Silver isotope fractionation in evaporation and redox processes: Implication to silver transport in hydrothermal systems

GE DONG [1], HAI-ZHEN WEI [1]*, A. E. WILLIAMS-JONES [2], SHAO-YONG JIANG [3], XI LIU [1]

[1]School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, PR China (haizhenwei@nju.edu.cn)
[2] Department of Earth and Planetary Sciences, McGill University, Montreal H3A 0E8, Canada (anthony.williams-jones@mcgill.ca)
[3] School of Earth Resources, China University of Geosciences, Wuhan 430074, PR China (shyjiang@cug.edu.cn)

Silver transport in hydrothermal deposits has been the subject of extensive study and shown to involve sulfide- and chloride-species, and to be significant in both aqueous liquids and vapours. In the case of $HCl-H_2O$ vapours, silver solubility as AgCl increases with increasing hydration number [1]. The fractionation of silver isotopes during evaporation and redox processes was explored experimentally and theoretically in the current work.

The experimental results show that the migration kinetics of silver from the liquid to the vapour follows a second-order kinetic reaction model, in which the activation energy and the apparent rate constant under neutral and acidic conditions are $E_a = 2.2\times10^4$ kJ/mol, $k_0 = 4.70\times10^5\ s^{-1}$ (pH 7) and $E_a = 3.6\times10^4$ kJ/mol，$k_0 = 5.12\times10^5\ s^{-1}$ (pH 3). During boiling and condensation, the vapour is generally enriched in ^{107}Ag while the liquid is enriched in ^{109}Ag. The kinetic silver isotope fractionation ($\Delta^{109}Ag_{liquid\text{-}vapour}$) during surface evaporation is negligible, whereas it can be as large as +0.4‰ during boiling. We have also quantified the equilibrium silver isotope fractionation during precipitation and redox processes and done this using density functional theory study (DFT). We found that silver is enriched in the heavy isotope in the reduced phase and determined isotope fractionation factors for argentite-fluid, $\alpha_{argentite\text{–}fluid}$ and reduced-oxidised silver, $\alpha_{Ag(0)\text{-}Ag(+1)}$ of 1.0009 and 1.0001, respectively, at 573 K. The results show that the source signatures of $\delta^{109}Ag$ are modified significantly by transport- and deposition-related processes during ore formation (e.g., phase separation, boiling, and reduction or oxidation) as proposed by Christopher et al. (2019) [2].

[1] Migdisov A.A., Williams-Jones A.E. (2013). Geochem. Cosmochim. Acta 104, 123-135.
[2] Christopher R.V., et al. (2019). Econ. Geol. 114, 233-242.