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

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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 (WO₄)²⁻ and its protonated forms¹ depending on pH. Chloride does not form stable complexes with W². However, polymeric W species such as the hexamer (H₆W₆O₂₁)⁶⁻ or alkali metal complexes such as NaWO₄ or KWO₄ may also exist, but there is currently no thermodynamic data to predict their abundance³.

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 (WO₄)²⁻, while in acidic solutions W speciation is far more complicated with the coexistence of (HWO₄)⁻ together with several polymeric species like (W₆O₁₉)⁵⁻ at low temperature, or the surprising predominance of the long chain, highly charged (W₁₀O₃₂)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.