Fundamental Studies of Laser Ablation ICPMS using a Nitrogen Plasma Source and Helium, Argon and Nitrogen as Carrier Gas

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Supporting information

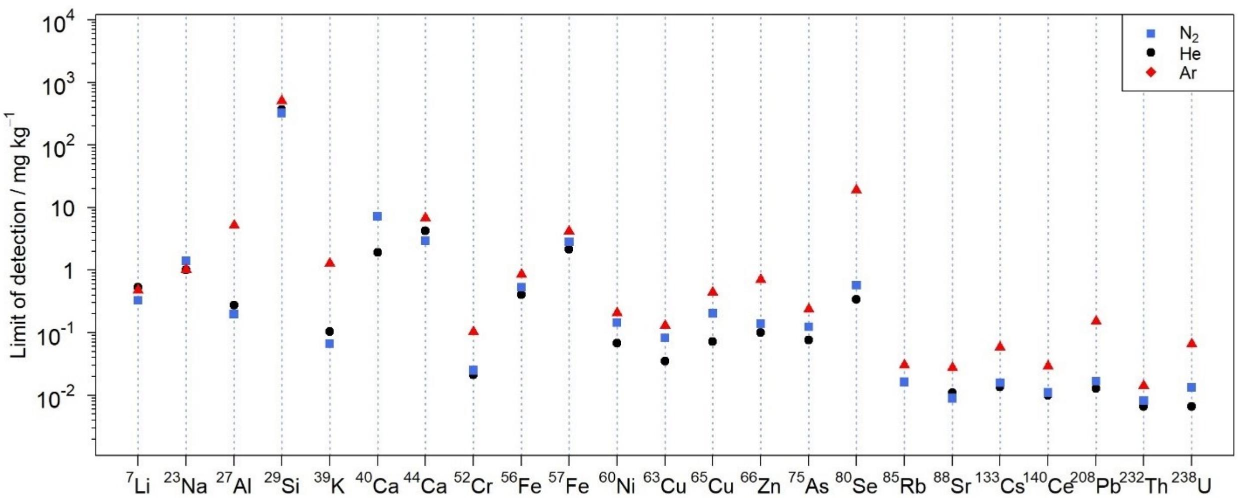

Figure S 1 : LODs obtained with helium (black), nitrogen (blue) or argon (red) as carrier gas using 19 J/cm² and a 90 µm spot for LA of NIST SRM 610. These data were calculated according to Longerich et al.[39] from the sensitivities given in Figure 2.

Figure S 2 : Ni-skimmer cone after one day of measurement using only nitrogen. After a second day of measurement using helium, the opening was widened by 10 %.

Table S 1 : Quantification of the USGS GSE-1G basaltic glass reference material using NIST SRM 610 as calibration standard, ^{40}Ca as internal standard and a fluence of 19 J/cm^2. The concentrations were expressed in mg/kg for the reference values as well as for the measured concentrations. Standard deviations (SD) indicate the measurement uncertainties for the present study and the reference values. ^{40}Ca was not measured for measurement using argon as carrier gas due to the high background caused by the $^{40}Ar^+$ ion and ^{44}Ca was used as internal standard. The deviation of measured concentration is provided for each gas in percent from the reference value. IS: used as internal standard.

	USGS GSE-1G										
	Reference		Nitrogen			Helium			Argon		
	Conc.	SD	Conc.	SD	Deviation	Conc.	SD	Deviation	Conc.	SD	Deviation
Li7	430	60	482	6	12	452.5	1.2	5	478	7	11
Na23	28935	1484	30100	600	4.0	30400	600	5	32280	150	12
Al27	68824	2118	77700	1200	13	73700	1100	7	73500	1100	7
Si29	250600	7000	266900	2800	6	276000	4000	10	253000	1600	0.9
K39	21574	830	24600	400	14	25300	300	17	24770	240	15
Ca40	52857	2143	IS			IS			-		
Ca44	52857	2143	51700	500	-2	50600	100	-4	IS		
Cr52	400	80	398	8	-0.4	397	6	-0.7	372.1	1.8	-7
Fe56	98699	2331	107700	1800	9	103480	600	5	92500	1600	-6
Fe57	98699	2331	105000	2500	6	100195	800	1.5	90300	700	-9
Ni60	440	30	486	7	11	460.8	1.8	5	422	9	-4
Cu63	380	40	426	11	12	399	10	5	363	26	-4
Cu65	380	40	432	12	14	395	11	4	359	24	-6
Zn66	460	10	456	6	-1.0	463	3	0.6	411	16	-11
As75	260	90	394	12	51	330	60	25	327	14	26
Se80	20	16	2.1	0.4	-90	4.59	0.07	-77	< 19		
Rb85	356	4	386	8	8	388	5	9	386	3	9
Sr88	447	5	468	6	5	458.7	2.8	2.6	462	5	3
Cs133	310	20	316	6	1.9	305	4	-1.7	303	5	-2.2
Ce140	414	4	439	11	6	421.75	0.26	1.9	416	3	0.5
Pb208	378	12	409	12	8	399	9	6	345	10	-9
Th232	380	20	405	15	6	393	8	3	373	20	-1.8
U238	420	30	443	10	5	430	4	2.4	408.2	0.3	-2.8

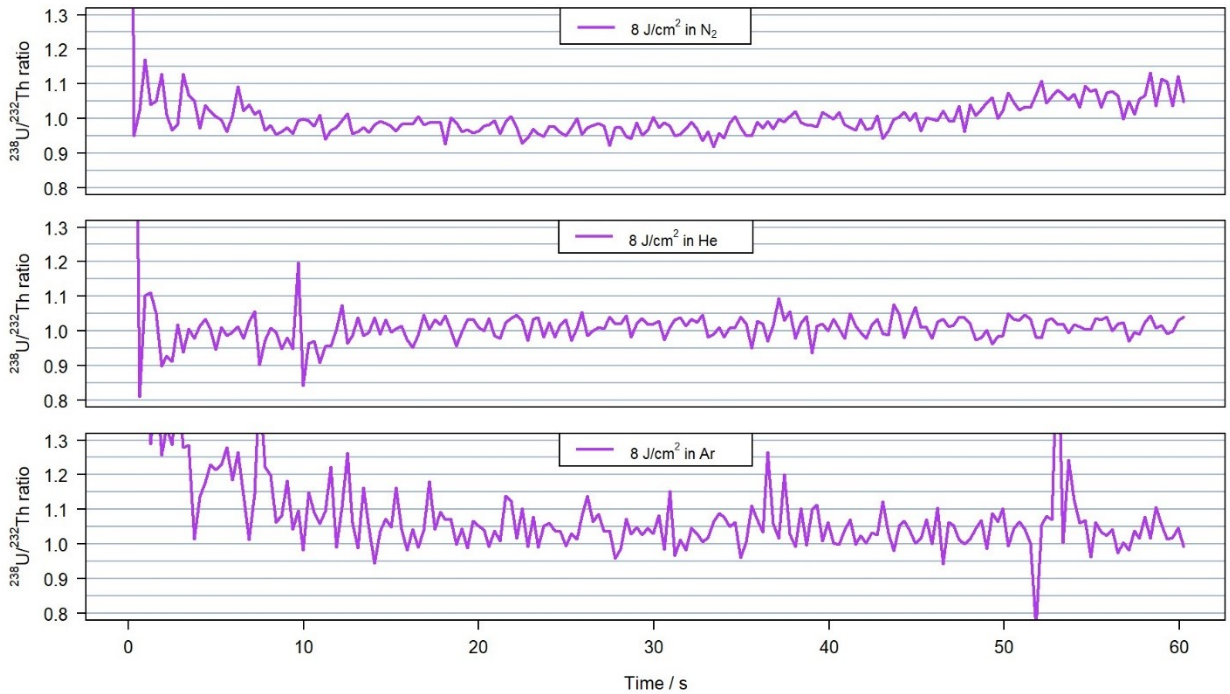

Figure S 3 : $^{238}U^{+}/^{232}Th^{+}$ ratio measured for 8 J/cm^2 in nitrogen at 1.00(4) on average (top), helium at 1.01(3) (middle) and argon at 1.05(8) (bottom) with 600 pulses at 10 Hz on NIST SRM 610. The time window illustrates the 60 s of ablation without background nor washout time. The $^{238}U^{+}$ transient signal corresponding to the experiment presented here can be visualized in Figure 4 at the corresponding fluence and carrier gas.

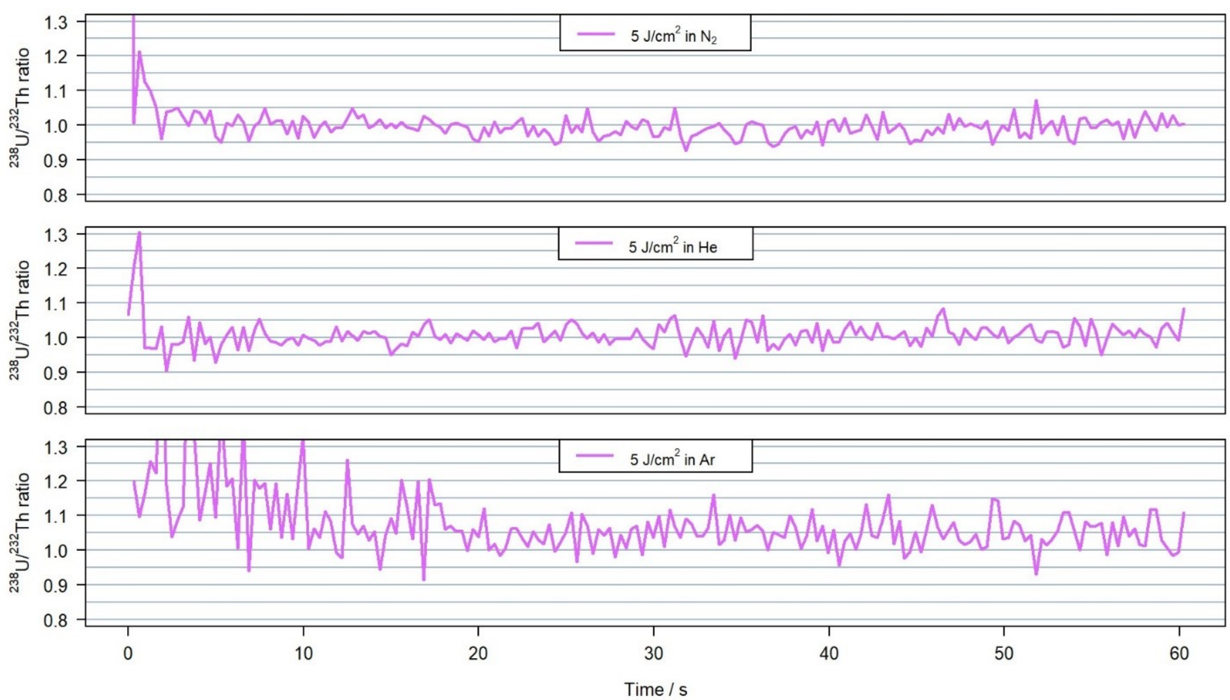

Figure S 4 : $^{238}U^{+}/^{232}Th^{+}$ ratio measured for 5 J/cm^2 in nitrogen at 0.99(3) on average (top), helium at 1.01(3) (middle) and argon at 1.05(5) (bottom) with 600 pulses at 10 Hz on NIST SRM 610. The time window illustrates the 60 s of ablation without background nor washout time. The $^{238}U^{+}$ transient signal corresponding to the experiment presented here can be visualized in Figure 4 at the corresponding fluence and carrier gas.

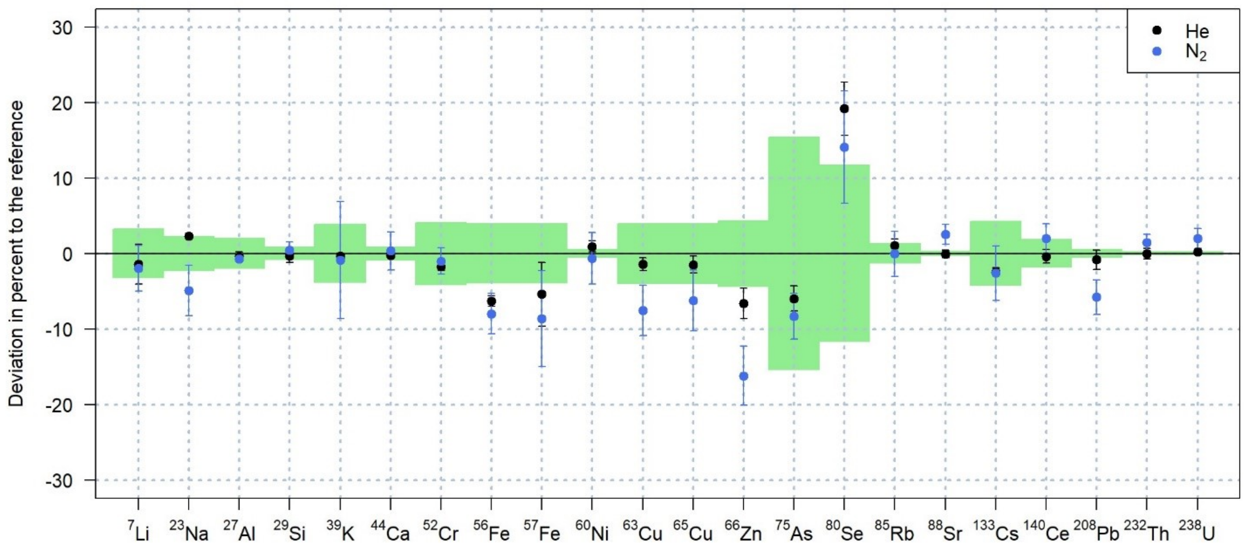

Figure S 5 : Quantification of NIST SRM 612 using nitrogen and helium as carrier gases and NIST SRM 610 as calibration standard. ^{40}Ca was used as internal standard and a fluence of 18 J/cm^2 was applied in combination with the MPFAC. Error bars represent the standard deviation of 6 replicate analysis, while the standard deviations of the reference values are indicated by the light green areas.

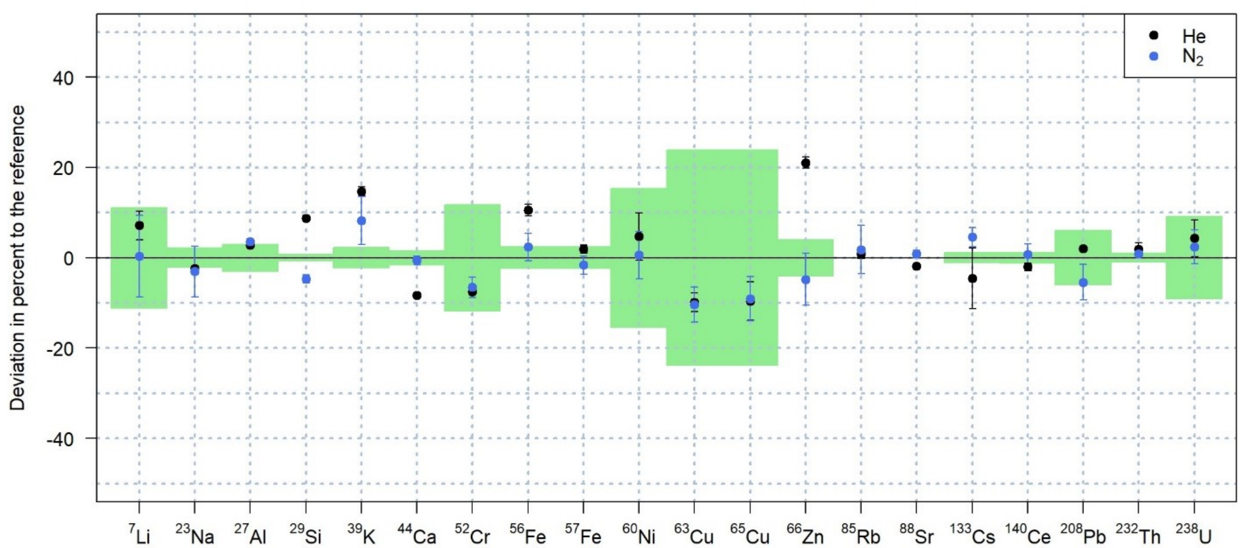

Figure S 6 : Quantification of USGS BCR-2G using nitrogen and helium as carrier gases and NIST SRM 610 as calibration standard. ^{40}Ca was used as internal standard and a fluence of 18 J/cm^2 was applied in combination with the MPFAC. Error bars represent the standard deviation of 3 replicate analysis, while the standard deviations of the reference values are indicated by the light green areas.

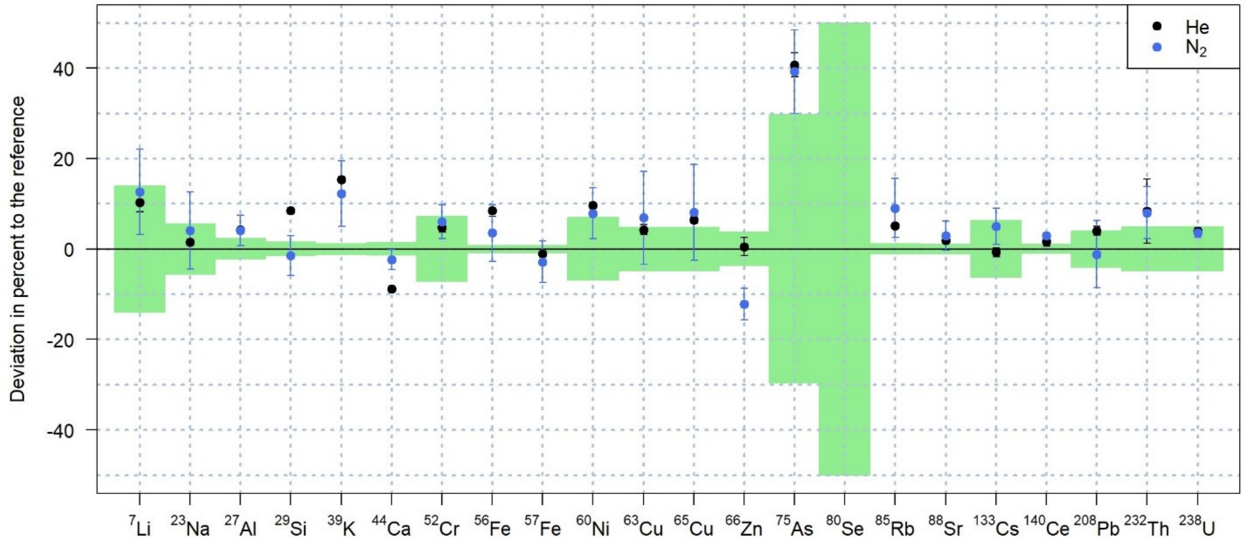

Figure S 7 : Quantification of USGS GSD-1G using nitrogen and helium as carrier gases and NIST SRM 610 as calibration standard. ^{40}Ca was used as internal standard and a fluence of 18 J/cm^2 was applied in combination with the MPFAC. Error bars represent the standard deviation of 3 replicate analysis, while the standard deviations of the reference values are indicated by the light green areas.

Table S 2 : Thermodynamic properties of the different carrier gases studied. It should be noted that the isobaric heat capacity was calculated by unit of volume instead of unit of mass by taking into account the density provided in the reference.[42]

Properties at 300 K and 1 bar	Argon	Helium	Nitrogen
Isobaric heat capacity C_p / kJ m^{-3} K^{-1}	0.836	0.833	1.169
Thermal conductivity / mW m^{-1} K^{-1}	17.84	156.0	25.97
Ionization energy / eV	15.76	24.59	15.58
Viscosity / µPa s	22.74	19.93	17.89

a) b) c)

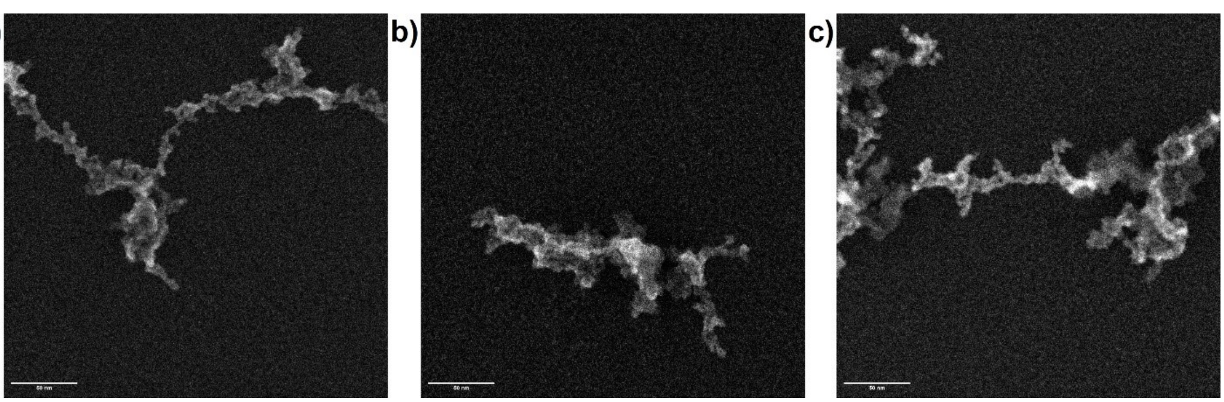

Figure S 8 : STEM images of laser-generated aerosol formed in nitrogen (a), helium (b) and argon (c) in a two-volume cell. The scale bar is 50 nm. The observation of the primary particles with the scale bar set at 50 nm can be compared to Figure 9b), Figure 10b) and Figure 11b), respectively for the same magnification and carrier gas but using the cylindrical ablation cell.