

Accurate determination of silver isotopic composition in silicate rocks with low silver abundance

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Due to the extremely low abundance of silver in the crust and mantle, the content of other metals is often thousands or even hundreds of thousands of times that of silver, such as Ti, Cr and Ni (Rudnick and Gao, 2004) [1]. It is very difficult to eliminate the influence of these impurities to obtain accurate silver isotope data in silicate rocks, which also makes it hard to define the silver isotopic composition of the major reservoirs in the Earth. To solve this problem, we have modified the pre-treatment procedures and assessed the matrix effect to achieve precise and accurate determination of silver isotopic composition in silicate rocks.

With the modified ion-exchange procedure, there is no obvious loss of silver with a total silver recovery of >95%. In order to better evaluate the matrix effect, we doped the major matrix elements (e.g., Ti, Cr, Ni and Si) into the NIST SRM 978a silver isotope standard solution with the molar ratios of Ti/Ag, Cr/Ag, Ni/Ag and Si/Ag of 0:1 to 600:1, 0:1 to 2000:1, 0:1 to 200:1, 0:1 to 600:1 respectively. The results indicate that the matrix effect from Ti and Cr could be better corrected with the internal standard Pd isotope pair of ^{108}Pd - ^{106}Pd while that from Ni can be corrected with the Pd isotope pair of ^{106}Pd - ^{105}Pd . As a result, the shifts in $\delta^{109}\text{Ag}$ of NIST SRM 978a caused by the cations are less than 0.02%. It is worth noting that there is an obvious shift up to 2.00% in $\delta^{109}\text{Ag}$ when soluble metasilicate existed in the solution.

This study might interpret the obvious discrepancy of measured $\delta^{109}\text{Ag}$ in basalts and granites. Compared to the very narrow distribution of $\delta^{109}\text{Ag}$ in ancient coins from different regions and periods (e.g., Fujii and Albarède (2018) [2] and Albarède et al. (2021) [3]), it is necessary to acquire silver isotopic compositions in magmatic, sedimentary and metamorphic rocks with abundant datasets.

[1] Rudnick, R.L. and Gao, S. (2004). *Treatise on Geochemistry*, 3, 1-65.

[2] Fujii, T., Albarède, F. (2018). *Geochimica et Cosmochimica Acta*, 234, 37-49.

[3] Albarède, F. et al., (2021). *Archaeometry* 63(1), 142-155.