Modification of high-precision silver stable isotope analysis and implications for mineralization processes associated with Ag-Au deposits

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Except for radiogenic variations with high $^{107}\text{Ag}/^{109}\text{Ag}$ ratios of up to 10, the variation of $\delta^{109}\text{Ag}$ values from -0.5 ‰ to +1.1‰ in terrestrial samples have been observed, showing the mass dependent stable isotope fractionation dominated by physicochemical processes (e.g., evaporation, diffusion, chemical exchange, etc.) during magmatic and hydrothermal alteration. In addition, as one of controls on Ag isotope fractionation in ore-forming processes is connected with changes in Ag valency state during mineral formation, the nontraditional silver isotope hold more potential insights for constraining ore deposits and hydrothermal geochemistry than other traditional stable isotope approaches.

We carried out a preliminary investigation using silver isotope geochemistry on a typical orogenic gold deposit in the Dazhuangzi gold deposit, Jiaodong, China, where the mineralization is strictly controlled by the fault structures related to the Mesozoic extensional events and tectonically induced fault activity provided channelways for fluid circulation and precious metal and sulfide precipitation. Previous studies on the source(s) of ore-related metals are controversial, in which some workers suggest a mantle source (e.g. from sulfur isotopes), while others imply multiple sources (e.g., from carbon and oxygen isotopes). Many of the metals (e.g., Cu, Pb, Zn, Fe, Cd) in minerals identified in the paragenetic sequence (e.g., chalcopyrite, sphalerite, galena, and pyrite etc.) are tens to thousands of times more abundant than silver in the ore minerals of gold-silver deposits. Therefore, a two-stage ion exchange procedure is modified for effective silver separation from minerals in our work, which ensures the full extraction of silver with an average recovery of 96.47% and also reduces the molar ratios of matrix metals to silver (M/Ag) down to 0.002~2.75 from 353~2200. Relevant isobaric inferences and the mass discrimination in MC-ICP-MS could be well corrected to achieve the largest tolerance capacities for metal impurities by using the selection of alternative Pd isotope pairs. As a result, we reported silver isotope compositions ($\delta^{109}\text{Ag}$) in geological standard materials from difference sources varying from -0.029 ‰ to +0.020 ‰ with an external reproducibility of ± 0.009 ‰.

A systemic survey of $^{109}\text{Ag}$ variations in minerals in the Dazhuangzi gold deposit is being processed, and a more abundant database of silver isotope variations will explore the dominant origins of ore metals and other potential controls (e.g., temperature, different host minerals) influencing silver isotope fractionations involved in the ore-forming process.