Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Table S1: Summary of chemical separation procedures

First column	based on Mortlock et al. (2005)	Ra column I	based on Koornneef et al. (2010)
resin volume	AG 1-X8 1 ml	resin volume	AG 50W-X8 20 ml
clean resin	4 CV 7N HNO_3 2 CV 0.1N HCl 2 CV 12N HCl 2 CV 0.13N HF in 12N HCl 2 CV H_2O repeat all 5 steps	clean resin	1 CV 6N HCl 2 ml H_2O 1 CV 7N HNO_3 1 CV 0.25N HNO_3
		condition with	2.5 CV 6N HCl
condition with	6 CV 7N HNO_3	load sample in	2 CV 6N HCl
load sample in	1 CV 7N HNO_3	wash with	55 ml 6N HCl 4 ml H_2O
elute Ra (+Ba and matrix)	3 CV 7N HNO_3 clean beaker with first CV	elute Ra (+Ba)	1 CV 7N HNO_3
elute Th	6 CV 12N HCl added dropwise	Ra column II	based on Koornneef et al. (2010)
elute Pa	5 CV 0.13N HF in 12N HCl added dropwise	resin volume	AG 50W-X8 10 ml
elute U	5 CV 1N HBr	clean resin	1 CV 6N HCl 2 ml H_2O 1 CV 7N HNO_3 1 CV 0.25N HNO_3
Th column	based on Mortlock et al. (2005)	condition with	2 CV 6N HCl
resin volume	same same	load sample in	0.5 CV 6N HCl
clean resin	4 CV 7N HNO_3 2 CV 0.1N HCl 2 CV 12N HCl 2 CV 0.13N HF in 12N HCl 2 CV H_2O repeat all 5 steps	wash with	6 CV 6N HCl
		elute Ra (+Ba)	9 CV 6N HCl
		Ra-Ba column	based on Koornneef et al. (2010)
condition with	6 CV 7N HNO_3	resin volume	Sr-Spec + Prefilter 1 ml
load sample in	1 CV 7N HNO_3	clean resin	0.1N H_2O 1 CV 3N HNO_3
wash with	3 CV 7N HNO_3	condition with	10 CV 3N HNO_3
elute Th	3 CV 6N HCl	load sample in	0.5 CV 3N HNO_3
Pa column	based on Mortlock et al. (2005)	wash with	1 CV 3N HNO_3
resin volume	same same	elute Ra	2 CV 3N HNO_3

clean resin	4 CV 7N HNO_3 2 CV 0.1N HCl 2 CV 12N HCl 2 CV 0.13N HF in 12N HCl 2 CV H_2O repeat all 5 steps	wash resin with	4x10 CV 3N HNO_3
condition with	6 CV 12N HCl	condition with	10 CV 3N HNO_3
load sample in	1 CV 12N HCl	load sample in	0.5 CV 3N HNO_3
wash with	5 CV 12N HCl	wash with	1 CV 3N HNO_3
elute Pa	5 CV 12N HCl + HF	elute Ra	2 CV 3N HNO_3

Table S2: Cup configurations used for mass spectrometric analyses

	H2	H1	Ax	L1	L2	IC0	L3	IC1	# of cycles
U		238		236	235	234			50
	238		236	235		233			50
Th			232			229			50/40
				232		230			50/40
Th Tailing				232		230			10
						230.5			10
						229.5			10
						228.5			10
Pa						233	232	231	60
Pa Tailing						233	232	231	5
						233.5		231.5	5
						232.5		230.5	5
Ra						228		226	60

Table S3: Uncertainties of the various ratios based on the propagation of all errors vs. the reproducibility of these ratios determined by the 1σ standard deviation

	uncertainty of the individual ratios (2σ standard error including propagation of errors from all corrections (for Pa quoted for each individual set)	reproducibility for each individual data set (1σ RSD)	reproducibility of all values (1σ RSD)
Natural-to-spike ratios WM1			
$^{231}Pa/^{233}Pa$	0.86 %	1.44 %	
	0.82 %	0.60 %	
	0.78 %	3.37 %	
	0.83 %	3.65 %	
$^{226}Ra/^{228}Ra$	35.58 %	4.56 %	4.25 %
		2.13 %	
		3.16 %	
		4.53 %	
$^{230}Th/^{229}Th$	0.33 %	0.24 %	0.22 %
		0.16 %	
		0.23 %	
		0.18 %	
$^{232}Th/^{229}Th$	43.92 %	4.41 %	8.95 %
		4.05 %	
		2.88 %	
		2.97 %	
$^{234}U/^{236}U$	0.17 %	0.12 %	0.19 %
		0.21 %	
		0.11 %	
		0.12 %	
Spike ratios:			
$^{229}Th/^{236}U$	0.35 %	0.20 %	0.27 %
		0.17 %	
		0.19 %	
		0.13 %	
$^{233}Pa/^{236}U$	0.95 %	1.47 %	
	0.86 %	0.59 %	
	0.78 %	3.54 %	
	0.84 %	4.02 %	
$^{228}Ra/^{236}U$	35.8 %	4.8 %	4.2 %
		2.3 %	
		3.1 %	
		4.5 %	

Isotope ratios BON:			
$^{234}U/^{238}U$	0.23 %		0.08 %
$^{230}Th/^{238}U$	0.63 %		0.39 %
$^{231}Pa/^{235}U$	2.23 %		1.21 %
$^{226}Ra/^{230}Th$	69.9 %		3.40 %
Isotope ratios AQB:			
$^{234}U/^{238}U$	0.27 %		
$^{230}Th/^{238}U$	0.62 %		
$^{231}Pa/^{235}U$	1.64 %		
	0.69%		
	2.73 %		
	2.96%		
$^{226}Ra/^{230}Th$	6.58 %		

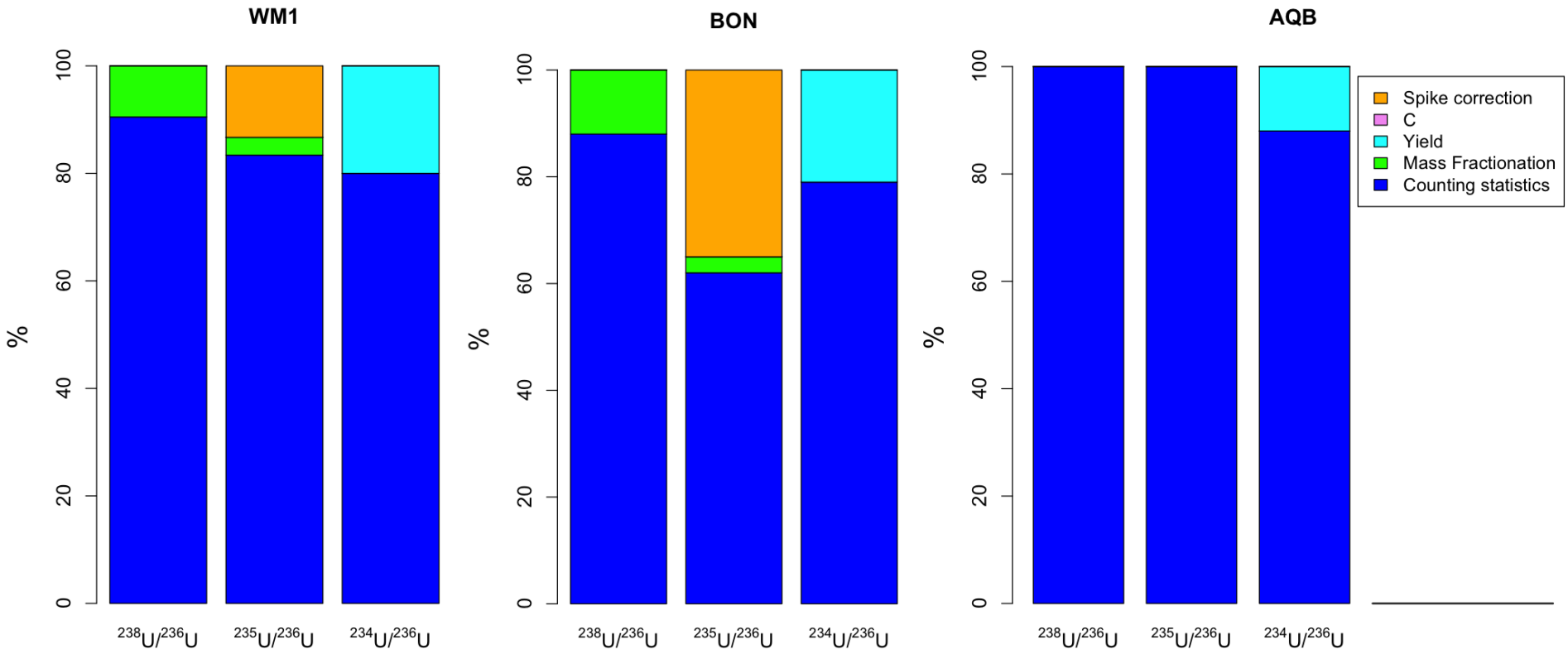

Figure S1: Error contributions of the different corrections on the final U isotope ratios for WM1, BON-5-A and AQB samples.

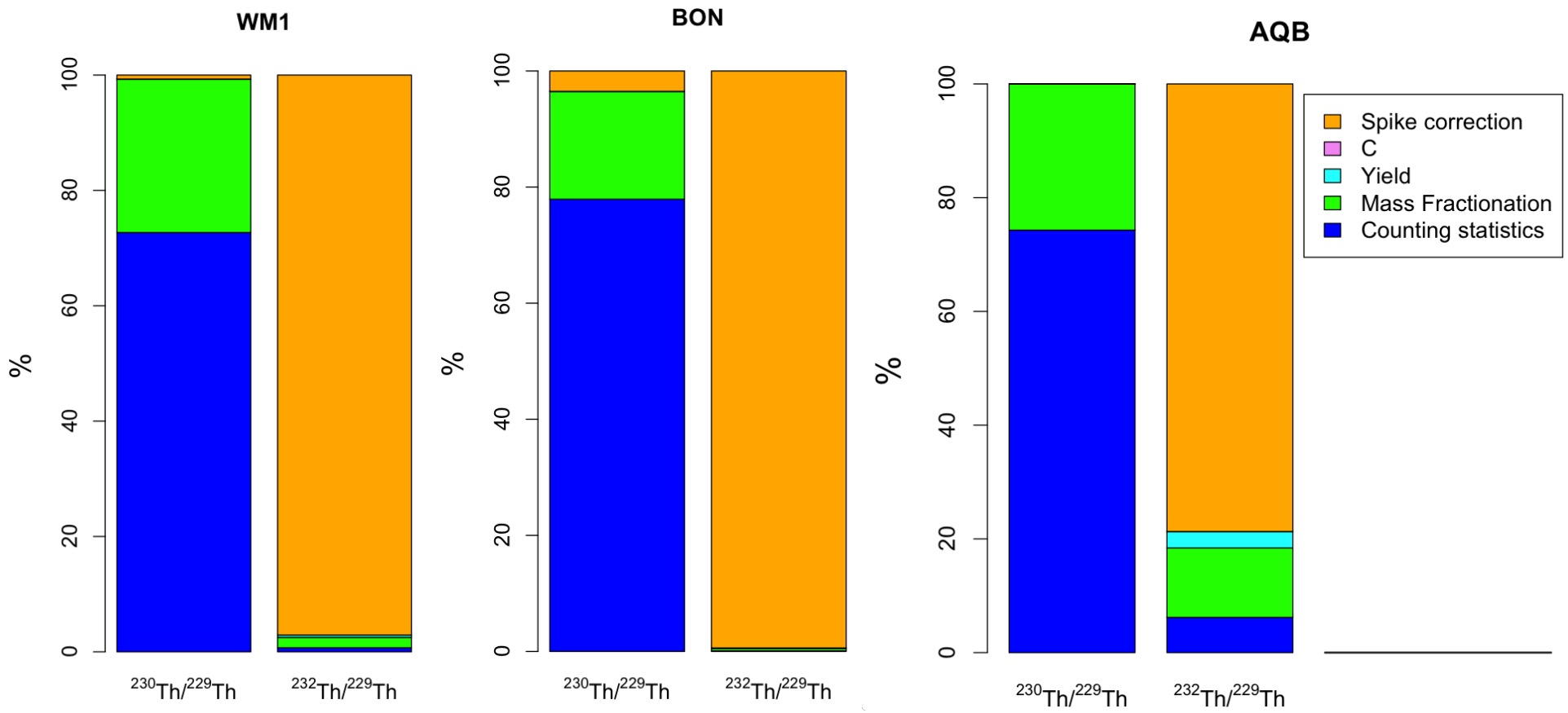

Figure S2: Error contributions of the different corrections on the final Th isotope ratios for WM1, BON-5-A and AQB samples.

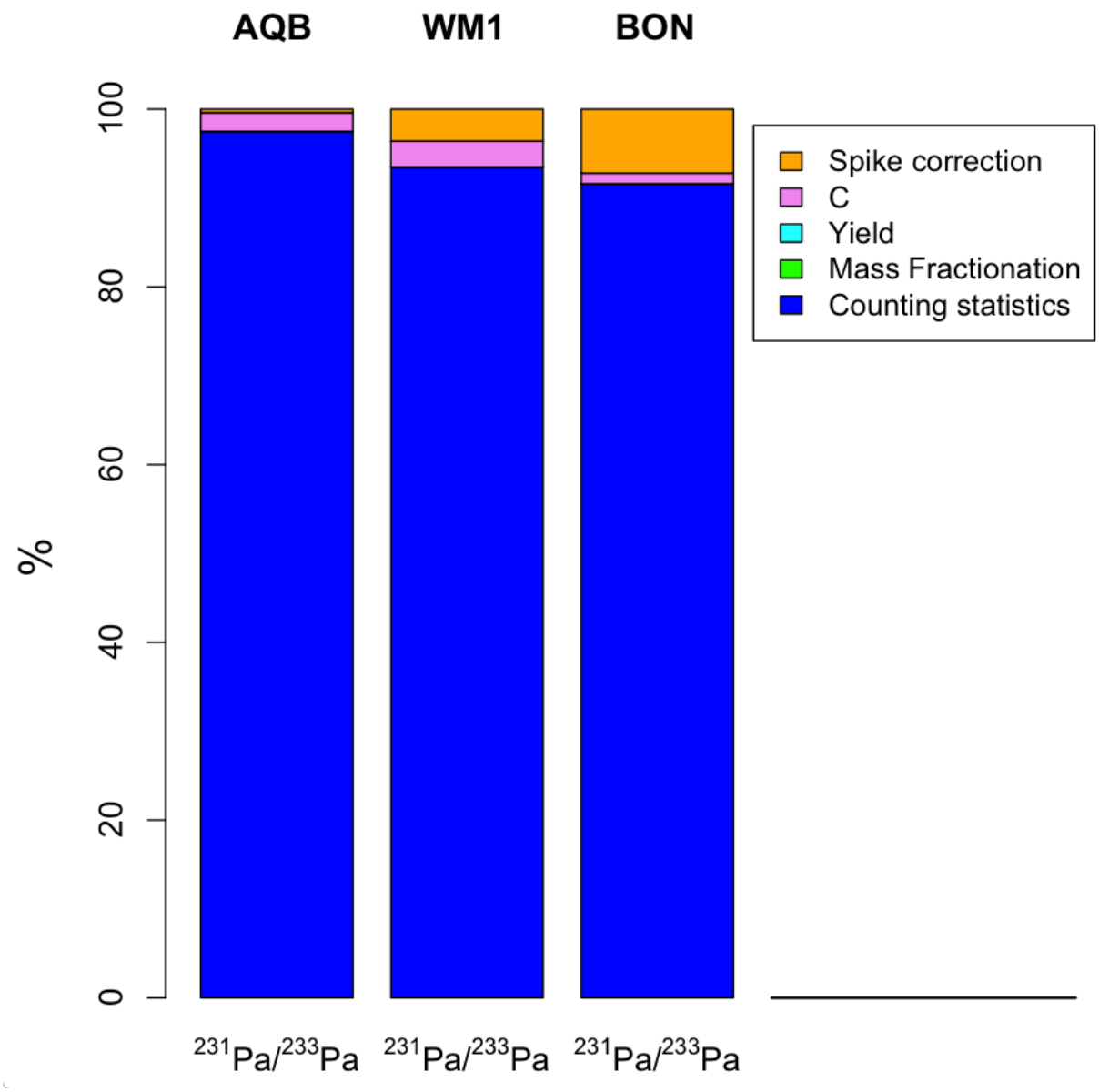

Figure S3: Error contributions of the different corrections on the final Pa isotope ratios for AQB, WM1, and BON-5-A samples.

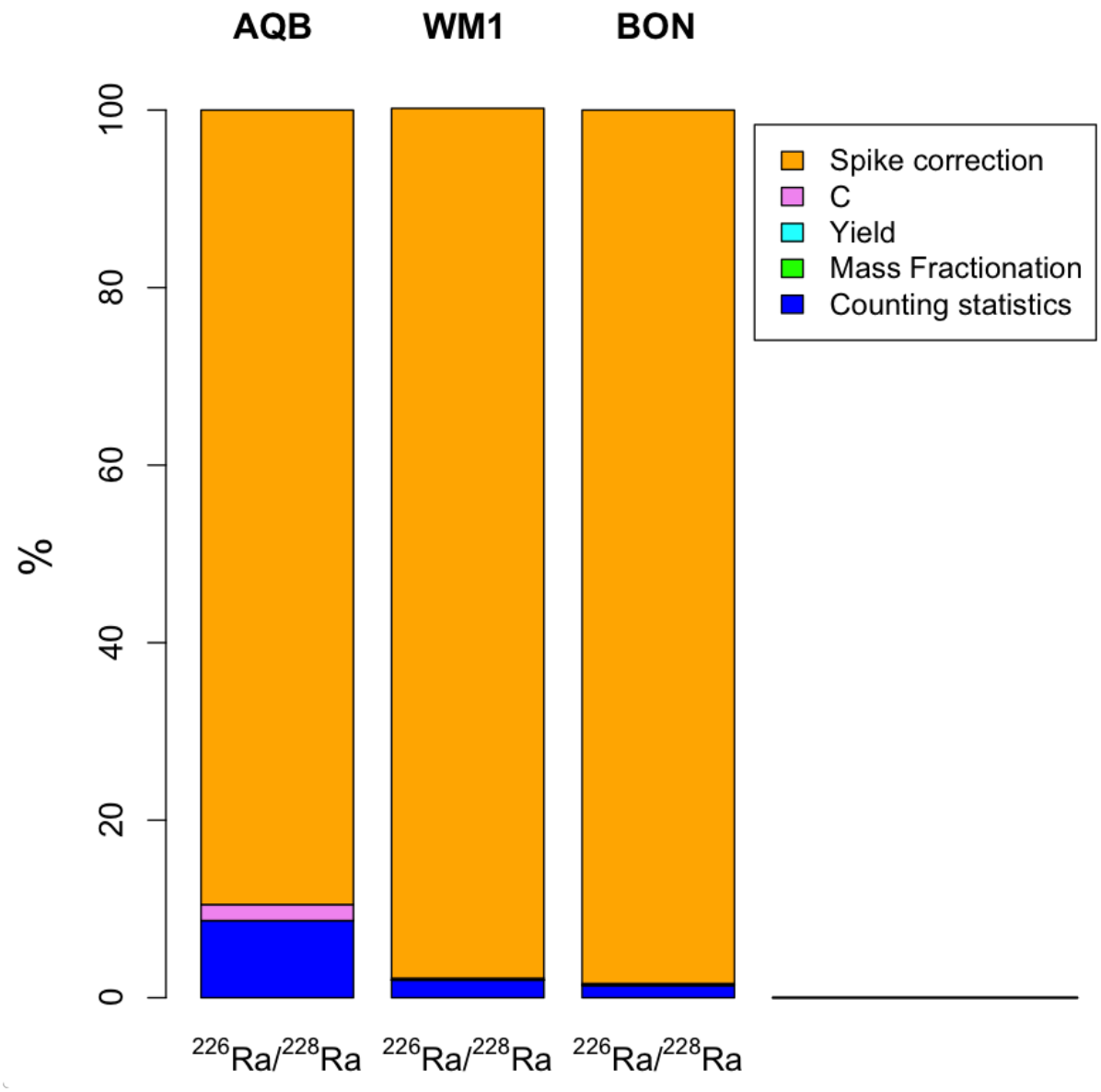

Figure S4: Error contributions of the different corrections on the final Ra isotope ratios for AQB, WM1, and BON-5-A samples.

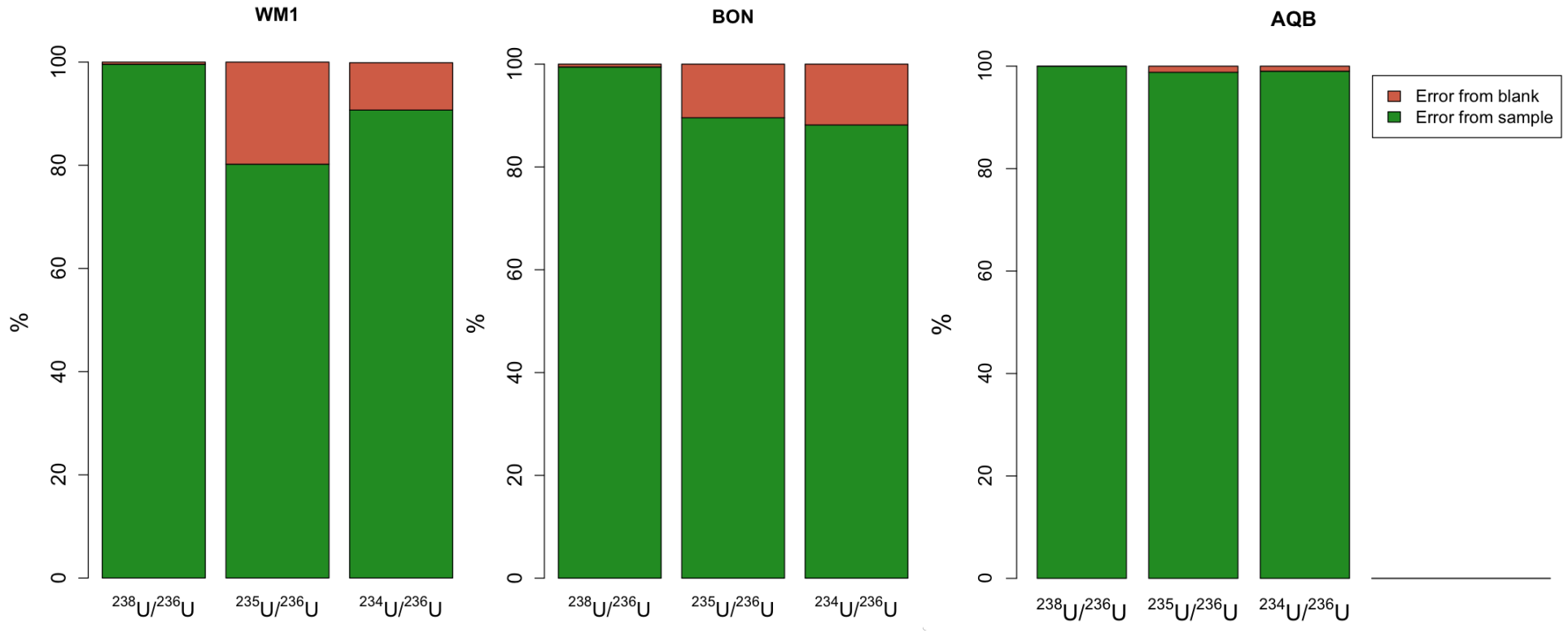

Figure S5: Error contributions of the blank and sample ratios on the blank corrected U isotope ratios for WM1, BON-5-A and AQB samples.

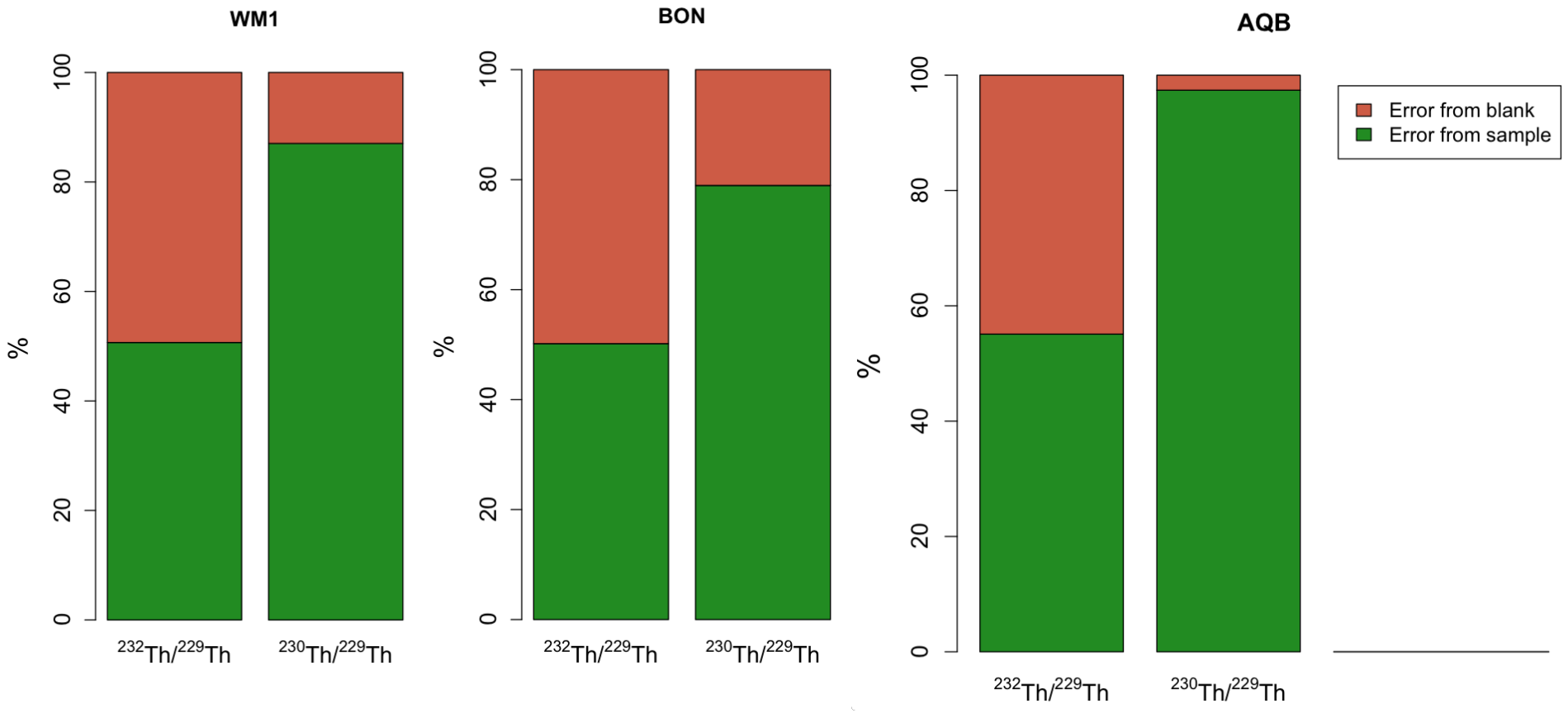

Figure S6: Error contributions of the blank and sample ratios on the blank corrected Th isotope ratios for WM1, BON-5-A and AQB samples.

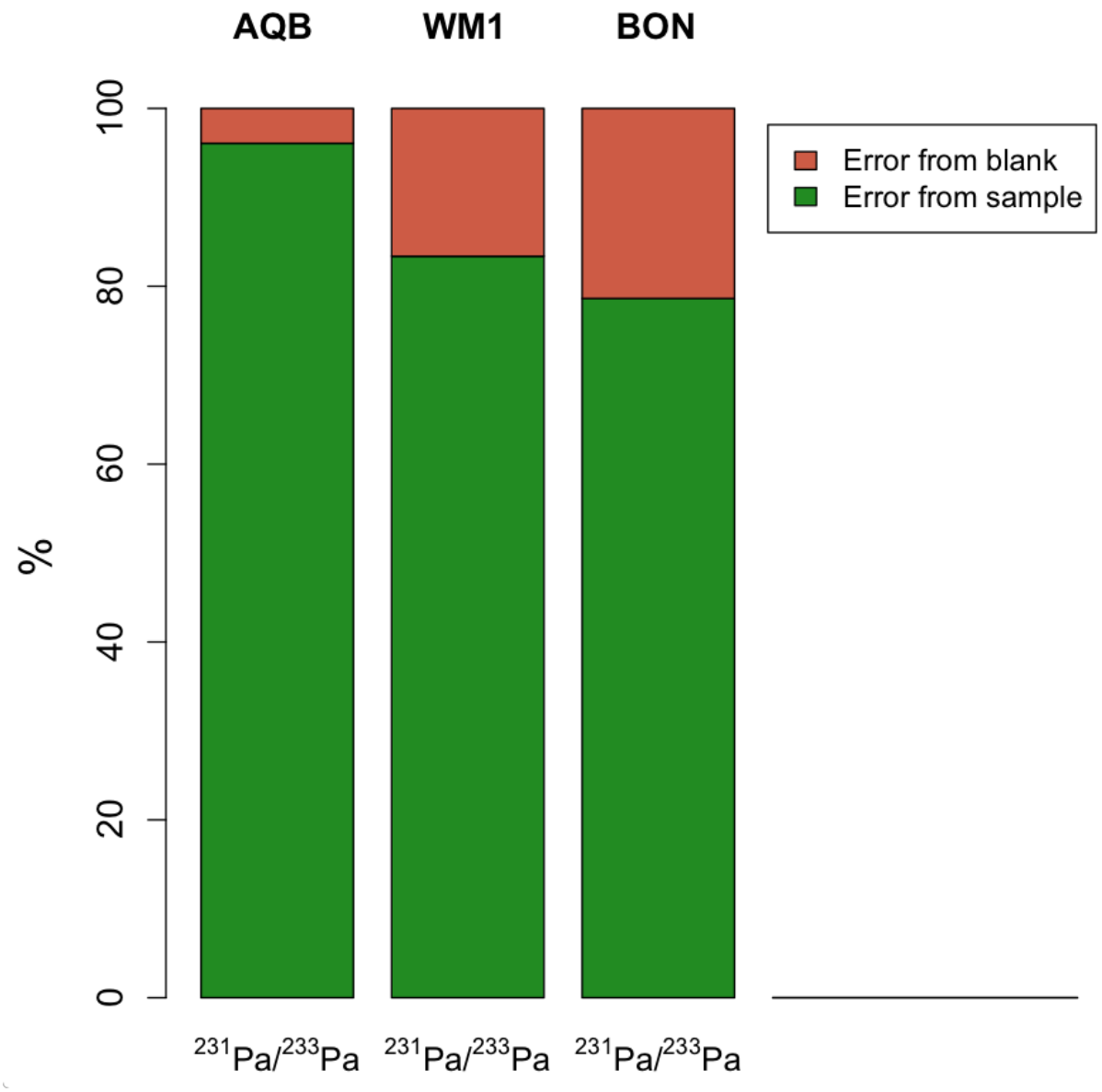

Figure S7: Error contributions of the blank and sample ratios of the blank corrected Pa ratios of AQB, WM1 and BON-5-A samples.

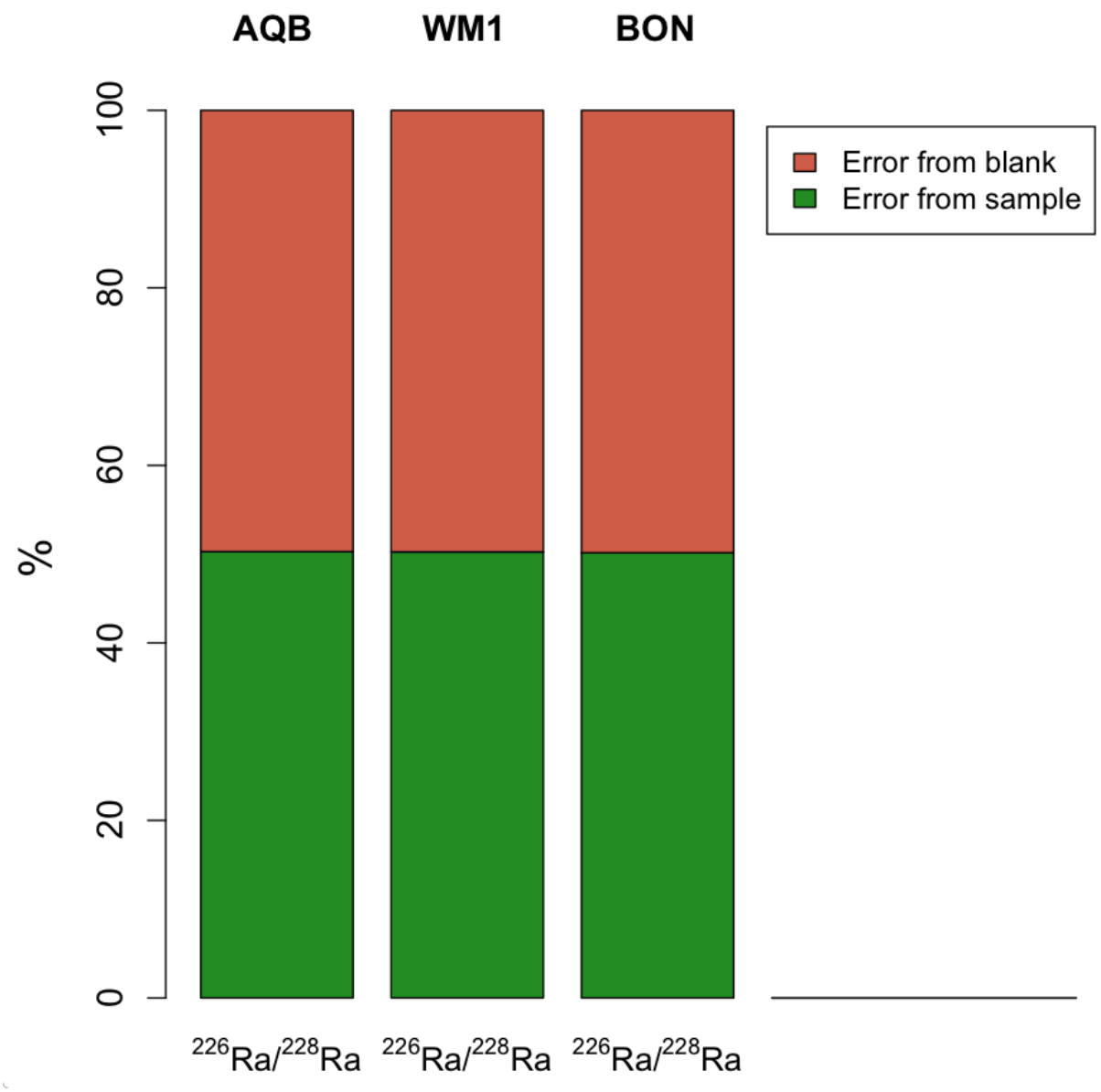

Figure S8: Error contributions of the blank and sample ratios of the blank corrected Ra ratios of AQB, WM1 and BON-5-A samples.

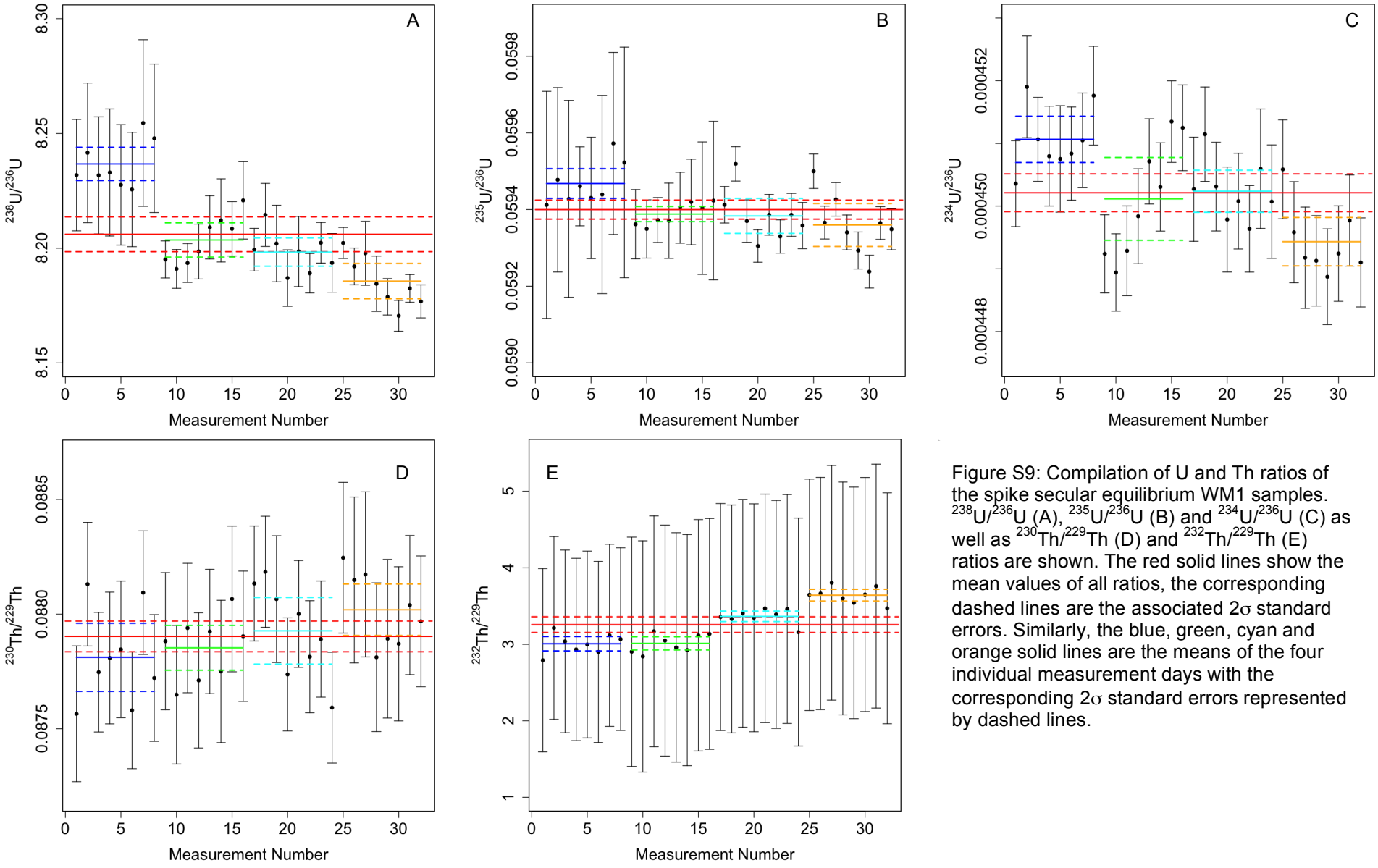

Figure S9: Compilation of U and Th ratios of the spike secular equilibrium WM1 samples. $^{238}U/^{236}U$ (A), $^{235}U/^{236}U$ (B) and $^{234}U/^{236}U$ (C) as well as $^{230}Th/^{229}Th$ (D) and $^{232}Th/^{229}Th$ (E) ratios are shown. The red solid lines show the mean values of all ratios, the corresponding dashed lines are the associated 2σ standard errors. Similarly, the blue, green, cyan and orange solid lines are the means of the four individual measurement days with the corresponding 2σ standard errors represented by dashed lines.

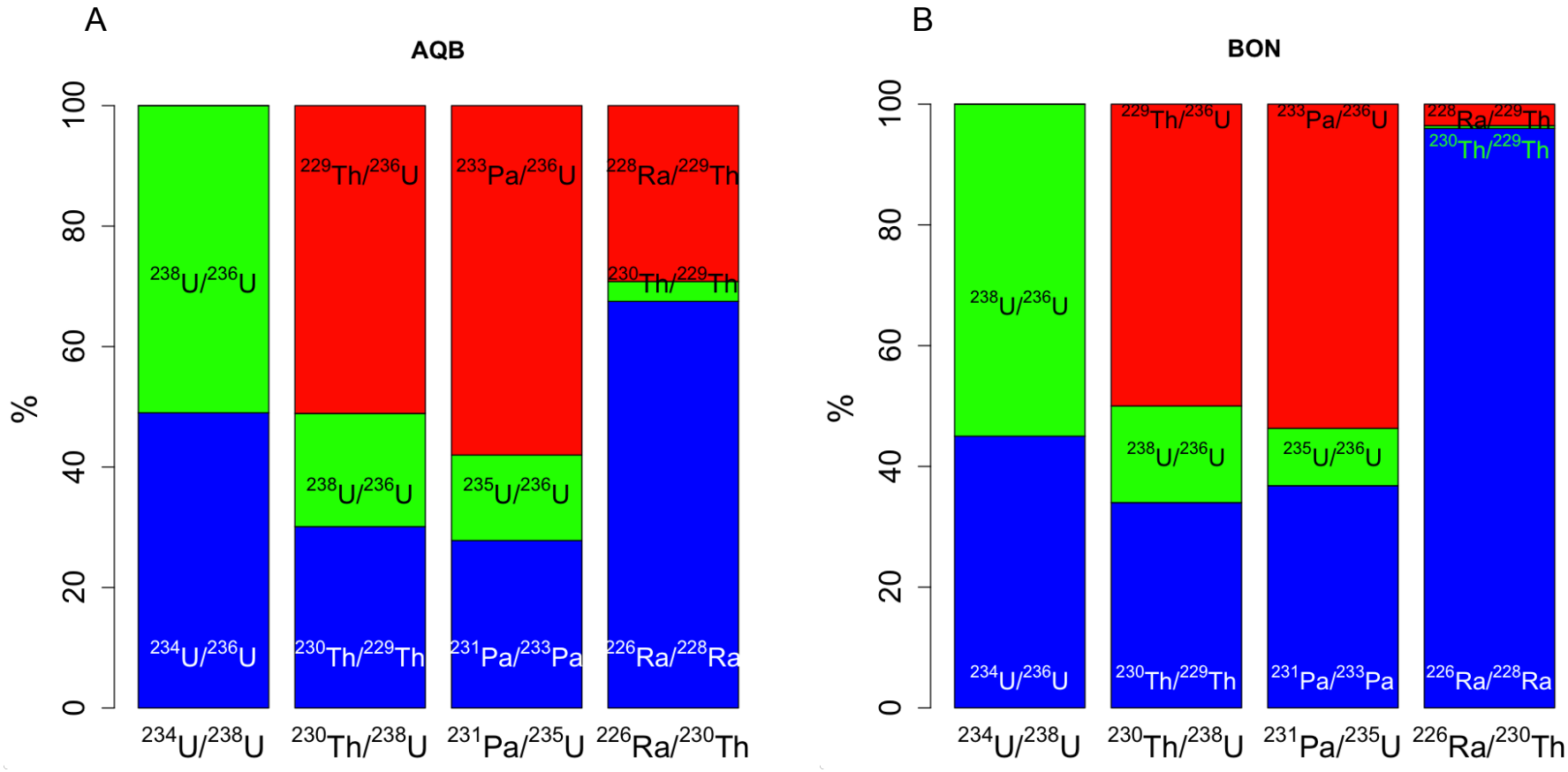

Figure S10: Compilation of the contributions of the uncertainties of the different isotope ratios used to calculate final isotope ratios to the total uncertainty of the coral AQB (A) and BON-5-A (B) samples.