

**Table S1. Contents of matrix / Ag ratios of BCR-2 and AGV-2 after four-step chromatography process**

Matrix / Ag ratio	BCR-2	AGV-2
Ti:Ag	0.12	0.04
Fe:Ag	0.29	0.07
Cu:Ag	0.18	0.30
Zn:Ag	0.00	0.04
Ge:Ag	0.00	0.04
Rb:Ag	0.44	0.00
Nb:Ag	0.02	0.01
Zr:Ag	0.00	0.00
Cd:Ag	0.00	0.00

**Table S2. Synthetic solutions with different matrix element ratios and Ag isotope compositions**

Synthetic																									
solution	Na <sup>+</sup>	Mg <sup>+</sup>	Al <sup>+</sup>	S	K <sup>+</sup>	Ca <sup>+</sup>	Ti	Mn	Fe <sup>+</sup>	Cu <sup>+</sup>	Zn <sup>+</sup>	Ga	As	Se	Sr	Y	Zr	Nb	Mo	Ag <sup>a</sup>	Cd	Sn	$\delta^{109}\text{Ag}$	2SD	N
I	-	2	-	-	-	-	20	-	2	1	1	-	20	-	20	20	10	10	20	1	30	10	0.02	0.05	6
II	1.0	1.5	4.0	20	1.5	12	5	10	14	5.0	5.0	10	20	20	10	10	-	-	100	2	200	15	0.03	0.04	12
III	1.0	1.5	4.0	5.0	1.5	12	2	2	14	0.5	0.1	10	10	20	10	10	-	-	50	0.5	200	15	0.03	0.04	12

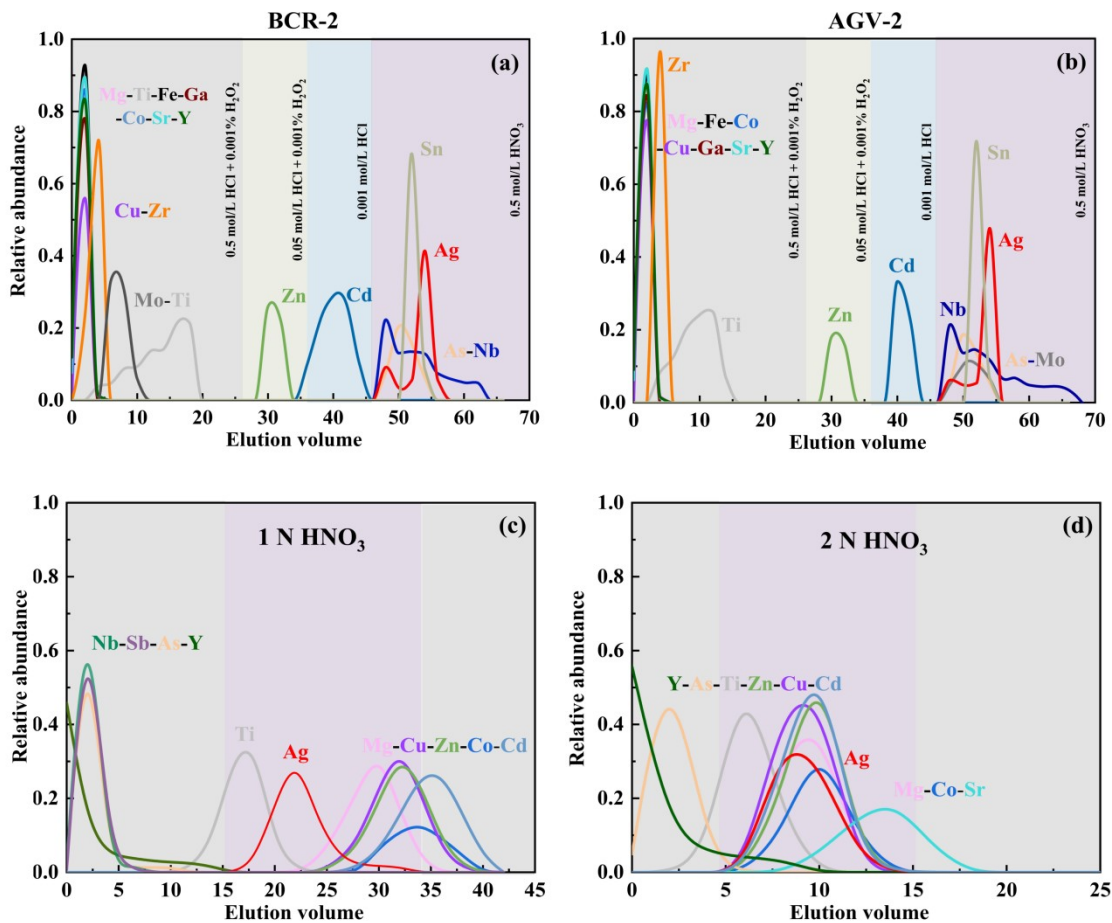
\* The unit of major elements is wt.%. The unit of trace elements is  $\mu\text{g/g}$ . <sup>a</sup> The reference material SRM978a.

2SD is the 2 standard deviation for the synthetic solution ( $n \geq 3$ ). N is the number of repeated measurements.

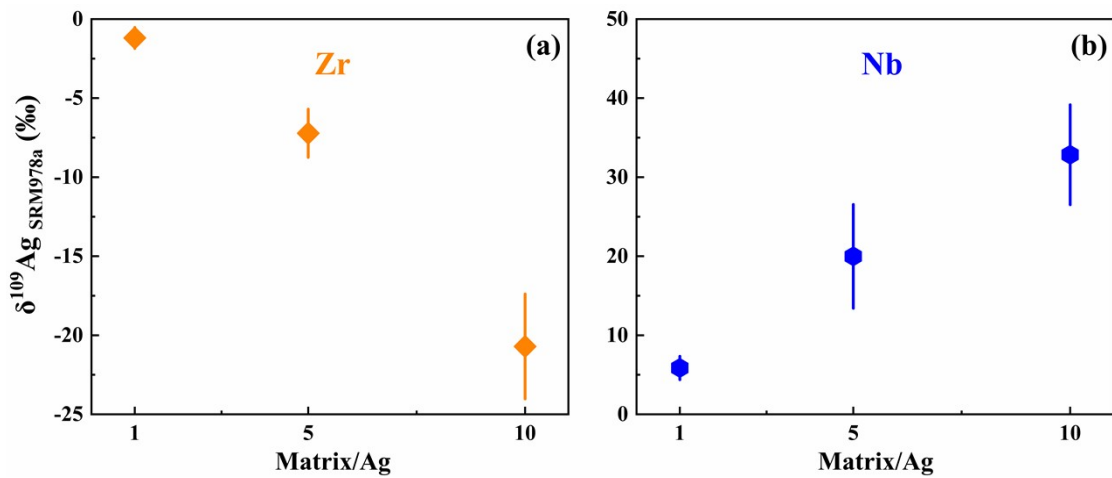
**Table S3. Ag isotope compositions of the doping solutions analyzed by MC-ICP-MS**

Molar element ratio	$\delta^{109}\text{Ag}_{\text{SRM978a}}$ (‰)	2SD (n=3)
Fe:Ag = 1:10	0.00	0.03
Fe:Ag = 1:1	0.07	0.05
Fe:Ag = 5:1	0.19	0.05
Cu:Ag = 1:2	0.00	0.04
Cu:Ag = 1:1	0.03	0.04
Cu:Ag = 2:1	0.17	0.02
Zn:Ag = 1:2	0.00	0.03
Zn:Ag = 1:1	0.01	0.04
Zn:Ag = 2:1	-0.26	0.04
Zr:Ag = 1:100	-0.01	0.02
Zr:Ag = 1:10	-0.08	0.05
Zr:Ag = 1:2	-0.39	0.04
Nb:Ag = 1:100	-0.02	0.01
Nb:Ag = 2:10	0.06	0.04
Nb:Ag = 1:2	0.26	0.03
Cd:Ag = 1:1	0.01	0.04
Cd:Ag = 5:1	-0.01	0.04
Cd:Ag = 10:1	0.08	0.06

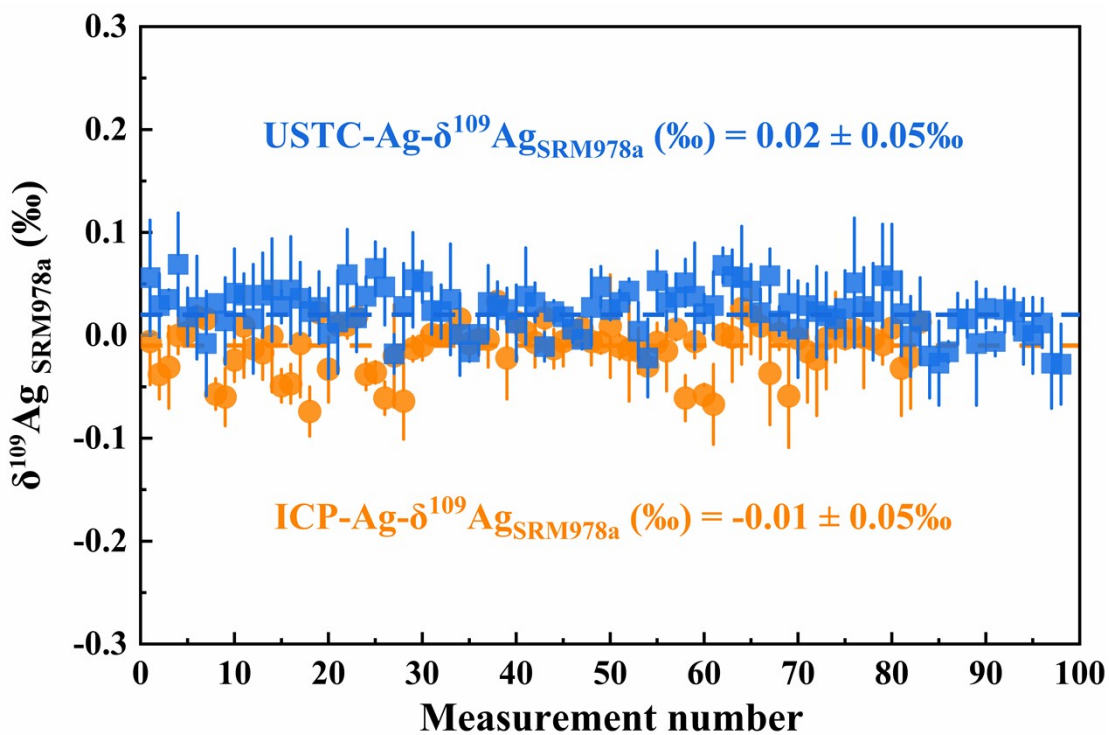
**Figure S1.** Elution curves of the Ag purification procedure using different rock standards, BCR-2 (a) and AGV-2 (b) with the same separation step as Figure 1. Elution curves of Ag purification with AG50 W-X8 resin as eluted at 1 mol/L (c) and 2 mol/L (d) HNO<sub>3</sub>.



**Figure S2. The effect of Zr and Nb doping on  $\delta^{109}\text{Ag}_{\text{SRM978}}$ .**  $\delta^{109}\text{Ag}_{\text{SRM978}}$  show an extreme drifting even when SRM978a was doped with tiny amounts of Zr and Nb solutions.



**Figure S3.** The Ag isotope data of the in-house laboratory standards ICP-Ag and USTC-Ag analyzed by MC-ICP-MS over 3 years.



Error bars represent the 2SD uncertainties for each measurement of  $0.05\text{‰}$  ( $n \geq 3$ ). The dashed lines represent the average  $\delta^{109}\text{Ag}_{\text{SRM978a}}$  values of both.