

Supporting Information

A synthesized sphalerite standard for in situ analysis of sulfur isotopes and trace elements by LA-MC-ICP-MS and LA-ICP-MS

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Supplementary Table 1. The published reference materials applied in microanalysis of sphalerite for LA-MC-ICP-MS and LA-ICP-MS.

	Name	Material	$\delta^{34}\text{S}_{\text{V-CDT}} (\text{‰})$	Ref.
LA-MC-ICP-MS	NBS123	Natural sphalerite	+17.75±0.17‰	Pribil et al. ⁵⁹
	PSPT-3	Pressed powder tablet	+26.4±0.21‰	Bao et al. ²³
	SPH-1	Natural sphalerite	-7.13±0.41‰	Lv et al. ⁵¹
	PAS-GBW0270	PAS-synthesized sphalerite	-5.44±0.2‰	Nie et al. ³¹
	Name	Material	Matrix	Ref.
LA-ICP-MS	MASS-1	Pressed powder tablet	Fe-Zn-Cu-S	Wilson et al. ²²
	MUL-ZnS-1	Sintering pressed pellet	Fe-Zn-S	Onuk et al. ¹
	STDGL2b2	Li-borate fused glass	Fe-Zn-Se-S	Danyushevsky et al. ¹⁹
	STDGL3	Li-borate fused glass	Fe-Zn-S	Belousov et al. ³⁰

Supplementary Table 2 Concentrations of different elements in quality control material (GBW07270) analyzed by ICP-MS ($\mu\text{g g}^{-1}$)

	Preferred value	Calibration values			
		Duplicate 1	Duplicate 2	Duplicate 3	RSD (%)
Ag	5	4.97	5.11	5.07	1.43
As	3.3	3.01	2.99	2.97	0.67
Bi	6.1	6.01	6.12	6.11	1.00
Cd	1500	1493	1497	1503	0.34
Co	491	487	481	489	0.86
Cu	1000	1015	1087	1032	3.60
Fe	21400	21378	21556	21474	0.41
Ga	251	259	254	253	1.26
Ge	6	6.19	6.24	5.87	3.29
In	21	20.76	21.03	20.97	0.68

Supplementary Table 3 S isotopes of quality control material analyzed by IRMS

	IAEA-S-1 (‰)	IAEA-S-2 (‰)	IAEA-S-3 (‰)
1	-0.13	+22.47	-32.41
2	-0.42	+22.72	-32.35
3	-0.42	+22.60	-32.67
4	-0.19	+22.90	-32.54
STDV	0.15	0.18	0.14
Mean	-0.29	+22.67	-32.49

Supplementary Table 4 Concentrations of different elements in quality control material analyzed by LA-ICP-MS ($\mu\text{g g}^{-1}$)

	SKLODG						USTC			SKLCD		
	GSE-1G (n=12)			MASS-1 (n=10)			GSE-1G (n=3)			GSE-1G (n=4)		
	Calibration values	Preferred value	Relative deviation	Calibration values	Preferred value	Relative deviation	Calibration values	Preferred value	Relative deviation	Calibration values	Preferred value	Relative deviation
Na	30603.61	28935.48	5.77	26358.00	24483.87	7.65	29779.06	28935.48	2.92	30583.54	28935.48	5.70
Mg	20161.19	21000.00	-3.99	34.09	-	-	19387.68	21000.00	-7.68	22570.58	21000.00	7.48
S	-	-	-	286710.20	276000.00	3.88	-	-	-	3114.18	-	-
Ca	49459.46	53586.21	-7.70	<DL	-	-	57380.74	53586.21	7.08	56936.14	53586.21	6.25
Sc	491.26	530.00	-7.31	<DL	-	-	503.43	530.00	-5.01	550.12	530.00	3.80
V	430.34	440.00	-2.20	63.55	63.00	0.87	424.29	440.00	-3.57	470.81	440.00	7.00
Cr	371.24	400.00	-7.19	65.09	65.00	0.14	387.08	400.00	-3.23	424.06	400.00	6.02
Mn	571.57	590.00	-3.12	266.51	280.00	-4.82	577.23	590.00	-2.17	624.67	590.00	5.88
Fe	101017.62	98700.00	2.35	164257.00	156000.00	5.29	99527.60	98700.00	0.84	103930.56	98700.00	5.30
Co	407.47	380.00	7.23	64.99	60.00	8.32	398.04	380.00	4.75	397.37	380.00	4.57
Ni	485.07	440.00	10.24	102.89	97.00	6.07	458.99	440.00	4.32	472.40	440.00	7.36
Cu	352.13	380.00	-7.33	137841.10	134000.00	2.87	390.93	380.00	2.88	388.10	380.00	2.13
Zn	496.00	460.00	7.83	204622.10	210000.00	-2.56	422.00	460.00	-8.26	479.00	460.00	4.13
Ga	534.44	490.00	9.07	57.81	64.00	-9.67	470.99	490.00	-3.88	437.73	490.00	-10.67
Ge	335.50	320.00	4.84	51.37	-	-	298.33	320.00	-6.77	327.14	320.00	2.23
As	247.43	260.00	-4.83	67.07	65.00	3.18	237.82	260.00	-8.53	260.07	260.00	0.03
Se	23.51	20.00	17.54	58.09	51.00	13.90	18.82	20.00	-5.90	-	20.00	-
Zr	383.42	410.00	-6.48	0.18	-	-	418.66	410.00	2.11	402.82	410.00	-1.75
Ag	219.71	200.00	9.85	54.49	50.00	8.99	184.46	200.00	-7.77	202.77	200.00	1.39
Cd	174.31	160.00	8.94	60.83	60.00	1.38	145.33	160.00	-9.17	172.83	160.00	8.02
In	390.48	370.00	5.53	53.77	50.00	7.53	365.70	370.00	-1.16	400.85	370.00	8.34
Te	230.73	-	-	16.94	15.00	12.96	249.56	-	-	-	-	-
Ba	391.43	427.00	-8.33	11.88	14.00	-15.13	395.11	427.00	-7.47	451.04	427.00	5.63
Pb	396.87	378.00	4.99	71.63	68.00	5.33	409.26	378.00	8.27	387.82	378.00	2.60
Bi	343.22	320.00	7.26	58.82	60.00	-1.97	324.75	320.00	1.48	320.02	320.00	0.01

Supplementary Table 5. Instrument parameters and data calibration for measurements of S isotopes and trace elements by LA-(MC)-ICP-MS.

LA-ICP-MS	SKLODG	USTC	SKLCD	
ICP-MS	Agilent 7700x	Agilent 7700e	Agilent 7700x	
Forward power	1400 W	1350 W	1400 W	
Carrier gas (Ar)	0.9 L min ⁻¹	0.7 L min ⁻¹	1.0 L min ⁻¹	
Oxide rate (Tho/Th)	<0.3%	<0.5%	<0.3%	
Doubly charged formation rate	<0.3%	<0.3%	<0.3%	
Plasma condition (U/Th)	0.95-1.05	0.95-1.05	0.95-1.05	
Laser ablation	Resolution-LR-S155	GeoLas pro, Coherent	GeoLas 2005, Lambda Physik	
Wavelength	193nm	193 nm	193 nm	
Energy density on sample	2 J cm ⁻²	3.0 J cm ⁻²	2.5 J cm ⁻²	
Pulse frequency	5 Hz	6 Hz	5 Hz	
Spot size	26 μm, 40μm	40 μm	37 μm	
Carrier gas (He)	350 ml min ⁻¹	900 ml min ⁻¹	370 ml min ⁻¹	
Standard	STDGL3, GSD-1G	STDGL3, GSD-1G	MASS-1, GSD-1G, BCR-2G	
Software	LADR	Iolite 4.0	ICPMSDataCal 10.0	
Calibration	Normalization	Normalization	Normalization	
LA-MC-ICP-MS	SKLODG	Nanjing FoucuMS	SKLCD	CAGS
MC-ICP-MS	Nu plasma III	Nu plasma II	Nu 1700	Finnigan Neptune
Forward power	1400 W	1300 W	1300 W	1300 W
Carrier gas (Ar)	0.85L min ⁻¹	0.9 L min ⁻¹	0.8 L min ⁻¹	0.9 L min ⁻¹
Integration time	0.4 s	0.3 s	0.4 s	0.3 s
Mass resolution	Medium resolution	Medium resolution	Medium resolution	Medium resolution
Laser ablation	Resolution-LR-S155	Teledyne Cetac Analyte Excite	CompexPro 102	Resolution-LR-S155
Wavelength	193 nm	193 nm	193 nm	193 nm
Energy density on sample	2 J cm ⁻²	2.5 J cm ⁻²	4 J cm ⁻²	5 J cm ⁻²
Pulse frequency	5 Hz	5 Hz	3 Hz	4 Hz
Spot size	60 μm	35 μm	37 μm	32 μm
Carrier gas (He)	200 ml min ⁻¹	800 ml min ⁻¹	300 ml min ⁻¹	200ml min ⁻¹
Standard	NBS123, PAS-GBW07270	NBS123, NWU-Zn	NBS123, PAS-SPH	NBS123
Mass bias	SSB	SSB	SSB	SSB