

Hydrothermal Transport and Deposition of Rhenium under Subcritical Conditions (up to 200°C) in Light of Experimental Studies

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Abstract

To investigate the aqueous species important for transport of rhenium under subcritical conditions, we conducted a series of solubility experiments from 100° to 200°C at vapor saturation pressures. In these experiments, oxygen fugacity was buffered by fixing the partial pressure of hydrogen gas, and pH was mainly buffered by $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$ and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ homogeneous aqueous buffers. These experimental solubility studies indicate that $\text{Re}(\text{OH})_4^0$ may be the predominant species over a wide range of pH from ~2.2 to ~8.8 in low-temperature solutions up to 200°C. The equilibrium constants in the temperature range from 100° to 200°C for the reaction $\text{Re}_{(\text{solid})} + \text{O}_{2(\text{gas})} + 2\text{H}_2\text{O} = \text{Re}(\text{OH})_4^0_{(\text{aqueous})}$ can be expressed as follows (temperature, T, is in degrees K):

$$\log K = -19.38 \pm 0.86 + \frac{29358 \pm 322}{T} \quad (2\sigma).$$

Sandstone copper deposits and black shales are typically enriched in rhenium, and our results may shed some light on their formation. As the formation temperature of such deposits is generally below 150°C, neutral species should be important for the transport of rhenium in them. Our evaluation further demonstrates that the species ReO_4^- is not important in the transport of rhenium, even under geologically relatively oxidizing conditions close to the $\text{HS}^-/\text{SO}_4^{2-}$ boundary in low-temperature environments typical of sandstone copper deposits and black shales. Our results suggest that several processes should be effective in concentration and deposition of rhenium, including (1) mixing of the fluids containing rhenium with cooler, sulfide-rich solutions, (2) decrease in temperature, (3) change in pH, and (4) redox reactions. Application of our results to sandstone copper deposits indicates that our findings are in good agreement with field observations, and it implies that mineralizing fluids responsible for the formation of sandstone copper deposits are capable of transporting thousands of tonnes of rhenium.

Extrapolation of our experimental results suggests that ReS_2 is important in controlling solubility in sulfur-bearing environments. Our calculations indicate that rhenium concentrations in the sulfide stability field, even close the $\text{HS}^-/\text{SO}_4^{2-}$ boundary, are very low ($\sim 10^{-6}$ to $\sim 10^{-5}$ ppm) in the temperature range from 100° to 200°C. This result may have important implications for the Re-Os isotopic system, implying that as long as low-temperature hydrothermal alteration is constrained to oxygen fugacity conditions under which sulfide is stable, disturbance of Re-Os systematics will not be severe.