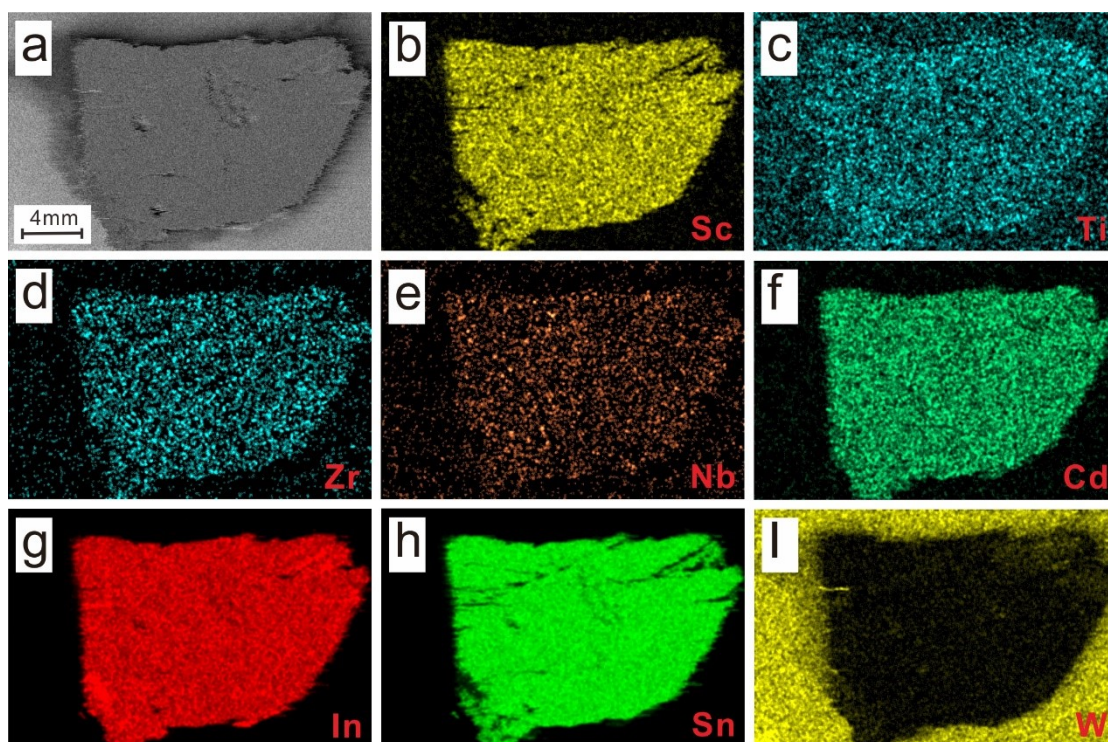
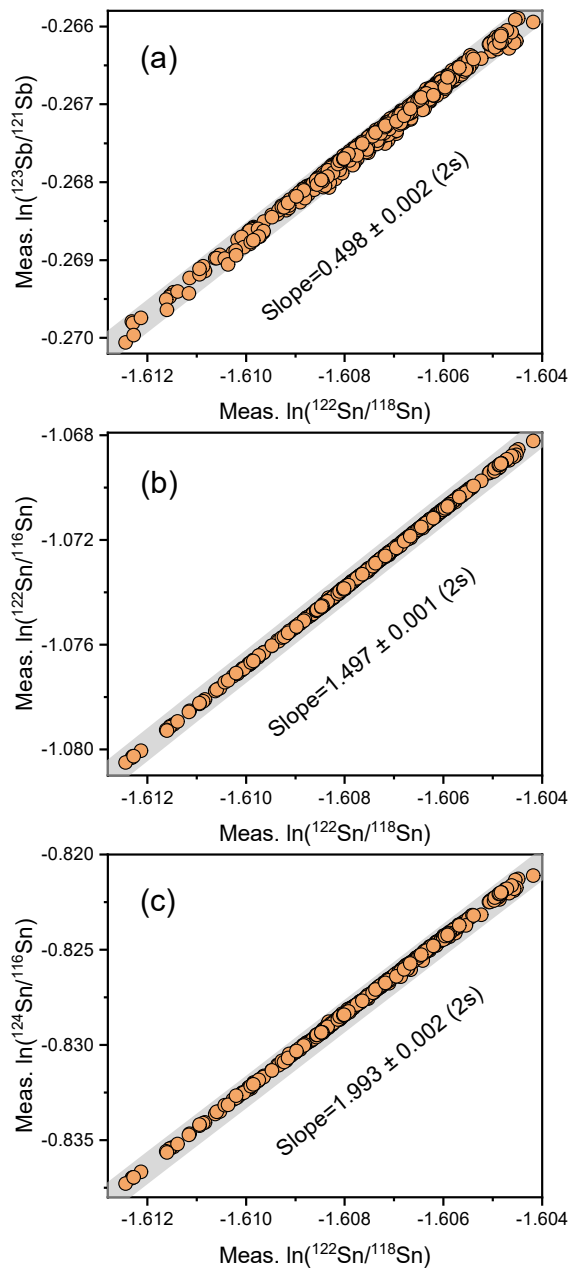


**Fig. S1.** Representative micro XRF maps (a-c), backscatter electron images (d-f) of cassiterite samples. a-c reveals the distribution of various elements of #cas 2 with a crack. d is the homogeneous cassiterite #cas 17. e represents the synthetic cassiterite. f shows the particle size of crushed cassiterite grains.



**Fig. S2.** Representative micro XRF maps of the homogeneous solid standard #cas 17. A represents the overlay of all elements.



**Fig. S3.** Logarithmic plots of raw ratio  $^{123}\text{Sb}/^{121}\text{Sb}$ ,  $^{122}\text{Sn}/^{116}\text{Sn}$ , and  $^{124}\text{Sn}/^{116}\text{Sn}$  versus  $^{122}\text{Sn}/^{118}\text{Sn}$  for the cassiterites analyzed by solution nebulization method in different sessions with experimentally determined regression (grey area).

**Table S1.**  $\delta^{122/118}\text{Sn}_{3161a}$  values for the decomposition experiments with various methods during the initial exploration stage.

sample	reagent	temperature	tool	time (h)	yield (%)
T1	9 mL HCl	200 °C	microwave	5	0.14
T2	8.5 mL HCl + 0.01115 g $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 0.5 mL HF	220 °C	microwave	5	0.48
T3	9 mL HCl + 0.01237 g $\text{NH}_2\text{OH}\cdot\text{HCl}$	220 °C	microwave	5	1.08
T4	8 mL HCl + 0.1 g $\text{NH}_2\text{OH}\cdot\text{HCl}$	200 °C	microwave	5	1.47
T5	9 mL HCl + 0.0442 g $\text{NH}_2\text{OH}\cdot\text{HCl}$	220 °C	microwave	5	1.50
T6	9 mL HCl + 0.03707 g $\text{NH}_2\text{OH}\cdot\text{HCl}$	220 °C	microwave	5	1.58
T7	9 mL HCl + 0.0541 g $\text{NH}_2\text{OH}\cdot\text{HCl}$	220 °C	microwave	5	1.63
T8	0.15 mL $\text{HClO}_4$ + 3mL HCl + 0.5 mL HF	200 °C	Parr bombs	48	2.29
T9	0.1 mL $\text{HClO}_4$ + 0.8 mL HF + 0.2 mL $\text{HNO}_3$	200 °C	Parr bombs	48	2.55
T10	0.1 mL $\text{HClO}_4$ + 1 mL HCl	200 °C	Parr bombs	48	3.09
T10	0.2 mL $\text{HClO}_4$ + 2 mL HCl	200 °C	Parr bombs	48	13.44
T12	5 mL HCl	200 °C	Parr bombs	48	31.96
T13	3.5 mL HCl + 0.01030 g $\text{NH}_2\text{OH}\cdot\text{HCl}$	200 °C	Parr bombs	48	37.20

**Table S2.**  $\delta^{122/118}\text{Sn}_{3161a}$  values for the decomposition experiments with the high-pressure bomb.

Experiments	sample	time (h)	yield (%)	$\delta^{122/118}\text{Sn}$	2sd
<b>EP A</b>	b03	32	39.19	0.15	0.10
	b04	65	18.62	-0.02	0.10
	b05	89	54.70	0.22	0.01
	b07	89	60.10	0.27	0.05
	b11	108	29.51	0.14	0.01
	b13	131	54.63	0.20	0.03
	b14	131	54.32	0.22	0.02
	b16	166	39.01	0.13	0.09
	b21	166	48.30	0.26	0.08
	b20	186	63.01	0.28	0.08
	b22	186	60.35	0.27	0.01
	b24	218	47.93	0.19	0.04
	<b>EP B</b>	B20	72	13.43	-0.13
B25		96	44.30	0.16	0.06
B24		120	55.62	0.20	0.02
B07		144	26.29	0.07	0.04
B03		192	58.51	0.17	0.02
B14		240	53.50	0.21	0.10
<b>EP C</b>	YT04-1	480	79.63	0.28	0.03
	YT41-1	480	100.00	0.27	0.03
	YT120-1	480	100.00	0.29	0.00
	YT130-1	480	96.21	0.28	0.04
	YT 41-2	480	100.00	0.28	0.04
	DK92	480	100.00	0.30	0.02