{19})^{2-}$ at low temperature, or the surprising predominance of the long chain, highly charged $(W_{10}O_{32})^{4-}$ species at high temperature. The polymeric species will probably play an important role in the W transport in acidic to neutral hydrothermal solutions. Carbonates have no effect on W speciation whatever T and pH. Obtained results demonstrate that Raman spectroscopy is the perfect tool to study the stability of the main undocumented tungsten-polymers at different pH, temperature and redox conditions.

[1] Wood, S. A. and Vlassopoulos, D. 1989. Experimental determination of the hydrothermal solubility and speciation of tungsten at 500°C and 1 kbar. *Geochim. Cosmochim. Acta*: 53, 303-12.

[2] Wood, S.A., 1992. Experimental determination of the solubility of WO_3(s) and the thermodynamic properties of H_2WO_4(aq) in the range 300–600 C at 1 kBar – calculation of scheelite solubility. *Geochim. Cosmochim. Acta*: 56, 1827–1836.

[3] Redkin, A.F. and Bondarenko, G.V., 2010. Raman spectra of tungsten-bearing solutions. *Journal of Solution Chemistry*: 39, 1549–1561.