



# Fractionation of silver isotopes in native silver explained by redox reactions

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## Abstract

Scant data exist on the silver isotope composition of native silver specimens because of the relative newness of the technique. This study increases the published dataset by an order of magnitude and presents 80 silver new isotope analyses from native silver originating from a diverse set of worldwide deposits (8 deposit types, 33 mining districts in five continents). The measured isotopic range (defined as  $\delta^{109}\text{Ag}/^{107}\text{Ag}$  in per mil units compared to NIST 978 Ag isotope standard) is +2.1 to  $-0.86\%$  ( $2\sigma$  errors less than 0.015); with no apparent systematic correlations to date with deposit type or even within districts. Importantly, the data centering on 0‰ all come from high temperature hypogene/primary deposits whereas flanking and overlapping data represent secondary supergene deposits. To investigate the causes for the more fractionated values, several laboratory experiments involving oxidation of silver from natural specimens of Ag-rich sulfides and precipitation and adsorption of silver onto reagent grade  $\text{MnO}_2$  and  $\text{FeOOH}$  were conducted. Simple leach experiments demonstrate little Ag isotope fractionation occurred through oxidation of Ag from native Ag ( $\Delta_{\text{solution-native Ag}}^{109} = 0.12\%$ ). In contrast, significant fractionation occurred through precipitation of native Ag onto  $\text{MnO}_2$  (up to  $\Delta_{\text{solution-MnO}_2}^{109} = 0.68\%$ , or 0.3amu). Adsorption of silver onto the  $\text{MnO}_2$  and  $\text{FeOOH}$  did not produce as large fractionation as precipitation (mean value of  $\Delta_{\text{solution-MnO}_2}^{109} = 0.10\%$ ). The most likely cause for the isotopic variations seen relates to redox effects such as the reduction of silver from Ag (I) to  $\text{Ag}^0$  that occurs during precipitation onto the mineral surface. Since many Ag deposits have halos dominated by  $\text{MnO}_2$  and  $\text{FeOOH}$  phases, potential may exist for the silver isotope composition of ores and surrounding geochemical haloes to be used to better understand ore genesis and potential exploration applications. Aside from the Mn oxides, surface fluid silver isotope compositions might provide information about geochemical reactions relevant to both environmental and hydrometallurgical applications.

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## 1. INTRODUCTION

Silver isotope geochemistry is a relatively new field in which the ratio of the two Ag isotopes ( $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ ) have been used to understand and measure a variety of nat-

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ural and technological processes, such the formation of the solar system (Woodland et al., 2005; Schönbacher et al., 2008), the transformation of environmental nanoparticles (Lu et al., 2016), improving analytical routines in multicollector mass spectrometry (Schönbacher et al., 2007; Yang et al., 2009; Luo et al., 2010), and unraveling the provenance and circulation of past silver coinage (Desauty et al., 2011). All of these studies found silver isotope variations, but no study has focused on silver ores or the natural processes that might have caused the observed variations. Among other applications, given that silver is a major commodity, understanding the variation of silver isotopes in natural ore deposits may shed light on their ore-forming process, which could enhance exploration and extraction techniques. Further, understanding the silver isotope variations and systematics in natural ores may help explain the variations seen in manufactured materials, in particular those of archaeological and recent historical interest. To address these issues, and explain the silver isotope variations observed, we present silver isotope data of native silver from a diverse set of deposit types coupled with experimental products.

All the primary silver ore deposits on Earth are of hydrothermal origin; i.e., where silver precipitates from an aqueous fluid (at temperatures of ~120 to ~400 °C; Bodnar et al., 2014) circulating within the Earth's crust as the fluid reacts to a variety of physical and chemical gradients. The principal silver and silver-bearing deposit types include epithermal (low-, intermediate- and high-sulfidation), volcanogenic massive sulfides (VMS), sedimentary-exhalative (SEDEX), sediment-hosted Ag–Cu, carbonate replacement and skarns, porphyry Cu, mesothermal Ag–Pb–Zn, and Ag–Co–Ni–As veins (Fig. 1, Table 1 (Graybeal and Vikre, 2010; Kesler and Simon, 2015).

Most primary silver mineralization in all deposit types occurs as one of four principal mineral groups consisting of hypogene sulfides, sulfosalts, tellurides-selenides, or native silver; silver in the distal parts of some deposits may also occur as a primary species adsorbed on and mixed

with manganese oxides. Through weathering and oxidation, the primary (hypogene) species may be transformed into secondary (supergene) minerals such as native silver, silver halides and complex silver-manganese compounds. Notably, native silver can be deposited as both a hypogene and supergene mineral, the latter largely through desulfurization of the silver sulfide acanthite (Ag<sub>2</sub>S). Similarly, the complex silver-adsorbed-on-manganese-oxide mixtures can form either as a secondary product or as a primary product where waning hydrothermal conditions overlap with those of the secondary environment (Megaw, 1998). This wide range of silver species and reformulations between primary and secondary phases opens the question of whether or not there is systematic fractionation of the silver isotope composition of species within and between the hypogene and supergene environments. One possibility is that different deposit types, or stages within them, show different silver isotopic values or systematic isotope shifts that can be used to characterize them consistently.

Since the fractionation of most isotopic systems is greater at low temperatures, we expect that greater differences will be observed between high and low temperature (hypogene vs supergene) conditions. Separately, adsorption of silver onto Mn oxides, as well as other general redox reactions, could lead to a fractionation of silver isotopes independent of temperature. Manganese oxides are common in all deposit types analyzed here and are known to form in both high and low (Sorem and Cameron, 1960; Larson, 1964) temperature environments. This family of minerals has highly charged surfaces which readily adsorb metals like silver (Anderson et al., 1973; McKenzie, 1980; Nicholson, 1992), and the charged surface of Mn oxide minerals is known to cause significant fractionation of isotopes of molybdenum (Arnold et al., 2004; Barling and Anbar, 2004) and copper (Pokrovsky et al., 2008; Bigalke et al., 2009, 2011; Little et al., 2014). By contrast, cadmium does not appear to be fractionated due to surface sorption on Mn oxide (Schmitt et al., 2009; Horner et al., 2010). Finally, electron transfer (redox reactions) occurring during



Fig. 1. Location map for deposits where native silver originated.

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