Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Supplementary information: the geometric inversion method (ESI A)

For the three-dimensional $^{117}Sn/^{118}Sn$-$^{120}Sn/^{118}Sn$-$^{122}Sn/^{118}Sn$ space, the true Sn isotope composition of the spike (T) and unknown sample (N) mixed along a mixing line TMN according to a mixing proportion of λ (Fig. 1). Generally, the sample-spike mixture and unknown sample are fractionated with two instrumental fractionation factors β and α, following the curves U and V. Note that β and α follow the exponential law. The uncertainty of the mixing line correlates with the angle ($\theta_{U\text{-}V}$) between the two instrumental fractionation curves (curves U and V), the spike composition, and spike to sample ratio. The results show that the accuracy of the data inversion is consistent with the Newton-Raphson iteration method, however, the geometric method is associated with larger errors (Fig. S1). The origin could be that our spike composition is not designed for the lowest and constant error of geometric method, as suggested by Johnson and Beard [1]. In addition, Rudge et al. [2] argue that the optimum of $\theta_{U\text{-}V}$ may not necessarily produce the optimal double spike compared to the Newton-Raphson iteration, which directly focuses on the error. Therefore, we prefer to use the Newton-Raphson iteration method in this study. The code for this method is listed below:

```
% Known: two curves, one point in a 3-d space
% Find: one line that crosses both curves and the point
% Solve: two fractionation factors(f1 and f2);
% two cross points of the line and two curves (with slopes k1 and k2)
clear all
% Sn isotopes atomic weights
Sn122 = 121.90344;
Sn120 = 119.902197;
Sn117 = 116.902954;
Sn118 = 117.901607;

% use the measured isotope ratios (122Sn/118Sn, 120Sn/118Sn, 117Sn/118Sn) to calculate the curves, which follow the exponential mass fractionation law
% x-axis: 122Sn/118Sn
% y-axis: 120Sn/118Sn
% z-axis: 117Sn/118Sn

% declare unknown variables
% f1: fractionation factor of natural sample
% f2: fractionation factor of the mixture
% k1 and k2: slopes of the line in the (y vs. x) and (z vs. x) direction
syms f1 f2 k1 k2
% define the variables
```

```
% 1. natural sample

x1=0.202006343*(Sn122/Sn118)^f1;
y1=1.383368191*(Sn120/Sn118)^f1;
z1=0.312473414*(Sn117/Sn118)^f1;

% 2. the mixture of natural sample and double spike
x2=1.8162026*(Sn122/Sn118)^f2;
y2=1.2381183*(Sn120/Sn118)^f2;
z2=1.7047163*(Sn117/Sn118)^f2;

% 3. double spike composition
x0=13.03162026;y0=0.180618718;z0=12.12788719;

% 4. use four equations to solve four unknowns
eqns = [y1-y0==k1*(x1-x0), y2-y0==k1*(x2-x0), z1-z0==k2*(x1-x0), z2-z0==k2*(x2-x0)];
S = vpasolve(eqns,[f1 f2 k1 k2]);
% The solutions of [f1 f2 k1 k2] are stored in S
```

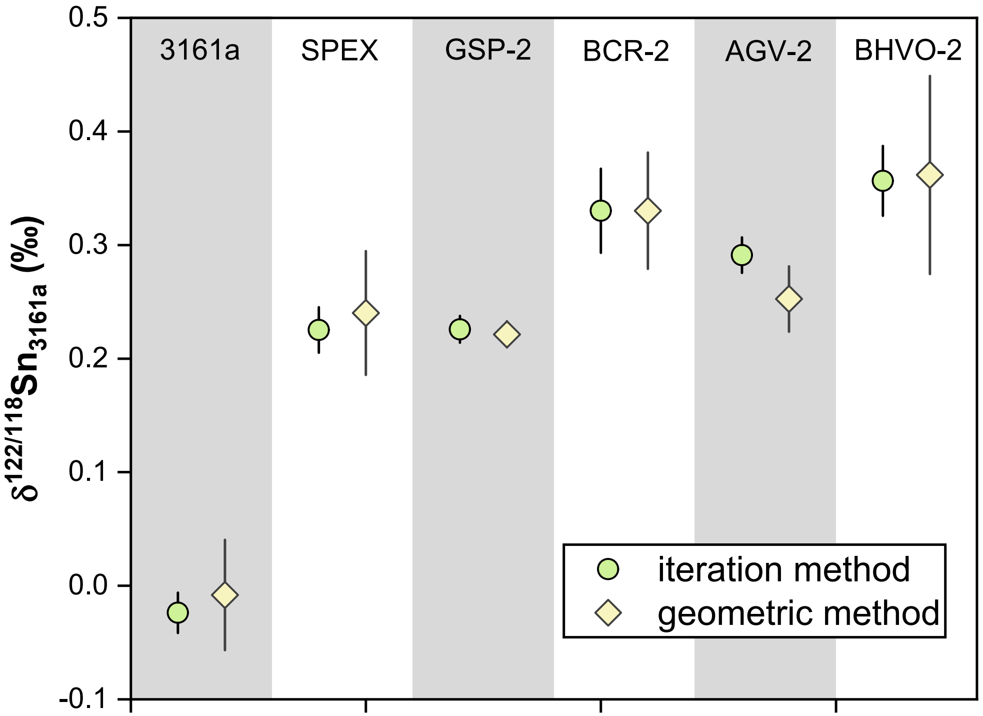

Fig. S1. Compilation of $\delta^{122/118}Sn_{3161a}$ data of pure and geological reference materials with various data reduction methods. In this study, we utilize a Newton-Raphson iteration method with ^{117}Sn-^{118}Sn-^{120}Sn-^{122}Sn inversion. Another geometric method with ^{117}Sn-^{118}Sn-^{120}Sn-^{122}Sn was also used for comparison. All uncertainties on individual data points reflect the 2SD of the samples.

Table S1. Potential elemental and molecular isobaric interferences on Sn isotopes. The interferences for Sb isotopes are also listed.

	^{124}Sn	^{123}Sb	^{122}Sn	^{121}Sb	^{120}Sn	^{119}Sn	^{118}Sn	^{117}Sn	^{116}Sn	^{115}Sn
Cd	$^{112}Cd^{12}C$, $^{110}Cd^{14}N$		$^{110}Cd^{12}C$					$^{116}Cd^{1}H$	^{116}Cd	
In									$^{115}In^{1}H$	^{115}In
Te	^{124}Te	^{123}Te	^{122}Te		^{120}Te					
Xe	^{124}Xe									
Mo									$^{100}Mo^{16}O$	
Ag		$^{107}Ag^{16}O$, $^{109}Ag^{14}N$		$^{109}Ag^{12}C$, $^{107}Ag^{14}N$		$^{107}Ag^{12}C$				
Ru					$^{104}Ru^{16}O$		$^{104}Ru^{14}N$, $^{102}Ru^{16}O$	$^{101}Ru^{16}O$	$^{102}Ru^{14}N$, $^{100}Ru^{16}O$	$^{101}Ru^{14}N$, $^{99}Ru^{16}O$
M^{++}						$^{238}U^{2+}$			$^{232}Th^{2+}$	

Table S2. The results of $\delta^{122/118}Sn_{3161a}$ for the cuts of the laboratory elemental solution eluted from the column with TRU resin.

step	**Volume (ml)**	**Yield (%)**	**$\delta^{122/118}$Sn**	**2sd**
1	2	0.33	□	□
2	4	0.01	□	□
3	6	0.01	□	□
4	8	0.24	□	□
5	10	0.20	□	□
6	12	0.08	□	□
7	13	0.22	□	□
8	15	28.94	0.218	0.073
9	16	39.11	-0.291	0.082
10	17	15.74	-0.196	0.028
11	19	9.16	-0.570	0.042
12	21	2.51	-0.100	0.042
13	23	2.21	0.545	0.011
14	25	1.26	1.138	0.053
mass balance	□	□	-0.111	0.063□
Sn single solution	□	□	-0.095	0.030

Table S3. Compilation of Sn mass fractions from literature[3-20] and this study

Sample	Reference	Sn µg/g	2s
GSP-2	This study	6.52	0.30
	Cotta and Enzweiler (2013)	6.4	0.1
	Creech et al. (2017)	8.32	
	Wang et al. (2022)	6.53	0.36
BCR-2	This study	2.22	0.03
	Braukmuller et al. (2020)	2.086	0.061
	GeoRem	2.28	0.13
	Kirchenbaur et al. (2018)	2.136	0.048
	Cotta and Enzweiler (2013)	2.03	0.03
	Braukmuller et al. (2018)	2.52	0.06
	Creech et al. (2017)	2.36	
	Hu and Gao (2008)	2.2	
	Marx and Kamber (2010)	2.37	0.3
	Jochum et al. (2016)	2.28	0.13
AGV-2	This study	2.03	0.19
	Braukmuller et al. (2020)	2.021	0.04
	Jochum et al. (2016)	1.83	0.25
	Gaschnig et al. (2014)	1.9	0.122
	Creech et al. (2017)	2.07	
	Hu and Gao (2008)	2.08	
	Marx and Kamber (2010)	2.24	0.36
	Wang et al. (2022)	2.01	0.14
	Marx and Kamber (2010)	2.242	0.36
BHVO-2	This study	1.83	0.05
	Braukmuller et al. (2020)	1.709	0.041
	Jochum et al. (2016)	1.776	0.059
	Kirchenbaur et al. (2018)	1.716	0.02
	Braukmuller et al. (2018)	1.73	0.04
	Bouman et al. (2004)	2.3	
	Creech et al. (2017)	1.9	
	Hu and Gao (2008)	1.8	
	Marx and Kamber (2010)	1.92	0.2
	Garbe-Schonber and Muller (2014)	2.04	0.02
	Weis et al. (2005)	1.7	0.02
	Wang et al. (2022)	1.81	0.02
	Wang et al. (2018)	1.83	
GSR-1	This study	11.78	0.20

	Cotta and Enzweiler (2013)	11.9	0.1
JG-2	This study	2.56	0.12
	Wang et al. (2022)	2.6	0.27
	Kon and Hirata (2015)	2.843	0.056
NOD-A-1	This study	3.36	0.01
	Wang et al. (2022)	3.03	0.75
	Axelsson et al. (2002)	3	0.16
BIR-1	This study	0.74	0.03
	Braukmuller et al. (2020)	0.692	0.024
	Jochum et al. (2016)	0.701	0.067
	Kirchenbaur et al. (2018)	0.706	0.02
	Yi et al. (1995)	0.76	0.09
	Gaschnig et al. (2014)	0.7	0.04
	Cotta and Enzweiler (2013)	0.76	0.04
	Hu and Gao (2008)	0.69	
	Jochum et al. (1993)	0.76	0.54
RGM-1	This study	4.21	0.12
	Braukmuller et al. (2020)	4.11	0.14
	Jochum et al. (2016)	4.34	0.61
	Hu and Gao (2008)	4.07	
	Cotta and Enzweiler (2013)	3.84	0.05

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