Supporting information:

Comparison and optimization of chromatographic separation methods for accurate measurement of antimony isotopic composition

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Table S1. Existing chromatographic separation strategies for Sb purification and isotope measurement

Reference	Sorbent used for Sb purification		Yield (%)	Antimony isotope analysis by MC-ICP-MS			
				Method of mass bias correction	Sample introduction system		Precision (‰, 2SD)
	Step 1	Step 2			Sb	Doping element	
Rouxel *et al.* (2003)[1]	Bio-Rad AG 50-X8 resin	Thiol cotton fiber (TCF)	—	SSB	HG	—	0.04
Asaoka *et al.* (2011)[2]	TCF	—	99.5± 3.6	RRL (Sn doping)	—	—	0.04
Tanimizu *et al.* (2011)[3]	TCF	—	—	RRL (Sn doping)	NSC	NSC	0.04
Lobo *et al.* (2012, 2013)[4, 5]	Dowex AG 50-X8 resin	Amberlite IRA 743 resin	>84	SSB and RRL (In doping)	NSC	NSC	0.02
Resongles *et al.* (2015)[6]	Thiol-cellulose powder (TCP)	—	96± 3	SSB	HG	—	0.06
Liu *et al.* (2020)[7]	AG 1-X4 resin	AG 50W-X8 resin	98.7± 5.6	SSB and RRL (Cd doping)	NSC	NSC	0.04
Li *et al.* (2021)[8]	Thiol–silica resin (Cleaner SH)	—	>95.2	SSB and RRL (In doping)	Desolvation system	Desolvation system	0.04
Ferrari *et al.* (2021)[9]	Thiol-functionalized silica powder (TSP)	—	100± 7	SSB	HG and SC	—	0.05
Sun *et al.* (2021)[10]	Bio-Rad AG 50w-X8 resin	Thiol–silica resin (Cleaner SH)	99.5± 4.1	SSB and RRL (Cd doping)	HG	Desolvation system	0.04
Kaufmann *et al.* (2021)[11]	Dowex AG 50-X8 resin	Amberlite IRA 743 resin	—	SSB and RRL (Sn doping)	NSC	NSC	<0.06
Fang *et al.* (2022)[12]	AG 50W-X8 resin	—	99.9 ± 2.8	SSB and RRL (Sn doping)	NSC	NSC	0.03
Ferrari *et al.* (2023)[13]	Thiol-functionalized silica powder (TSP)	—	>93	SSB	HG and SC	—	<0.06
Veldhuizen *et al.* (2023)[14]	Eichrom 1-X8 resin	—	100± 5	SSB	HG	—	0.06
Xia *et al.* (2023)[15]	Thiol–silica resin (Cleaner SH)	—	>94	SSB and RRL (Cd doping)	HG	Desolvation system	0.04
Li *et al.* (2024)[16]	Bio-Rad AG 50w-X8 resin	Thiol–silica resin (Cleaner SH)	100	SSB and RRL (In doping)	Desolvation system	Desolvation system	0.04
Zhu *et al.*(2024)[17]	Bio-Rad AG 50w-X8 resin	thiol-functionalized mesoporous powder (TSP)	>95.6	SSB and RRL (Cd doping)	HG	Desolvation system	<0.09
Chen *et al.*(2025)[18]	HPLC: Hamilton PRP-X100 anion-exchange column	—	103 ± 3 99 ± 1	SSB and RRL (In doping)	HG	Desolvation system	0.05
Kaufmann *et al.* (2025)[19]	Bio-Rad AG MP-1 resin	Dowex AG 50-X8 (same resin for step 3)	—	SSB and RRL (Sn doping)	Desolvation system	Desolvation system	<0.1
Li *et al.* (2025)[20]	HG	Thiol–silica resin (Cleaner SH)	100	SSB and RRL (In doping)	Desolvation system	Desolvation system	<0.07
Kaufmann *et al.* (2021)[11] and Wang *et al.*(2024)[21]	—	—	—	SSB and RRL (Sn doping)	Laser-ablation	NSC	0.06

The following abbreviations are used: standard-sample bracketing method (SSB), revised Russell's Law (RRL), hydride generation system (HG), spray chamber (SC), nebulizer and spray chamber (NSC), and High-Performance Liquid Chromatography (HPLC).

Table S2. Instrument settings and parameters for the HG-MC-ICPMS system

Instrument and component	Parameters
Nu Plasma III MC-ICP-MS	
Cup configuration	L5(^{111}Cd), L4(^{113}Cd), Ax(^{117}Sn), H1(^{118}Sn), H3(^{120}Sn), H4(^{121}Sb), H6(^{123}Sb), H7(^{125}Te)
Sample cone	Nickel
Skimmer cone	Nickel
RF power	1300 W
Resolution	Low
Coolant gas (L min^{-1})	13
Auxiliary gas (L min^{-1})	1.2
Sample gas (L min^{-1})	0.02
Quad 1	-27.9
Quad 2	200.3
Number of blocks	1
Number of cycles	30
Integration time per cycle	10s
Aridus II: introduction of Cd	
PFA nebulizer	100 μL min^{-1}
Nebulizer gas (Psi)	30
Sweep gas in Aridus II (L min^{-1})	2.66
Hydride generator: introduction of Sb	
Flow rate of reductant	0.5 mL min^{-1}
Flow rate of sample solution	0.5 mL min^{-1}
Washing solution	3 M HCl

Table S3. The Sb recovery rates and difference between measured and reported δ^{123}Sb values (expressed as $\Delta^{123}Sb = |\delta^{123}Sb_{measured} - \delta^{123}Sb_{reported}|$) for geological samples before modification for Protocol 2

Sample	Recovery	Measured δ^{123}Sb value (‰, ±2SD, n=3)	Reported δ^{123}Sb value	Δ^{123}Sb
BCR-2	84.4%	0.03 ± 0.02	0.26 ± 0.04[22]	0.23
BHVO-2	93.7%	0.13 ± 0.04	-0.10 ± 0.06[19]	0.23
AGV-2	82.8%	-0.03	0.23 ± 0.11[17]	0.26
GBW03104	80.2%	-0.03	0.29 ± 0.06[10]	0.32
GSS-5	77.8%	-0.19 ± 0.03	0.21 ± 0.02[10]	0.40
GSS-14	80.6%	-0.12 ± 0.04	0.34 ± 0.03[10]	0.46
GSD-3a	86.6%	-0.06 ± 0.04	0.20 ± 0.07[10]	0.26
GSD-11	84.8%	0.16 ± 0.04	0.17 ± 0.05[10]	0.01
BCR-482	109.6%	0.17 ± 0.01	0.20 ± 0.05[10]	0.03
GSB-11	99.7%	0.20 ± 0.03	0.24 ± 0.10[17]	0.04
GSP-2	85.8%	-0.05 ± 0.00	—	—
JG-2	100.3%	0.20 ± 0.07	—	—
GBW07314	79.1%	-0.10 ± 0.00	—	—
GBW07333	75.3%	0.02 ± 0.01	—	—
Nist 2702	96.9%	-0.13 ± 0.03	—	—

Table S4. Sb recovery (%) for the analytical protocol using a final KI–AA concentration of 0.5% during reduction in 0.5 M HCl, together with sample loss on ignition (LOI) and Fe content in geological samples[23]

Sample name	W(Fe_2O_3t) /% *	Mean value of LOI (%)*	Sb recovery
BCR-2	13.77	0.27	84.4%
BHVO-2	12.39	-0.05	93.7%
AGV-2	6.69	1.33	82.8%
GBW03104	5.67	4.17	80.2%
GSS-5	12.62	9.14	77.8%
GSS-14	5.32	—	80.6%
GSD-3a	4.72	—	86.6%
GSD-11	4.30	3.02	84.8%
BCR-482	0.11	—	109.6%
GSB-11	0.07	—	99.7%
GSP-2	4.90	1.18	85.8%
JG-2	0.97	1.34	100.3%
GBW07314	5.36	—	79.1%
GBW07333	6.77	—	75.3%
Nist 2702	11.30	—	96.9%

* Data collected from the GeoReM website: http://georem.mpch-mainz.gwdg.de[23]

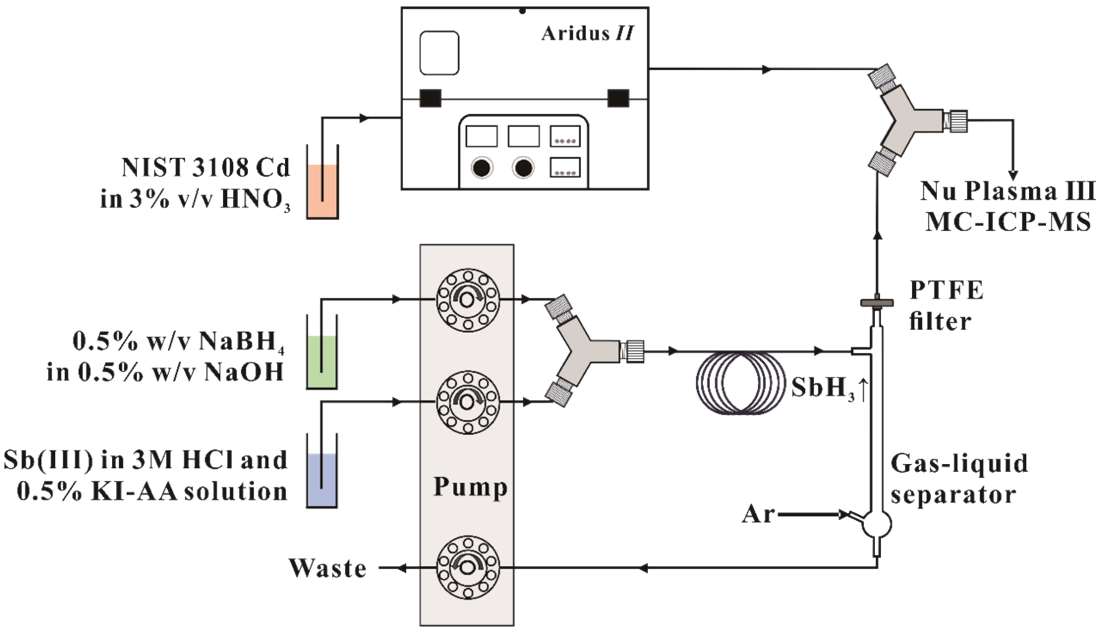

Fig. S1. A schematic diagram illustrating the connection between the hydride generator, the membrane desolvation system (Aridus II), and the MC-ICP-MS instrument (Nu Plasma III) for antimony isotope analysis. (Modified from Sun *et al.*, 2021)

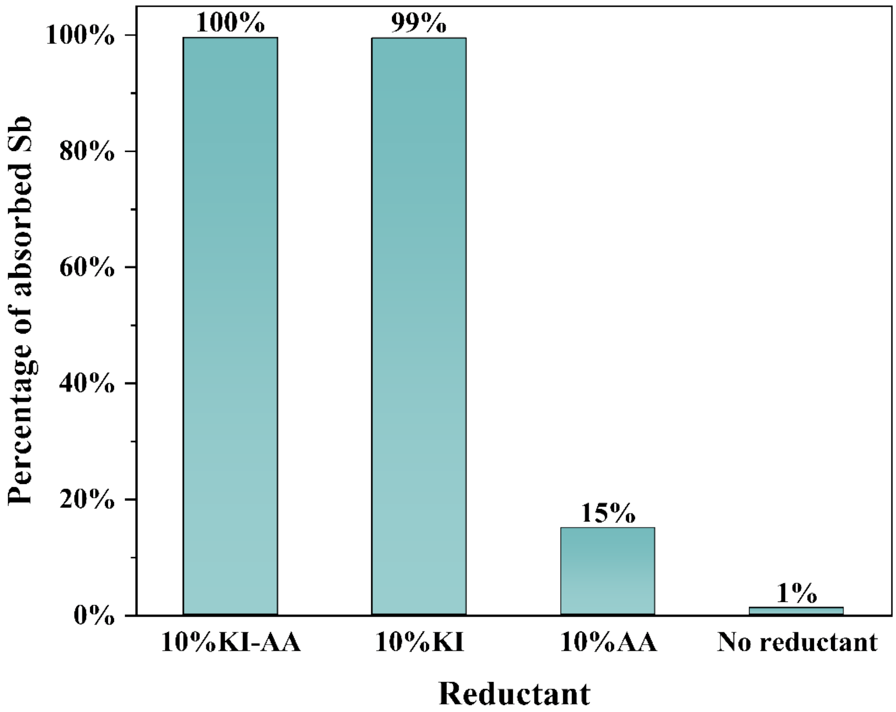

Fig. S2. Sb recovery from the 1.2 mL AG 1-X4 resin column using different reductant

Experiment condition: Four 1 mL aliquots of 2 M HCl (each containing ~1000 ng Sb and Fe) were treated separately with: (a) 110 µL of 10% (w/v) KI–AA mixture, (b) 110 µL of 10% (w/v) KI solution, (c) 110 µL of 10% (w/v) AA solution, and (d) 110 µL Milli-Q H_2O. After >8 h reaction, each solutions was loaded onto a 1.2 mL AG 1-X4 resin column. Effluents from sample loading and a subsequent 10 mL rinse with 0.5 M HCl were combined. Each combined fraction then received 1 mL HNO_3 and 0.5 mL H_2O_2. Following overnight reaction, samples were degassed, refluxed at 100°C for 0.5 h, cooled, evaporated to dryness at 85°C, and reconstituted in 10 mL of 3% HNO_3. Sb concentrations were quantified via ICP-MS to determine resin adsorption percentages.

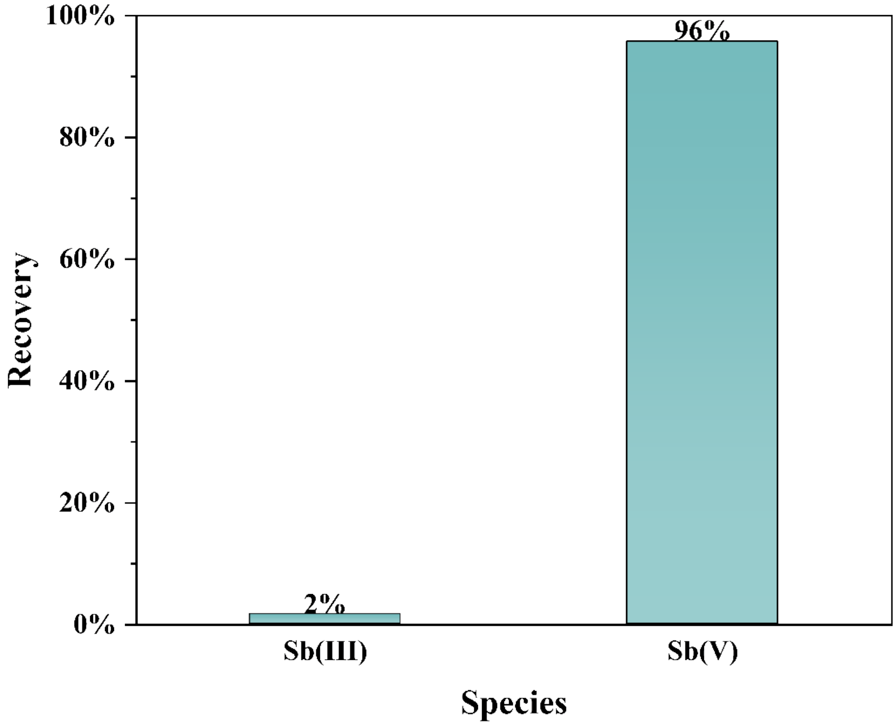

Fig. S3. Recovery of Sb(III) and Sb(V) from a 1 mL AG 50W-X8 resin column eluted with 0.1 M HNO_3

Experiment condition: Solutions containing exclusively Sb(III) or Sb(V) were prepared using potassium antimonyl tartrate sesquihydrate and potassium hexahydroxidoantimonate(V), respectively. Aliquots of approximately 700 ng Sb(III) and 500 ng Sb(V) in 0.5 mL of 0.1 M HNO_3 matrix were loaded onto preconditioned 1 mL AG 50W-X8 resin columns, followed by rinsing with 4 mL of 0.1 M HNO_3. Effluent fractions were collected and analyzed for Sb quantification.

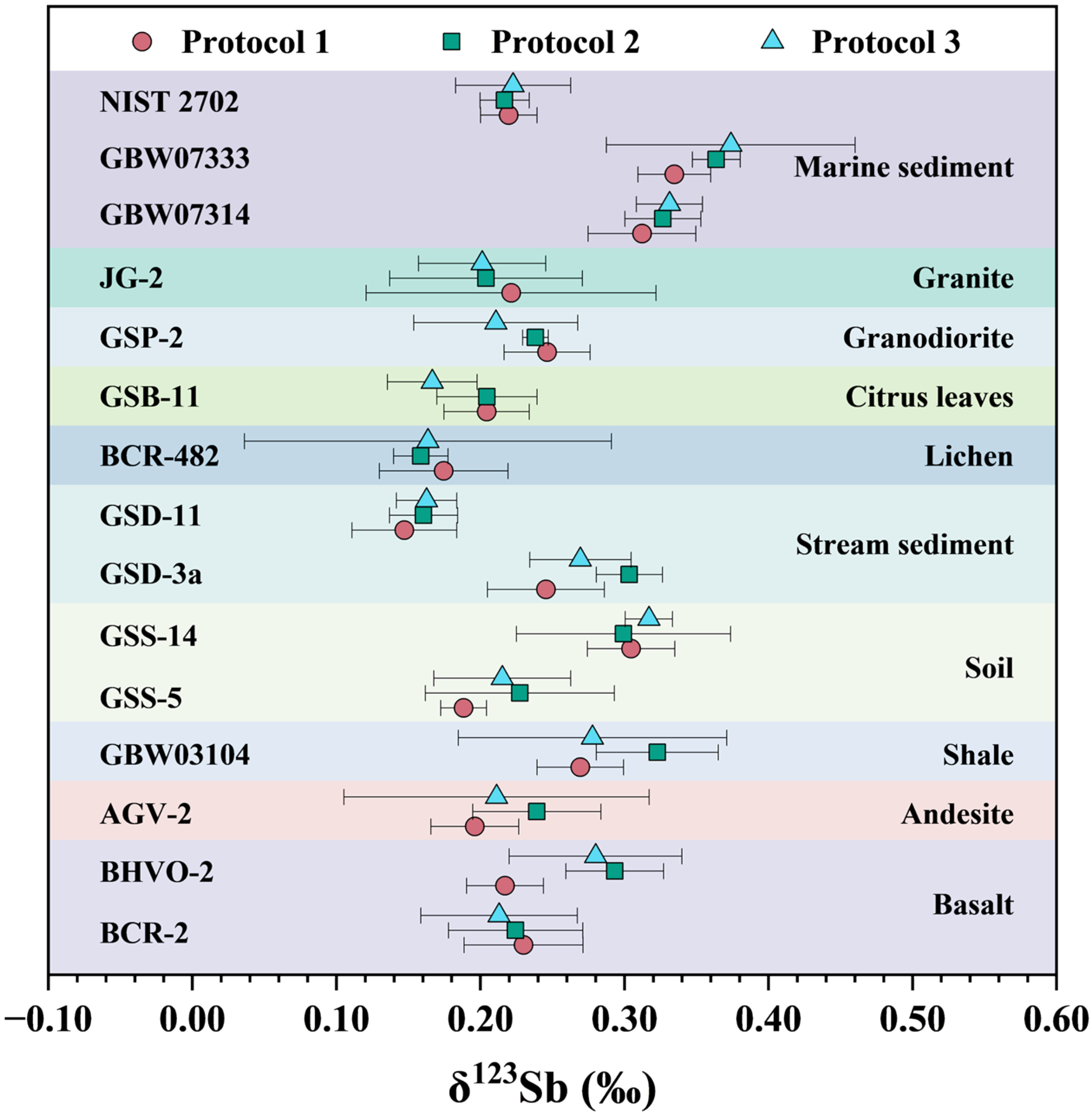

Fig. S4. Comparison of δ^{123}Sb values in selected geological reference materials obtained using the three optimized analytical protocols. Error bars represent ±2SD.

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