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Supplemental information for Classification of Zirconium-Rich Engineered and Natural Nano Particles using Single Particle ICP-TOFMS

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ICP Parameters						
Nebulizer gas	0.68 L min ⁻¹					
Auxillary gas	1.48 L min ⁻¹					
Cool gas	13 L min ⁻¹					
RF power	1550 W					
Sampling depth	4.9 mm					
Torch/Injector	iCAP Q Quartz torch with 2.5 mm					
	quartz injector					
Skimmer/sampler cone	iCAP Q Nickel Samples (X Series)					
	with Skimmer (with insert)					
Mass Spectrometer Parameter	rs					
Extraction Lens	-180 V					
CCT mass	222 V					
CCT Bias	-1.7 V					
Deflection entry	-29.8 V					
Deflection exit	35 V					
CCT H ₂ flow rate	3.8 mL min ⁻¹					
Notch filter (m/z)	19, 31.5, 37, 39.5					
Time resolution	1.19 ms					
Number of mass spectra	99					
averaged per time point						

Table S1. ICP-TOFMS instrument parameters

Table S2: Element names, measured Isotopes, sensitivities and critical masses obtained from
spICP-TOFMS measurements

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Element Name	Isotopes Used	Sensitivity (TofCts/g)	X ^{mass} _{C,sp} (g)			
Mg	²⁴ Mg+ ²⁵ Mg	2.70E+15	2.89E-15			
Al	²⁷ Al	8.93E+15	9.00E-16			
Ti	⁴⁶ Ti or ⁴⁸ Ti	5.39E+16	1.37E-16			
Mn	⁵⁵ Mn	1.18E+17	7.14E-17			
Fe	⁵⁶ Fe	1.17E+17	1.57E-16			
Y	⁸⁹ Y	3.01E+17	2.07E-17			
Zr	⁹⁰ Zr	1.70E+17	2.65E-17			
Nb	⁹³ Nb	2.97E+17	2.39E-17			
Cs	¹³³ Cs	3.45E+17	2.21E-17			
La	¹³⁹ La	5.47E+17	1.03E-17			
Ce	¹⁴⁰ Ce	5.35E+17	1.06E-17			
Но	¹⁶⁵ Ho	2.76E+17	1.92E-17			
Hf	¹⁷⁷ Hf+ ¹⁷⁸ Hf+ ¹⁷⁹ Hf+ ¹⁸⁰ Hf	2.67E+17	1.49E-17			
Та	¹⁸¹ Ta	5.22E+17	1.04E-17			
Pb	²⁰⁶ Pb+ ²⁰⁷ Pb+ ²⁰⁸ Pb	3.00E+17	1.84E-17			
Bi	²⁰⁹ Bi	2.55E+17	1.87E-17			
Th	²³² Th	2.55E+17	1.76E-17			
U	²³⁸ U	2.83E+17	1.68E-17			

Elements	Zr-eng	Zr-nat				
Mg	na	0.2 ± 0.1%				
Al	na	3.1 ± 0.3%				
Ti	na	0.1 ± 0.1%				
Mn	na	0.010 ± 0.001%				
Fe	na	18 ± 2%				
Y	na	0.8 ± 0.4%				
Zr	98.2 ± 0.1%	73 ± 2%				
Sn	na	0.03 ± 0.01%				
La	na	0.36 ± 0.02%				
Ce	na	0.70 ± 0.09%				
Но	na	0.03 ± 0.02%				
Hf	$1.8 \pm 0.1\%$	0.78 ± 0.02%				
Та	na	0.06 ± 0.05%				
Pb	na	0.030 ± 0.003%				
Th	na	3.4 ± 0.1%				
U	na	0.22 ± 0.07%				

Table S3: Mass fractions of each element in Zr-eng and Zr-nat particles. Mass fractions are calculated based on the total mass of each element present in Zr-eng and Zr-nat particles by spICP-TOFMS.



Figure S1: Boxplots showing mass distribution of Zr and Hf in single element (sm) and multielement (mm) Zr-eng and Zr-nat particles.

AI	1.00	0.27	0.50	0.05	0.05	0.30	0.25	0.01	0.04	0.14	0.10	0.01		- 1.00
Ti	0.27	1.00	0.29	0.04	0.04	0.02	0.01	0.01	0.04	0.01	0.03	0.01		0.75
Fe	0.50	0.29	1.00	0.16	0.08	0.17	0.21	0.12	0.07	0.34	0.18	0.08		
Y	0.05	0.04	0.16	1.00	0.15	0.16	0.12	0.93	0.15	0.06	0.22	0.05		- 0.5
Zr	0.05	0.04	0.08	0.15	1.00	0.02	0.03	0.03	0.89	0.08	0.05	0.18		- 0.25
La	0.30	0.02	0.17	0.16	0.02	1.00	0.89	0.12	0.03	0.45	0.35	0.02		
Ce	0.25	0.01	0.21	0.12	0.03	0.89	1.00	0.09	0.02	0.48	0.23	0.04		- 0.00
Но	0.01	0.01	0.12	0.93	0.03	0.12	0.09	1.00	0.03	0.04	0.13	0.04		-0.25
Hf	0.04	0.04	0.07	0.15	0.89	0.03	0.02	0.03	1.00	0.04	0.05	0.11		
Pb	0.14	0.01	0.34	0.06	0.08	0.45	0.48	0.04	0.04	1.00	0.32	0.61		0.50
Th	0.10	0.03	0.18	0.22	0.05	0.35	0.23	0.13	0.05	0.32	1.00	0.04		0.75
U	0.01	0.01	0.08	0.05	0.18	0.02	0.04	0.04	0.11	0.61	0.04	1.00		
	Al	Ti	Fe	Y	Zr	La	Ce	Но	Hf	Pb	Th	U		1.00

Figure S2: Correlation matrix of mass amounts of each element in Zr-nat particles. Correlation matrix is generated using Streamlit webapp based on Pearson correlation coefficient.



Figure S3: Pie charts of the multi-elemental signature measured by spICP-TOFMS for a) Zr-eng and b) Zr-nat particles. Only particles with recorded and multi-metal zirconium (mm-Zr) signatures are included in the pie charts.