

Supporting Information

A Natural Reference Material OOID for Calibrating *In Situ* Trace Element Measurements in the Carbonate Matrix

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SUPPORTING TABLES

Table S1. Operating parameters for the LA-ICP-MS measurements

Facility 1 - SWPU				Facility 2 - Chuangyuan Microspectrum			
ICP-MS system	Agilent 7800	LA system	ESI NWR 193UC	ICP-MS system	Thermo iCAP TQ	LA system	RESolution LR S155
RF power (W)	1400	Wavelength (nm)	193	RF power (W)	1550	Wavelength (nm)	193
Nebulizer gas (L/min)	0.56	Spot size (μm)	60 or 70	Nebulizer gas (L/min)	0.90 to 1.01	Spot size (μm)	67
		Fluence (J/cm ²)	2.5 to 3			Fluence (J/cm ²)	2.5 to 3
		Warm up time (s)	10			Warm up time (s)	15
		Rep. Rate (Hz)	7 or 9			Rep. Rate (Hz)	8 or 10
		Pre-ablation time	No			Pre-ablation	3 pulses
		Duration (s)	69.6			Duration (s)	51
		Wash-out time (s)	50			Wash-out time (s)	5
		Carrier gas	He+N ₂ mixture			Carrier gas	He or He+N ₂ mixture
		Current flow (mL/min)	650±2			Current flow (mL/min)	300 or 350±5

Table S2. Contents of Ca, Si, and Al oxides in the reference material OOID (wt %; EPMA)

No.	CaO %	SiO ₂ %	Al ₂ O ₃ %
1	52.618	0	0
2	53.282	0	0
3	52.383	0	0
4	52.490	0	0.017
5	52.749	0	0
6	51.217	0	0.021
7	52.724	0	0.006
8	53.026	0	0.01
9	52.941	0	0.025
10	51.912	0	0

Gd	155																	0.347	4.6	0.349	6.8
Gd	157	0.099	5.5	0.105	9.1	0.101	9	0.111	7.8									2.36	8.6	2.33	6.9
Gd	158									0.086	7	0.081	7.6	0.084	10	0.086	5.7	0.084	6.4	0.087	11
Tb	159	0.017	7.5	0.017	6.7	0.016	7.4	0.017	6.6	0.014	9.9	0.014	7.3	0.013	9.6	0.013	7.3	0.013	7.6	0.014	7.9
Dy	163	0.118	5.2	0.124	5.1	0.116	5.4	0.126	5.8	0.1	5.5	0.096	4.9	0.097	5.7	0.098	5.6	0.095	5.5	0.103	7.5
Ho	165	0.029	5.1	0.031	5.7	0.029	3.8	0.031	2.8	0.025	6.9	0.024	5.4	0.024	5.8	0.025	7.5	0.024	3.9	0.025	6.2
Er	166	0.09	4.9	0.096	7.3	0.09	5.8	0.095	4	0.075	4	0.074	4.8	0.074	6.8	0.075	6.6	0.073	5.1	0.077	6.3
Tm	169	0.012	6.3	0.013	7.8	0.012	6	0.013	7.3	0.0098	10	0.0097	5.8	0.0097	5.8	0.0097	7.4	0.0096	5.5	0.01	5.1
Yb	171	0.075	6.9	0.079	7.8	0.074	7.5	0.078	6.6			0.061	6.9	0.062	8.9	0.063	8	0.062	4.2	0.066	7.5
Yb	172									0.062	7.9										
Lu	175	0.012	6.3	0.012	7.5	0.011	7.2	0.012	6.6	0.0094	6.1	0.0092	6.6	0.0091	7	0.0091	5.7	0.0091	5.7	0.0097	6.4
Pb	208									0.632	5.5	0.546	5.6	0.532	7.6	0.524	7.1	0.559	5.4	0.562	2.5
Th	232	0.027	19	0.027	24	0.028	29	0.027	36	0.023	10.2	0.023	14	0.022	20	0.023	12	0.023	12	0.024	22
U	238	2.59	3.9	2.26	5.5	2.23	5.7	2.37	5.6	2.53	3.2	2.13	2.1	2.03	2	2.03	2.6	2.21	2.6	2.22	3.2

Gd	155																	0.344	4.1	0.34	6.2
Gd	157	0.102	6.1	0.1	10	0.1	11	0.105	9.4									1.35	5.8	1.31	5.7
Gd	158									0.09	7.4	0.093	7.1	0.093	11	0.098	6.5	0.093	6.7	0.095	10
Tb	159	0.016	7.4	0.016	7.5	0.015	8.1	0.015	10	0.014	10	0.015	8	0.014	10	0.015	7.6	0.014	7.8	0.015	8
Dy	163	0.12	5.6	0.116	6.4	0.113	7.2	0.116	8.5	0.103	6.3	0.107	4.9	0.105	6.8	0.11	5.5	0.103	6.2	0.11	7
Ho	165	0.03	5.5	0.029	6.9	0.028	4.9	0.028	6.2	0.025	7.3	0.027	5.6	0.026	6.3	0.028	8.1	0.026	5.1	0.027	6.2
Er	166	0.092	5.2	0.089	8	0.086	6.4	0.087	8.4	0.077	3.2	0.083	4.8	0.081	7.5	0.084	6.9	0.08	5.8	0.082	5.9
Tm	169	0.012	6.8	0.012	9.1	0.011	6.6	0.012	11	0.0099	10	0.011	6.6	0.01	6.6	0.011	7.6	0.01	6.2	0.011	5.5
Yb	171	0.074	7.5	0.071	7.4	0.068	8.4	0.069	9.1			0.066	7.3	0.065	9.5	0.067	8.8	0.065	5	0.067	6.9
Yb	172									0.061	6.7										
Lu	175	0.012	6.6	0.011	8.1	0.011	8.3	0.011	10	0.0096	5.5	0.01	7.2	0.01	7.7	0.01	6	0.01	6.2	0.01	5.7
Pb	208									0.588	5.5	0.606	5.6	0.577	7.9	0.591	6.9	0.602	5.6	0.593	2.9
Th	232	0.028	19	0.026	22	0.027	28	0.024	33	0.024	10	0.026	14	0.025	20	0.026	11	0.025	14	0.026	21
U	238	2.81	14	2.76	5.8	2.64	32	2.73	17	2.66	15	2.68	7.8	2.69	7.1	2.33	26	2.53	20	2.58	7.5

Table S5. Results of means and relative standard deviations (RSDs) of measured elements in MACS-3 calibrated against NIST 612. Laser ablation-based element reference values (RV-LA) of MACS-3 from reference¹⁹; solution-based element reference values (RV-solution) of MACS-3 from reference⁹. Note that the isotopes used for measurements are not provided along with the laser ablation-based element reference values. The isotopes used for measurements are provided along with the solution-based element reference values and a few adopted isotopes not listed are enclosed in brackets

Element	Isotope	MACS-3		Session 1 (n = 32)		Session 2 (n = 16)		Session 3 (n = 15)		Session 4 (n = 9)		Session 5 (n = 12)		Session 6 (n = 22)		Session 7 (n = 16)		Session 8 (n = 16)		Session 9 (n = 18)		Session 10 (n = 12)		
		RV-LA ¹⁹	RV-solution ⁹	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	
		(µg/g)	(µg/g)	(µg/g)	(%)	(µg/g)	(%)	(µg/g)	(%)	(µg/g)	(%)	(µg/g)	(%)	(µg/g)	(%)	(µg/g)	(%)	(µg/g)	(%)	(µg/g)	(%)	(µg/g)	(%)	(µg/g)
Na	23	5850	6069	6099	2.7	5385	5.5	5443	2.8	5820	6.8	6972	3.9											
Mg	25	1720	1886	2002	2.8	1843	12.2	1858	7.1	1901	5.7	2137	3.5	2017	4	2058	4.5	2105	4.1	2055	2.4	2082	2.7	
Al	27	396	427	424	19	439	6.4	417	7.3	410	7.9	435	2.8	402	4.4	424	14	384	4.5	414	3.7	411	3.8	
Sc	45	20.3	21.6	18.9	4.1	19.2	9.4	19.2	7	20.1	5.6			16.9	2.7	17.1	2.7	16.6	3	17.7	2.8	18.3	2.3	
Ti	47	53.1	60.2 (49)	54.6	5	52.9	8.4					52.6	5.3	47	5.2	49	7.4	46.1	4.5	51.9	4.5	51.4	5.6	
V	51	44.8	46.4	46.4	4.1	41.8	6.2	44	11	42.3	4.1	46.4	3.9	40.1	4.4	42.1	6.6	39.3	4.3	44.7	4.7	44.2	4.9	
Cr	52	114		118	4.6	109	8.7	109	5.8	103	4.6													
Cr	53		111											107	4.3	116	7.5	107	5.1	116	4.9	116	4.4	
Mn	55	512	526	540	2.4	493	6.2	511	2.1	509	4	581	3.3	527	4.1	544	3.7	536	5.2	536	3	555	3.6	
Fe	57	10500	10981	4707	19	3081	33.1	3750	26	5273	4.9			9351	3.7	8144	5.8	7806	3.5	6934	5.9	7772	2.9	
Co	59	55.3	58.9	54.5	3.3	48.8	3.1	51.6	5.7	52.1	6.1			55.2	3.7	80.4	5.3	80.9	4.4	55.2	3.6	56.7	3.7	
Ni	60	56.2	59.3	55.8	2.8	50.4	3.9	50.5	5.9	52.2	5.2	60.1	1.8	52.4	2.7	54	4.2	52.4	1.8	55.2	3	56.2	3.3	
Ni	62													53.8	4.2	55.9	4	56.3	2.4					
Cu	65	116	117 (63)									128	3.1	110	3.5	111	3.4	111	3.9	113	2.8	116	3.5	
Zn	66	124	106	85.3	5.8	68.7	5	71.9	3.3	65.5	7.6	75.5	5.8	73.4	6.9	78.4	5.2	74.9	6.1	75.3	5.1	73.6	3.5	
Ga	71	15.6	15.1											16	3.2	16.7	5.8	16.3	4	17	4	17	3.5	
Sr	86	6640										7315	3.4	7169	3.1	7260	2	7540	2.8	7073	2.7	7172	2	
Sr	88		6640	6684	2.4	6283	2.3	6468	3.9	6676	3.6													
Y	89	20.7	23	20.7	2.5	23	3.7	22.3	3.7	22.5	3.4	20.9	3	18.8	3.1	19.1	3	18.5	2.7	19.5	2.9	19.7	2.5	
Zr	90	8.5	8.36 (91)	8.45	4.5	9.38	4.9	8.85	6.9	8.87	4.7	8.39	4	8.03	4.1	8.47	6.7	7.85	4.3	8.54	3.8	8.55	4.2	
Mo	95		1.19			1.16	14	1.13	6.2	1.13	15	1.28	17	1.16	9.6	1.19	12	1.15	6.4	1.25	11	1.27	9.1	
Ba	137	59.6	56.9	57.5	3	50.4	3.3	54.1	4.7	54	2.7	63.5	3.3	59.2	3.1	59.9	3.9	59.8	2.2	58.2	2.7	58.6	3.4	
La	139	10.6	10.6	10.1	3.6	10.2	4.7	10.1	4.9	10.5	6.2	10.6	4.4	10.4	3.9	10.6	3.7	10.4	5.5	10.4	3.7	10.6	3.2	
Ce	140	10.9	11	10.5	3.6	9.5	4.7	9.52	4.6	9.92	5.4	10.9	2.9	10.4	3.9	10.8	2.9	10.5	3.6	10.3	3.8	10.5	2.6	
Pr	141	11.5	11.7	10.9	3.5	10.4	4.7	10.3	5	10.7	5.3	11.1	3.9	10.9	3.6	11.3	4	11	4.9	10.9	3.5	11.1	2.9	
Nd	146	10.6	11.1 (143)	10.3	3.3	10.4	4.5	10.2	3.6	10.8	5.1	10.4	4.2	9.91	3.7	10.1	3.2	9.98	4.9	10	3.8	10.2	2	
Sm	147	10.3	10.8	10.1	3.3	10.4	4.3	10.1	4.3	10.6	4.7	10.1	4.3	9.41	3.7	9.61	3.1	9.33	4.4	9.52	4.1	9.71	2.2	

Eu	151	11.1	11.2									10.8	3.2	10.4	3.2	10.7	2.7	10.5	4.9	10.5	4.1	10.6	2.9
Eu	153			10.7	3.4	10.5	4.4	10.4	4.3	10.9	5.2												
Gd	155	9.72	10.3																	9.81	3.8	10	2.4
Gd	157			9.39	3	10.2	4	9.76	3.7	10.2	4									17	7.1	17.3	8.9
Gd	158											9.33	4	8.52	3	8.79	3.2	8.54	4.3	8.75	3.6	8.95	2.7
Tb	159	9.49	10.6	9.6	3.1	10.4	4.4	10	3.9	10.4	4.3	9.59	3	8.71	3	8.93	2.9	8.65	3.6	8.9	3.8	9.07	2.2
Dy	163	9.9	10.9	9.72	3	10.6	4.1	10.2	3.4	10.7	4.5	9.68	3.1	8.88	3.1	9.12	3	8.85	3.2	9.16	3.6	9.32	2.5
Ho	165	10.3	10.9	10	2.8	11.1	4.1	10.6	3.8	11.1	4.2	10	2.9	9.17	3.1	9.39	3.1	9.1	2.7	9.41	3.3	9.64	2.6
Er	166	10.3	10.7	10.1	2.9	11.1	4.2	10.6	3.1	11.1	4.2	10	3	9.19	3.2	9.42	2.8	9.14	2.4	9.45	3.1	9.66	2.5
Tm	169	10.4	11.4	10.3	2.9	11.4	4.1	10.9	3.5	11.4	4.2	10.3	2.4	9.44	3.1	9.7	2.9	9.39	2.2	9.68	3.2	9.92	2.4
Yb	171	10.2	10.8 (173)	10.4	2.9	11.4	4.2	10.9	3.5	11.5	4.3			9.53	3.3	9.82	3.2	9.56	2.4	9.81	3	10	2.8
Yb	172											10.3	2.8										
Lu	175	10	10.7	9.77	2.8	10.8	3.9	10.4	3.3	10.8	4.1	9.75	2.6	8.86	3.3	9.1	3.1	8.8	2.3	9.11	3	9.35	2.6
Pb	208	59.7	52.6									63.9	3.3	53.8	2.6	55	4.1	52.9	2.3	55.5	2.5	56.6	2.4
Th	232	51.9	53.9	51.1	2.8	54.3	4.4	53.7	3.8	55.9	5.1	50.5	3.1	46.3	3.4	46.8	3.4	45.4	2.2	47.4	3.6	48.9	3.4
U	238	1.41	1.45	1.33	13.4	1.16	10	1.28	22	1.28	15	1.38	16	1.13	8.5	1.07	6.6	1.34	32	1.29	23	1.22	7.6
