Spatial micro-analysis of natural $^{13}C/^{12}C$ abundance in environmental samples using laser-ablation isotope-ratio-mass spectrometry

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Supporting Information

The stable $^{13}C/^{12}C$ isotope composition usually varies among different organic materials due to isotope fractionation during biochemical synthesis and degradation processes. Here we introduce a novel laser-ablation stable isotope-mass-spectrometry methodology (LA-IRMS) that allows highly resolved spatial analysis of carbon isotope signatures in solid samples down to a spatial resolution of 10 µm.

As Supporting Information we present one table and six figures showing the determination of carbon amount by measurements of crater depth on an acryl plate (Table S-1), configuration of the newly developed laser cells (Fig. S-1), images of press-pellets from the ground und mixed standard substances (Fig. S-2), images of spot depth and surface mapping of ablated spots (Fig. S-3), deviation of the $\delta^{13}C$ signal from referenced values due to the contribution of the blank signal (Fig. S-4), adjustment of loading times in the cryo-trap (Fig. S-5), and stable C isotope signatures of a *Miscanthus* rhizome and the surrounding soil.

Tables and Figures

Table S-1: Determination of carbon amount by multiple measurements of crater depth in matrix of ablation spot size and number of shots using surface mapping on acryl plate (mass fraction of carbon 0.6; acryl density 1.19 g cm^3).

Figure S-1: Configuration of the newly developed laser cells. Design was optimized to have a low active cell volume and a proper helium circulation on the sample surface allowing suspension and transport of ablated particles (3.8 ml volume cell, scale in mm).

Figure S-2: Images of (a) press-pellets from the ground und mixed standard substances, (b) steel slots for separate tests, and (c) acryl plate slots for parallel measurements of different standards and soil samples.

Figure S-3: Acryl plate (a) after laser ablation for determination of spot depth in combination with increased number of shots (10, 20, 30, and 40, respectively); (b) surface mapping of ablated spots using sub-angstrom optical profiler; and (c) an example of a flat-bottom crater profile for shape and depth determination.

Figure S-4: a) deviation of the $\delta^{13}C$ signal (given as $\Delta\delta^{13}C$) from the referenced value due to the contribution of the blank signal. If the ablated sample amount increased (controlled by spot size and shot number), the blank contribution decreased linearly, allowing for correction of the blank signal contribution (see text for blank correction calculation). (b) deviation of the blank corrected $\delta^{13}C$ signal correlated to sample peak area (without peak area of the blank). If the amount of ablated material was reduced to a sample peak area of 0.3Vs, the signal became unstable (data produced with 20 sec loading time in 3.8 ml active cell volume).

Figure S-5: Contribution of blank to total $\delta^{13}C$ as influenced by different loading times in the cryo-trap (sample: acryl plate, 0.4 mL active volume cell, pure blank detection limit at 20 mV and -19.09±0.30‰ (grey symbols)). (a) In the 0.4 ml cell, a 10 sec loading time produced a stable $\delta^{13}C$ signal. If the loading time was set to 15 sec, the blank contribution increased significantly. (b) the blank contribution changed the $\delta^{13}C$ value systematically with increasing amount of ablated material when the loading time was < 10 sec. If the loading time was set to less than 10 sec, the blank corrected signal became unstable.

Figure S-6: Stable C isotope signature of a *Miscanthus* rhizome and the surrounding soil, detected with constant spot size of 30 µm and 40 shots per ablation in a 3.8 ml cell (in-house reference acryl = -29.75±0.18‰).

Table S-1.

Spot size µm	Number of shots	Crater depth[1)] µm	s.d.[2)]	RSD[3)] %	Carbon amount ng
10	10	1.8	0.1	7.7	0.1
	20	4.0	0.1	3.3	0.2
	30	6.1	0.1	1.4	0.3
	40	7.6	0.1	1.6	0.4
20	10	1.8	0.1	5.1	0.4
	20	3.3	0.1	3.1	0.7
	30	5.2	0.0	0.9	1.2
	40	7.1	0.1	1.3	1.6
30	10	1.6	0.0	0.0	0.8
	20	3.3	0.0	1.4	1.7
	30	5.3	0.1	1.6	2.7
	40	6.8	0.2	2.8	3.4
40	10	1.7	0.0	2.7	1.5
	20	3.2	0.0	1.4	2.9
	30	5.3	0.1	1.7	4.8
	40	6.2	0.1	1.5	5.6

[1)] Mean value, n = 5

[2)] Standard deviation

[3)] Relative standard deviation

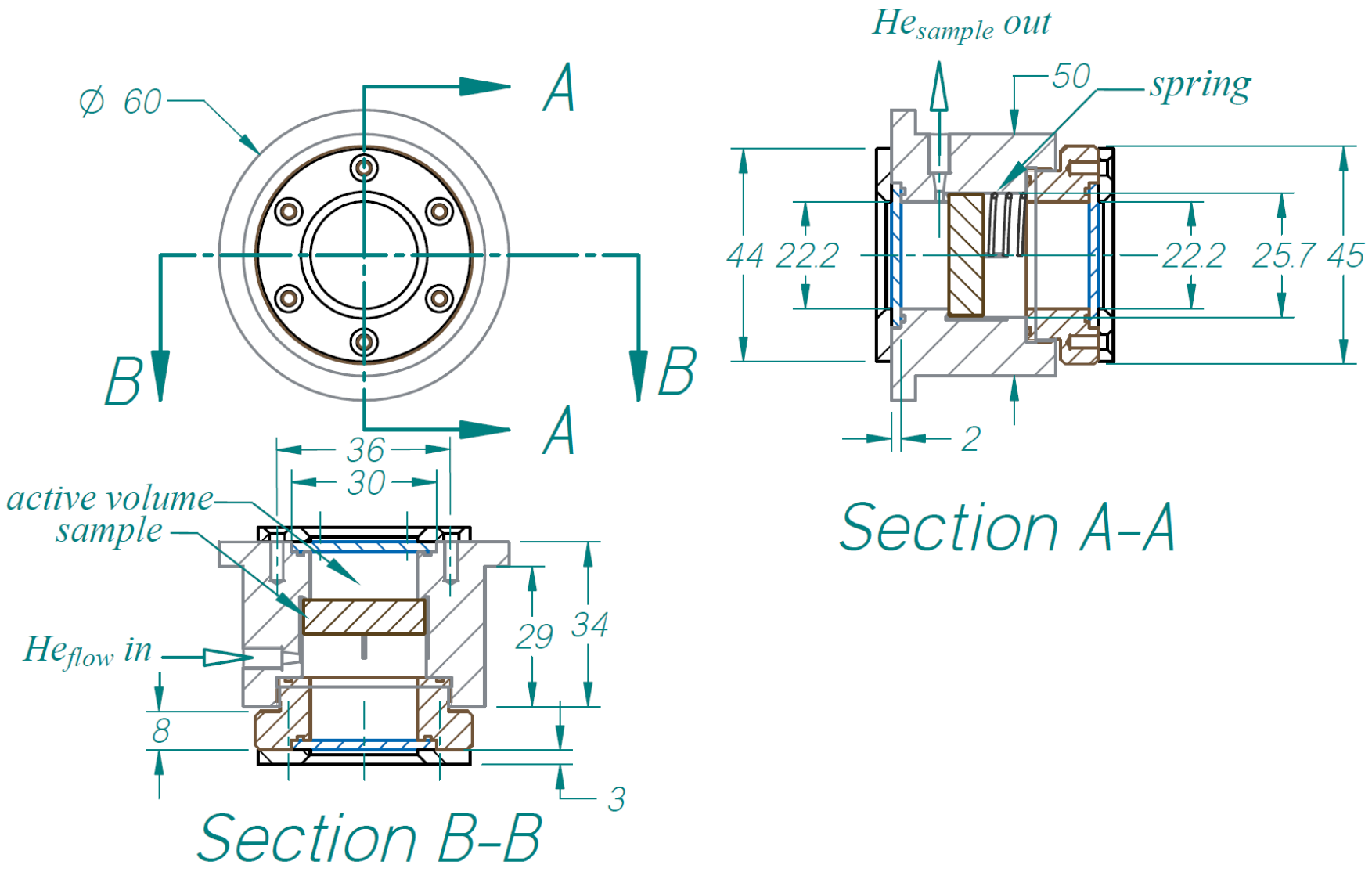
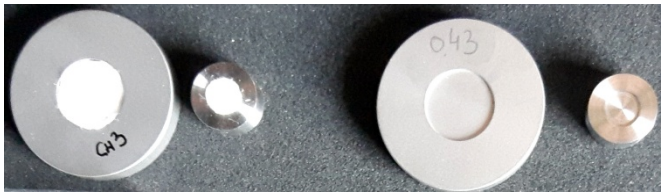

Ø 60
A
B
B
A
36
30
active volume
sample
He flow in
8
29
34
3
Section B-B
He sample out
50
spring
44
22.2
22.2
25.7
45
2
Section A-A

Figure S-1.

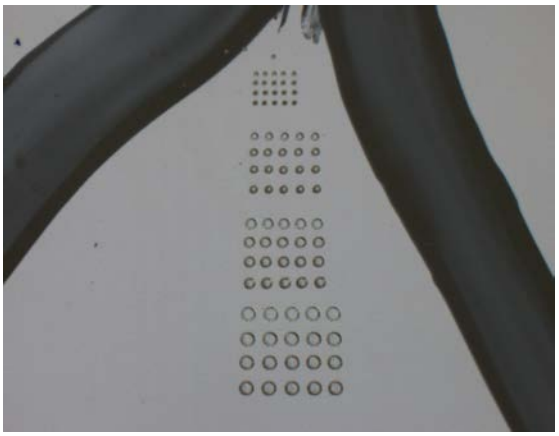
a)

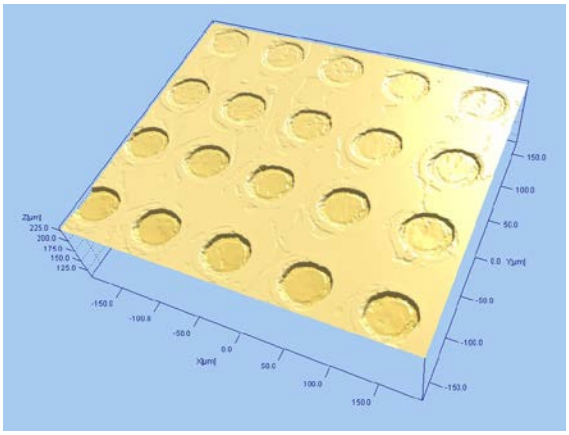
b)



c)

Figure S-2.

a) 

b) 

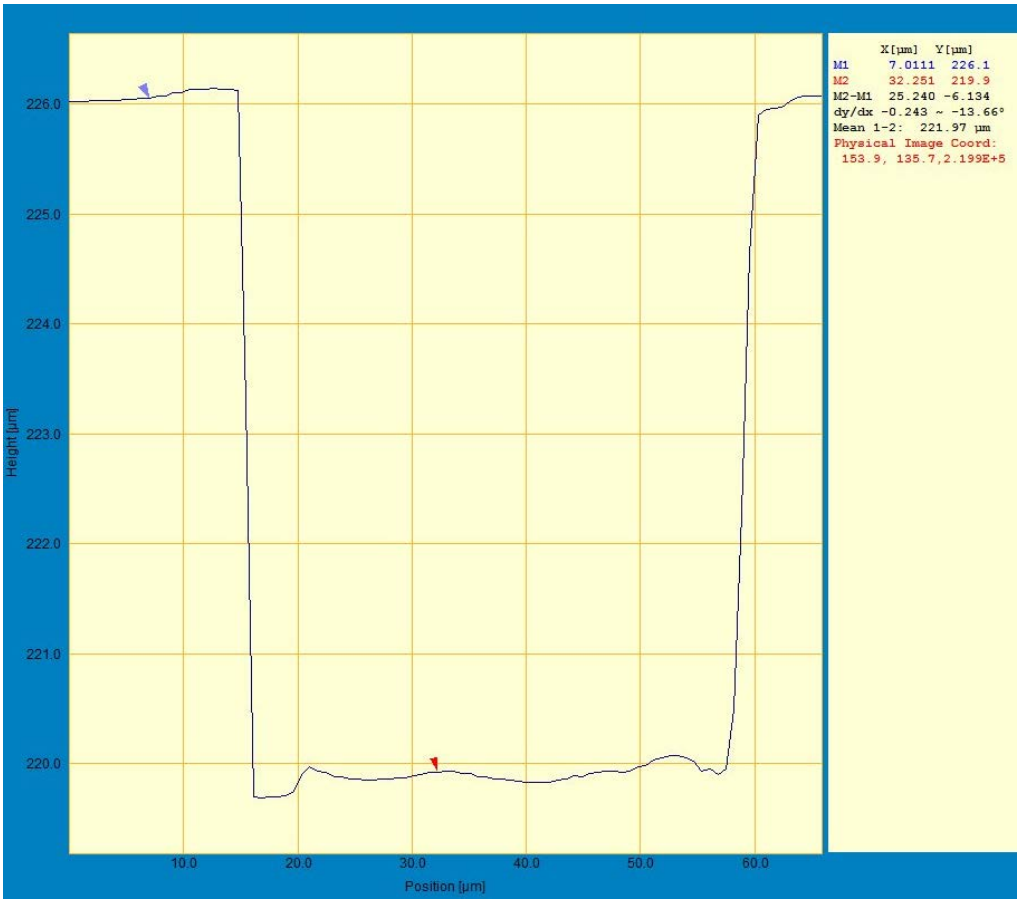
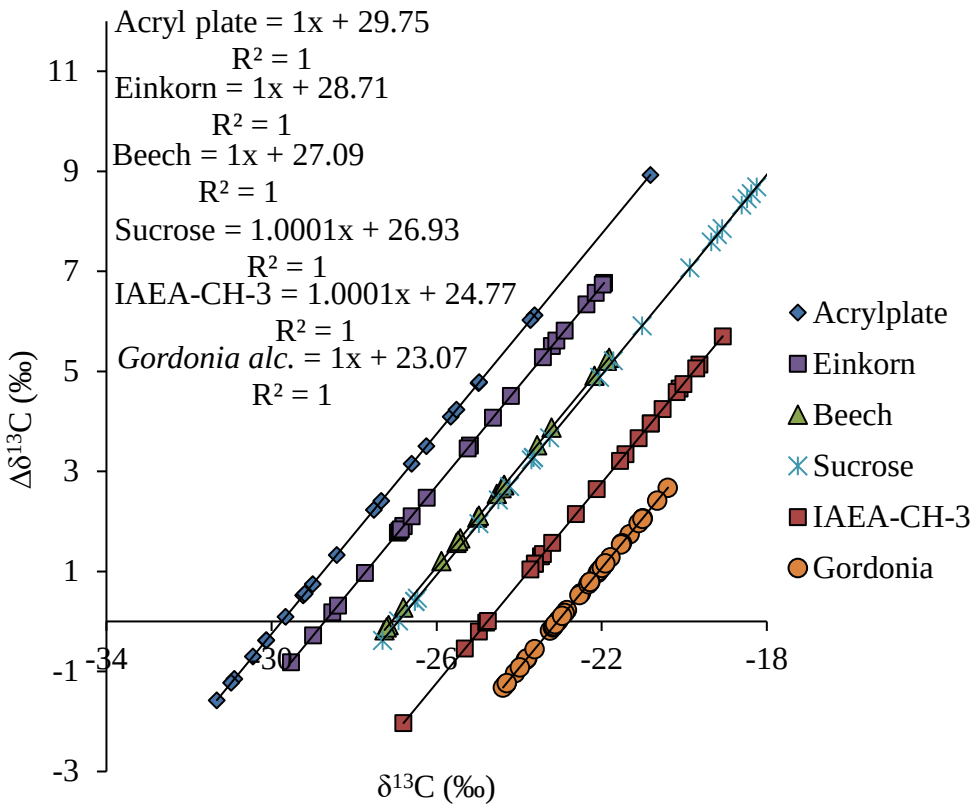
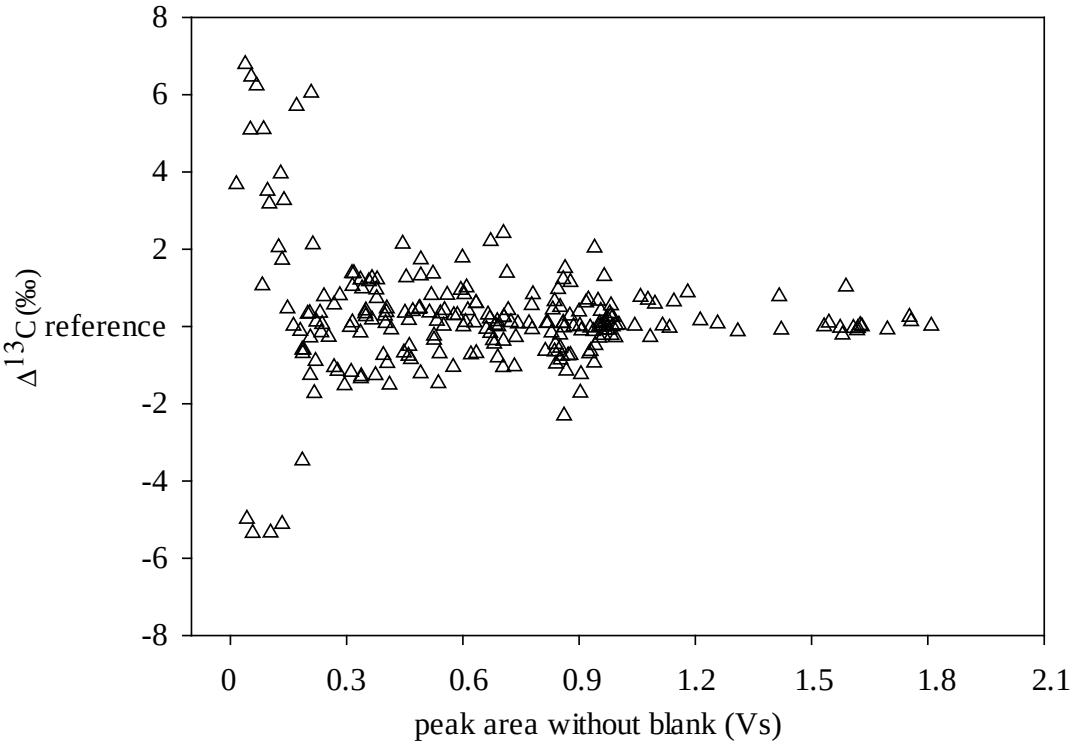
c) 

Figure S-3.

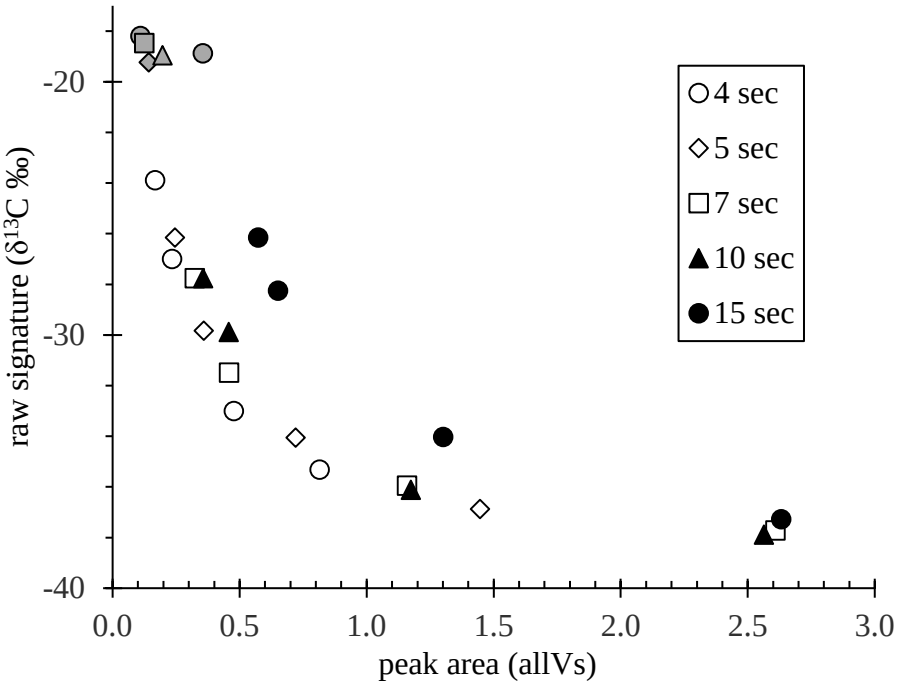

Acryl plate = 1x + 29.75
R² = 1
Einkorn = 1x + 28.71
R² = 1
Beech = 1x + 27.09
R² = 1
Sucrose = 1.0001x + 26.93
R² = 1
IAEA-CH-3 = 1.0001x + 24.77
R² = 1
Gordonia alc. = 1x + 23.07
R² = 1
Δδ13C (‰)
δ13C (‰)
Acrylplate
Einkorn
Beech
Sucrose
IAEA-CH-3
Gordonia

a)

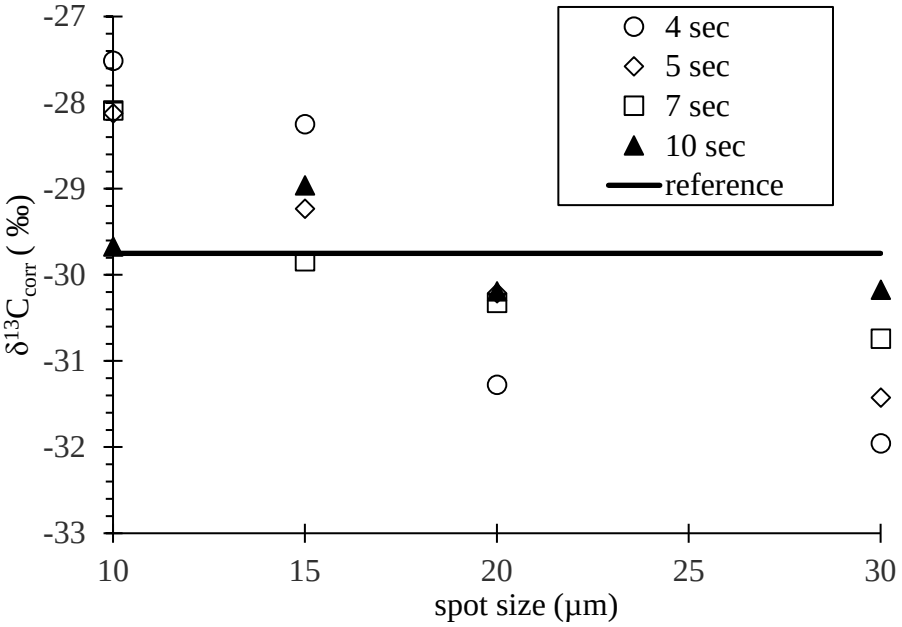

Δ13C (‰) reference
peak area without blank (Vs)

b)

Figure S-4.


raw signature (δ13C ‰)
-20
-30
-40
0.0
0.5
1.0
1.5
2.0
2.5
3.0
peak area (allVs)
4 sec
5 sec
7 sec
10 sec
15 sec

a)


δ13Ccorr (‰)
-27
-28
-29
-30
-31
-32
-33
10
15
20
25
30
spot size (µm)
4 sec
5 sec
7 sec
10 sec
reference

b)

Figure S-5.

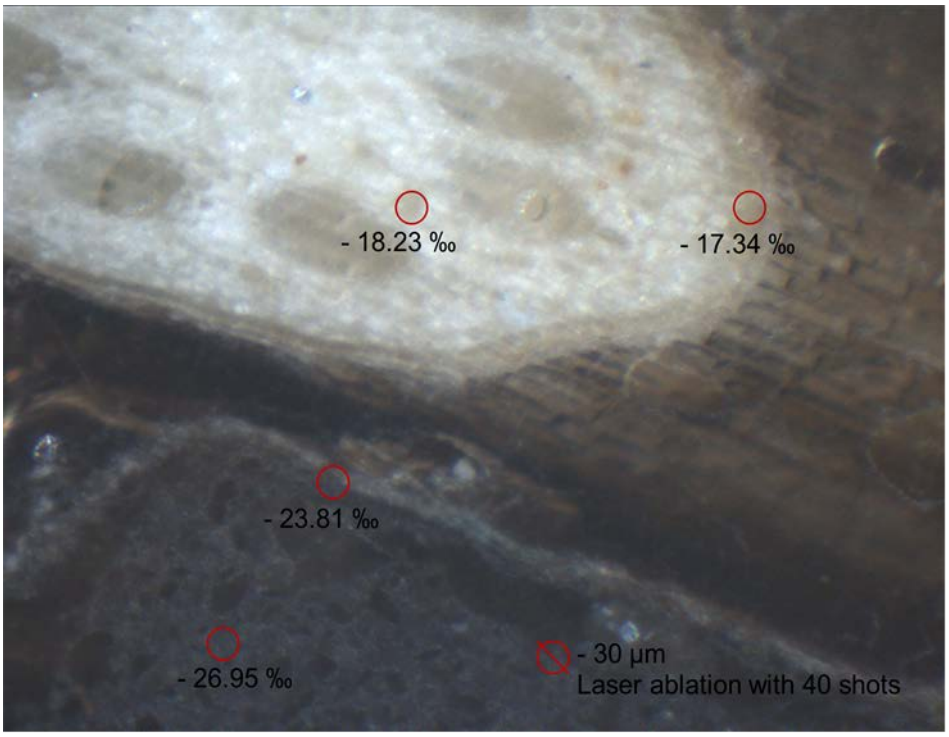


Figure S-6.