The Hydrothermal Geochemistry of Tungsten in Granitoid Environments: I. Relative Solubilities of Ferberite and Scheelite as a Function of T, P, pH, and m_{NaCl}

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Abstract

The characteristics of granitoid-related tungsten deposits hosted in siliceous (carbonate-free) rocks (e.g., Panasqueira, Cligga Head, Pasto Bueno) are reviewed and the ranges of physicochemical parameters of the ore-forming fluids are summarized. The two important tungsten minerals in these deposits are wolframite and scheelite, which were deposited mostly between 200° and 500°C and 200 and 1,500 bars. The salinities of the mineralizing fluids were typically less than 15 wt percent but commonly were significantly higher (up to 55 wt %). The two predominant dissolved components are Na^+ and Cl^- with subordinate Ca^{2+}, K^+, and carbonate species (CO_3^{2-}/HCO_3^-). The contents of CO_2 are highly variable, but X_{CO2} values typically range from 0 to 0.1. Limited pH and f_{O2} estimates indicate a moderately acidic fluid with oxygen fugacities between those of the QFM and HM buffers. These parameters were used to guide solubility and speciation modeling of W in hydrothermal fluids in granitoid environments.

Experimentally derived thermodynamic data for scheelite, ferberite, aqueous Ca, Fe, and W species, and other required aqueous species were critically evaluated and the most reliable data were adopted. Where necessary, missing data were estimated. The resultant thermodynamic database provides a basis for solubility and speciation calculations in the system Ca-Fe-W-Cl-O-H. The simultaneous solubilities of scheelite and ferberite in NaCl-HCl-H_2O solutions were calculated at temperatures from 200° to 600°C, pressures from 500 to 1,000 bars, pH from 3 to 6, and m_{NaCl} from to 0.1 to 5.0 moles/kg H_2O. The solubility model takes account of the species H^+, OH^-, Na^+, Cl^-, $NaCl^0$, HCl^0, $NaOH^0$, $H_2WO_4^0$, HWO_4^-, WO_4^{2-}, Fe^{2+}, $FeCl^+$, $FeCl_2^0$, $FeOH^+$, FeO^0, $HFeO_2^-$, Ca^{2+}, $CaCl^+$, $CaCl_2^0$, $CaOH^+$, $NaHWO_4^0$, and $NaWO_4^-$. The calculations indicate the following: (1) solubilities of scheelite and/or ferberite can attain values as high as hundreds to thousands of parts per million as the tungstate species $H_2WO_4^0$, HWO_4^-, WO_4^{2-}, $NaHWO_4^0$, and $NaWO_4^-$; thus, tungsten-chloride, -fluoride, or -carbonate complexes, or more exotic species are not required to transport sufficient W to form an ore deposit; (2) the tungsten concentration in equilibrium with scheelite and ferberite increases strongly with increasing temperature, increasing NaCl concentration and decreasing pH, but is only weakly dependent on pressure; (3) the Ca/Fe ratio of a solution in equilibrium with both scheelite and ferberite decreases strongly with increasing temperature, i.e., the field of stability of scheelite expands with increasing temperature; the implication, therefore, is that simple cooling of a solution with a constant Ca/Fe ratio cannot result in the replacement of ferberite by scheelite, and that field observations of the late-stage replacement of ferberite by scheelite require an increase in the Ca/Fe ratio concomitant with cooling; (4) the Ca/Fe ratio is relatively independent of pH; and (5) the effect of NaCl concentration on this ratio changes

as a function of temperature and pressure. At less than 400°C the ratio is independent of, or decreases with, increasing NaCl concentration; at higher temperatures the ratio first decreases and then increases with increasing NaCl concentration. Experimental data on the solubility of scheelite and the Ca/Fe ratio of fluids in equilibrium with scheelite + ferberite, and which are not used in parameterizing our model, generally agree with the results of calculations performed using our thermodynamic database within an order of magnitude. However, our critical examination of available thermodynamic data reveals that significant uncertainty remains in several parameters (e.g., the solubility products of scheelite and ferberite and the association constants for alkali tungstate ion pairs). This uncertainty can only be reduced via carefully conceived, executed, controlled, and interpreted experiments, taking into account the various experimental pitfalls identified in this paper.