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Dynamic implantation - An improved approach for a large area SIMS measurement

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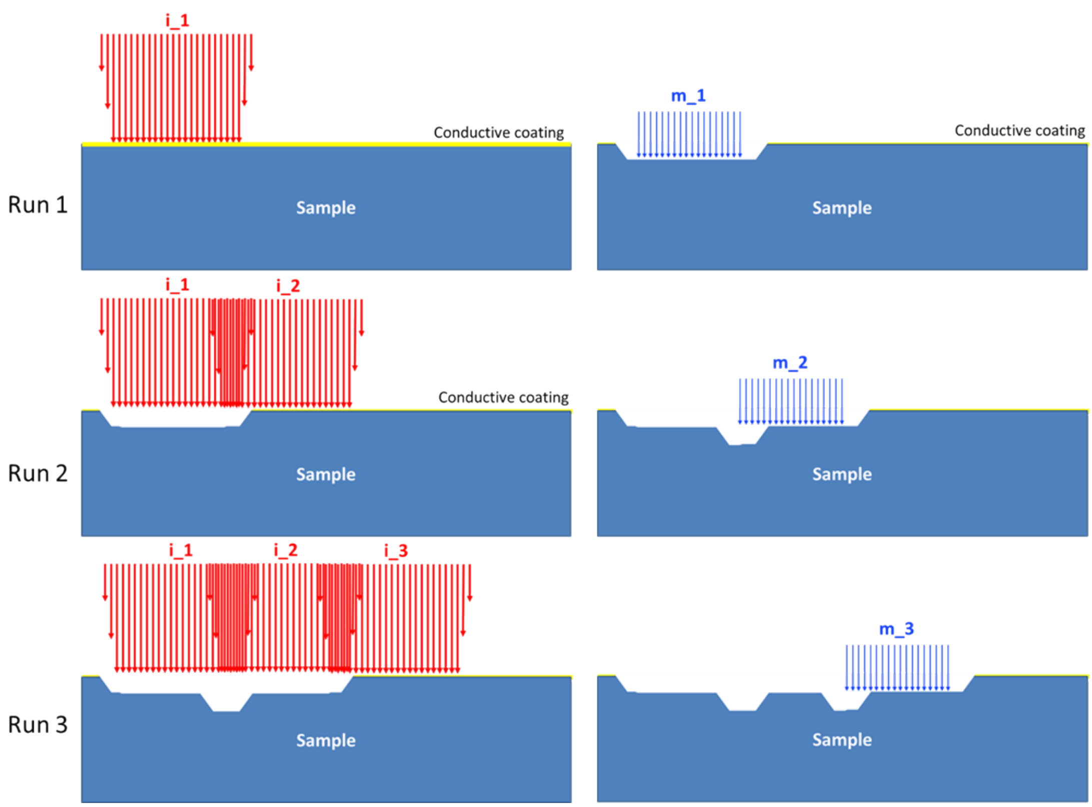
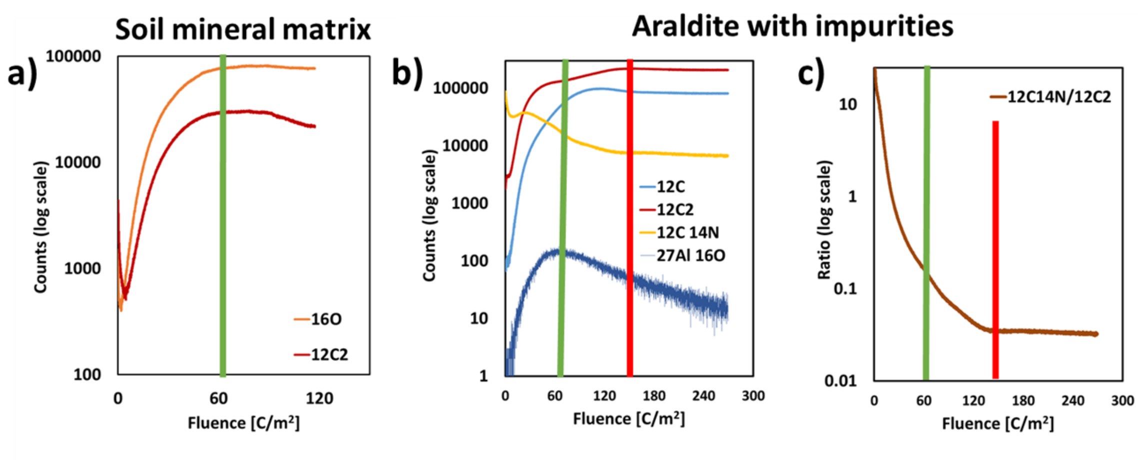


Fig. S1 Schematics illustrating the artifacts introduced by the traditional pre-sputtering/implantation of single spots in a row of measurements as line scan. Red colored arrows indicate the Cs dose entering the sample due to pre-sputtering at successive implantation steps (i_i). The much lower Cs dose impacting the sample during the measurement (m_i) is indicated by the blue arrows. Crater edge effects must be avoided by pre-sputtering area larger than the measurement size. At overlapping regions the different depths are measured due to the double implantation

Fig. S2 Exemplary graph showing the progression of the secondary ions escaping the sample surface. It is useful to determine the implantation fluence to reach a regime appropriate for performing the measurements. Once selected, the fluence should be kept constant for measuring the samples and the standards; a) depth profile of soil mineral matrix at a test position (10 µm x 10 µm, 12 pA). We choose a fluence of 60 C m^{-2} (vertical green line), corresponding to a dose of 3.7E+16 Cs ions/cm^2, to perform our measurements on the embedded soil aggregate as at this fluence the $^{16}O^-$ signal becomes sufficiently constant. b) and c) depth profiles on the araldite embedding media presenting impurities illustrated by their secondary ion counts (b) and the $^{12}C^{14}N^-/^{12}C_2^-$ elemental ratio (c). The vertical green line shows favorable fluence (60 C m^{-2}) for measuring minor features like AlO which diminish with increasing fluence, while the vertical red line shows favorable fluence (150 C m^{-2}) when measuring at the steady state in the araldite matrix.



Terms and formulas for calculating the parameters necessary to perform the dynamic implantation for any geometry of

Input				Calculations					
comment	*raster*	*I-Fco*	*time*	*time*	*area*	*charge*	*fluence*	*dose*	*dose*
	[µm]	*[pA]*	*[s]*	*[hh:mm:ss]*	*[m^2]*	*[C]*	*[C/m^2]*	*[$ions/m^2$]*	*[$ions/cm^2$]*
Fluence $1C/m^2$	10	10	10	00:00:10	1.0E-10	1.0E-10	1.0	6.2E+18	6.2E+14
Implantation check	10	12	500	00:08:20	1.0E-10	6.0E-09	60.0	3.7E+20	3.7E+16
Implantion, high current, $60C/m^2$	50	260	580	00:09:40	2.5E-09	1.5E-07	60.3	3.8E+20	3.8E+16
Measurement, 1 plane, 256 pixels	30	2	66	00:01:06	9.0E-10	1.3E-10	0.1	9.1E+17	9.1E+13
Measurement, 20 planes, 256 pixels	30	2	1312	00:21:52	9.0E-10	2.6E-09	2.9	1.8E+19	1.8E+15
Implantation steady state	50	260	1445	00:24:05	2.5E-09	3.8E-07	150.3	9.4E+20	9.4E+16

Table 1 Determination of the fluence for different steps. In a first step (Implantation check) the fluence necessary to reach a regime appropriate for performing measurements is calculated based on the secondary ion evolution as shown in Fig. S2 (60 C m^{-2}). To avoid deterioration of the electron detectors (Electron Multipliers for NanoSIMS) the primary current (I-Fco) is limited and would be lower (e.g. 12 pA) than the high primary beam used for the dynamic implantation (e.g. 260 pA). To speed up, the raster size can be small (e.g. 10 µm). In a second step, the time necessary for implantation of the region to be measured at the found fluence (60 C m^{-2}) with high current (260 pA, while protecting the detectors) is determined (580 s). Furthermore, the fluence during the measurement is calculated. For example, during one plane of a measurement 30 µm x 30 µm consisting e.g. of 256 pixels at a dwell time of 1ms/pixel a dose of 0.1 C m^{-2} Cs ions enter the surface. More planes can be recorded according to statistical requirements for the precision of the measurement (e.g. 20 planes), while the fluence accumulates. To perform an implantation of an area of 50 µm x 50 µm in steady state (150 C m^{-2}) with a high current of 260 pA, about 24 minutes are necessary.

analysis:

m_x_start = x coordinate of the first measurement [µm]
m_y_start = y coordinate of the first measurement [µm]
m_x_stop = x coordinate of the last measurement [µm]
m_y_stop = y coordinate of the first measurement [µm]
m_x_center = x coordinate of the center of the measured area [µm]
m_y_center = y coordinate of the center of the measured area [µm]
m_scan = scanning size (raster) of one single measurement [µm]
m_x_n = number of measurements in x direction (= 1 for line scan in y)
m_y_n = number of measurements in y direction (= 1 for line scan in x)

i_x_start = x coordinate of the starting position for implantation [µm]
i_y_start = y coordinate of the starting position for implantation [µm]
i_x_stop = x coordinate of the end position for implantation [µm]
i_y_stop = y coordinate of the end position for implantation [µm]
i_x_step = step width during implantation in x direction [µm], “+” is up, “-“ is down
i_y_step = step width during implantation in y direction [µm], “+” is right, “-“ is left
i_x_nsteps = number of steps in x direction during implantation

i_y_nsteps = number of steps in y direction during implantation
i_nsteps = number of total steps during implantation (for area scan)
i_scan = scanning size during implantation [µm]
i_pixel = number of pixels for implantation (e.g. 64, 128 or 256), we recommend 64 when working with high current settings
i_pixel_width = pixel size during the implantation
i_current = current of primary beam during implantation [pA]
i_fluence = fluence to be reached through implantation [C/m^2] or [pC/µm^2], 1 pC/µm^2 = 1 C/m^2
i_scan_area = area of an implantation step with the i_scan size [µm^2]

t_scan_area= time we need to reach the desired fluence in case we stay all the time at one spot with a given i_scan
t_step = time for one implantation step
t-tot = total time for implantation without software overhead
t_dwell = dwell time per pixel

Calculations formulas:

m_x_stop [µm] = m_x_start + ((m_x_n – 1) * m_scan)
m_y_stop [µm] = m_y_start + ((m_y_n – 1) * m_scan)
m_x_center [µm] = (m_x_start + m_x_stop) / 2
m_y_center [µm] = (m_y_start + m_y_stop) / 2
i_x_start [µm] = m_x_start – m_scan / 2 - i_scan
i_y_start [µm] = m_y_start – m_scan / 2 - i_scan
i_x_stop [µm] = m_x_stop + m_scan / 2 + i_scan
i_y_stop [µm] = m_y_stop + m_scan / 2 + i_scan
i_x_nsteps = (i_x_stop – i_x_start) / i_x_step
i_y_nsteps = (i_y_stop – i_y_start) / i_y_step
i_scan_area [µm^2] = i_scan [µm] * i_scan [µm]
i_pixel_width [nm]= i_scan [nm] / i_pixel
t_scan_area [s] = (i_fluence * i_scan_area) / i_current
t_tot [s] = i_nsteps * t_step
t_dwell [µs] = t_step [µs] / i_pixel^2

charge [pC] = I [pA] * time [s]; charge [C] = I [A] * time [s]
fluence [pC/µm^2] = charge [pC] / area = (I [pA] * time [s]) / i_scan [µm]^2
fluence [C/m^2] = fluence [pC/µm^2] =(I [A] * time [s]) / i_scan [m]^2
dose [ions/m^2] = fluence [C/m^2] / e; e = 1.6 10^{-19} C

-for line scan:
t_step [s] = t_scan_area / (i_scan / i_x/y_step)
line scan Y: i_x_start = m_x_start = m_x_center = i_x_stop = m_x_stop
line scan X: i_y_start = m_y_start = m_y_center = i_y_stop = m_y_stop

-for area scan:
i_nsteps = i_x_nsteps * i_y_nsteps
i_x_step = i_y_step = i_step
t_step [s] = t_scan_area / (i_scan / i_step)^2

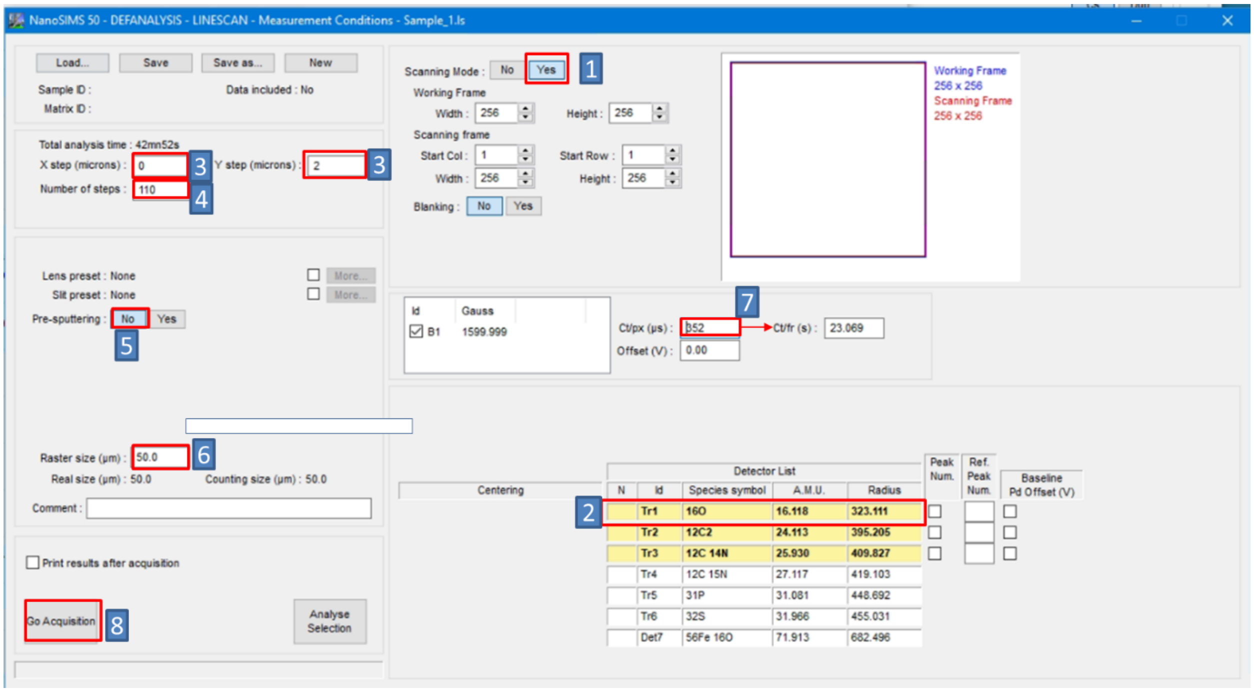


Fig. S3 Screenshot showing the step by step implementation of the line scan dynamic implantation in Cameca NanoSIMS Software

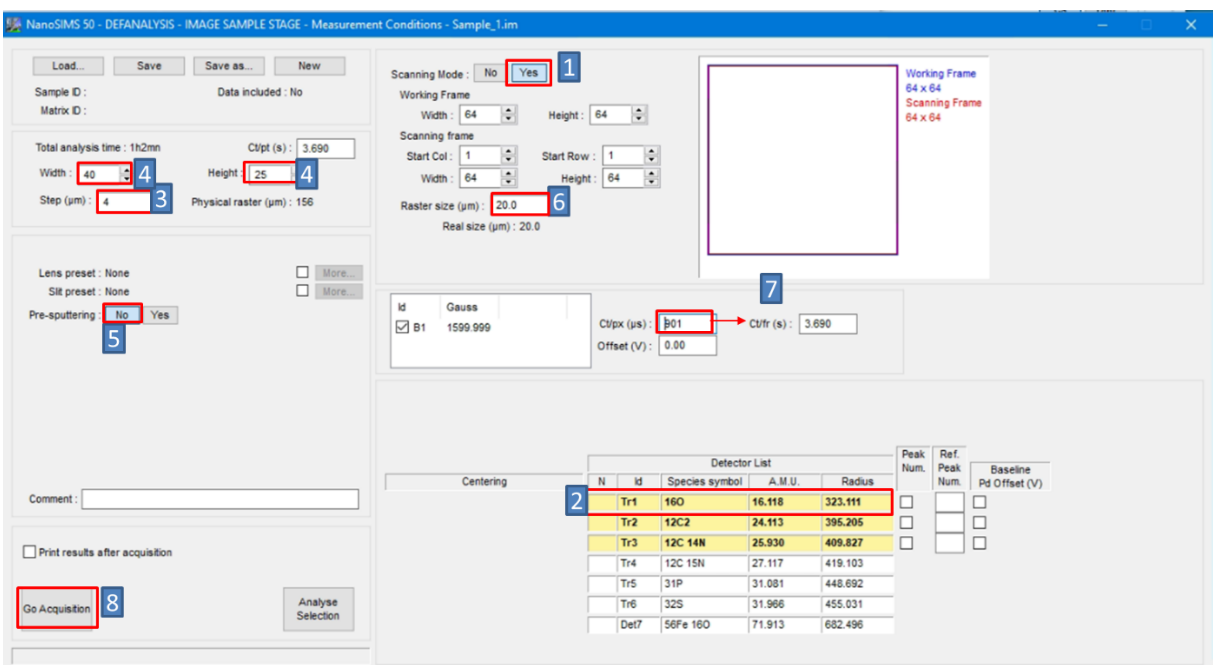


Fig. S4 Screenshot showing the step by step implementation of the area scan dynamic implantation in Cameca NanoSIMS Software

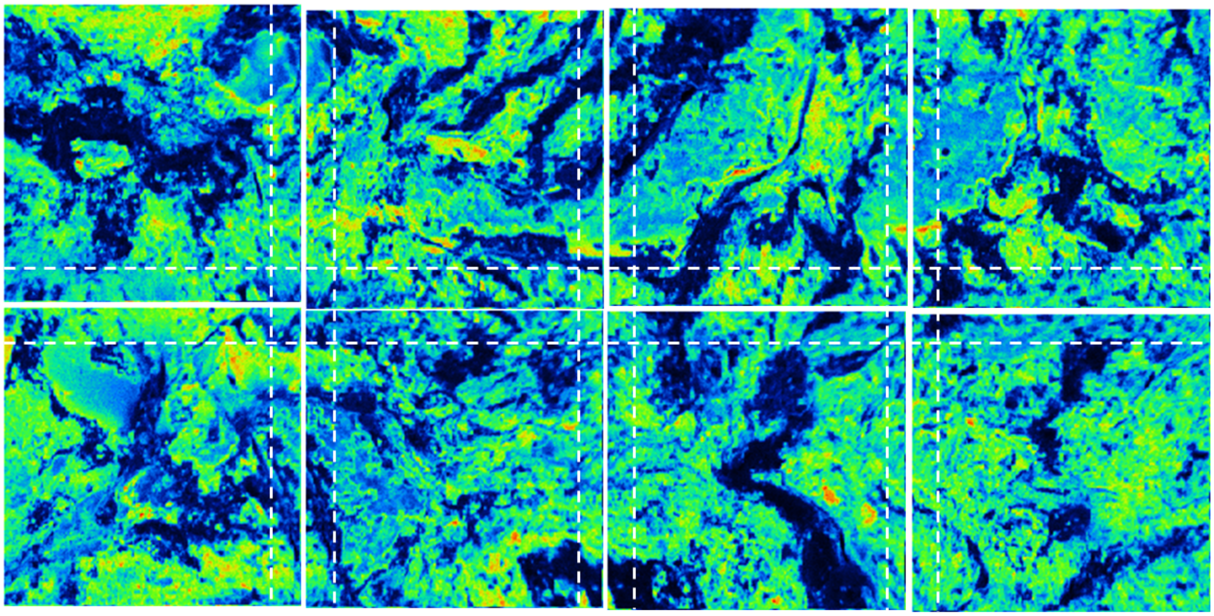


Fig. S5 NanoSIMS images ($^{16}O^-$) of the area dynamically implanted (the same area shown in Fig. 4b for $^{12}C_2^-$) consisting of 4 x 2 measurements of 30 µm x 30 µm size performed with an overlap of 3 µm, indicated by the white dashed lines. Due to the homogeneous dynamic implantation of the large area done previously to the measurements (60 C m^{-2}), at the zones twice measured with a low surplus dose of 2.9 C m^{-2}, no differences in the ion yield are visible. This would be different using classical implantation, when the overlap zones suffer a double pre-sputtering and so a surplus dose of (60+2.9) C m^{-2}. Using the overlap, these measurements can be assembled as a mosaic without artefacts.