The Thermodynamic Properties of Carrollite (CuCo2S4) and Their Application in Modeling Hydrothermal Co(-Cu) Ore-formation

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The production of electric vehicles has fueled a strong demand for Co, a critical component of the batteries used by these vehicles, and is projected to drive Co demand for the foreseeable future. Recently, much of this demand has been accommodated by increased production in the Central African Copperbelt (CACB), particularly in the Democratic Republic of the Congo (DRC), which accounts for ~70% of global Co production (2021). In the absence of robust Co recycling programs, increased exploration in this region and elsewhere will be required to meet future demand. However, the processes responsible for hydrothermal Co mineral deposition, the main means of Co concentration, are poorly understood, hampering exploration for this critical metal. A major reason for this poor understanding is that there are few thermodynamic data for Co minerals and none for carrollite ($CuCo_2S_4$), the principal ore mineral of Co in sediment-hosted deposits of the type exploited in the CACB. Consequently, it has not been possible to model the physicochemical conditions of hydrothermal Co transport and deposition and develop quantitative models of oregenesis on which to base exploration strategies.

In this study, calorimetry and solubility measurements are used to determine values of the standard thermodynamic parameters ($\Delta_f G°_{Tr,Pr}$, $\Delta_f H°_{Tr,Pr}$, $S°_{Tr,Pr}$, $C°p$, and $V°_{Tr,Pr}$) for carrollite at reference conditions (i.e., T_r = 25 °C and P_r = 1 bar). A value for $V°_{Tr,Pr}$ was calculated from published unit cell parameters. Low-temperature calorimetry measurements of $C°_p$ have been made in order to calculate $S°_{Tr,Pr}$. These data, in conjunction with solubility data collected for carrollite in equilibrium with an aqueous NaCl-HCl solution at 200 °C and saturated water vapor pressure, permit calculation of $\Delta_f H°_{Tr,Pr}$ and $\Delta_f G°_{Tr,Pr}$. Using the Python libraries Reaktoro and ThermoFun, we employ these new data for carrollite to build plausible geochemical models for the formation of sediment-hosted Cu-Co deposits.