Supporting information:

Quantitative analysis of radium-226 at the microscale by NanoSIMS

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Material and methods

^{226}Ra reference material A

The ^{226}Ra solution for reference material A was first prepared with 1.3 g of uraninite dissolved in 20 mL of 3 mol.L-1 HNO_3 at 90°C. 2 mL of 3 mol.L^{-1} HNO_3 at 90°C were added and resulted in the observation of a gray precipitate at the bottom of the tube and a yellow-green supernatant of approximately 15 mL. The supernatant solution of 15 mL was then successively passed 4 times through a 20 mL UTEVA column. At the end of each passage, a 50 µL aliquot of the solution was taken for ICP-MS analyses. Parallel ICP-MS analyses validate the complete extraction of ^{238}U and ^{232}Th. The analysis of the first two solutions after passing through the column confirmed the absence of ^{238}U and ^{232}Th. These two solutions were combined and then dried in a Savillex vessel at 140°C. 7.5 mL of 2 mol.L^{-1} HCl was used to dissolve the residue obtained after heating. At the end of this step, a white precipitate and a green supernatant solution were obtained. The supernatant was then poured into an AG1-X8 column to extract Pb and bismuth from the solution.

A microprecipitation process was then used to create the Ra-barite reference material. The resulting solution was mixed with 1 mL of 0.1 mol.L^{-1} Na_2SO_4 solution and 1 mL of 0.1 mol.L^{-1} $Ba(NO_3)_2$ solution. The precipitation of a white solid was instantaneous.

50 µL of supernatant was taken after centrifugation at 3500 rpm during 15 min for ICP-MS analyses to access the amount of ^{226}Ra precipitated as barite.

The precipitated was dried at 75°c during several hours until mass stabilization.

^{226}Ra reference material B

This reference material was created from an initial 2 mL ^{226}Ra solution of 8.8 kBq with 200 µL of a ^{232}Th solution of 0.001 mg.L^{-1}. To this mixture was added 1 mL of 0.1 mol.L^{-1} Na_2SO_4 solution and 1 mL of 0.1 mol.L^{-1} $Ba(NO_3)_2$ solution. Precipitation and validation process were the same as the precedent reference material.

Barite reference materials dopped with Pb

To study the effect of the $^{208}Pb^{18}O$ interference, three barite dopped with the following amount of Pb: 100 µg.g^{-1}, 1000 µg.g^{-1} and 10000 µg.g^{-1}, were synthetized with the same protocol previously presented using a Pb solution of 981 mg.L^{-1} instead of the ^{226}Ra and ^{232}Th solutions. Precipitation and validation process were the same as precedent reference materials.

Blank

The processus was also realized without any Ra elemental solution to obtain a blank. Precipitate from this process was conserved to ensure that the ^{226}Ra count detected by NanoSIMS is not influenced by other elements present in the barite.

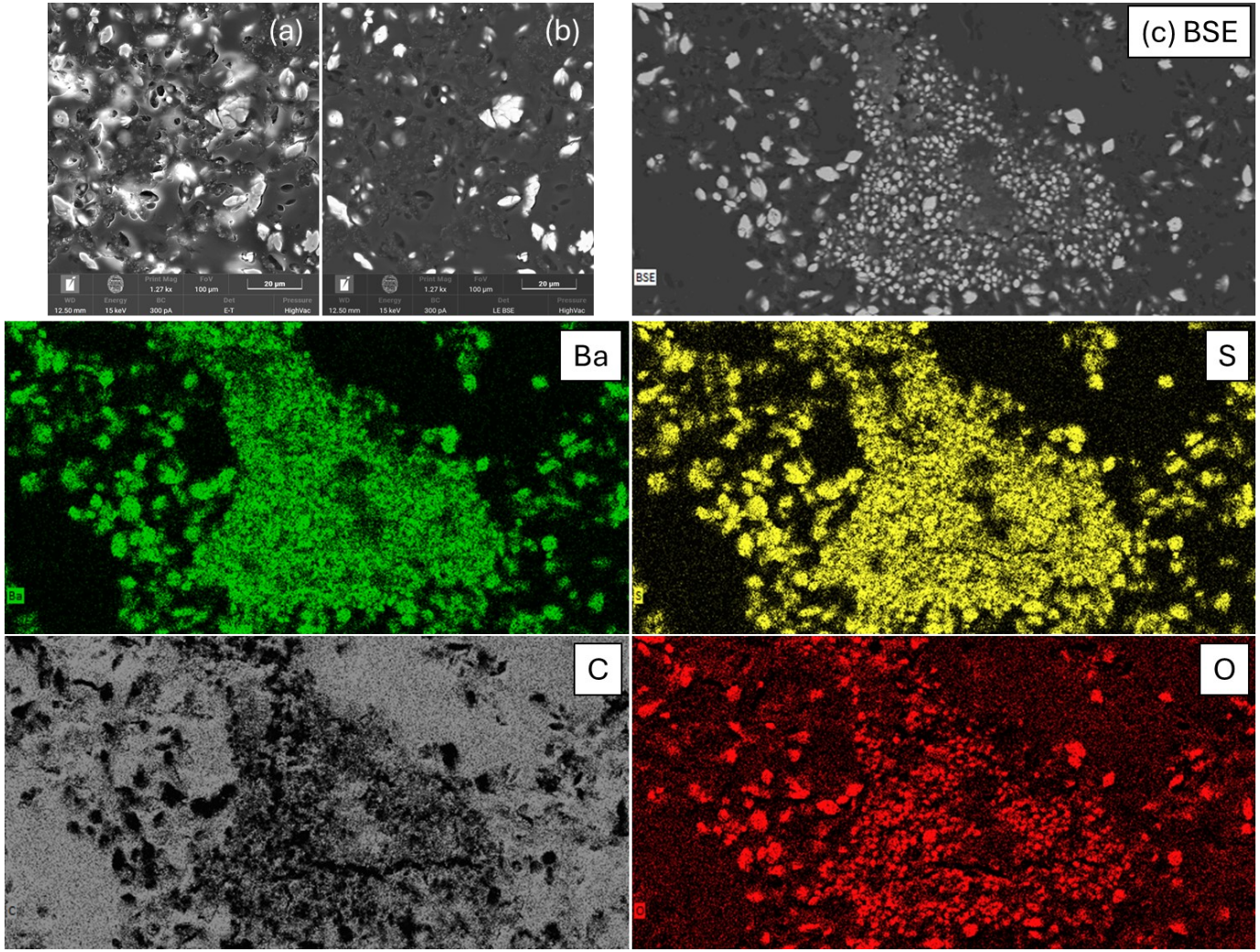
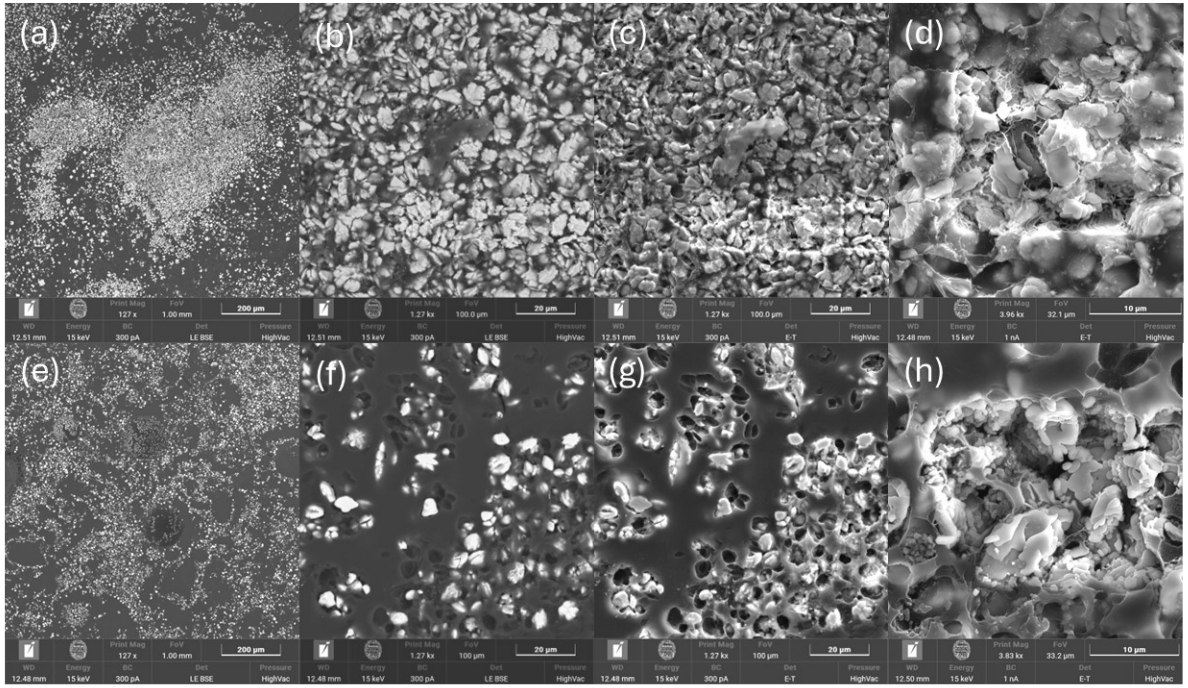


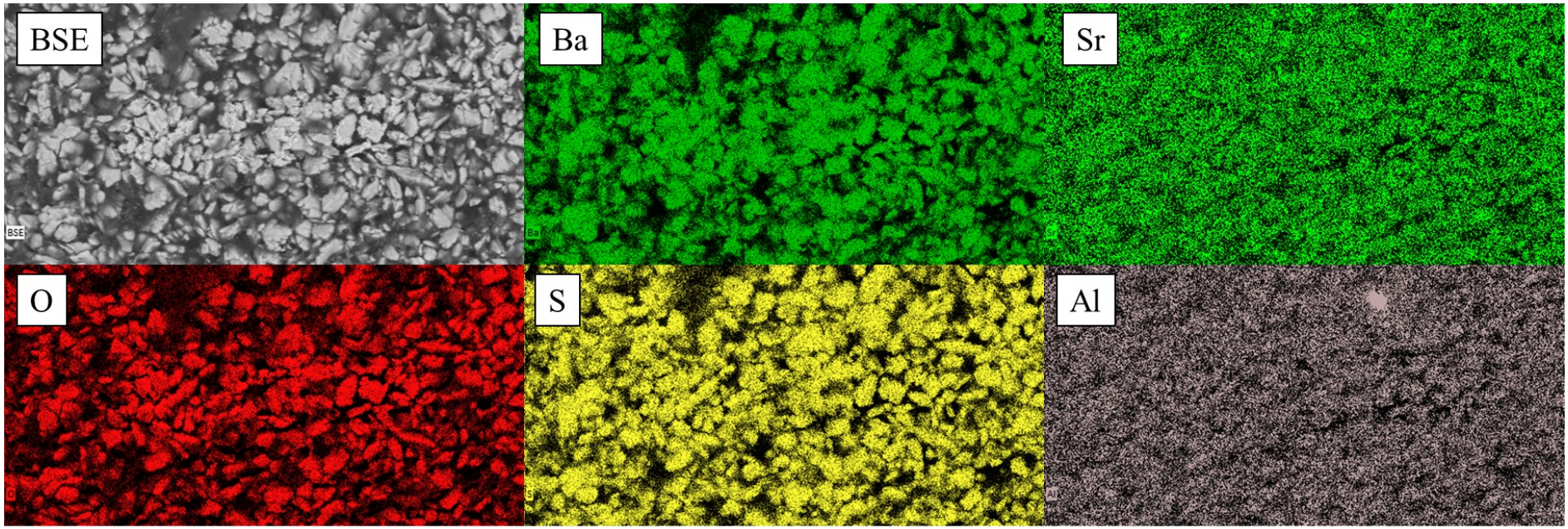
Figure SI-1: SEM images of blank synthetized material with (a) and (c) secondary electrons (SE) and (b) backscattered electrons (BSE) images of barite grains and elemental maps obtained with EDX analyzes of Ba, S, C and O.



	at%	O	S	Cl	Ba	Ba/S	
Blank	2	66.63	15.14	0.36	17.86	1.18	
	1	68.18	14.23	0.34	17.25	1.21	
	4	65.57	14.51	0	19.82	1.37	
	5	66.9	16.06	0	17.04	1.06	
	6	67.17	15.23	0.24	17.36	1.14	
	7	67.48	14.53	0.1	17.89	1.23	
	8	63.84	16.7	0.36	19.1	1.14	stdev
	avge	66.54	15.2	0.2	18.05	1.19	0.1
Reference material A – ^{226}Ra 2.89 µg.g^{-1}	nano	58.96	13.59	7.82	19.37		
	3	64.98	16.89	2.42	15.72	0.93	
	4	63.77	17.61	0.84	17.79	1.01	
	5	65.56	15.23	0.99	18.21	1.2	
	6	67.49	14.11	1.53	16.87	1.2	
	7	64.13	16.58	1.19	18.1	1.09	
	8	64.07	16.24	0.94	18.74	1.15	
	9	64.16	16.78	0.59	18.46	1.1	stdev
	avge	64.88	16.21	1.21	17.7	1.19	0.1
Reference material B – ^{226}Ra 9.65 µg.g^{-1}	nano	59.78	14.46	4.37	21.39		
	2	63.34	17	0.45	19.21	1.13	
	1	66.34	15.52	0.54	17.6	1.13	
	4	64.76	15.86	0.44	18.94	1.19	
	5	66	15.46	0.32	18.022	1.18	
	6	66.23	15.4	0.18	18.19	1.18	
	7	66.05	15.47	0.41	18.07	1.17	
	8	66.24	15.78	0.44	17.55	1.11	
	9	66.7	15.01	0.3	17.98	1.2	stdev
	avge	65.05	15.55	0.83	18.57	1.16	0.03

Figure SI-2: SEM (a), (c) et (d) SE and (b) BSE images of reference material A with 2.89 µg.g^{-1} of ^{226}Ra and SEM (e), (g) and (h) SE and (f) BSE images of reference material B with 9.65 µg.g^{-1} of ^{226}Ra, with table results of O, S, Cl and Ba (at%) beside obtain from some area analyzed of the blank and reference material A and B. SE images (d) and (h) show area analyzed by NanoSIMS.

Reference material A - barite with 2.89 µg.g^{-1}



Reference material B - barite with 9.65 µg.g^{-1}

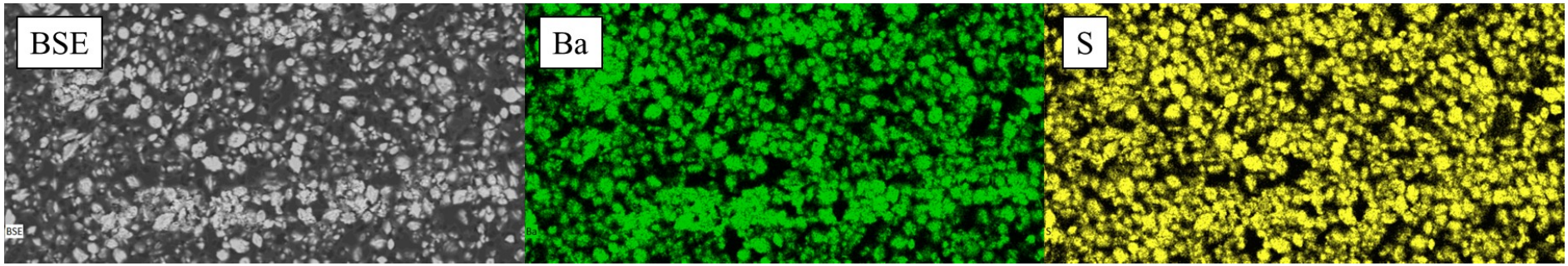


Figure SI-3: SEM BSE and Ba, Sr, O, S and Al elemental images of reference material A with 2.89 µg.g^{-1} of ^{226}Ra and SEM BSE and Ba, and S elemental images of reference material B with 9.65 µg.g^{-1}. In these areas, some of NanoSIMS images presented in the paper were acquired.

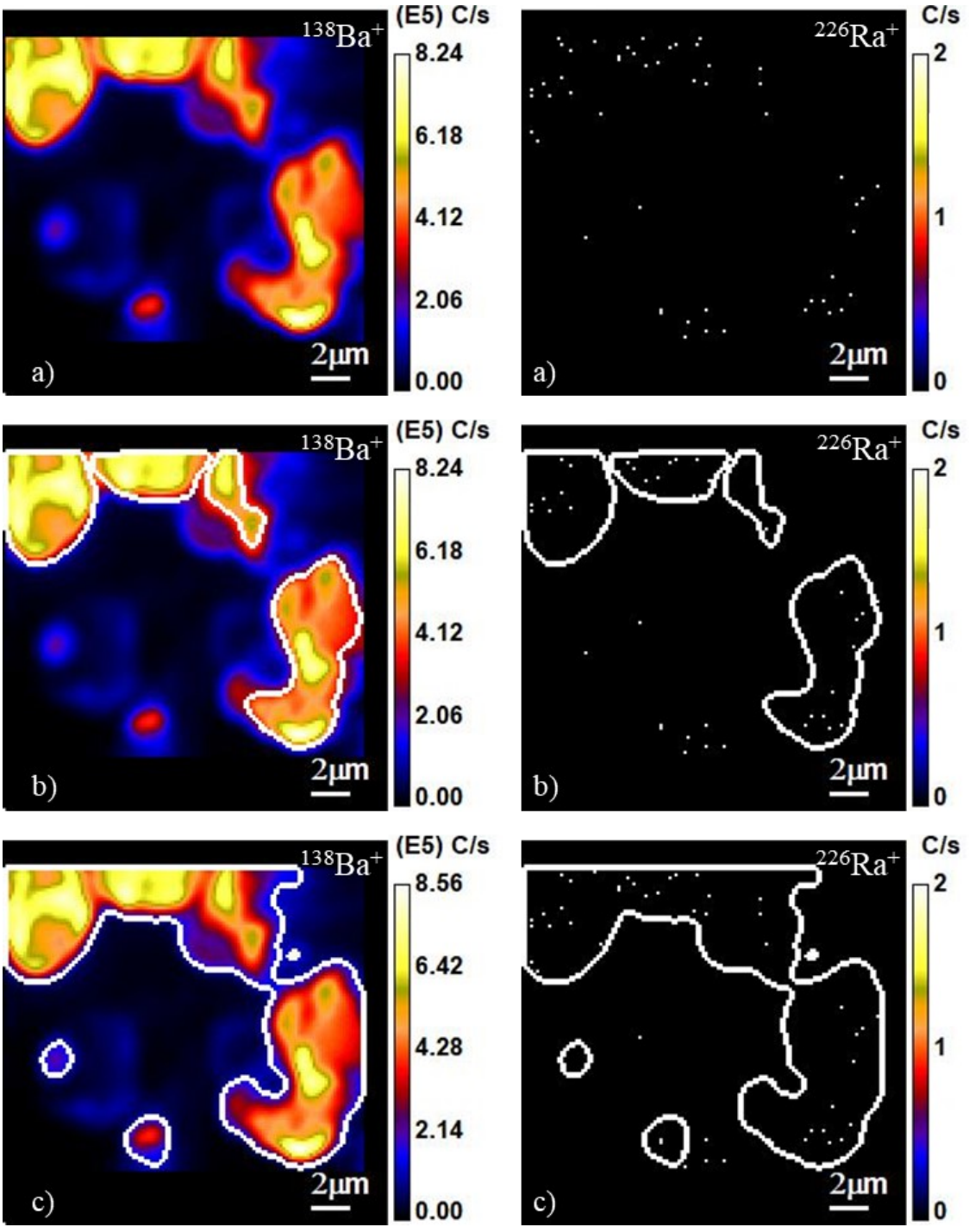


Figure SI-4: a) NanoSIMS images obtain of ^{138}Ba and ^{226}Ra for the blank (barite synthetized without addition of ^{226}Ra), in white line : b) "grain" ROI delimitation and c) "bulk" ROI delimitation.

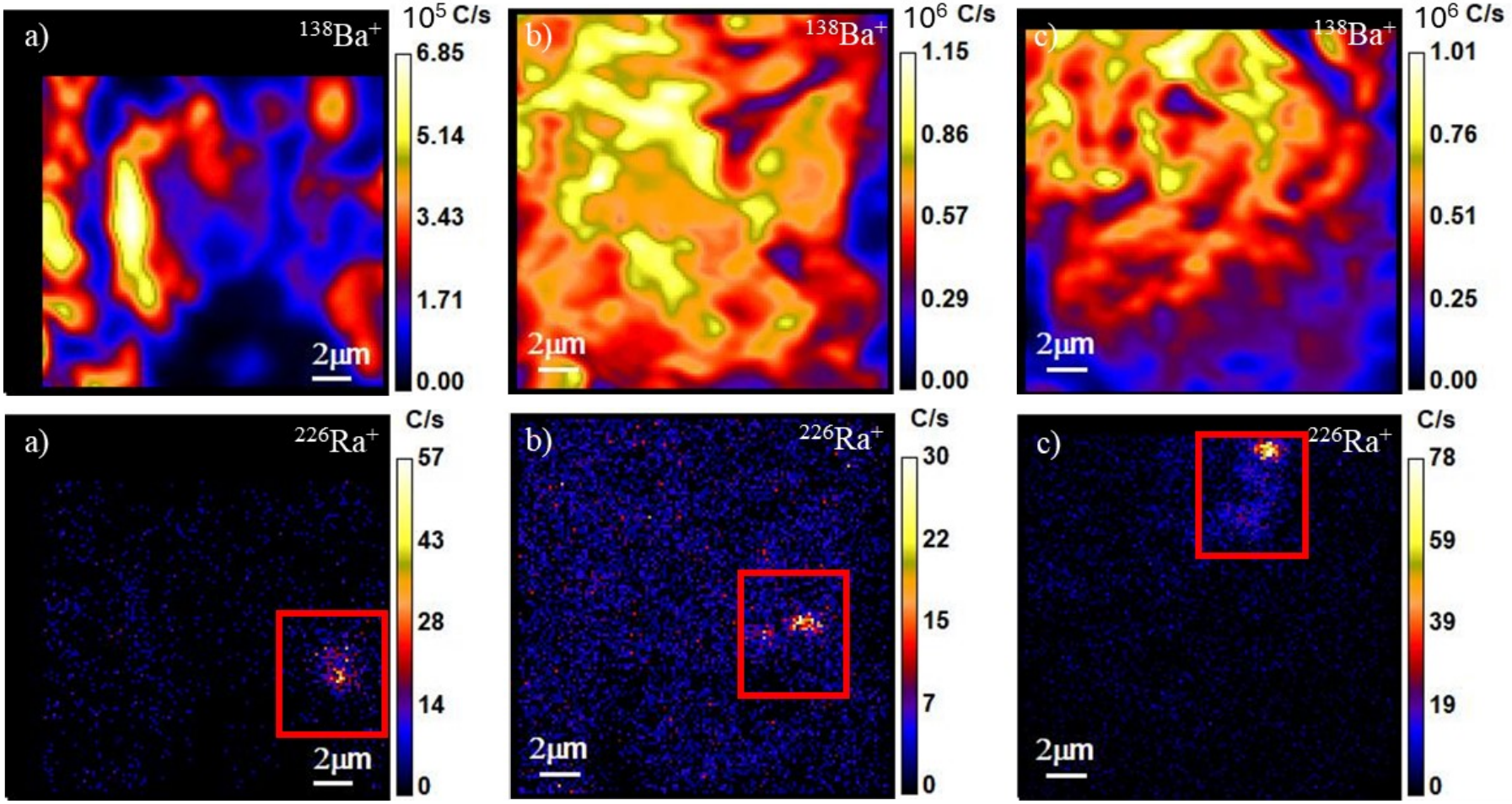


Figure SI-5: NanoSIMS image of the inhomogeneity observed for reference material A with 2.89 µg.g^{-1} of ^{226}Ra, with a) b) and c) three different area analyzed of the solid.

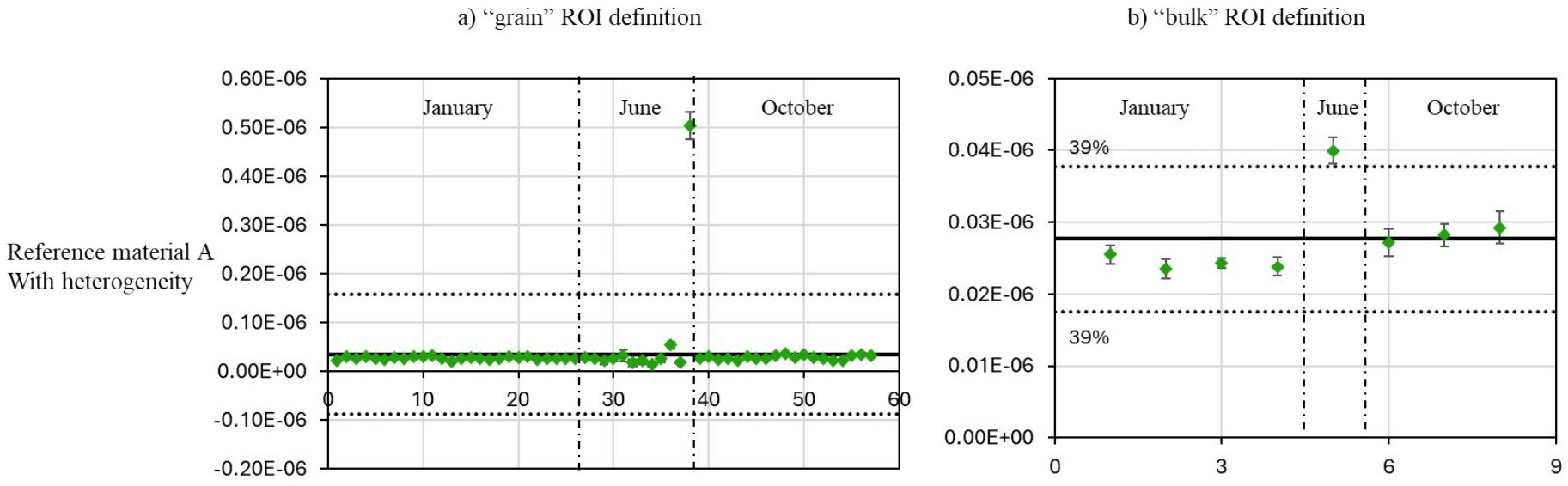


Figure SI 6: $^{226}Ra^{+}/^{138}Ba^{+}$ ratio calculated for reference material A including the heterogeneity observed in Figure SI-3 with a) the grain ROI definition and b) the bulk ROI definition along the session of January, June and October of 2024. The black lines are the mean values while dotted lines present the relative reference material deviation (2 sd) in % associated

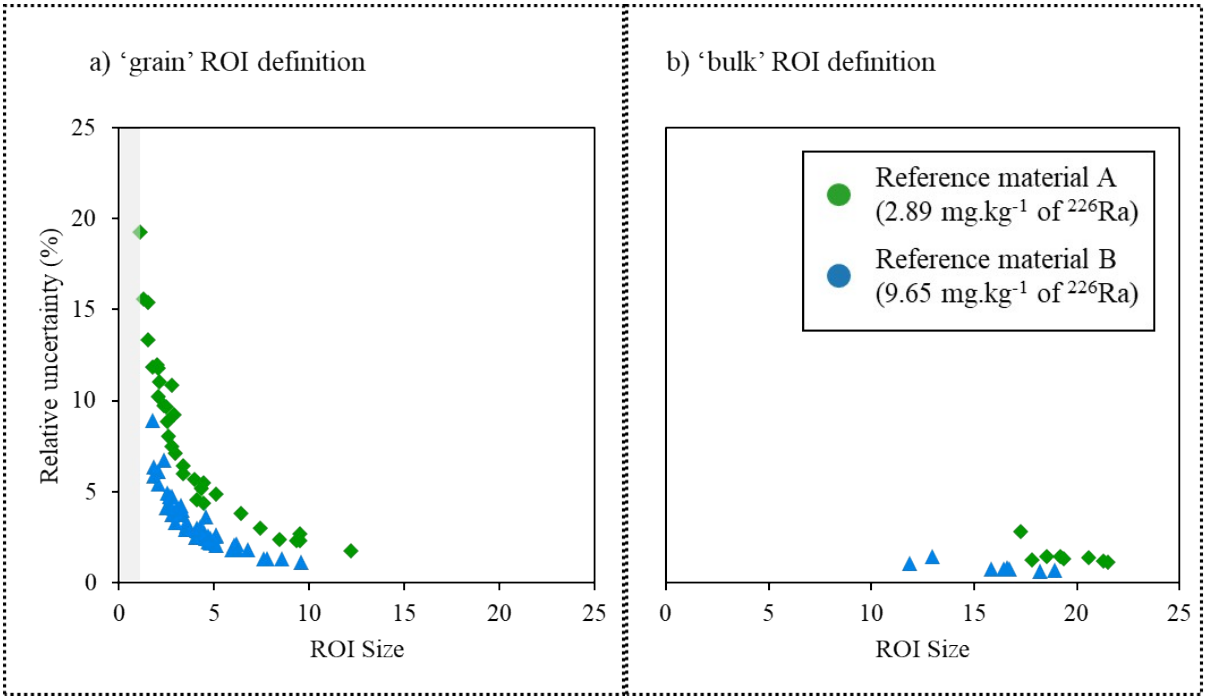


Figure SI-7: Relative uncertainty (%) associated to $^{226}Ra^{+}/^{138}Ba^{+}$ ratio estimated using ROI selected (a) by "grain" method (Figure 3-(1), Figure SI-2-b), or (b) by "bulk" method (Figure 3-(2), Figure SI-2-c), depending on ROI size (in equivalent diameter - µm²) for the two reference materials A and B.

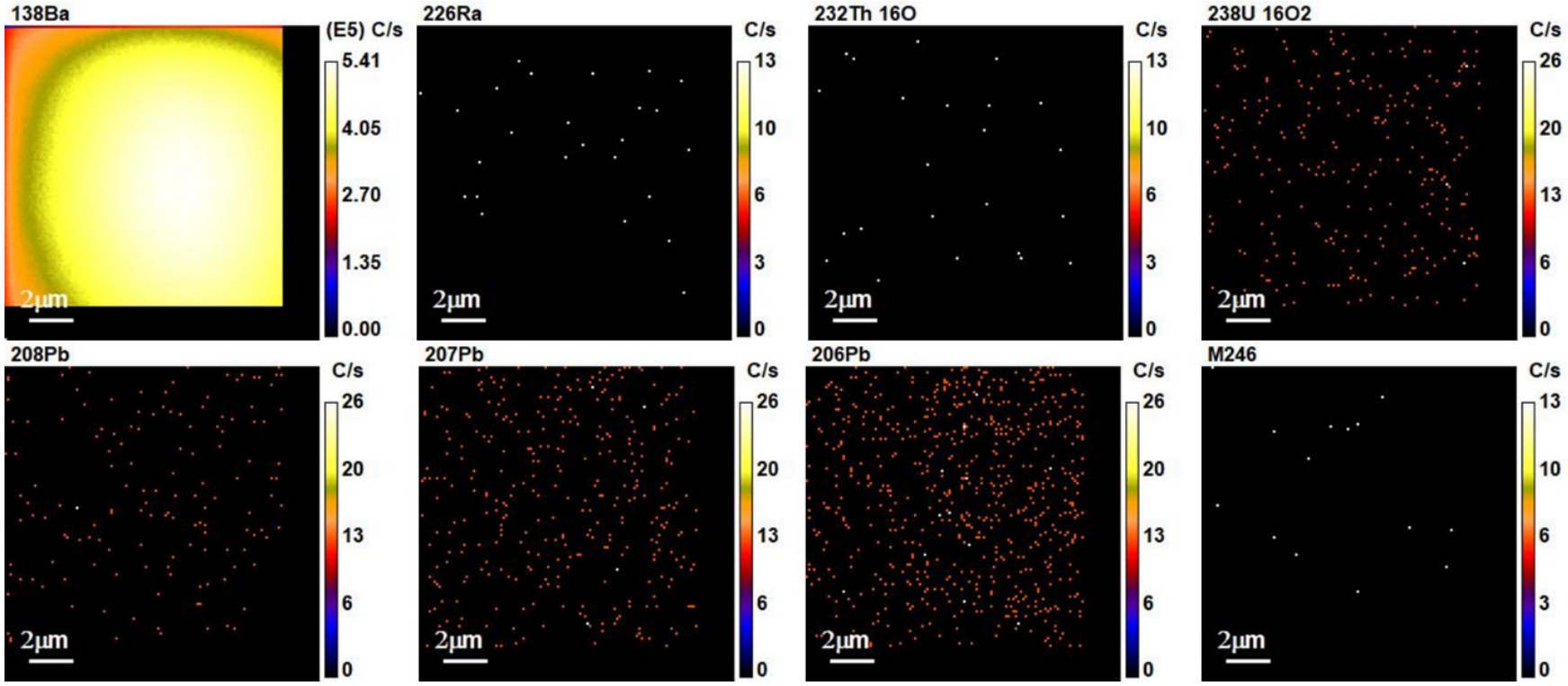


Figure SI-8: NanoSIMS images obtain of ^{138}Ba, ^{226}Ra, ^{232}Th, ^{238}U, ^{208}Pb, ^{207}Pb, ^{206}Pb, and ^{230}Th for the natural barite from Le Maine.