Supplementary Information (SI) for Analyst.

The necessity of matrix-matched standards usage in quantitative imaging of specimens with calcareous skeleton by LA-ICP-MS

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Table S1 *Operating conditions*

ICP-MS spectrometer				**Laser system**		
parameter	**wet analysis**	**LA analysis**		**parameter**	**UP-266**	**ESL 213**
	ELAN DRC-e	**ELAN DRC-e**	**NexION 5000**			
RF power [W]	1300	1300	1600	Wavelength [nm]	266	213
Nebuliser gas [L min^{-1}]	1.08	1.08	0.65	Ablation mode	line	line (imaging)
Auxiliary gas [L min^{-1}]	1.02	1.02	1.20	Spot size [μm]	20	20 x 20 (XYR Shutter)
Plasma gas [L min^{-1}]	17.00	17.00	16.00	Scan speed [μm s^{-1}]	80	
Sweeps	30	1	1	Offset between lines [μm]	20 (no gap)	
Reading	2	adjusted to the size of the analysed sample		Repetition rate [Hz]	10	
Replicate	3	1	1	Power [%]	100	25
Dwell time [ms]	50	40		Energy density [J cm^{-2}]	7.22	8.86
Measured masses	^{24}Mg, ^{88}Sr, ^{138}Ba, ^{43}Ca			He carrier gas flow rate [L min^{-1}]	0.8	

Table S2 *Digestion programme*

Stage	Time [min]	Max. pressure [bar]	Min. pressure [bar]	Max. temperature [°C]	Min. temperature [°C]	Power [%]
I	5:00	20	18	260	250	60
II	5:00	28	26	280	270	85
III	10:00	40	38	290	285	100

Fig. S1 *The comparison of elements distribution without and with internal standardisation*

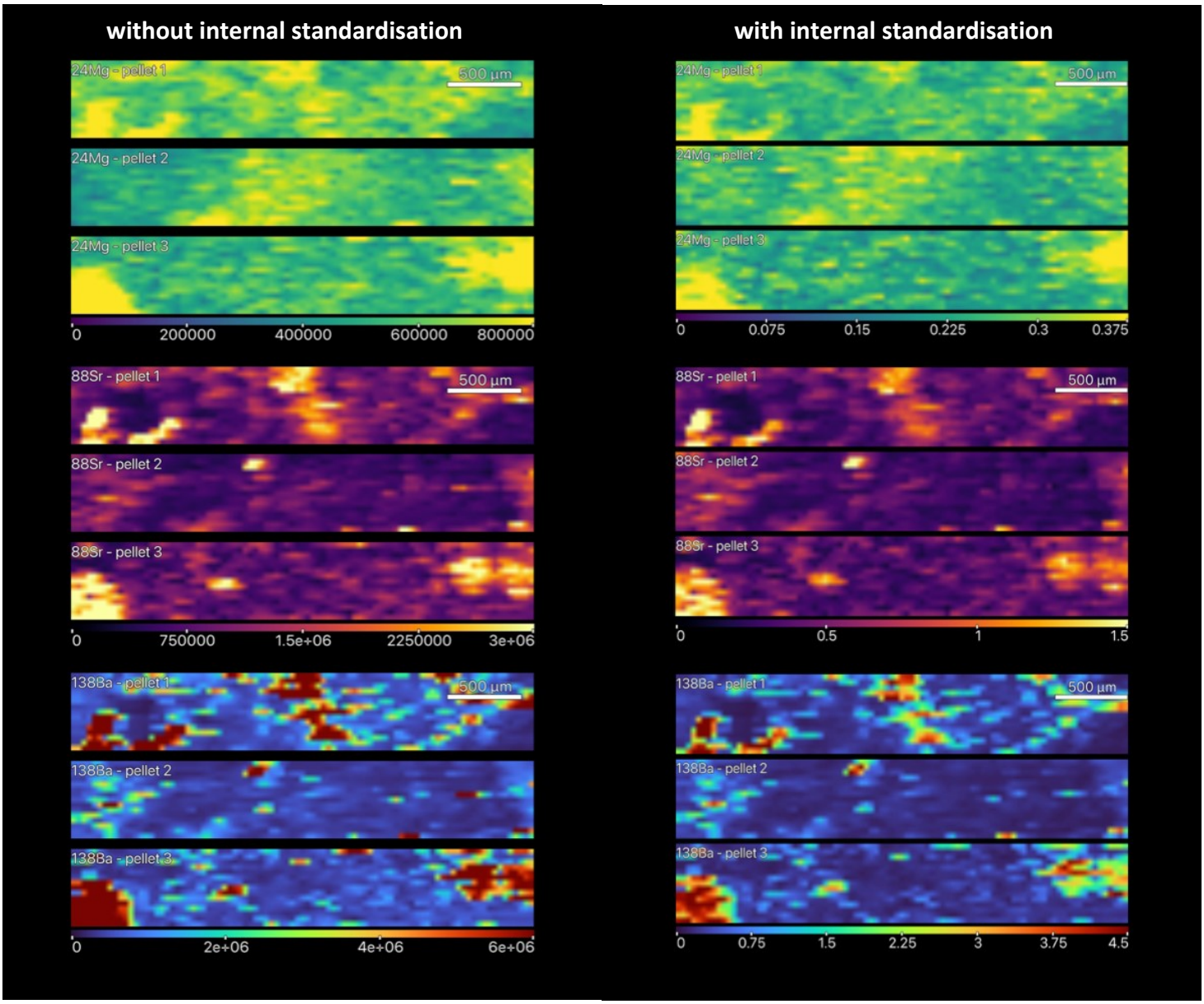

Fig. S2 *Examples of 3D distribution maps: Ca, Mg, and Mg standardised against Ca*

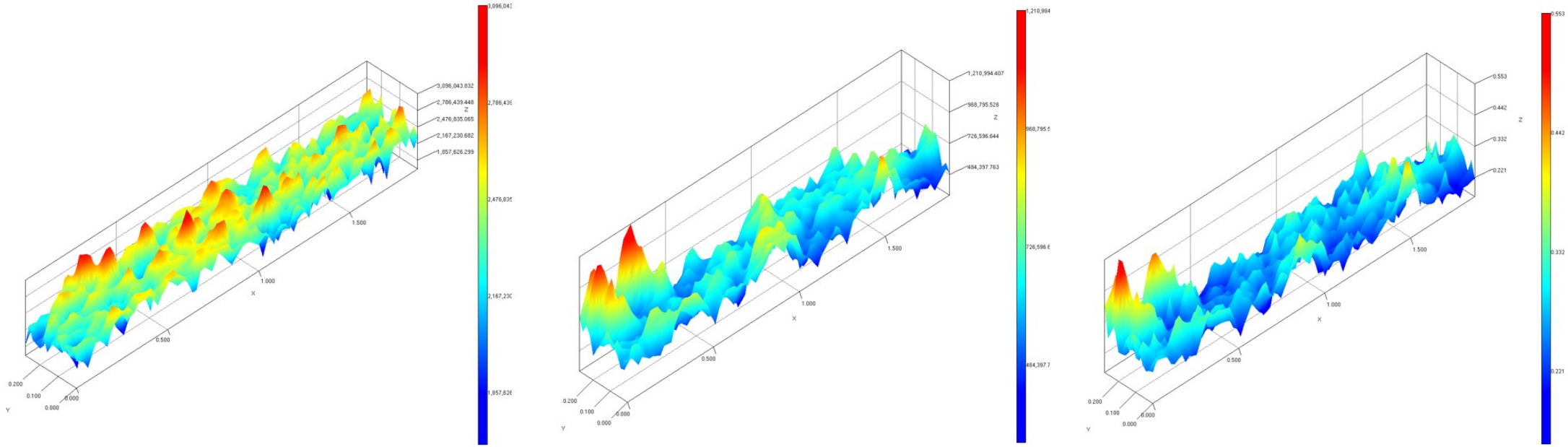

Table S3 *Minimal, maximal, mean intensity and coefficient of variation (standard deviation/ mean value x 100%) of the normalised against Ca signals in the obtained pellets images and of the averaged standardised signals from the five ablated lines located randomly at each pellet*

Ablation type	Pellet	^{24}Mg				^{88}Sr				^{138}Ba			
		Min. int.	Max. int.	Mean int.	CV (%)	Min. int.	Max. int.	Mean int.	CV (%)	Min. int.	Max. int.	Mean int.	CV (%)
rectangular area of 15 lines	1	0.154	0.553	0.268	18	0.131	3.847	0.488	65	0.036	7.675	0.810	138
	2	0.140	0.523	0.267	17	0.119	1.992	0.375	51	0.065	4.519	0.326	144
	3	0.125	0.553	0.256	25	0.134	2.178	0.488	62	0.051	6.426	0.752	148
5 lines located randomly	1	0.151	0.450	0.261	8	0.675	6.839	0.502	14	0.300	5.072	0.770	28
	2	0.169	0.452	0.268	7	0.472	8.948	0.481	54	0.178	5.803	0.758	12
	3	0.176	0.494	0.272	4	0.896	3.896	0.560	15	0.269	5.732	0.882	41

Table S4 *Minimal, maximal, mean intensity and coefficient of variation (standard deviation/ mean value x 100%) of the non-normalised signals in the obtained pellets images and of the averaged signals from the five ablated lines located randomly at each pellet*

Ablation type	Pellet	^{24}Mg				^{88}Sr				^{138}Ba			
		Min. int. [cps]	Max. int. [cps]	Mean int. [cps]	CV [%]	Min. int. [cps]	Max. int. [cps]	Mean int. [cps]	CV [%]	Min. int. [cps]	Max. int. [cps]	Mean int. [cps]	CV [%]
rectangular area of 15 lines	1	325,207	1,210,994	632,866	18	295,474	7,743,583	1,162,928	67	81,210	18,453,375	1,938,846	139
	2	307,089	2,804,460	567,611	24	280,820	3,215,789	786,164	49	149,645	9,218,855	684,701	147
	3	308,553	1,201,083	600,207	27	310,591	4,416,103	1,161,799	65	114,440	14,825,949	1,831,928	153
5 lines located randomly	1	315,382	1,138,577	586,165	12	301,053	5,254,136	1,129,936	18	129,490	12,495,567	1,738,197	31
	2	371,406	996,389	607,622	4	260,375	7,299,223	1,078,714	50	163,632	20,764,737	1,673,484	16
	3	278,660	1,088,650	605,332	8	291,584	3,516,461	1,243,942	15	151,657	13,157,906	1,963,881	41

Fig. S3 *Calibration curves used for LOD and LOQ establishment*

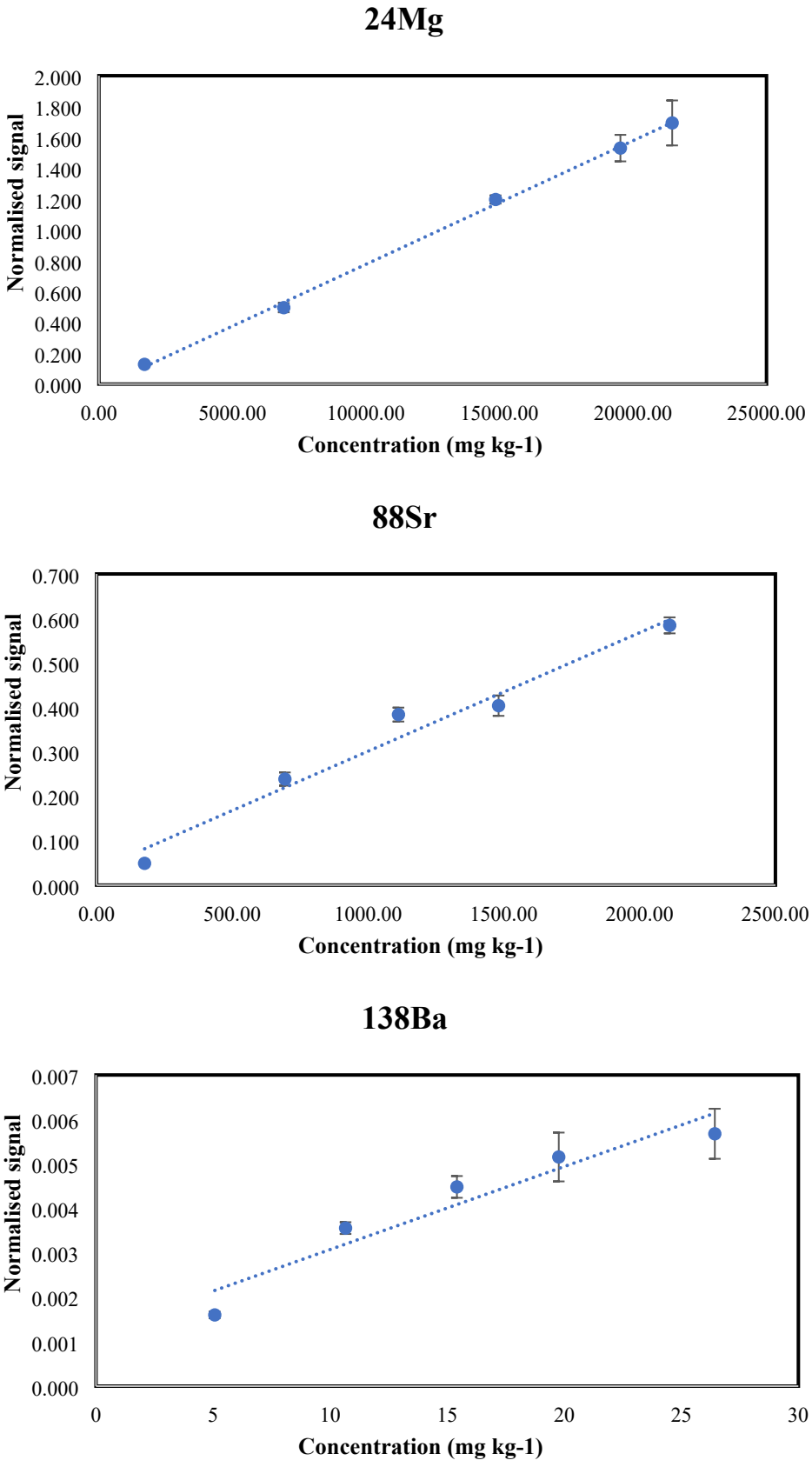

Table S5 *The concentration of elements in the in-house reference material established against various calibration standards without internal standardisation*

Element	Laser wavelength (nm)	calibration standard NIST 610		calibration standard NIST 612		liquid-powder calibration standards	
		c (mg kg^{-1})	RE (%)	c (mg kg^{-1})	RE (%)	c (mg kg^{-1})	RE (%)
^{24}Mg	266	141.9 ± 4.9	30	28.8 ± 0.9	-74	<LOD	-
	213	97.2 ± 0.5	-11	11.7 ± 0.2	-89		
^{88}Sr	266	19,840 ± 790	721	25,900 ± 1,000	973	1,787 ± 69	-26
	213	11,380 ± 260	371	8,650 ± 200	258	1,741 ± 39	-28
^{138}Ba	266	193.8 ± 8.1	883	213 ± 9	985	19.6 ± 0.9	-1
	213	114.9 ± 2.9	483	61.3 ± 1.6	211	26.8 ± 0.7	36

Fig. S4 *Internal standardisation problem with a settlement plate*