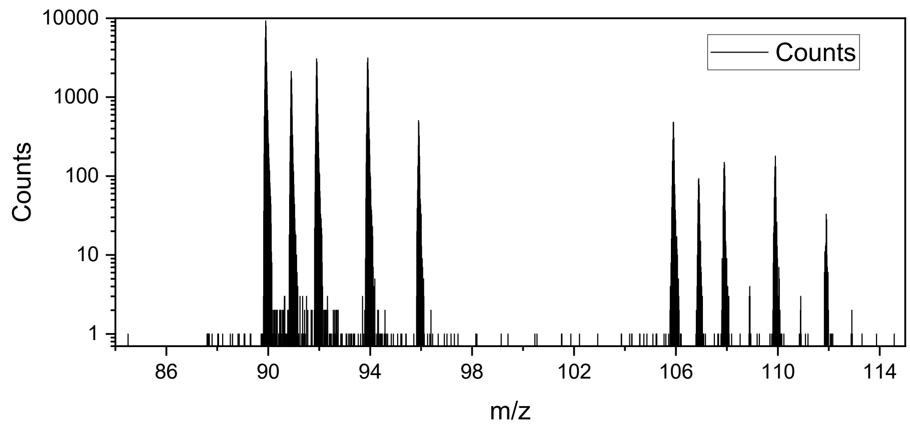
Supplementary Information

SI-Table 1: Resonant excess between Zr lasers on- and off-resonance of sample A-40 from Figure 6

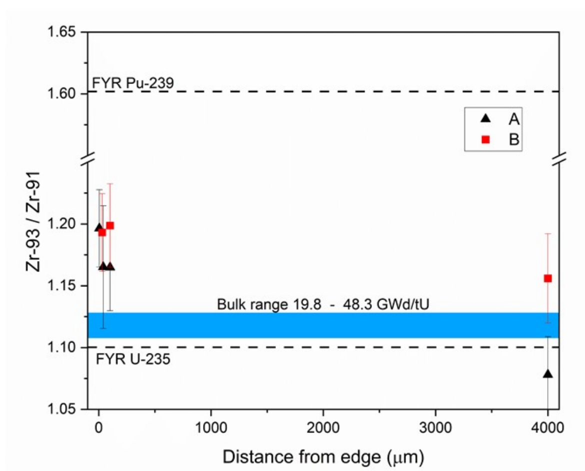
Mass	88	90	91	92	93	94	96	99
Resonant counts	185	1055	1515	1549	1766	1759	1867	555
Detuned counts	184	83	17	14	8	18	11	430

SI-Table 2: Measured Zr isotopic ratios with 1 sigma uncertainties

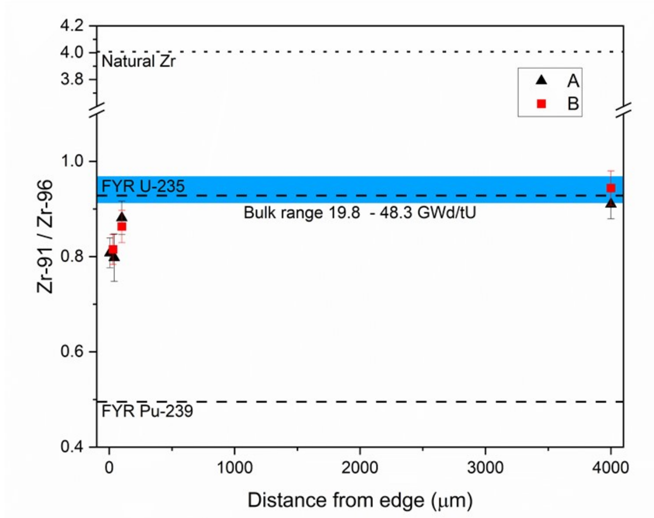
Sample	Distance to edge in µm	Zr-93/Zr-91	1σ (Zr-93/Zr-91)	Zr-94/Zr-91	1σ (Zr-94/Zr-91)	Zr-96/Zr-91	1σ (Zr-96/Zr-91)
A-5	5	1.196	0.017	1.203	0.018	1.237	0.024
A-40	40	1.165	0.033	1.195	0.034	1.253	0.039
A-100	100	1.164	0.019	1.138	0.019	1.133	0.023
A-4000	4000	1.078	0.016	1.138	0.017	1.099	0.019
B-30	30	1.193	0.017	1.211	0.018	1.226	0.024
B-100	100	1.198	0.019	1.149	0.019	1.159	0.023
B-4000	4000	1.156	0.017	1.086	0.017	1.059	0.020



SI-Figure 1: Mass spectra of natural Zr metal. No other peaks are visible besides the Zr elemental and oxide species. Some molecules with very strong bonds like ZrO may survive the sputtering process intact. The ionization potential of ZrO is 5.8(2) eV, which is lower than that of atomic Zr (6.6 eV), so the two photons have more than enough energy to ionize it. The required energy is further lowered because molecules exit the surface with rotational and vibrational (and perhaps electronic) energy due to the sputtering process. Metal monoxides have twice as many electronic energy levels as the metal atoms from which they are derived, and each level has many associated rotational and vibrational levels, leading to a much greater number of possible transitions and thus more likelihood of absorbing laser photons. For this reason, ionization due to molecular absorption is often observed in RIMS spectra.



SI-Figure 2: Measured $^{93}Zr/^{91}Zr$ ratios as a function of distance from the pellet edge. The blue band shows the range of $^{91}Zr/^{96}Zr$ ratios measured in bulk sample with burnups ranging from 19.8 to 48.3 GWd/tU. Uncertainties on data points are 2σ. The ratio shifts from that expected from ^{235}U fission (FYR U-235, lower dashed line) towards the ratio expected from ^{239}Pu (FYR Pu-239, upper dashed line). While the ^{93}Zr counts in this work could not be corrected for bias due to laser fractionation the expected overestimation of around 4% is neglectable. The bulk $^{93}Zr/^{91}Zr$ ratios remain intermediate between the center and edge samples measured by RIMS. Natural Zr is missing the anthropogenic ^{93}Zr and an influx from the cladding would lower the $^{93}Zr/^{91}Zr$ ratio at the edge, rather than raise it as seen here.



SI-Figure 3: Measured $^{91}Zr/^{96}Zr$ ratios as a function of distance from the pellet edge. The ratio shifts from that expected from ^{235}U fission (FYR U-235, upper dashed line) towards the ratio expected from ^{239}Pu (FYR Pu-239, lower dashed line). The ratio of natural Zr (4.01(3)) is much higher. Therefore, any significant influence of the Zr cladding would shift the ratio upwards instead of down. The blue band shows the range of $^{91}Zr/^{96}Zr$ ratios measured in bulk sample with burnups ranging from 19.8 to 48.3 GWd/tU. Uncertainties on data points are 2σ.