

Ag isotope fractionation in fluids with applications to ore deposits, archeometry, and cosmochemistry

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We calculated the reduced partition functions for silver isotopes in various dissolved Ag species by *ab initio* methods in order to evaluate the extent of Ag fractionation in fluids and the potential of Ag isotopes to discriminate between different metal sources. The ratios $\ln \beta$ of reduced partition functions were for the free Ag^+ ion with various degrees of hydration, hydrates, chloride complexes, sulfides, sulfates, Sb-As sulfosalts, and Ag-ammines. At 0°C, the magnitude of the Nuclear Field Shift effect is -1×10^{-4} . Only weak Ag isotope fractionation is expected in the Ag-Cl-S system regardless of the pH of hydrothermal solutions at 300°C. Stronger effects are predicted when Sb and As are added to the solutions. Bonding with SbS_3 and AsS_3 reduces $\ln \beta$ values by $\sim 2 \times 10^{-4}$. Under the more oxic conditions of the subsurface and at the temperatures of groundwater, Ag is present as Ag^+ and, at higher chlorinity, as AgCl^0 . The latter component is isotopically heavier than Ag^+ . Di-ammine silver $\text{Ag}(\text{NH}_3)_2^+$ forms in groundwater underneath forests and grasslands. Upon reduction or nitrification, $\text{Ag}(\text{NH}_3)_2^+$ precipitates as metallic Ag(0). Both chlorargyrite (AgCl) and native Ag are found among the weathering products (gossan) of bedrock ore deposits. The high end of the $^{109}\text{Ag}/^{107}\text{Ag}$ histogram of silver coinage from around the Mediterranean and from Spanish Americas, particularly well-represented in Mexican silver ore, therefore attests to the presence of gossan silver, while the variability at the low end is more likely to represent temperature effects and variable abundances of S, Sb, and As in hydrothermal fluids. Should the yield of Ag during separation chemistry be $< 100\%$, or samples be altered by metamorphism, low-temperature Ag isotope fractionation becomes an issue seriously affecting (i) so-far published $^{109}\text{Ag}/^{107}\text{Ag}$ data on chondrites, (ii) ages derived from the extinct ^{107}Pd - ^{107}Ag chronometer ($T_{1/2} = 6.5$ Ma), and (iii) inferences about the volatile content of the Earth. It is argued that the NIST SRM 978a value should be retained to represent the Bulk Silicate Earth and not the literature values on basalts, which clearly have been affected by incomplete Ag separation.