

Supporting Information for

Accurate determination of ultra-trace rare earth elements by LA-ICP-MS/MS and its application to cassiterite for effective elimination of Gd and Tb false positive anomalies

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Table S1 Instrumental operation parameters used for LA-ICP-MS/MS and LA-SF-ICP-MS analysis.

Analysis	LA-ICP-MS/MS	LA-SF-ICP-MS
Laser ablation system	New Wave Research, NWR 193 HE	Coherent, Geolas HD ArF excimer
Ablation Cell	Two volume cell	In-house cell, aerosol dispersion volume <3 cm ³
Wavelength (nm)	193	193
Laser fluence (J cm ⁻²)	3.5	5
Ablation frequency (Hz)	8	6
Laser spot size (μm)	120	120
Ablation duration (s)	60	60
Ablation mode	Spot	Spot
Ablation gas flow (L min ⁻¹)	0.72 (He)	0.75 (He)
Mass spectrometry	PeikinElmer NexION5000 ICP-MS/MS	Thermo Fisher Scientific Element XR SF-ICP-MS
RF power (W)	1350	1320
Mass resolution (m/Δm)	-	300
Cool gas flow rate (L min ⁻¹)	15 (Ar)	15 (Ar)
Auxiliary gas flow rate (L min ⁻¹)	1.0 (Ar)	0.8 (Ar)
Carrier gas flow rate (L min ⁻¹)	0.85 (Ar)	0.95 (Ar)
Cell gas flow rate (mL min ⁻¹)	1.1 (O ₂)	None
Analytical mode	Mass-shift	E-scan
Isotopes measured and dwell time (ms)	¹³⁹ La ¹⁶ O (15), ¹⁴⁰ Ce ¹⁶ O (15), ¹⁴¹ Pr ¹⁶ O (15), ¹⁴⁶ Nd ¹⁶ O (15), ¹⁴⁷ Sm ¹⁶ O (15), ¹⁵³ Eu ¹⁶ O (15), ¹⁵⁷ Gd ¹⁶ O (15), ¹⁵⁹ Tb ¹⁶ O (15), ¹⁶³ Dy ¹⁶ O (15), ¹⁶⁵ Ho ¹⁶ O (15), ¹⁶⁶ Er ¹⁶ O (15), ¹⁶⁹ Tm ¹⁶ O (15), ¹⁷² Yb ¹⁶ O (15), ¹⁷⁵ Lu ¹⁶ O (15)	¹³⁹ La (15), ¹⁴⁰ Ce (15), ¹⁴¹ Pr (15), ¹⁴⁶ Nd (15), ¹⁴⁷ Sm (15), ¹⁵³ Eu (15), ¹⁵⁷ Gd (15), ¹⁵⁹ Tb (15), ¹⁶³ Dy (15), ¹⁶⁵ Ho (15), ¹⁶⁶ Er (15), ¹⁶⁹ Tm (15), ¹⁷² Yb (15), ¹⁷⁵ Lu (15)

Table S2 Rare earth element contents obtained by solution-based methods.

□	ICP-MS/MS (Sol.)						SF-ICP-MS (Sol.)						Ref. ²³	
	19HS		XBD		GSR-3		19HS		XBD		GSR-3		GSR-3	
	n=1	2SE	n=1	2SE	n=1	2SE	n=1	2SE	n=1	2SE	n=1	2SE	n=1	2SD
La	210	8.00	3.12	0.12	57.4	1.38	208	6.2	3.19	0.10	58.0	1.63	56.0	2.10
Ce	785	29.9	129	4.92	107	2.23	784	23.5	129	3.86	108	2.29	105	4.00
Pr	73.5	2.79	1.13	0.04	13.0	0.20	74.0	2.22	1.14	0.03	13.3	0.35	13.2	0.50
Nd	309	11.8	1.69	0.06	53.8	0.22	308	9.30	1.66	0.05	54.9	1.16	54.0	1.80
Sm	109	4.14	1.07	0.04	10.4	0.20	109	3.27	1.09	0.03	10.5	0.24	10.2	0.40
Eu	60.8	2.31	1.64	0.06	3.30	0.10	60.8	1.82	1.64	0.05	3.31	0.11	3.20	0.11
Gd	160	6.09	1.33	0.05	8.75	0.26	159	4.78	1.37	0.04	8.70	0.25	8.50	0.19
Tb	40.3	1.53	1.09	0.04	1.18	0.02	40.3	1.21	1.19	0.04	1.22	0.04	1.20	0.04
Dy	343	13.0	13.3	0.51	5.75	0.15	343	10.3	13.3	0.40	5.79	0.17	5.60	0.17
Ho	82.4	3.14	7.26	0.28	0.91	0.03	82.9	2.49	7.26	0.22	0.90	0.03	0.88	0.05
Er	298	11.3	69.3	2.64	2.05	0.05	298	8.90	69.7	2.09	2.03	0.07	2.00	0.10
Tm	60.4	2.30	42.0	1.60	0.27	0.01	60.4	1.81	42.3	1.27	0.28	0.01	0.28	0.01
Yb	622	23.7	808	30.8	1.47	0.03	622	18.7	809	24.3	1.52	0.05	1.50	0.07
Lu	118	4.49	279	10.6	0.19	0.01	118	3.55	280	8.40	0.20	0.01	0.19	0.01
Ce/Ce*	1.55		16.9		0.96		1.55		16.6		0.96		0.95	
Eu/Eu*	1.41		4.18		1.06		1.41		4.09		1.06		1.05	
(La/Yb) _N	0.242		0.003		28.0		0.239		0.003		27.9		26.8	

Note:

$$1. Ce/Ce^* = Ce_N / \sqrt{La_N * Pr_N}; Eu/Eu^* = Eu_N / \sqrt{Sm_N * Gd_N}.$$

2. "N" represents normalized by Chondrite values ³¹; "SE" means standard error; "SD" means standard deviation.

3. Rare earth element contents in cassiterite samples are given in ng g⁻¹ and given in μg g⁻¹.

4. All analyzed cassiterite samples are heterogeneous. Even though chondrite-normalized REE patterns are similar within individual grains, the corresponding REE contents may vary by two orders of magnitude.

Table S3 Rare earth element contents of cassiterite samples investigated in this study obtained by LA-SF-ICP-MS.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce/Ce*	Eu/Eu*	(La/Yb) _N
19HS, Huangsha quartz-vien type tin deposit, Jiangxi Province, China																	
19HS-1	2.00	30.7	2.80	7.80	2.90	2.35	1520	126	4.70	0.96	3.70	2.90	22.0	6.20	3.18	0.11	0.065
19HS-2	3.62	41.4	3.20	20.8	11.4	5.90	1442	126	9.00	6.70	24.0	6.60	88.0	16.6	2.98	0.14	0.030
19HS-3	12.0	103	13.2	27.4	8.70	6.35	1448	124	9.10	2.30	11.4	2.80	32.0	6.00	2.01	0.17	0.269
19HS-4	8.50	73.5	6.90	25.0	5.70	5.90	1495	124	8.90	2.50	8.60	2.80	26.3	4.90	2.35	0.20	0.232
19HS-5	1.50	21.7	1.60	5.20	1.90	3.75	1550	140	9.20	0.91	2.90	0.90	23.0	5.90	3.43	0.21	0.047
19HS-6	37.0	230	24.2	81.0	46.0	17.4	1625	148	124	31.0	127	24.5	220	39.0	1.88	0.19	0.121
19HS-7	20.0	161	17.4	76.5	24.0	16.7	1702	154	17.0	6.60	24.6	4.30	63.0	12.9	2.12	0.25	0.228
19HS-8	76.0	362	31.1	106.5	26.0	13.9	1785	174	74.0	21.4	63.0	16.7	124	19.7	1.83	0.20	0.440
19HS-9	41.0	252	15.5	60.0	19.5	9.60	1801	157	18.0	4.30	16.6	5.40	52.0	10.7	2.45	0.16	0.566
XBD, Xuebaoding pegmatite tin deposit, Sichuan Province, China																	
XBD-1	0.40	19.3	1.60	4.25	1.40	0.89	1372	111	10.6	6.50	56.0	32.2	722	177	5.91	0.06	0.0004
XBD-2	3.90	22.8	2.20	2.00	1.70	0.75	1336	97	15.0	12.4	120	58.2	1172	328	1.91	0.05	0.0024
XBD-3	3.60	21.5	2.10	1.30	1.20	0.61	1360	110	32.0	12.4	101	46.6	970	278	1.92	0.05	0.0027
XBD-4	3.60	17.9	2.40	1.75	1.10	0.68	1318	109	24.3	3.50	41.9	21.6	466	132	1.49	0.05	0.0055
XBD-5	3.51	21.4	1.00	1.50	1.90	0.88	1393	105	24.0	5.50	34.9	21.0	439	117	2.80	0.05	0.0057
XBD-6	2.60	15.6	2.20	1.75	0.73	0.40	1402	112	24.0	6.10	73.0	40.0	857	236	1.60	0.04	0.0022
XBD-7	1.60	21.0	1.10	1.70	0.70	0.77	1429	122	18.9	3.80	52.1	29.6	714	177	3.88	0.07	0.0016
XBD-8	4.00	23.9	2.00	2.00	0.62	0.35	1464	114	12.8	5.00	41.2	26.2	523	120	2.07	0.04	0.0055
XBD-9	1.70	29.1	2.20	3.40	1.80	1.45	1479	136	60.0	16.2	116	64.0	1178	272	3.69	0.09	0.0010
XBD-10	2.20	15.1	1.70	1.60	0.61	1.70	1428	125	28.0	6.80	55.9	38.9	733	180	1.91	0.18	0.0022
Glass reference materials' results obtained by LA-SF-ICP-MS																	
Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce/Ce*	Eu/Eu*	(La/Yb) _N
NIST612-1	35.8	37.8	37.2	35.6	37.2	35.6	37.0	37.8	35.7	37.7	37.5	37.9	38.8	36.4	-	-	-
NIST612-2	36.5	40.5	40.7	38.6	40.4	38.5	40.8	41.5	39.3	39.3	38.8	41.6	39.9	38.0	-	-	-
NIST612-3	35.8	38.6	38.3	35.6	38.6	35.8	37.7	38.3	36.0	37.9	37.7	37.6	38.9	36.6	-	-	-
NIST612-4	36.2	39.1	38.9	36.7	38.5	36.7	38.6	39.3	37.1	38.7	38.3	39.1	39.6	37.5	-	-	-
NIST612-5	36.0	37.2	36.4	34.1	36.2	34.3	35.9	36.4	34.2	38.2	37.9	35.3	39.1	36.8	-	-	-

Table S3 (Continued) Rare earth element contents of cassiterite samples investigated in this study obtained by LA-SF-ICP-MS.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce/Ce*	Eu/Eu*	(La/Yb) _N
NIST612-6	36.0	38.6	38.2	35.8	37.6	35.7	37.5	37.8	35.7	38.4	38.1	37.0	39.3	37.1	-	-	-
NIST612-7	36.1	39.6	38.9	36.2	38.8	36.8	38.8	39.0	37.0	38.5	38.2	38.0	39.4	37.2	-	-	-
NIST612-8	35.8	36.5	36.5	34.0	36.2	33.6	35.8	35.9	33.6	37.8	37.6	34.9	38.8	36.5	-	-	-
NIST612-9	36.0	37.7	36.6	34.1	36.6	34.1	36.0	36.1	33.9	38.3	38.0	35.1	39.2	37.0	-	-	-
NIST612-10	36.0	37.6	37.5	35.5	37.8	35.6	37.2	37.5	35.4	38.3	38.0	36.6	39.2	37.0	-	-	-
NIST612-11	36.0	39.9	39.5	36.6	39.1	37.1	38.5	38.8	36.8	38.4	38.1	37.7	39.3	37.1	-	-	-
NIST612-12	35.9	37.9	36.7	34.5	36.6	34.5	36.3	36.5	34.3	38.1	37.8	35.6	39.1	36.8	-	-	-
NIST612-13	36.0	38.4	37.9	35.8	37.4	35.5	37.1	37.5	35.2	38.3	38.0	36.7	39.2	37.0	-	-	-
NIST612-14	36.0	38.8	38.5	35.9	38.4	36.2	37.8	38.2	36.2	38.3	38.0	37.7	39.2	37.0	-	-	-
NIST612-15	35.9	38.4	37.8	35.3	37.6	35.5	37.2	37.4	35.4	38.2	38.0	36.6	39.1	37.0	-	-	-
NIST612-16	36.2	38.4	38.0	35.7	37.8	35.9	37.5	37.9	35.6	38.4	38.0	37.1	39.3	37.0	-	-	-
NIST612-17	36.0	38.3	37.8	35.8	37.6	35.7	37.3	37.7	35.7	38.4	38.0	37.1	39.2	37.1	-	-	-
NIST612-18	35.9	38.4	38.0	35.5	37.8	35.4	37.2	37.5	35.4	38.2	38.0	36.6	39.2	36.9	-	-	-
NIST612-19	35.6	38.3	37.6	35.3	37.1	35.2	36.8	36.9	35.1	37.8	38.0	36.3	38.9	36.7	-	-	-
NIST612-20	36.7	38.5	38.2	35.8	38.5	36.2	38.0	38.6	36.2	38.9	38.0	37.7	39.7	37.4	-	-	-
NIST612-21	32.6	38.4	37.8	25.6	35.9	34.7	36.4	36.3	34.2	37.2	38.0	35.2	38.9	36.6	-	-	-
NIST612-22	36.6	38.5	38.6	35.5	38.5	37.4	38.0	39.5	37.1	39.4	38.1	37.9	39.8	37.5	-	-	-
NIST612-23	36.2	38.4	37.8	35.4	37.8	35.8	37.4	37.7	35.7	38.5	38.0	37.2	39.1	37.0	-	-	-
NIST612-24	35.9	38.4	38.0	35.9	37.8	35.6	37.5	37.7	35.6	38.4	38.0	36.8	39.3	37.0	-	-	-
NIST612-25	36.0	38.4	37.8	35.8	37.5	35.4	37.1	37.4	35.4	38.2	38.0	36.7	39.1	37.0	-	-	-
NIST612-26	34.9	38.3	37.4	34.8	36.3	34.9	35.8	35.9	34.1	36.7	37.9	34.9	37.9	35.5	-	-	-
NIST612-27	37.6	38.5	38.4	36.7	39.6	36.6	39.2	39.8	37.8	41.3	38.2	39.8	41.5	39.9	-	-	-
NIST612-28	33.1	38.0	36.2	32.5	34.9	32.4	34.5	34.4	33.0	34.9	37.8	34.1	36.3	34.3	-	-	-
NIST612-29	36.8	38.7	38.4	36.1	38.6	36.4	38.0	38.1	36.3	38.9	38.1	37.6	40.1	37.7	-	-	-
NIST612-30	35.5	38.3	37.7	35.3	37.1	35.1	36.7	36.8	34.9	37.7	38.0	35.9	38.7	36.4	-	-	-
NIST612-31	36.2	38.5	38.0	36.1	38.2	35.9	37.6	38.1	36.2	38.7	38.0	37.3	39.6	37.4	-	-	-
NIST612-32	35.6	38.3	37.6	34.9	37.4	35.3	36.8	36.9	34.8	37.7	38.0	36.2	39.0	36.5	-	-	-
NIST612-33	36.2	38.5	38.2	35.5	37.8	35.8	37.6	38.1	35.8	38.6	38.0	37.1	39.3	37.2	-	-	-

Table S3 (Continued) Rare earth element contents of cassiterite samples investigated in this study obtained by LA-SF-ICP-MS.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce/Ce*	Eu/Eu*	(La/Yb) _N
ARM-3-1	3.97	5.65	3.90	5.33	4.18	3.86	4.01	4.46	4.14	4.23	3.74	4.36	5.70	3.92	-	-	-
ARM-3-2	4.06	5.35	3.66	4.96	3.86	3.64	3.75	4.06	3.77	4.28	3.89	4.03	5.65	3.98	-	-	-
ARM-3-3	3.93	5.07	3.53	4.86	3.62	3.56	3.64	3.98	3.77	4.17	3.64	3.82	5.51	3.82	-	-	-
ARM-3-4	4.89	5.37	3.84	5.13	4.12	3.82	3.95	4.34	3.94	5.07	4.53	4.12	6.69	4.62	-	-	-
ARM-3-5	4.29	5.56	3.85	5.21	4.13	3.89	3.99	4.39	4.23	4.59	4.04	4.18	6.16	4.27	-	-	-
ARM-3-6	4.88	5.55	3.95	5.27	4.08	3.94	4.01	4.34	4.06	5.13	4.67	4.27	6.77	4.76	-	-	-
ARM-3-7	4.25	5.46	3.80	5.13	3.95	3.83	3.97	4.23	4.02	4.42	3.90	4.25	5.83	4.08	-	-	-
ARM-3-8	4.24	5.52	3.72	4.94	3.77	3.66	3.70	3.98	3.76	4.32	3.82	3.88	5.87	4.00	-	-	-
ARM-3-9	4.17	5.38	3.65	5.08	3.87	3.59	3.69	4.02	3.83	4.35	3.99	3.91	5.84	4.10	-	-	-
ARM-3-10	4.43	5.43	3.72	5.15	3.94	3.84	3.94	4.24	4.02	4.63	3.91	4.19	5.96	4.15	-	-	-
ARM-3-11	5.06	6.32	4.35	5.76	4.55	4.23	4.36	4.71	4.51	5.22	4.58	4.64	6.81	4.69	-	-	-
ARM-3-12	4.65	5.90	4.04	5.39	4.21	3.94	4.14	4.35	4.12	4.85	4.37	4.36	6.46	4.46	-	-	-
ARM-3-13	4.27	6.01	3.87	5.14	3.77	3.68	3.65	3.92	3.78	4.35	3.35	3.91	5.73	3.90	-	-	-
ARM-3-14	4.54	5.18	3.84	5.17	4.18	3.90	3.89	4.17	4.03	4.58	3.74	4.14	6.04	4.22	-	-	-
ARM-3-15	3.99	3.95	3.08	4.60	3.56	3.37	3.49	3.87	3.79	4.22	3.51	3.86	5.46	4.09	-	-	-
ARM-3-16	4.09	5.10	3.63	4.77	3.80	3.51	3.64	3.97	3.70	4.28	3.74	3.93	5.53	3.91	-	-	-
ARM-3-17	4.46	5.34	3.79	5.19	4.16	3.92	4.05	4.39	3.99	4.79	4.18	4.34	6.38	4.43	-	-	-

Note:

1. $Ce/Ce^* = Ce_N / \sqrt{La_N * Pr_N}$; $Eu/Eu^* = Eu_N / \sqrt{Sm_N * Gd_N}$.

2. "N" represents normalized by Chondrite values ³¹.

3. Rare earth element contents in cassiterite samples are given in ng g⁻¹ and glass reference materials are given in μg g⁻¹.

Table S4 Rare earth element contents of cassiterite samples investigated in this study obtained by LA-ICP-MS/MS.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce/Ce*	Eu/Eu*	(La/Yb) _N
19HS, Huangsha quartz-vien type tin deposit, Jiangxi Province, China																	
19HS-1	242	883	83.7	324	77.6	28.4	84.4	15.8	121	28.5	97.0	21.9	254	45.1	1.52	1.07	0.682
19HS-2	478	1987	228	1029	386	244	599	163	1461	377	1462	307	3014	568	1.48	1.55	0.114
19HS-3	104	498	38.1	152	49.0	29.4	73.2	17.7	153	36.3	120	24.4	267	49.0	1.94	1.50	0.280
19HS-4	324	923	93.9	415	181	95.4	251	59.7	490	103	345	57.2	643	117	1.30	1.37	0.362
19HS-5	149	577	50.0	214	70.5	42.1	125	34.5	312	72.5	265	59.0	572	104	1.64	1.37	0.187
19HS-6	87.3	298	18.5	66.3	15.8	7.86	16.1	3.50	23.4	5.34	21.3	4.06	52.2	13.4	1.82	1.51	1.199
19HS-7	15.8	145	5.49	23.2	6.13	4.07	6.57	1.08	7.14	2.27	8.27	2.21	28.5	6.64	3.83	1.96	0.397
19HS-8	22.8	153	6.37	20.4	7.03	3.76	6.27	0.96	7.29	2.27	7.91	1.75	22.6	7.17	3.12	1.73	0.725
19HS-9	317	1181	101	377	128	60.5	181	42.2	325	73.5	220	40.3	472	85.4	1.62	1.22	0.482
19HS-10	127	349	28.7	130	48.5	26.7	83.4	20.6	155	33.8	109	20.0	218	56.6	1.41	1.28	0.420
XBD, Xuebaoding pegmatite tin deposit, Sichuan Province, China																	
XBD-1	7.27	95.7	1.59	3.60	2.86	4.61	1.92	0.70	13.6	7.17	62.0	39.5	638	251	6.90	6.01	0.008
XBD-2	2.47	76.6	1.30	1.13	0.67	0.43	1.13	0.59	6.89	5.43	50.4	32.8	610	203	10.5	1.52	0.003
XBD-3	3.18	86.7	1.08	1.14	1.34	0.97	1.92	0.59	10.9	4.81	32.9	14.8	572	189	11.4	1.85	0.004
XBD-4	1.96	88.9	0.59	1.30	0.54	1.50	0.61	0.48	12.5	7.14	69.6	42.1	721	289	20.3	8.01	0.002
XBD-5	2.79	97.8	0.82	1.34	0.50	2.43	1.25	0.86	13.9	7.84	82.1	50.4	849	290	15.9	9.41	0.002
XBD-6	1.14	142	0.94	0.94	0.42	1.94	0.68	1.04	6.78	3.20	35.4	18.3	620	236	33.6	11.1	0.001
XBD-7	1.36	138	0.55	1.09	0.57	0.97	0.79	0.35	10.8	5.40	47.5	30.8	721	199	39.0	4.43	0.001
XBD-8	1.73	139	0.59	1.14	0.47	0.31	0.75	1.04	12.2	7.25	79.6	47.5	863	298	33.7	1.60	0.001
XBD-9	2.62	141	1.64	1.14	0.67	0.43	0.69	0.38	16.6	9.56	93.9	56.6	876	282	16.7	1.96	0.002
XBD-10	3.32	146	0.96	2.27	1.51	0.97	2.15	0.94	14.2	6.89	64.3	41.5	734	254	20.1	1.65	0.003
Glass reference materials' results obtained by LA-ICP-MS/MS																	
Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce/Ce*	Eu/Eu*	(La/Yb) _N
NIST614-1	0.74	0.82	0.78	0.77	0.79	0.79	0.80	0.78	0.77	0.79	0.77	0.78	0.77	0.77	-	-	-
NIST614-2	0.76	0.87	0.82	0.79	0.80	0.81	0.81	0.79	0.81	0.79	0.79	0.77	0.77	0.77	-	-	-
NIST614-3	0.71	0.80	0.76	0.76	0.74	0.76	0.75	0.72	0.73	0.72	0.72	0.71	0.71	0.71	-	-	-

Table S4 (Continued) Rare earth element contents of cassiterite samples investigated in this study obtained by LA-ICP-MS/MS.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce/Ce*	Eu/Eu*	(La/Yb) _N
NIST614-4	0.67	0.76	0.72	0.68	0.69	0.72	0.69	0.67	0.67	0.69	0.67	0.67	0.67	0.68	-	-	-
NIST614-5	0.73	0.82	0.77	0.79	0.77	0.78	0.78	0.77	0.77	0.76	0.77	0.76	0.79	0.76	-	-	-
NIST614-6	0.70	0.78	0.76	0.73	0.75	0.77	0.78	0.75	0.76	0.76	0.75	0.75	0.81	0.75	-	-	-
NIST614-7	0.70	0.79	0.75	0.74	0.75	0.74	0.75	0.73	0.75	0.75	0.72	0.72	0.74	0.73	-	-	-
NIST614-8	0.72	0.82	0.78	0.76	0.75	0.78	0.76	0.73	0.75	0.74	0.72	0.72	0.80	0.72	-	-	-
NIST614-9	0.74	0.85	0.79	0.74	0.76	0.80	0.77	0.75	0.75	0.76	0.75	0.74	0.80	0.73	-	-	-
NIST614-10	0.72	0.81	0.76	0.76	0.76	0.76	0.74	0.71	0.71	0.72	0.72	0.69	0.73	0.70	-	-	-
NIST614-11	0.75	0.84	0.80	0.76	0.77	0.81	0.78	0.78	0.79	0.78	0.75	0.76	0.80	0.77	-	-	-
NIST614-12	0.70	0.78	0.74	0.75	0.78	0.77	0.77	0.74	0.74	0.75	0.75	0.73	0.75	0.74	-	-	-
NIST614-13	0.71	0.81	0.77	0.74	0.75	0.73	0.77	0.75	0.74	0.75	0.73	0.73	0.76	0.73	-	-	-
NIST614-14	0.75	0.84	0.79	0.78	0.76	0.81	0.78	0.75	0.75	0.78	0.77	0.76	0.79	0.76	-	-	-
NIST614-15	0.70	0.80	0.76	0.72	0.74	0.76	0.74	0.71	0.72	0.71	0.72	0.70	0.77	0.69	-	-	-
NIST614-16	0.70	0.80	0.76	0.76	0.72	0.75	0.74	0.71	0.74	0.73	0.72	0.72	0.79	0.71	-	-	-
NIST614-17	0.73	0.81	0.76	0.74	0.75	0.76	0.78	0.75	0.76	0.76	0.74	0.75	0.78	0.75	-	-	-
NIST614-18	0.73	0.82	0.78	0.77	0.78	0.78	0.79	0.75	0.75	0.76	0.75	0.76	0.76	0.75	-	-	-
NIST614-19	0.71	0.80	0.75	0.75	0.74	0.76	0.75	0.73	0.73	0.74	0.74	0.73	0.77	0.72	-	-	-
NIST614-20	0.71	0.80	0.75	0.74	0.74	0.77	0.74	0.73	0.73	0.74	0.71	0.72	0.78	0.72	-	-	-
NIST614-21	0.74	0.84	0.79	0.75	0.77	0.78	0.77	0.74	0.75	0.74	0.75	0.71	0.77	0.73	-	-	-
NIST614-22	0.71	0.81	0.78	0.76	0.75	0.77	0.74	0.73	0.75	0.75	0.75	0.72	0.80	0.73	-	-	-
NIST614-23	0.66	0.76	0.70	0.70	0.69	0.74	0.71	0.69	0.69	0.71	0.69	0.68	0.74	0.68	-	-	-
NIST614-24	0.67	0.78	0.73	0.71	0.71	0.72	0.71	0.71	0.72	0.72	0.73	0.71	0.72	0.71	-	-	-
NIST614-25	0.77	0.85	0.81	0.80	0.81	0.79	0.80	0.77	0.79	0.77	0.77	0.76	0.79	0.76	-	-	-
NIST614-26	0.78	0.86	0.83	0.80	0.80	0.83	0.83	0.79	0.78	0.79	0.78	0.77	0.85	0.78	-	-	-
NIST612-1	36.2	40.6	38.6	35.6	37.4	35.4	38.2	37.3	36.3	38.8	38.0	38.0	37.7	37.5	-	-	-
NIST612-2	37.5	41.8	39.5	36.5	38.4	36.2	39.4	38.6	37.5	39.8	39.5	39.0	38.8	38.6	-	-	-
NIST612-3	35.8	39.8	37.8	34.9	36.5	34.7	37.3	36.4	35.2	37.6	37.0	36.6	36.4	36.3	-	-	-
NIST612-4	35.7	39.7	37.8	34.9	36.4	34.4	37.1	36.2	35.2	37.3	36.8	36.6	36.4	36.2	-	-	-
NIST612-5	34.0	37.2	35.7	34.1	35.0	33.6	35.7	34.8	33.4	36.3	35.8	35.8	37.6	35.2	-	-	-

Table S4 (Continued) Rare earth element contents of cassiterite samples investigated in this study obtained by LA-ICP-MS/MS.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce/Ce*	Eu/Eu*	(La/Yb) _N
NIST612-6	36.2	39.3	37.4	36.1	36.9	35.4	38.3	37.4	36.0	39.0	38.8	38.2	40.3	37.9	-	-	-
NIST612-7	36.2	39.6	38.0	36.3	37.2	35.2	38.4	37.3	36.2	39.1	38.4	38.0	40.1	37.3	-	-	-
NIST612-8	36.8	40.3	38.3	36.5	37.5	35.7	38.4	37.3	36.4	39.1	38.5	38.1	40.3	37.5	-	-	-
NIST612-9	36.3	39.9	37.8	36.1	36.7	35.2	37.6	36.4	35.2	38.0	37.2	36.9	39.1	36.3	-	-	-
NIST612-10	39.3	43.5	41.2	39.0	39.6	38.1	40.6	39.4	38.2	41.0	40.5	39.9	42.2	39.2	-	-	-
NIST612-11	35.4	38.1	36.2	34.6	36.2	34.1	36.9	35.9	34.8	37.8	37.3	37.2	39.5	36.8	-	-	-
NIST612-12	37.2	40.3	38.5	36.6	38.1	35.9	39.2	38.3	36.9	39.9	39.6	39.3	41.1	38.7	-	-	-
NIST612-13	37.5	40.9	38.6	37.0	38.1	36.2	38.9	38.4	36.9	40.1	39.4	39.4	41.5	38.9	-	-	-
NIST612-14	37.1	40.7	38.6	36.9	38.1	36.1	38.4	38.2	36.6	39.4	39.2	39.0	41.1	38.4	-	-	-
NIST612-15	37.2	40.1	38.2	36.7	38.1	36.4	38.2	37.9	36.7	39.6	39.1	38.9	41.2	38.6	-	-	-
NIST612-16	38.8	42.9	40.3	38.6	39.3	37.6	39.4	39.0	37.2	40.5	39.8	39.7	42.0	39.4	-	-	-
NIST612-17	37.0	40.9	38.3	36.5	37.5	35.8	39.0	38.2	36.3	39.5	39.1	39.0	41.0	38.5	-	-	-
NIST612-18	36.5	39.2	37.3	35.6	36.8	35.7	38.5	37.9	36.3	39.4	38.8	38.7	40.3	38.3	-	-	-
NIST612-19	37.4	40.1	38.0	36.7	37.4	35.9	39.3	38.7	37.2	40.3	39.8	39.6	41.0	39.2	-	-	-
NIST612-20	37.6	39.8	38.3	37.2	37.2	36.2	39.3	38.7	37.2	40.5	39.9	39.6	41.2	39.1	-	-	-
NIST612-21	37.9	40.5	38.6	37.5	37.9	36.4	40.3	39.5	38.0	40.9	40.8	40.4	41.9	40.2	-	-	-
NIST612-22	39.1	42.6	40.0	38.1	39.2	37.7	41.0	40.2	38.3	41.4	41.0	40.9	42.8	40.3	-	-	-
NIST612-23	33.7	36.8	35.6	33.0	34.6	33.2	35.6	35.3	34.1	36.4	36.3	36.1	38.3	35.8	-	-	-
NIST612-24	35.1	37.9	36.4	34.1	36.1	34.3	36.7	36.4	35.2	37.6	37.3	37.1	39.6	36.8	-	-	-
NIST612-25	38.7	41.4	40.1	37.6	39.2	36.8	39.8	39.0	37.3	40.0	39.6	39.3	42.8	39.2	-	-	-
NIST612-26	38.9	41.7	40.0	37.9	39.3	36.8	39.8	39.1	37.6	40.2	39.9	39.7	43.3	39.5	-	-	-

Note:

1. $Ce/Ce^* = Ce_N / \sqrt{La_N * Pr_N}$; $Eu/Eu^* = Eu_N / \sqrt{Sm_N * Gd_N}$.

2. "N" represents normalized by Chondrite values ³¹.

3. Rare earth element contents in cassiterite samples are given in ng g⁻¹ and glass reference materials are given in μg g⁻¹.

Table S5 Signal intensity data (cps) obtained by LA-ICP-MS/MS in this study.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
19HS, Huangsha quartz-vien type tin deposit, Jiangxi Province, China														
19HS-1	77223	261201	29232	32384	8776	2504	7651	5099	13285	10556	20046	8435	24482	15585
19HS-2	152616	587553	79688	102750	43621	21539	54303	52400	160231	139320	302136	118005	290133	196029
19HS-3	33328	147314	13321	15207	5540	2594	6641	5693	16721	13416	24903	9374	25704	16914
19HS-4	103580	273038	32792	41446	20451	8417	22748	19232	53719	38227	71266	21991	61861	40505
19HS-5	47617	170701	17458	21379	7973	3711	11366	11113	34225	26802	54812	22682	55065	35860
19HS-6	27885	88018	6463	6619	1786	694	1463	1126	2569	1976	4411	1559	5027	4622
19HS-7	5033	42995	1917	2318	694	359	595	348	782	838	1710	851	2742	2292
19HS-8	7285	45369	2225	2035	795	332	568	309	799	838	1635	673	2171	2475
19HS-9	101199	349273	35442	37663	14445	5340	16370	13589	35586	27162	45421	15488	45411	29504
19HS-10	40732	103223	10024	13001	5488	2353	7563	6621	16942	12488	22549	7693	20963	19557
XBD, Xuebaoding pegmatite tin deposit, Sichuan Province, China														
XBD-1	2322	28311	557	360	323	407	175	224	1486	2651	12817	15187	61371	86585
XBD-2	790	22663	453	113	76	38	103	190	755	2006	10413	12594	58697	70232
XBD-3	1017	25630	379	114	152	86	175	190	1198	1777	6798	5707	55044	65138
XBD-4	625	26272	206	129	61	132	55	155	1366	2640	14391	16167	69394	99737
XBD-5	890	28922	287	133	57	214	113	276	1522	2900	16968	19381	81748	100133
XBD-6	365	41908	327	94	48	171	61	336	743	1185	7317	7023	59676	81500
XBD-7	436	40835	193	108	64	86	72	112	1186	1996	9825	11837	69375	68693
XBD-8	553	41100	207	114	53	32	68	336	1342	2682	16449	18239	83028	102893
XBD-9	837	41651	572	114	76	38	62	121	1822	3534	19407	21738	84271	97516
XBD-10	1062	43289	334	227	171	86	195	302	1558	2547	13284	15968	70637	87585
Glass reference materials														
NIST614-1	235788	238152	266083	77298	88335	69444	73173	254084	84818	297927	162969	305682	76733	272702
NIST614-2	242749	250680	278551	78447	89848	71680	74176	256100	89311	295733	166359	302096	78998	271695
NIST614-3	225474	232510	259823	76322	83060	66762	67862	233559	80945	270399	152361	279878	73376	251610
NIST614-4	211839	220812	245482	68389	77763	63458	62623	216431	74053	259945	141476	262982	68939	238765
NIST614-5	235788	238152	266083	77298	88335	69444	73173	254084	84818	297927	162969	305682	76733	272702
NIST614-6	235788	238152	266083	77298	88335	69444	73173	254084	84818	297927	162969	305682	76733	272702
NIST614-7	235788	238152	266083	77298	88335	69444	73173	254084	84818	297927	162969	305682	76733	272702
NIST614-8	242749	250680	278551	78447	89848	71680	74176	256100	89311	295733	166359	302096	78998	271695
NIST614-9	225474	232510	259823	76322	83060	66762	67862	233559	80945	270399	152361	279878	73376	251610
NIST614-10	211839	220812	245482	68389	77763	63458	62623	216431	74053	259945	141476	262982	68939	238765
NIST614-11	236154	245101	276568	74073	85272	69421	69302	243836	84796	277849	149555	283349	75975	257489
NIST614-12	222085	227629	258294	73055	85881	65777	68125	232588	79279	268898	151022	269348	71729	247177
NIST614-13	224777	235723	265941	72292	82810	62628	68208	233975	79441	266633	146134	270160	72064	246486

Table S5 (Continued) Signal intensity data (cps) obtained by LA-ICP-MS/MS in this study.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
NIST614-14	235759	243882	273949	75651	83876	69392	69607	236260	80832	276949	153442	281394	75416	255689
NIST614-15	222300	232036	264122	69595	81262	65194	66227	221807	77159	255050	144807	259854	73740	230788
NIST614-16	221547	231125	262472	74226	79257	64406	65687	223415	79408	259624	143923	266796	74857	237254
NIST614-17	233722	242465	272380	74389	85693	67457	69298	235799	82282	272378	149157	278482	74469	251687
NIST614-18	233883	243256	278196	77424	89536	68727	70231	236476	81510	275501	151546	282279	72202	253061
NIST614-19	228747	237861	268057	75708	85114	67306	67071	230590	78859	266598	148650	271677	73335	242905
NIST614-20	229057	239729	268015	73861	85430	68273	66281	228668	79413	267138	143557	269804	74922	242412
NIST614-21	236886	249124	283836	75286	88088	68818	68651	232838	81057	267328	150026	265474	73449	247102
NIST614-22	228772	242301	278009	75946	86377	68001	66123	229381	80923	270305	150967	268808	76849	244996
NIST614-23	211493	237459	249661	70867	78848	66903	65738	225582	77418	268406	144564	265517	68873	231775
NIST614-24	216013	244184	259814	72232	81360	65185	65885	232602	79985	273713	152513	274732	66973	242723
NIST614-25	245782	267316	287810	81192	92789	71684	73829	253476	88568	292547	161007	295279	73497	259309
NIST614-26	250655	270311	293597	80846	91216	75759	76687	259836	87724	298237	163908	299724	79278	266557
NIST612-1	11556936	11370345	13232689	3561458	4283832	3162618	3431280	12296299	3950072	14492777	8003454	14515559	3739417	13112809
NIST612-2	11980657	11684623	13532838	3648511	4398864	3237833	3541994	12696358	4085395	14869007	8310015	14886189	3876519	13518510
NIST612-3	11438786	11143493	12951634	3493039	4181287	3099890	3347125	11983919	3836827	14059565	7797134	13996492	3701188	12695627
NIST612-4	11399417	11099651	12962039	3486841	4172466	3077329	3332167	11926677	3835258	13961165	7751429	13990440	3688450	12666070
NIST612-5	11556936	11370345	13232689	3561458	4283832	3162618	3431280	12296299	3950072	14492777	8003454	14515559	3739417	13112809
NIST612-6	11556936	11370345	13232689	3561458	4283832	3162618	3431280	12296299	3950072	14492777	8003454	14515559	3739417	13112809
NIST612-7	11556936	11370345	13232689	3561458	4283832	3162618	3431280	12296299	3950072	14492777	8003454	14515559	3739417	13112809
NIST612-8	11980657	11684623	13532838	3648511	4398864	3237833	3541994	12696358	4085395	14869007	8310015	14886189	3876519	13518510
NIST612-9	11438786	11143493	12951634	3493039	4181287	3099890	3347125	11983919	3836827	14059565	7797134	13996492	3701188	12695627
NIST612-10	11399417	11099651	12962039	3486841	4172466	3077329	3332167	11926677	3835258	13961165	7751429	13990440	3688450	12666070
NIST612-11	11209169	10685972	12610396	3375585	4065445	2969258	3236426	11419036	3692076	13451779	7464845	13429794	3621246	12237293
NIST612-12	11777687	11302915	13422942	3562317	4276593	3126911	3440888	12188649	3916698	14194633	7926176	14186782	3772997	12886391
NIST612-13	11873954	11453178	13437570	3600493	4282205	3153720	3416597	12215290	3914879	14260392	7892824	14219593	3803264	12925095
NIST612-14	11740999	11407333	13445028	3597241	4284810	3143178	3371510	12155448	3878654	14020919	7849393	14077948	3770312	12757825
NIST612-15	11798726	11231104	13326132	3578796	4280348	3173089	3356101	12067345	3891722	14091216	7832775	14064895	3782479	12826855
NIST612-16	12287700	12028330	14047233	3759776	4419811	3273491	3457967	12421077	3943003	14417821	7961154	14331451	3849028	13088936
NIST612-17	11531885	11346060	13249838	3540508	4235501	3099457	3306023	11740343	3742509	13678653	7596000	13640157	3716776	12404393
NIST612-18	11383542	10882607	12901776	3448013	4163217	3084018	3260807	11631172	3739926	13637358	7527175	13528129	3655598	12340327
NIST612-19	11674373	11144534	13126971	3558845	4226290	3108431	3332942	11896757	3835661	13952084	7723733	13844986	3715916	12624718
NIST612-20	11718501	11061043	13233620	3601531	4209943	3126709	3330827	11887935	3827202	14042174	7751006	13839850	3739508	12588734
NIST612-21	11818666	11251356	13337865	3636087	4288727	3145542	3412805	12127762	3911571	14168643	7917967	14111448	3799494	12944805
NIST612-22	12182568	11827414	13835090	3692224	4427629	3256433	3472392	12352920	3948229	14352128	7958053	14288479	3881988	13004431

Table S5 (Continued) Signal intensity data (cps) obtained by LA-ICP-MS/MS in this study.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
NIST612-23	10856053	11151456	12663414	3349217	4029691	3059401	3246403	11746786	3765986	13730713	7634801	13626676	3506802	12106730
NIST612-24	11299884	11476102	12948506	3468110	4201332	3152845	3349090	12115345	3890536	14182209	7830788	14005854	3618386	12438699
NIST612-25	12462166	12544424	14264443	3817511	4562623	3389684	3629458	12993943	4120330	15061689	8316654	14808300	3916282	13265846
NIST612-26	12548327	12615071	14239863	3845882	4573945	3388519	3627563	13038202	4147066	15152759	8387236	14951220	3960805	13352303

Note:

1. Calculated background counts (cps): La (60), Ce (60), Pr (60), Nd (30), Sm (30), Eu (30), Gd (30), Tb (60), Dy (30), Ho (60), Er (60), Tm (60), Yb (30), Lu (60).
2. Calculated detection limit (ng g⁻¹): La (0.19), Ce (0.20), Pr (0.17), Nd (0.30), Sm (0.27), Eu (0.30), Gd (0.33), Tb (0.19), Dy (0.27), Ho (0.16), Er (0.29), Tm (0.16), Yb (0.31), Lu (0.17).
3. The detection limit is calculated to be three times the background ion count. All signal intensity data are above detection limit.