

An experimental study of the elemental and isotopic fractionation of copper between aqueous vapour and liquid to 450°C and 400 bar in the systems CuCl-NaCl-H₂O and CuCl-NaHS-NaCl-H₂O

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The vapour-liquid (V-L) fractionation of Cu has been studied at 350, 400 and 450°C and 140 to 400 bar in the CuCl-NaCl-H₂O system to better elucidate the behaviour of copper in magmatic-hydrothermal ore-forming fluids. The effect of sulphur on the Cu V-L fractionation has been additionally studied at 400 °C by the addition of NaHS to the experimental system. The V-L fractionation of NaCl in the sulphide absent experiments corresponds very well to previous data for the H₂O-NaCl system, whereas the addition of NaHS caused a narrowing of the V-L coexistence field. The copper partition coefficients (DCuV/L) measured in sulphur absent fluids are higher than those measured in earlier works, but those for sulphur bearing fluids are in the same range as previous data. Our results are in accordance with a significant increase in DCuV/L in the presence of reduced sulphur. We also present data for the vapour-liquid fractionation of the stable isotopes of copper (⁶⁵Cu/⁶³Cu) in the CuCl-NaCl-H₂O system. The isotopic compositions of individual vapour and liquid sample pairs are generally indistinguishable within analytical uncertainty. However, from the compositions of the starting solutions to those of the final, lowest-pressure V and L sample pairs extracted from the autoclave, a shift to heavier values of $\delta^{65}\text{Cu}$ was seen. Specifically, between the starting compositions and those of the lowest-pressure vapour samples, the differences in $\delta^{65}\text{Cu}$ values were 0.16, 0.69 and 0.10‰ (all $\pm 0.07\%$ at 350, 400 and 450°C, respectively). This compositional shift is roughly proportional to the volume of vapour extracted between sample sets (6-35% of the total bulk fluid removed as vapour), indicating that ⁶⁵Cu/⁶³Cu fractionation follows a Rayleigh distillation process. Our results suggest that in a closed, boiling hydrothermal ore-forming environment, Cu isotopes exhibit conservative fractionation, and coexisting V and L will preserve the isotopic signature of the fluid source. However, in a structurally open system in which periodic vapour removal occurs, the movement of the escaped vapour outward from the magmatic source will result in cooling and the condensation of liquid droplets with heavier $\delta^{65}\text{Cu}$ values. This process will give the evolving vapour a progressively lighter $\delta^{65}\text{Cu}$ than the residual fluid near the source, although individual liquid droplets will be only marginally heavier in composition than the vapour from which they condensed. It follows that vapour and liquid fluid inclusions trapped at shallower depths (e.g., epithermal vein systems) will likely have lighter $\delta^{65}\text{Cu}$ values than their deeper magmatic counterparts and the source of the ore fluids.