Supporting Information for

Bulk analysis of columbite ores by LA-ICP-MS: development of reference materials and investigation into matrix effects

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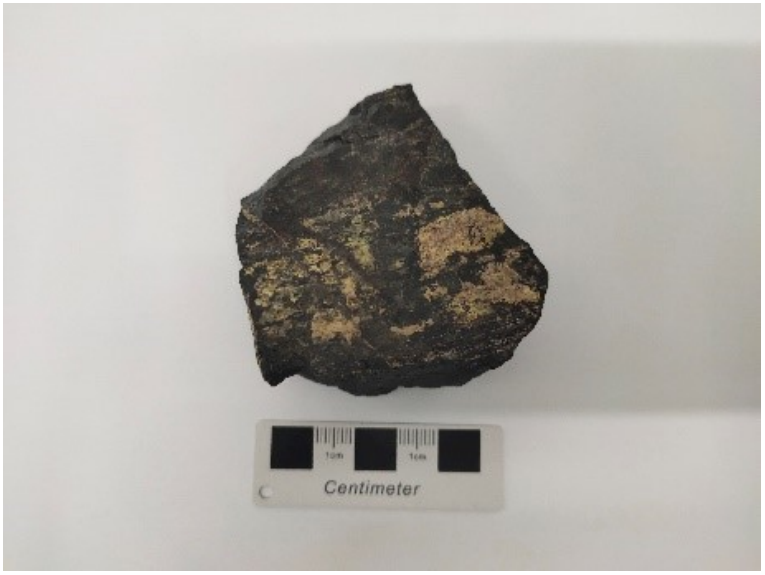
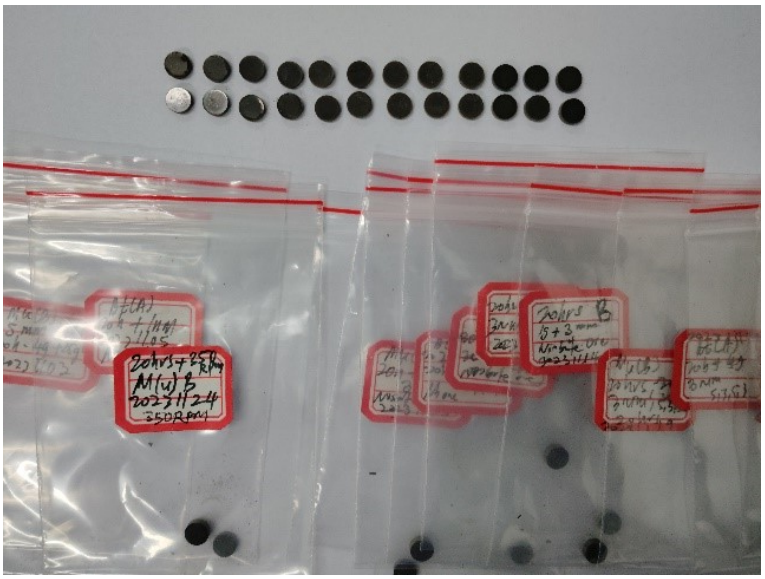
S1. Fig. S1: The photograph of the natural columbite ore



S2. Fig. S2: The photographs of HSC and LSC pellets



S3. Determination of HSC and LSC using "Standard Addition" method and ICP-MS

The sample of HSC and LSC was digested and analyzed using the solution ICP-MS method, which was used as a reference method to ascertain the accuracy of the developed LA-ICP-MS methodology. The sample decomposition used an in-house cleaned stainless-steel bomb consisting of a 10 mL PTFE inner vessel with a lid, which fitted tightly into an outer stainless steel pressure jacket. Approximately 25 mg of each sample in triplicates was weighed and placed into a pre-cleaned 10 ml PTFE vessel. 1.5 ml HF and 0.5 ml HNO_3 were added slowly to the digestion vessel and sealed. Then, the stainless-steel bomb was tightly screwed and heated to 190 ºC in an electric oven (Shanghai Jing Hong Laboratory Instrument Co., Ltd., Shanghai, China) for 48 hours. After cooling down, the clear solution obtained was transferred to a polyethylene bottle, and final volumes were made up to 100 g with ultrapure water. A procedural blank solution was prepared in the same way without the addition of any sample into PTFE vessel.

The prepared series solutions were analyzed using a high-resolution sector field ICP-MS instrument (Element XR, Thermo Fisher Scientific, Bremen, Germany) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences in Wuhan. Details of the operating condition and measurement parameters are summarized in Table S1.

Table S1. Instrumental operating conditions for ICP-MS

ICP-MS: Element XR	
Torch Position X	3.7 mm
Torch Position Y	1.0 mm
Torch Position Z	-3.0 mm
Cooling Gas Flow Rate	16.00 L min^{-1}
Auxiliary Gas Flow Rate	1.00 L min^{-1}
Sample Gas Flow Rate	1.16 L min^{-1}
RF Power	1200 W
Peristaltic Pump Sped	8.00 rpm
Sample Cone	Standard sampler cone, Nickel
Skimmer Cone	H skimmer
Spray Chamber	Quartz double pass spray chamber
Resolution	Low (R = 300)
Mass Window	100%
Sample Time	50 ms
Sample Per Peak	25
Integration Window	60%
Integration Type	Average
Scan Type	Escan
Detection System	Triple

To accurately quantify trace elements in the high and low standard concentration (HSC and LSC) samples, the standard addition method was employed, addressing the inherent matrix effect challenges. This technique is paramount when internal standards (In, Rh, Ge, Sc, Y, Bi) are

rendered ineffective due to pre-spiked elements within the sample.

The gravimetric standard addition method, substantiated by the work of Kelly et al. (2008), is encapsulated by the formula:

$$\left(\frac{m_x + m_s + m_d}{m_x}\right) I = k\left(\frac{m_s}{m_x} C_s\right) + kC_x$$

which has been foundational in determining the concentrations of trace elements in our study. Here, m_x is the mass of the sample, m_s the mass of the standard, m_d the mass of the diluent (I) the instrumental response, C_s the mass fraction of the analyte in the standard, C_x the mass fraction of the analyte in the sample, and (k) the instrument sensitivity. Usually, the masses of the sample and standard are determined during the sample preparation and can be plotted as $y = ax + b$ with $a = k$ and $b = kC_x$. C_x can then be determined by dividing the y-intercept by the slope of the linear regression $(C_x = b/a)$.This robust equation allowed for precise calculations of the elemental concentrations and facilitated the direct comparison between LA-ICP-MS and solution ICP-MS findings.

The ICP-MS signal of three replicates of the spiked and unspiked samples was average. The linear regression showed exemplary quantifications, exceeding 0.999, indicating the strong linear relationship between the added standard concentration and the observed intensities. The analytical results of trace elements in HSC and LSC are listed in Table S2. The concentrations of the elements spiked into samples, which were subsequently used for quantitative calibrations in LA-ICP-MS, were established utilizing the values obtained through the method of standard addition in ICP-MS. This approach ensures the accuracy of the calibration process by directly accounting for matrix effects and enhancing the reliability of the quantitative analysis performed with LA-ICP-MS.

References

Kelly, W.R., Toth, R.A., Wiese, K. (2008). Gravimetric Standard Addition for the Determination of Trace Elements in Geological Samples. Analytical Chemistry, 80(13), 5157-5163.

S4. Table S2. Results for trace elements in HSC, LSC, HMIE-NP and MAKR-NP using solution method and LA-ICP-MS. The reference values of HMIE-NP and MAKR-NP are from certificates approved by the "myStandards GmbH".

	Solution analysis				Certified values			
	HSC		LSC		HMIE-NP		MAKR-NP	
	Mean	SD (n=6)	Mean	SD (n=6)	Mean	*U**	Mean	*U*
Li	80.0	3.2	38.9	2.1	29.2	3.6	-	-
Be	80.2	1.9	39.1	2.0	13.5	2.0	-	-
Sc	80.6	1.4	41.6	1.9	3.70	0.5	-	-
V	73.7	1.1	38.5	0.9	25.0	3.0	541	13
Cr	79.8	6.3	36.0	4.5	107	22	106	9
Co	87.6	2.6	44.9	0.8	5.35	0.47	99	7
Ni	79.5	2.1	37.7	2.1	41.8	4.0	109	9
Cu	102	3	58.1	0.9	201.0	14.0	211	19
Zn	474	19	508	10	74.5	13.3	920	111
As	95.5	7.1	54.8	2.3	12.4	1.2	29.3	4.4
Rb	97.1	2.2	35.8	1.1	24.0	1.3	6.63	0.75
Sr	94.6	2.6	53.1	2.2	43.6	2.1	61.1	2.4
Y	57.0	3.9	32.9	2.3	7.97	1.08	30.0	2.8
Zr	963	35	944	68	14.1	2.4	18.1	4.8
Nb	-	-	-	-	1.7	0.5	2.06	0.29
Mo	95.2	2.1	57.3	1.1	9.2	2.2	-	-
Sn	212	6	104	7	5.0	1	16.5	2.0
Sb	251	11	126	7	5.4	0.7	-	-
Cs	75.7	3.8	35.1	2.8	5.4	0.5	1.81	0.23
Ba	147	5	112	3	62.0	5.2	31.8	1.9
La	54.9	1.5	34.5	1.2	3.1	0.5	17.7	1.6
Ce	64.4	2.0	36.1	1.1	6.2	1.1	36.1	3.2
Pr	51.7	1.5	24.1	1.0	0.80	0.16	4.38	0.4
Nd	56.2	0.7	28.0	1.3	3.30	0.7	17.1	1.5
Sm	54.7	1.9	29.2	1.8	0.81	0.15	3.53	0.30
Eu	52.5	1.1	26.1	1.3	0.19	0.05	0.65	0.06
Gd	55.3	1.3	30.0	2.2	1.03	0.24	4.4	0.4
Tb	52.6	0.8	24.1	1.8	0.19	0.05	0.71	0.07
Dy	58.5	2.0	31.3	1.6	1.2	0.3	4.60	0.50
Ho	73.7	1.7	39.3	2.1	0.26	0.07	0.92	0.09
Er	54.1	2.2	25.6	1.1	0.76	0.18	2.60	0.30
Tm	52.9	1.5	22.6	1.5	0.11	0.03	0.33	0.03
Yb	55.4	1.1	23.6	1.8	0.73	0.15	1.90	0.21
Lu	51.2	1.1	22.9	2.0	0.11	0.03	0.28	0.03
Hf	281	7	226	2	0.3	0.1	0.50	0.10
Ta	-	-	-	-	1.2	0.3	0.20	-
Tl	158	2	77.8	1.5	0.11	-	-	-
Pb	972	10	993	5	203	18	78	14
Bi	174	4	153	4	0.62	-	-	-

Th	-	-	-	-	1.07	0.18	2.10	0.45
U	-	-	-	-	2.97	0.21	0.49	0.09

*: U means "Uncertainty (95% CL) "

（Continued）

□	Ns-LA analysis											
	LSC* (Si as ID**)			LSC (Fe as ID)			MAKR-NP*** (Si as ID)			MAKR-NP (Fe as ID)		
	Mean	SD (n=15)	***RD (%)***	Mean	SD (n=15)	***RD (%)***	Mean	SD (n=15)	***RD (%)***	Mean	SD (n=15)	***RD (%)***
Li	36.6	1.0	***-6.0***	35.3	1.1	***-9.3***	10.8	1.4	-	11.3	1.2	-
Be	39.4	0.8	***0.8***	38.0	1.0	***-2.7***	33.9	4.4	-	35.7	5.3	-
Sc	39.0	0.9	***-6.3***	37.7	0.8	***-9.5***	3.67	0.20	-	3.84	0.23	-
V	36.4	0.7	***-5.3***	35.2	0.6	***-8.6***	540	14	***-0.1***	541	11	***-0.1***
Cr	36.5	1.6	***1.4***	35.2	1.5	***-2.1***	116	7	***9.5***	123	9	***15.6***
Co	38.0	0.1	***-15.5***	36.6	0.3	***-18.4***	98.6	2.2	***-0.4***	98.6	2.5	***-0.4***
Ni	32.4	0.6	***-14.1***	31.2	0.3	***-17.1***	107	6	***-1.4***	108	6	***-1.2***
Cu	68.3	5.8	***17.5***	65.9	5.4	***13.4***	221	33	***4.9***	229	37	***8.6***
Zn	527	28	***3.7***	508	28	***0.0***	924	34	***0.5***	929	24	***0.9***
As	52.5	0.8	***-4.2***	50.7	0.9	***-7.6***	32.0	11.2	***9.1***	32.0	11.7	***9.3***
Rb	37.0	0.4	***3.3***	35.7	0.5	***-0.3***	7.15	0.36	***7.9***	7.50	0.27	***13.1***
Sr	50.2	1.5	***-5.5***	48.4	1.4	***-8.8***	60.7	2.4	***-0.7***	61.5	1.7	***0.6***
Y	34.7	0.6	***5.7***	33.5	0.7	***2.1***	29.8	3.0	***-0.5***	29.8	2.8	***-0.7***
Zr	971	7	***2.8***	937	9	***-0.8***	19.2	3.2	***6.1***	19.8	3.1	***9.4***
Nb	-	-	-	-	-	-	1.90	0.09	***-8.0***	1.86	0.12	***-9.7***
Mo	52.6	0.7	***-8.2***	50.8	0.4	***-11.4***	55.0	13.9	-	57.6	16.3	-
Sn	101	1	***-2.3***	97.9	0.8	***-5.7***	17.3	3.3	***4.6***	17.2	3.0	***4.5***
Sb	129	1	***3.0***	125	2	***-0.6***	12.0	0.7	-	12.6	1.1	-
Cs	33.0	1.6	***-5.9***	31.8	1.4	***-9.2***	1.92	0.15	***6.1***	2.01	0.14	***10.9***
Ba	109	5	***-2.7***	105	5	***-6.1***	33.2	1.8	***4.5***	34.6	1.5	***8.8***
La	31.9	1.5	***-7.7***	30.8	1.4	***-10.9***	17.7	2.3	***0.1***	17.6	2.4	***-0.4***
Ce	31.5	0.3	***-12.6***	30.5	0.3	***-15.6***	36.3	4.4	***0.4***	36.3	4.9	***0.6***
Pr	23.9	0.4	***-0.8***	23.1	0.4	***-4.3***	4.38	0.39	***0.0***	4.38	0.39	***0.1***
Nd	27.3	0.4	***-2.4***	26.4	0.5	***-5.8***	17.1	1.3	***0.0***	17.1	1.3	***0.1***
Sm	27.0	0.4	***-7.7***	26.0	0.5	***-10.9***	3.57	0.35	***1.0***	3.59	0.30	***1.6***
Eu	24.4	0.4	***-6.7***	23.5	0.3	***-9.9***	0.64	0.04	***-1.4***	0.64	0.05	***-1.4***
Gd	28.3	0.7	***-5.8***	27.3	0.7	***-9.1***	4.35	0.32	***-1.0***	4.34	0.28	***-1.3***
Tb	24.6	0.3	***2.2***	23.8	0.3	***-1.3***	0.70	0.06	***-0.8***	0.70	0.06	***-0.9***
Dy	30.4	0.5	***-2.7***	29.4	0.4	***-6.1***	4.73	1.05	***2.7***	4.72	1.03	***2.5***
Ho	34.0	0.6	***-13.5***	32.8	0.6	***-16.5***	0.92	0.11	***-0.3***	0.92	0.10	***-0.5***
Er	26.1	0.4	***2.1***	25.2	0.5	***-1.4***	2.57	0.26	***-1.0***	2.57	0.24	***-1.3***
Tm	23.4	0.4	***3.7***	22.6	0.3	***0.1***	0.32	0.03	***-1.6***	0.32	0.03	***-2.1***
Yb	26.5	0.4	***12.1***	25.6	0.4	***8.2***	1.89	0.18	***-0.6***	1.89	0.16	***-0.4***
Lu	23.4	0.3	***2.1***	22.6	0.3	***-1.5***	0.27	0.02	***-2.3***	0.27	0.02	***-2.6***
Hf	207	2	***-8.8***	199	2	***-11.9***	0.52	0.10	***3.6***	0.52	0.10	***4.5***
Ta	-	-	-	-	-	-	0.23	0.02	***17.0***	0.25	0.02	***23.8***

Tl	76.4	0.6	***-1.8***	73.7	0.5	***-5.3***	0.07	0.01	**-**	0.08	0.01	**-**
Pb	970	7	***-2.3***	936	12	***-5.7***	97.8	18.6	***25.4***	105.8	22.6	***35.6***
Bi	149	1	***-2.2***	144	2	***-5.6***	1.46	0.17	**-**	1.53	0.17	**-**
Th	-	-	**-**	-	-	**-**	1.98	0.14	***-5.5***	1.95	0.18	***-7.1***
U	-	-	**-**	-	-	**-**	0.42	0.02	***-15.0***	0.42	0.02	***-13.6***

*: HSC and HMIE-NP were used as external standard for LA analysis
**: ID means "internal standard"