

Supplementary material to:

Simplifying silver isotope analysis of metallic
samples: Using silver nitrate precipitation to avoid
perilous chloride formation.

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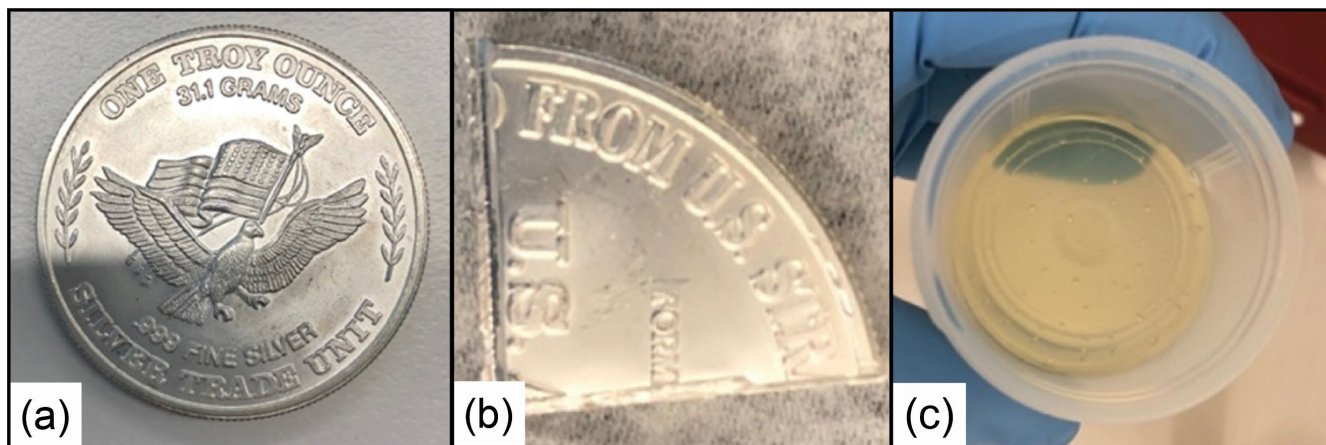


Figure S1: A) Silver coin used for method development. B) The silver coin was cut into quarters and used during different aspects of method development. C) Silver nitrate solution following dissolving the silver coin portion in 8 M HNO₃.

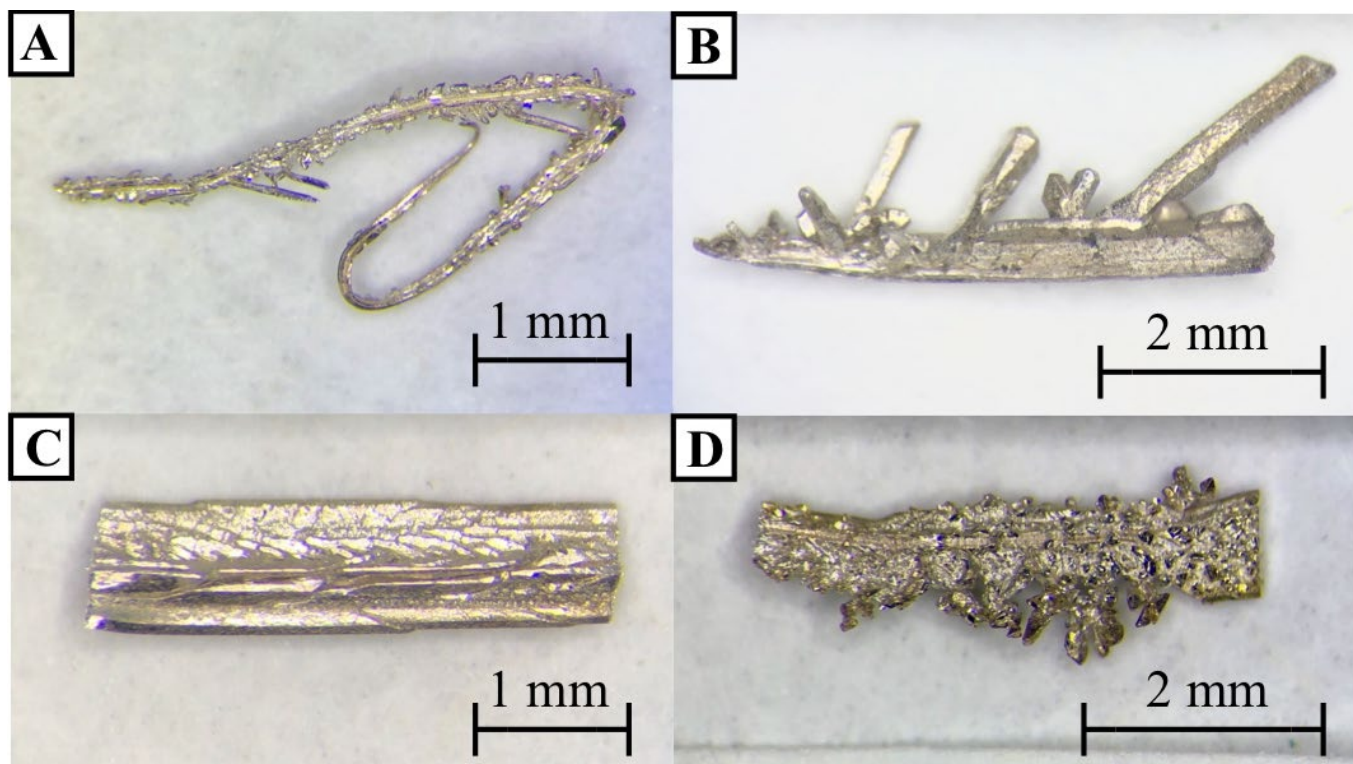


Figure S2: Native Ag wires SW01 – SW04 (A-D, respectively) from Eleura Mine in Cobar, New South Wales.

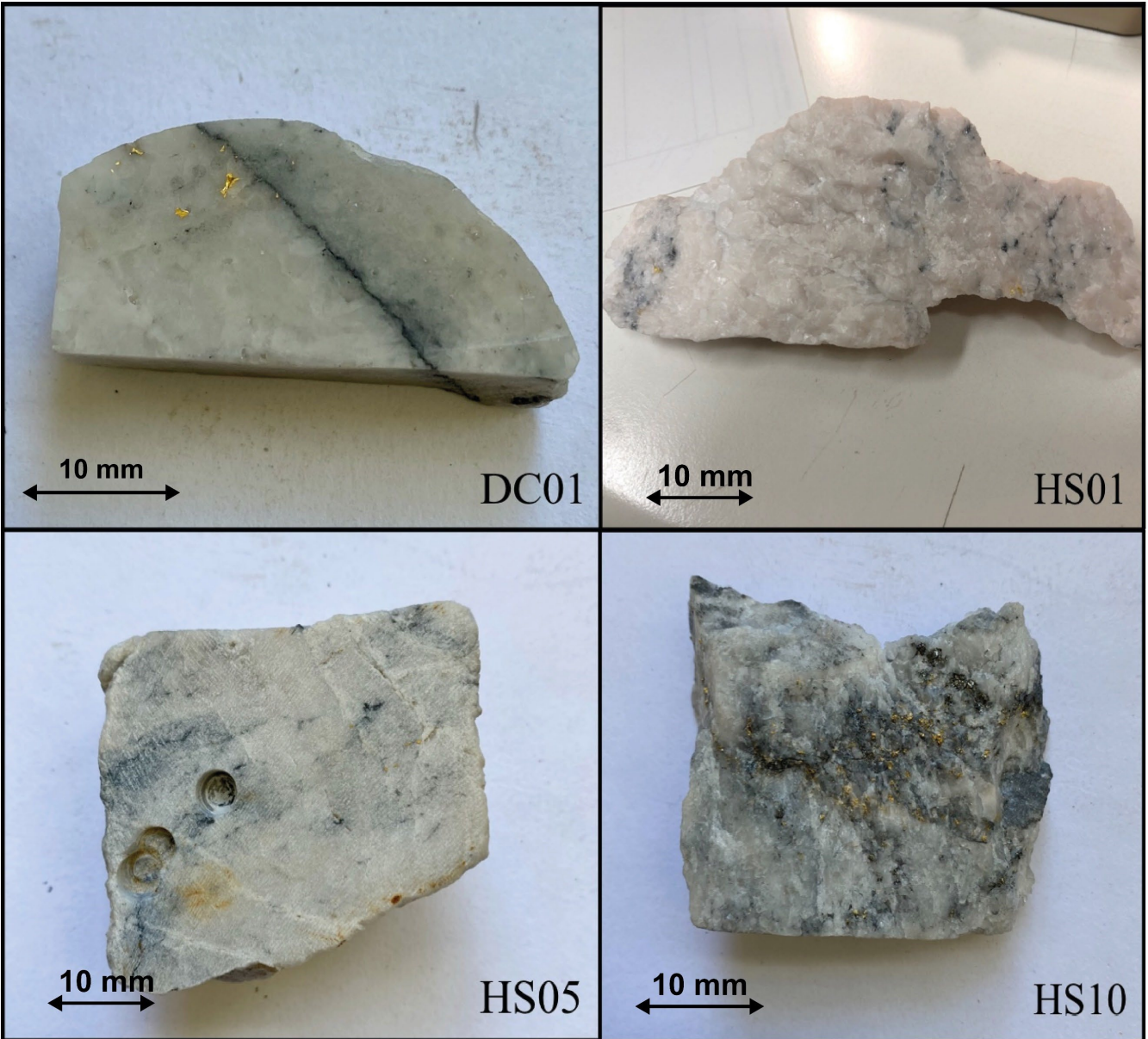


Figure S3: Hand samples of quartz veins from the Fosterville Gold Mine, which contain visible native gold.

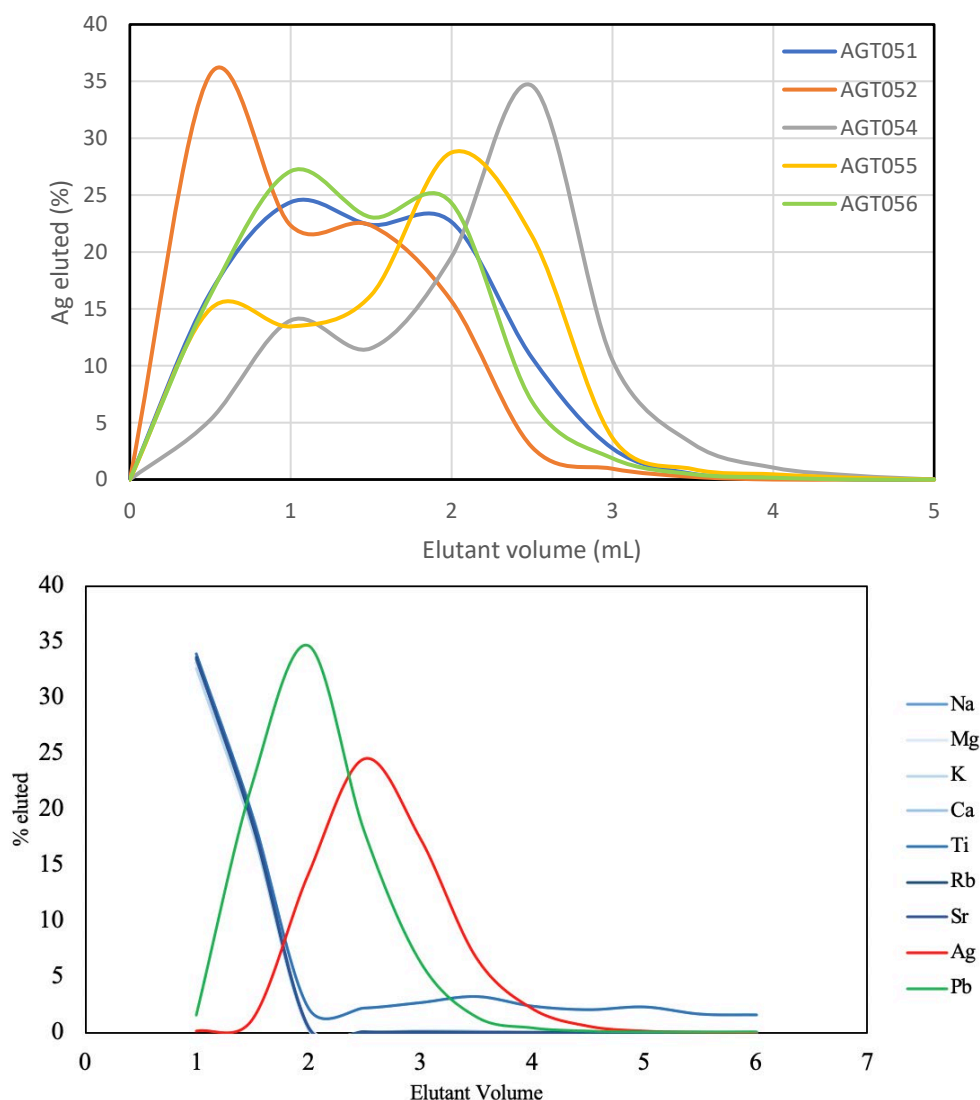


Figure S4: Elution curves for AG1-X8 anion exchange columns obtained during this study. Shown elutant volume is in mL. A total of 5 mL of 6 M HCl is collected off the columns during the procedure to ensure complete Ag yield.

Top: Stacked elution curves for Ag from 5 different synthetic Ag-Au-Pd mixtures based on 0.5 mL elution steps. Synthetic compositions were as follows: AGT051 (Ag = 300 μg ; Au = 1700 μg); AGT052 (Ag = 100 μg ; Au = 1900 μg); AGT054 (Ag = 600 μg ; Au = 100 μg); AGT055 (Ag = 600 μg ; Au = 1400 μg); AGT056 (Ag = 300 μg ; Au = 30 μg). All samples contained 30 μg Pd. In metallic Au and Ag samples multi element calibration is less important given the limited range of matrix elements. Au and Pd are the most important matrix elements to consider. Au because it comprises the majority of the sample, and Pd, although it should be in very low (ng/g) concentration in most sample types, must be removed as it can potentially interfere during mass bias corrections. However, elution curves are not shown for these elements (i.e. Au, Pd) as they remain strongly bonded to the AG1-X8 resin and are hence not eluted (see Fig. S5c). In samples with less Ag (i.e. AGT052) the Ag is eluted more rapidly from the column. Whereas samples with > 300 μg of Ag (i.e. AGT054 and AGT055) have more protracted elution curves and may have a small proportion of Ag retained on the column after 5 mL, therefore a maximum Ag load of 300 μg is recommended in this work.

Bottom: Elution curve for AG1-X8 ion exchange column loaded with a multi-element ICP solution. The main overlap in elution is with Pb, which although this should be in low concentrations (< $\mu\text{g/g}$) in native Au samples, may be present in metallic coins or in sulfide inclusions within native Au. The overlap in elution would ordinarily be problematic for a single step ion exchange procedure but the chemical conversion step of this method acts as a 'clean up' process for elements such as Pb. When metallic Ag is precipitated from the ammonium hydroxide solution, Pb will stay in solution and can be discarded.

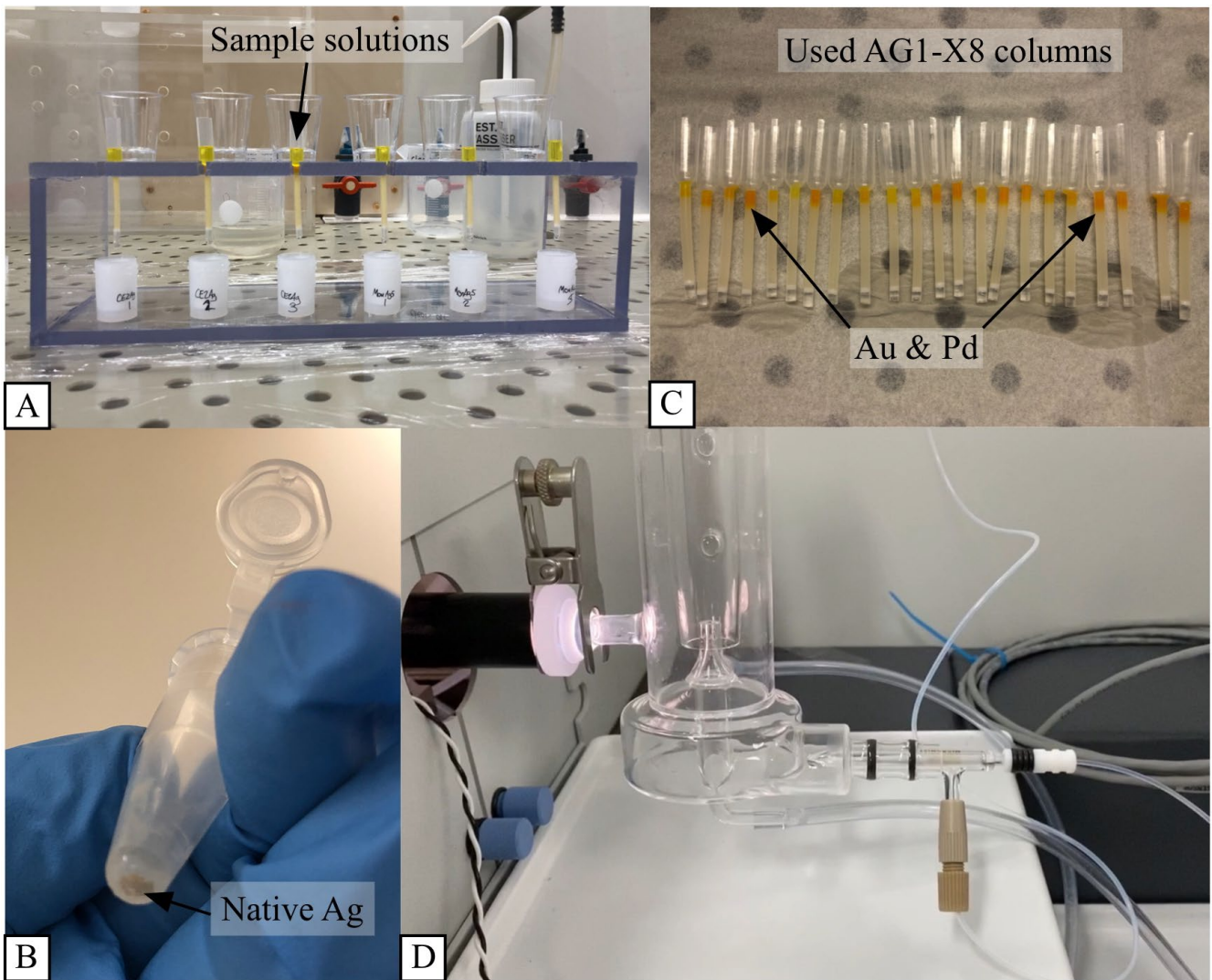


Figure S5: A) Typical set-up from ion-exchange chromatography, showing columns immediately after sample solutions have been loaded onto the columns; B) Native Ag powder in a 1.5 mL polypropylene centrifuge tube formed following the ammonia - ascorbic acid chemical conversion process; C) Used ion-exchange columns prior to being discarded. The dark yellow/orange band at the top of the resin bed is the Au and Pd bonded to the resin; D) Typical set up of the introduction system for the Neptune MC-ICP-MS, with the borosilicate glass nebuliser (Glass Expansion MicroMist nebulizer) and quartz glass dual cyclonic Scott spray chamber.

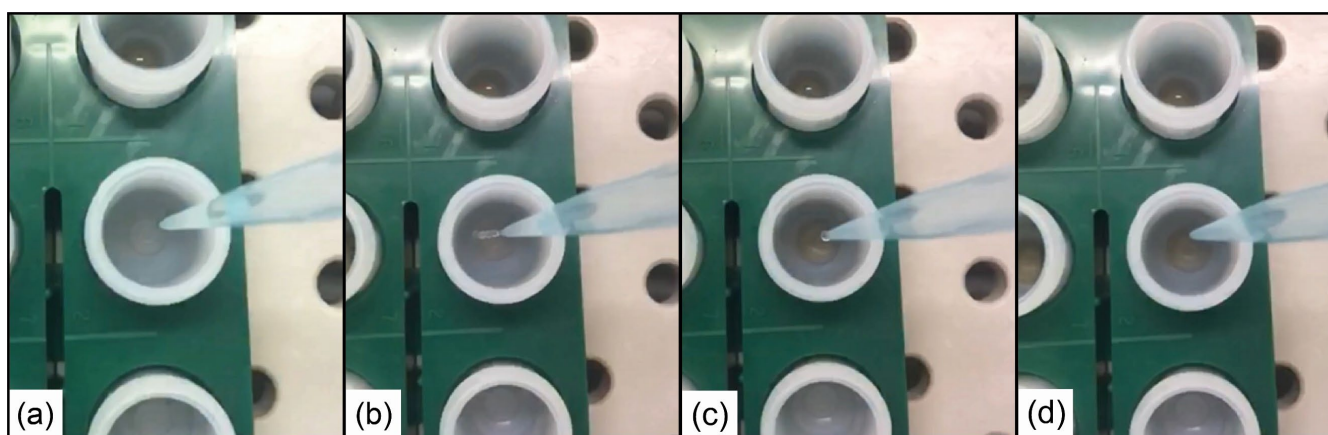


Figure S6: The chemical conversion process taking place in a Teflon Beaker. Image A shows the clear silver-bearing ammonium hydroxide solution prior to the ascorbic acid being pipetted in. Image B, C and D show the ascorbic acid solution being progressively added and precipitation of fine native silver particles. This process was found to be more efficient in a centrifuge vial.

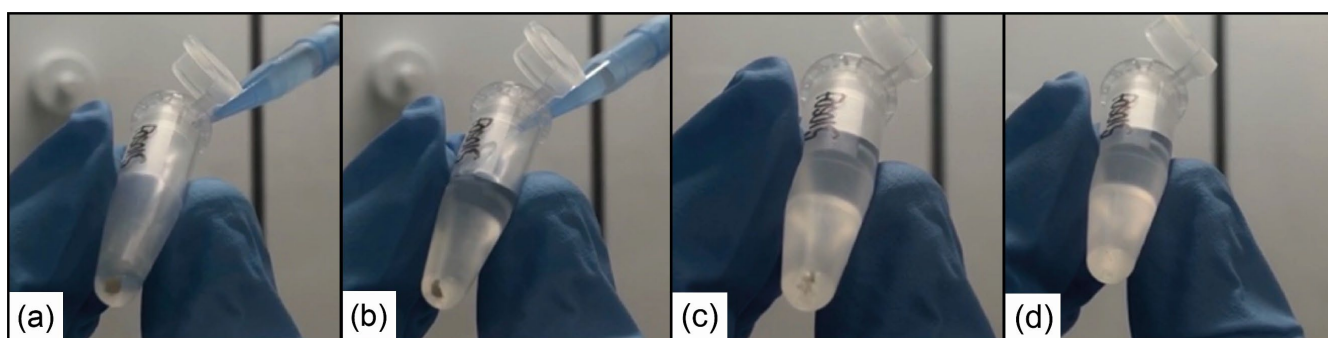


Figure S7: Dissolution of native silver particles with 1 mL of 8 M HNO_3 (50 % nitric acid). Images A-D show the progression of the dissolution process over less than 1 minute. This dissolution step must be completed immediately after the conversion as the Ag particles begin to oxidise rapidly.

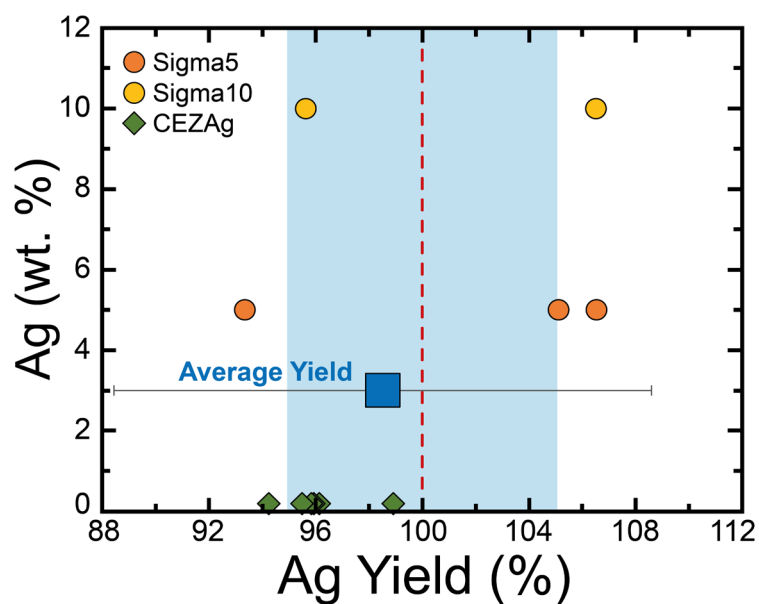


Figure S8: Yield measurements on Au samples relative to their Ag concentration. The shaded field represents an ideal Ag yield of $100 \pm 5\%$. The average Ag yield herein of $98.5 \pm 10.1\%$ (2s.d.; $n = 11$) is also shown. Samples scatter equally to values higher and lower than 100 %, consistent with the variability being the result of aliquoting errors due to the extreme dilution factors required to make the measurements.

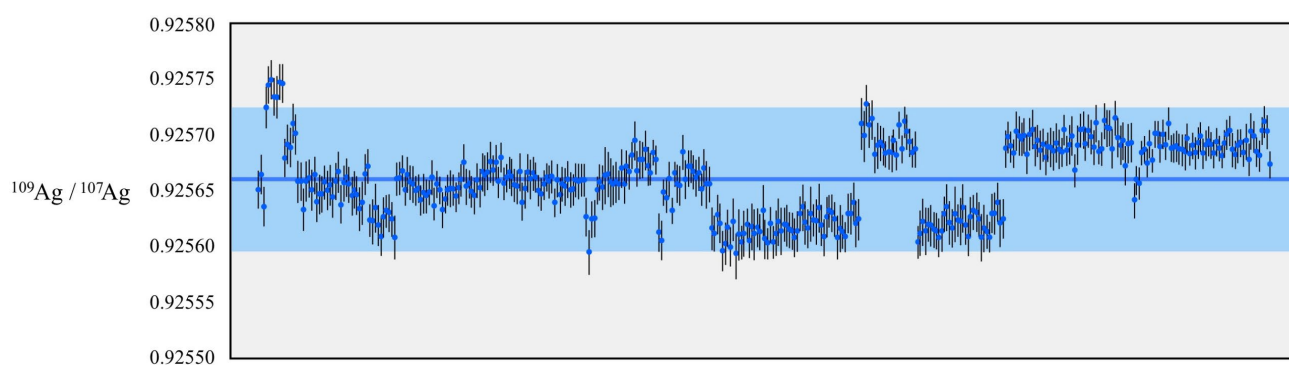


Figure S9: The long-term stability of Ag isotope measurements at Monash University is represented by the mass-bias corrected $^{109}\text{Ag}/^{107}\text{Ag}$ ratio of the NIST SRM978a Ag standard. The blue line represents the long-term average over a 2-year period and the shaded blue rectangle represents the long term 2 s.d. of the population ($^{109}\text{Ag}/^{107}\text{Ag} = 0.92566 \pm 0.0000646$; 2 s.d.; $n = 380$). Error bars shown represent 2 s.e. of individual measurements.

Table S1: Summary of instrument settings for Ag isotopic ratio measurements via MC-ICP-MS

RF power	1200 W
Cooling gas flow rate	16 L min ⁻¹
Auxiliary gas flow rate	0.7 L min ⁻¹
Carrier gas flow rate	1.0 L min ⁻¹
Cones	X-skimmer cone
Cup Configurations	L2 (¹⁰⁵ Pd), L1 (¹⁰⁶ Pd), C (¹⁰⁷ Ag), H1 (¹⁰⁸ Pd), H2 (¹⁰⁹ Ag), H4 (¹¹¹ Cd)
Mass resolution	Low resolution
Sensitivity	~4.7 V for ¹⁰⁷ Ag at 100 ppb
Blocks and cycles	1 block x 45 cycles
Integration time	4.194 s
Spray chamber	Stable sample introduction (SSI) borosilicate glass dual cyclonic Scott spray chamber
Nebuliser	Glass Expansion MicroMist nebulizer
Solution uptake rate	50 µl min ⁻¹
