

Silver isotope fractionation in native silver: Potential mechanisms and implications to ore genesis

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Scant data exist on the Ag isotope composition of native silver specimens because of the relatively new technique. This study increases the published dataset by an order of magnitude and presents 74 Ag isotope values from native silver originating from a diverse set of worldwide deposits (defined 24 districts, 6 deposit types). The measured isotopic range (defined as $d^{109}\text{Ag}/^{107}\text{Ag}$ in per mil units compared to NIST 978 Ag isotope standard) is -0.78 to +2.1‰ with 2σ errors less than 0.015. No relationship appears to exist with deposit type or even within districts to this point. However, the data cluster into 3 general groups, with the largest cluster centered on 0‰ ($n=35$) and two clusters flanking this at -0.3 and +0.35 per mil. Importantly, the data centering on 0‰ all come from high temperature hypogene/ primary deposits whereas flanking clusters represent secondary supergene or remobilized deposits. To investigate the causes for the more fractionated values, several laboratory experiments involving oxidation of Ag from natural specimens of native Ag and Ag-rich sulfides and adsorption of Ag onto reagent grade MnO_2 were conducted. Little fractionation occurred through oxidation of Ag from native Ag ($\Delta_{\text{solution-native }^{109}\text{Ag}}=0.12\text{‰}$). In contrast, significant fractionation occurred through adsorption and precipitation onto MnO_2 (up to $\Delta_{\text{solution-MnO}_2}^{109}\text{Ag}=0.68\text{‰}$). The experimentation revealed that fractionation of Ag onto MnO_2 remains consistent from pH5 to pH8 and increases at pH9. SEM images with EDS chemical data of the Mn oxides show that some have native Ag and adsorbed Ag occurred on the Mn oxide surface. The most likely cause for the isotopic variations is the reduction of Ag from Ag(I) to Ag^0 that occurs during precipitation onto the mineral surface. Since many Ag deposits have halos dominated by MnO_2 and related manganese-oxide phases; potential may exist for the Ag isotope composition of the Mn oxides to be used as exploration vectors and to understand fluid flow pathways. Aside from the Mn oxides, surface fluid Ag isotope compositions might provide current information about geochemical reactions relevant to both environmental and exploration efforts.