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The mechanisms of replacing wolframite by scheelite in hydrothermal fluids: insights from thermodynamic modeling

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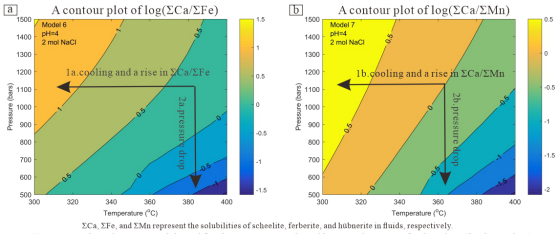

ΣCa, ΣFe, and ΣMn represent the solubilities of scheelite, ferberite, and hübnerite in fluids, respectively.

Two mechanisms are identified to cause scheelite replace to ferberite (hübnerite)

The occurrence of either scheelite ($CaWO_4$) or wolframite ([Fe,Mn]WO_4) in tungsten deposits is generally explained by the Ca content of the host rocks, but this cannot fully explain why the scheelite/wolframite ratios are highly variable and why wolframite is commonly replaced by scheelite or vice versa. To fill this gap in understanding the stabilities of wolframite and scheelite under hydrothermal conditions, the relative solubilities of scheelite and wolframite in hydrothermal fluids were constrained using two modeled chemical systems: W-Ca-Mn-Cl-Na-O-H and W-Ca-Fe-Cl-Na-O-H. The thermodynamic parameters of major species in the models come from the thermodynamic database SUPCRT and the update of [1-2] and this study. The concentrations of aqueous species and the solubility of wolframite (or scheelite) were calculated by the method of equilibrium constants using the R language free package CHNOSZ [3].

The two modeled chemical systems can well reproduce the available experimental data for scheelite, ferberite($FeWO_4$), and hübnerite ($MnWO_4$) solubilities under hydrothermal conditions. The modeling results indicate that scheelite is more soluble than hübnerite and ferberite under typical W-mineralizing conditions (300–400 °C, 500–1500 bars, and 1–3 mol/kg NaCl). Scheelite can replace ferberite (hübnerite) over a wide range of temperatures and pressures; therefore, the replacement of ferberite (hübnerite) by scheelite does not necessarily represent late stages of mineralization. Two mechanisms can cause scheelite to replace ferberite (hübnerite). The first mechanism is cooling with an increase in the Ca/Fe (Ca/Mn) molality ratio in fluids, and the second mechanism is a decrease in fluid pressure with constant Ca/Fe (Ca/Mn). Neither leaching Ca from Ca-rich wallrocks nor removing Fe (Mn) from hydrothermal fluids is required for the second mechanism. The second mechanism may account for vein-type or disseminated scheelite mineralization in host rocks whose Ca is low compared to carbonates.

[1] Miron, G.D., Wagner, T., Kulik, D.A., Heinrich, C.A., 2016. Geochimica et Cosmochimica Acta, 187: 41-78.

[2] Miron, G.D., Wagner, T., Kulik, D.A., Lothenbach, B., 2017.. American Journal of Science, 317(7): 755-806.

[3] Dick, J.M., 2019.. Frontiers in Earth Science, 7(180): 1-18.