

Supplementary materials

Table S1. Limits of detection for ICP-MS, and pXRF. LODs were provided by instruments based on the calibration curve of ICP-MS and the factory calibration of pXRF. ICP-MS undiluted was calculated to account for the dilution of the sample during acid digestion.

Limits of Detection			
Element	ICP-MS (ug/L)	ICP-MS undiluted dilution (mg/kg)	pXRF (mg/kg)
P	0.01	2220.56	477.00
S	NA	NA	87.00
Cl	NA	NA	43.00
K	2.43	485.72	194.00
Ca	17.43	3486.87	32.00
Ti	0.13	25.84	30.00
Cr	0.06	12.43	2.30
Mn	0.06	11.70	3.70
Fe	3.02	604.86	11.00
Co	0.01	1.04	7.00
Ni	0.01	1.93	8.00
Cu	0.08	16.36	3.90
Zn	0.38	76.99	2.10
As	0.04	8.35	1.50
Se	0.72	144.21	1.00
Rb	NA	NA	1.20
Sr	0.03	6.28	0.80
Zr	NA	NA	1.60
Mo	0.02	3.70	2.30
Ag	NA	NA	11.00
Cd	0.02	4.86	13.00
Sn	0.01	2.91	20.00
Sb	0.01	2.66	22.00
Ba	0.19	38.82	4.20
Hg	0.01	2.79	3.10
Pb	0.01	2.45	2.40

Table S2. Concentrations used to calibrate ICP-MS.

ICP-MS Calibration curves		
Elements	(ug l ⁻¹)	accounting for dilution (mg kg ⁻¹)
P, Ti, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag Cd, Sn, Sb, Ba, Hg, Pb	0	0
	25	5,000
	50	10,000
	75	15,000
	100	20,000
K, Ca	0	0
	250	50,000
	500	100,000
	750	150,000
	1,000	200,000
Fe	0	0
	275	55,000
	555	111,000
	825	165,000
	1,100	220,000

Figure S1. Regression of samples (n=102) collected from an iron slag heap in Teesside, UK. Showing As, Ni, Ti, Zn, P, and K concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross) standard deviation error bars (black solid lines).

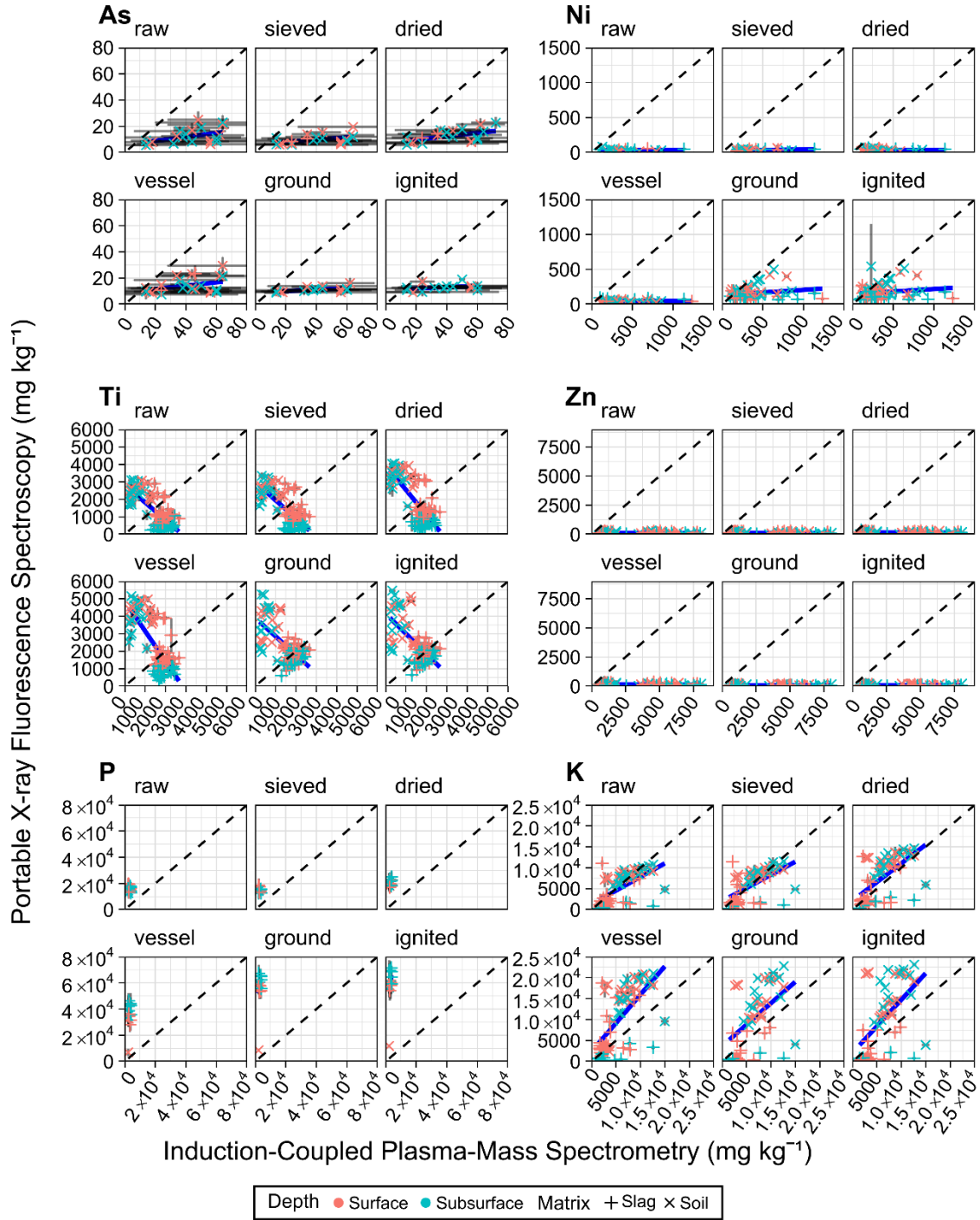


Figure S2. Regression of samples (n=102) collected from an iron slag heap in Teesside, UK, showing Fe and Ca concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross). error bars (black solid lines).

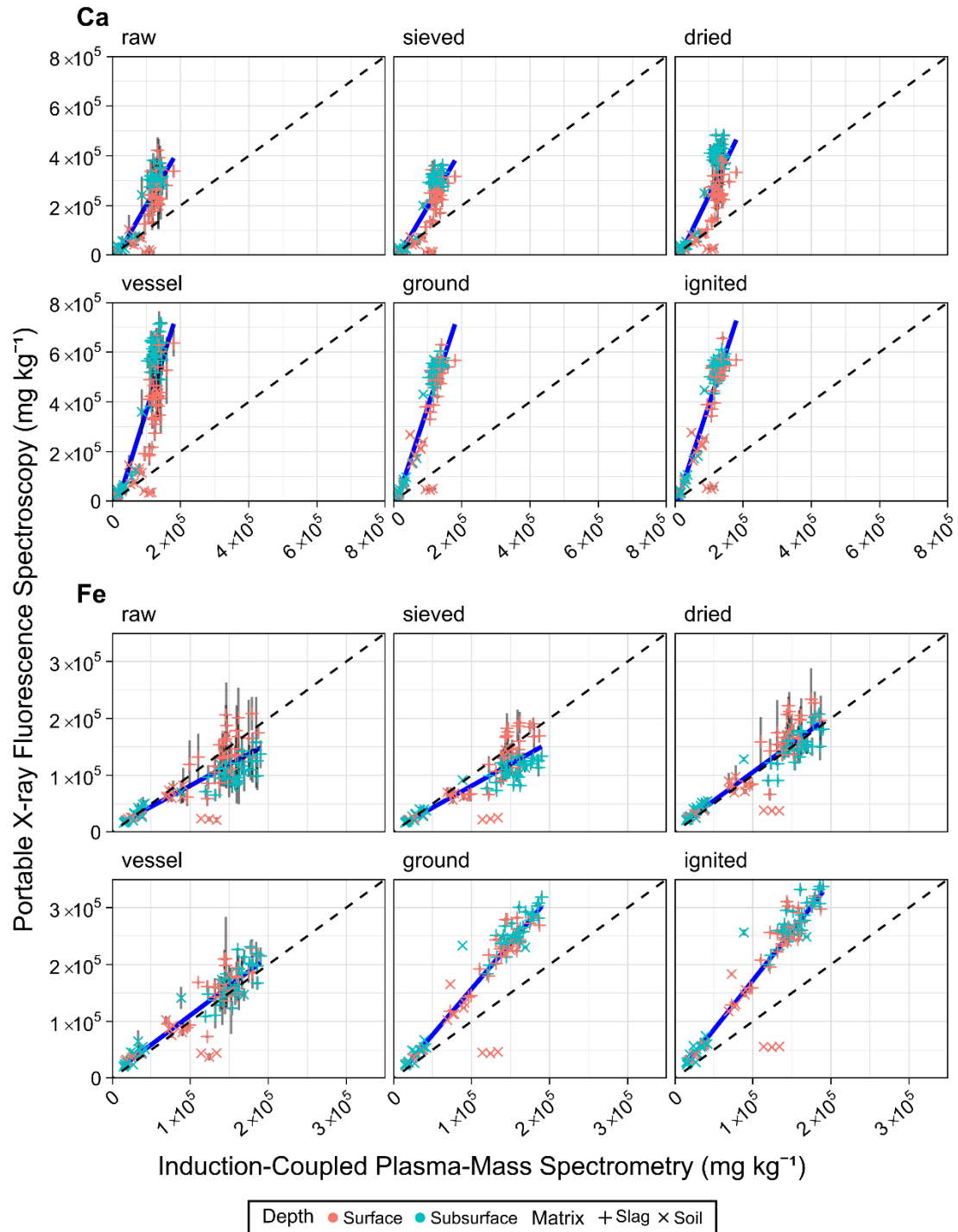


Figure S3. Regression of samples (n=102) collected from an iron slag heap in Teesside, UK, showing Cr and Mn concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross). error bars (black solid lines).

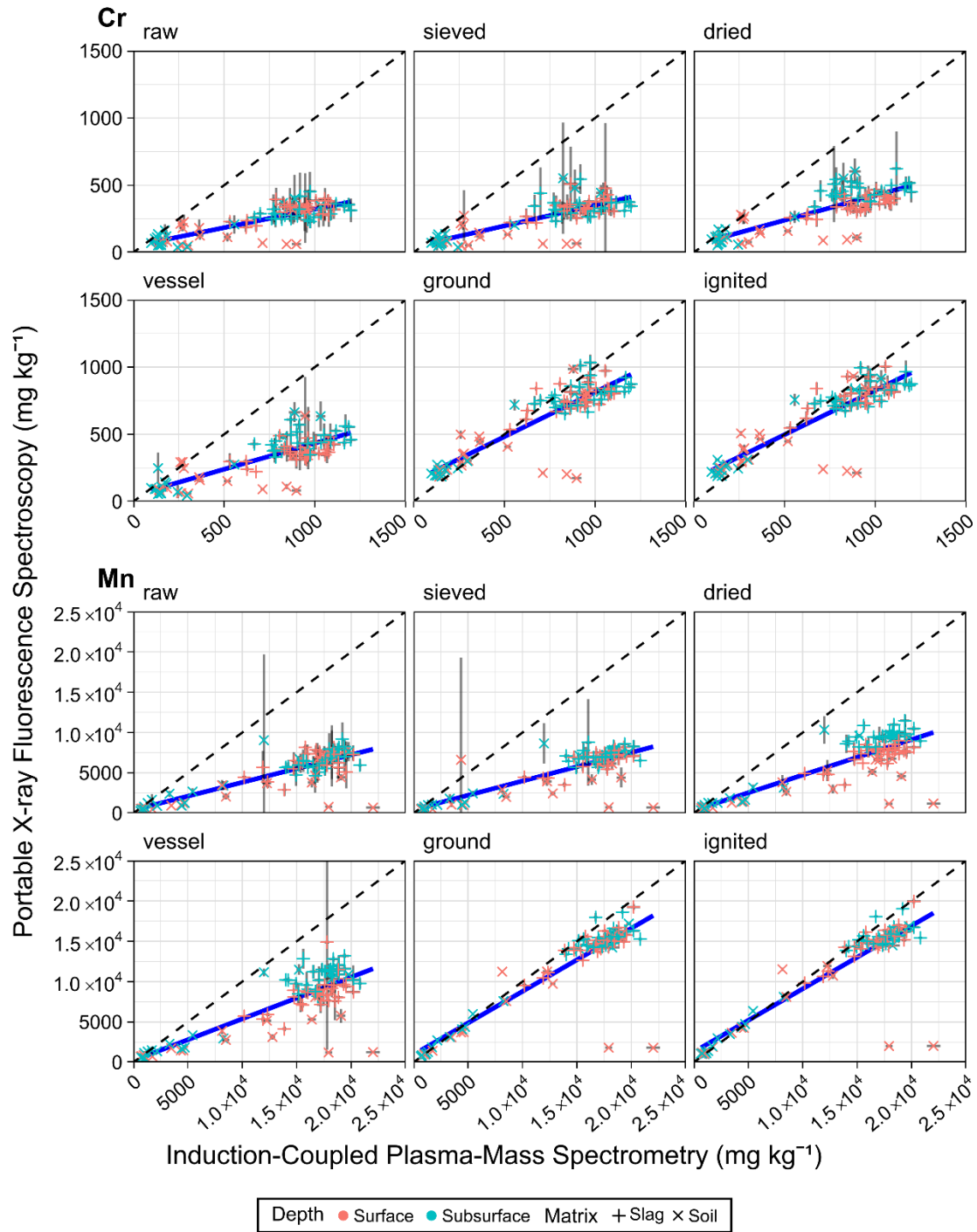


Figure S4. Regression of samples (n=102) collected from an iron slag heap in Teesside, UK, showing Pb and Sr concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross). error bars (black solid lines).

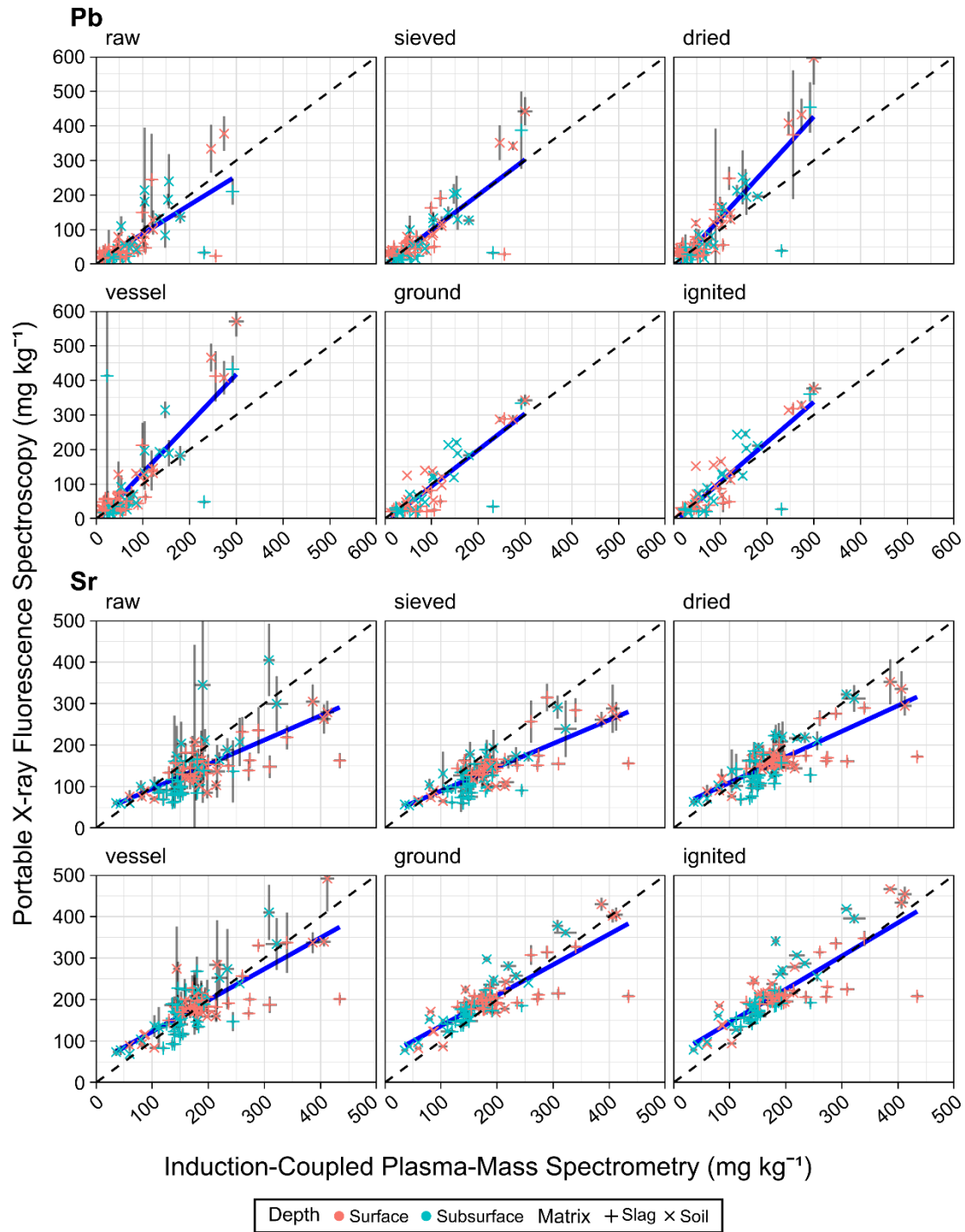


Table S3. Additional summary statistics of ordinary least squared regression on pXRF and ICP-MS measurements of samples (n=102). n is the number of samples above pXRF and ICP-MS LOD; residual prediction deviation (RPD); Person's correlation coefficient squared (r^2); ratio of performance to inter-quartile Distance (RPIQ); Lin's concordance correlation coefficient (r_c); mean absolute error (MAE); coefficient of determination (R^2); relative standard deviation (RSD); data quality assessment levels as defined by EPA [30].

Element	Processing Step	n	RPD	r^2	RMSE	RPIQ	r_c	MAE	R^2	RSD	Intercept	Slope	Intercept 95% CI	Slope 95% CI	Data Quality
As	Raw	32	0.50	0.20	34.13	0.64	0.07	30.71	-3.27	20.46	5.80	0.15	(-1, 13)	(0.006, 0.302)	No Correlation
	Sieved	33	0.52	0.20	34.45	0.93	0.04	30.33	-2.84	15.81	6.45	0.09	(3, 10)	(0.002, 0.172)	No Correlation
	Dried	31	0.54	0.25	33.03	0.89	0.07	29.05	-2.56	17.84	7.12	0.13	(2, 12)	(0.026, 0.237)	No Correlation
	Vessel	40	0.57	0.14	30.28	1.06	0.07	25.95	-2.25	18.29	9.27	0.13	(3, 15)	(-0.006, 0.259)	No Correlation
	Ground	21	0.53	0.25	33.13	0.83	0.03	28.96	-2.82	19.80	9.06	0.06	(7, 11)	(0.001, 0.11)	No Correlation
	Ignited	20	0.56	0.09	30.48	1.05	0.03	25.97	-2.41	14.57	11.37	0.04	(8, 15)	(-0.043, 0.131)	No Correlation
Pb	Raw	86	1.24	0.53	50.53	1.24	0.72	31.27	0.34	25.14	5.13	0.83	(-12, 22)	(0.655, 1.01)	No Correlation
	Sieved	82	1.40	0.67	49.00	1.44	0.80	30.44	0.48	19.30	-3.57	1.02	(-20, 13)	(0.856, 1.185)	Qualitative
	Dried	88	1.10	0.80	61.12	1.05	0.78	36.59	0.16	22.01	-14.95	1.47	(-31, 1)	(1.31, 1.633)	Quantitative
	Vessel	88	0.89	0.67	74.98	0.81	0.69	39.88	-0.28	19.85	-10.32	1.43	(-32, 11)	(1.203, 1.649)	Qualitative
	Ground	61	1.72	0.77	41.96	1.45	0.86	27.57	0.65	9.30	-11.19	1.05	(-29, 7)	(0.895, 1.205)	Quantitative
	Ignited	56	1.47	0.75	49.76	1.47	0.83	33.61	0.53	8.89	-10.99	1.16	(-33, 11)	(0.975, 1.348)	Quantitative
Sr	Raw	102	1.11	0.49	65.56	0.79	0.59	49.80	0.19	18.17	36.23	0.59	(12, 60)	(0.465, 0.709)	No Correlation
	Sieved	99	1.14	0.60	65.16	0.81	0.59	49.39	0.22	10.04	32.55	0.57	(14, 51)	(0.474, 0.667)	No Correlation
	Dried	102	1.46	0.61	49.95	1.03	0.72	35.58	0.53	9.23	47.83	0.62	(28, 67)	(0.519, 0.718)	Qualitative
	Vessel	102	1.53	0.61	47.57	1.08	0.78	33.90	0.57	10.98	47.63	0.75	(24, 72)	(0.631, 0.876)	Qualitative
	Ground	102	1.71	0.70	42.69	1.21	0.81	30.46	0.65	3.71	62.92	0.74	(44, 82)	(0.64, 0.835)	Quantitative
	Ignited	102	1.40	0.67	51.98	0.99	0.76	39.35	0.49	3.55	64.55	0.80	(42, 87)	(0.688, 0.916)	Qualitative
Cr	Raw	99	0.65	0.69	530.72	1.24	0.19	464.87	-1.40	18.80	46.89	0.28	(17, 77)	(0.237, 0.314)	Qualitative
	Sieved	96	0.69	0.65	509.55	1.33	0.23	440.69	-1.10	15.17	43.97	0.31	(7, 81)	(0.26, 0.355)	Qualitative
	Dried	98	0.77	0.69	455.51	1.46	0.30	390.59	-0.71	12.67	55.35	0.37	(15, 96)	(0.317, 0.42)	Qualitative
	Vessel	96	0.76	0.66	453.35	1.42	0.31	393.76	-0.73	11.91	45.97	0.39	(0, 92)	(0.33, 0.447)	Qualitative
	Ground	100	1.80	0.77	192.04	3.36	0.81	144.81	0.69	3.41	150.23	0.66	(91, 210)	(0.588, 0.739)	Quantitative
	Ignited	100	1.90	0.79	182.26	3.54	0.82	139.21	0.72	3.67	167.47	0.66	(111, 224)	(0.589, 0.731)	Quantitative
Ni	Raw	40	0.55	0.00	439.61	0.50	0.00	368.57	-2.39	19.93	37.11	0.00	(26, 48)	(-0.025, 0.021)	No Correlation
	Sieved	44	0.55	0.10	410.73	0.54	0.01	348.64	-2.47	21.18	28.59	0.02	(20, 37)	(-0.002, 0.035)	No Correlation
	Dried	52	0.58	0.01	379.46	0.59	0.00	310.35	-2.05	21.52	42.06	0.00	(34, 50)	(-0.023, 0.014)	No Correlation
	Vessel	59	0.59	0.00	437.81	0.62	0.00	355.23	-1.94	18.21	48.76	0.00	(40, 58)	(-0.019, 0.018)	No Correlation
	Ground	97	0.78	0.04	299.70	0.77	0.08	198.55	-0.66	13.86	132.28	0.08	(97, 167)	(-0.007, 0.159)	No Correlation
	Ignited	99	0.80	0.03	290.91	0.76	0.08	186.91	-0.57	14.83	149.13	0.07	(110, 189)	(-0.025, 0.166)	No Correlation
Ti	Raw	101	0.45	0.54	1475.12	0.67	-0.68	1368.15	-3.95	22.02	2836.97	-1.00	(2526, 3148)	(-1.195, -0.815)	No Correlation

	Sieved	98	0.44	0.53	1529.70	0.71	-0.68	1402.84	-4.17	11.43	3006.23	-1.05	(2672, 3341)	(-1.251, -0.842)	No Correlation
	Dried	102	0.37	0.59	1816.72	0.52	-0.61	1551.33	-6.56	11.75	3980.78	-1.43	(3589, 4373)	(-1.668, -1.19)	No Correlation
	Vessel	101	0.30	0.56	2218.51	0.44	-0.45	1754.94	-10.17	10.30	4885.29	-1.72	(4378, 5393)	(-2.033, -1.414)	No Correlation
	Ground	102	0.37	0.42	1791.06	0.53	-0.41	1181.68	-6.35	3.78	3916.31	-1.06	(3506, 4326)	(-1.31, -0.809)	No Correlation
	Ignited	102	0.35	0.43	1918.80	0.50	-0.38	1246.43	-7.44	3.44	4161.60	-1.15	(3717, 4606)	(-1.425, -0.882)	No Correlation
Zn	Raw	95	0.63	0.00	3866.63	1.06	0.00	3015.38	-1.56	22.09	134.28	0.00	(109, 160)	(-0.008, 0.005)	No Correlation
	Sieved	92	0.64	0.01	3750.18	1.08	0.00	2880.86	-1.46	15.32	141.12	0.00	(115, 167)	(-0.01, 0.003)	No Correlation
	Dried	94	0.63	0.00	3841.95	1.06	0.00	2976.65	-1.52	14.66	163.94	0.00	(137, 191)	(-0.009, 0.005)	No Correlation
	Vessel	93	0.64	0.01	3827.65	1.06	0.00	2953.09	-1.49	15.83	167.06	0.00	(139, 195)	(-0.01, 0.004)	No Correlation
	Ground	90	0.64	0.00	3853.04	1.05	0.00	2989.87	-1.51	10.06	77.31	0.00	(63, 92)	(-0.003, 0.005)	No Correlation
	Ignited	90	0.64	0.01	3845.79	1.05	0.00	2979.57	-1.49	10.49	83.10	0.00	(66, 100)	(-0.003, 0.006)	No Correlation
P	Raw	57	0.05	0.00	12653.65	0.09	0.00	12455.28	-439.42	19.55	15628.81	-0.04	(9316, 21942)	(-2.079, 1.992)	No Correlation
	Sieved	58	0.05	0.01	12043.25	0.09	0.00	11916.04	-439.46	18.62	15470.79	-0.21	(10203, 20739)	(-1.964, 1.549)	No Correlation
	Dried	65	0.03	0.02	17831.68	0.06	0.00	17697.17	-873.63	17.45	19155.57	0.52	(12767, 25544)	(-1.539, 2.581)	No Correlation
	Vessel	100	0.02	0.05	34502.26	0.03	0.00	33375.75	-3207.38	17.56	26479.46	3.30	(2609, 50350)	(-4.499, 11.098)	No Correlation
	Ground	100	0.01	0.07	54404.54	0.02	0.00	52900.50	-7693.93	12.90	39451.18	5.45	(4078, 74824)	(-6.013, 16.91)	No Correlation
	Ignited	100	0.01	0.12	57118.08	0.02	0.00	55726.43	-8792.02	11.72	37013.67	7.24	(3990, 70037)	(-3.551, 18.027)	No Correlation
K	Raw	75	1.12	0.40	3101.67	1.69	0.62	2094.43	0.20	21.83	1324.43	0.65	(-20, 2669)	(0.45, 0.849)	No Correlation
	Sieved	69	1.10	0.36	3177.33	1.59	0.60	2135.33	0.15	9.02	2028.60	0.63	(514, 3543)	(0.41, 0.848)	No Correlation
	Dried	74	0.84	0.39	4169.31	1.24	0.55	3179.41	-0.45	11.02	2102.08	0.89	(201, 4003)	(0.612, 1.176)	No Correlation
	Vessel	79	0.48	0.42	7187.06	0.76	0.39	5666.95	-3.32	9.09	2374.62	1.36	(-182, 4931)	(0.968, 1.747)	No Correlation
	Ground	52	0.46	0.23	7324.65	0.76	0.30	6136.14	-3.81	4.51	3632.63	1.03	(-603, 7869)	(0.47, 1.582)	No Correlation
	Ignited	61	0.45	0.30	7758.42	0.72	0.34	6132.34	-3.92	6.48	2042.89	1.27	(-1763, 5849)	(0.736, 1.799)	No Correlation
Mn	Raw	100	0.68	0.71	9692.21	0.84	0.24	8578.54	-1.21	17.47	405.32	0.34	(-278, 1089)	(0.297, 0.388)	Quantitative
	Sieved	97	0.70	0.71	9433.14	1.00	0.26	8336.62	-1.06	11.81	458.72	0.35	(-269, 1187)	(0.306, 0.402)	Quantitative
	Dried	100	0.78	0.71	8332.14	0.97	0.35	7277.00	-0.65	7.64	344.79	0.44	(-530, 1219)	(0.381, 0.497)	Quantitative
	Vessel	100	0.88	0.70	7409.55	1.09	0.44	6353.54	-0.31	8.14	209.45	0.52	(-853, 1271)	(0.447, 0.588)	Quantitative
	Ground	100	1.89	0.81	3466.43	2.36	0.85	2135.64	0.72	1.28	960.72	0.78	(-224, 2146)	(0.705, 0.861)	Quantitative
	Ignited	100	1.98	0.81	3301.39	2.47	0.86	1917.49	0.74	1.93	1287.60	0.78	(98, 2477)	(0.704, 0.861)	Quantitative
Ca	Raw	102	0.35	0.75	132687.87	0.49	0.36	106837.19	-7.34	20.05	-35599.57	2.36	(-65624, -5575)	(2.086, 2.636)	Quantitative
	Sieved	99	0.37	0.76	125474.64	0.55	0.39	99947.27	-6.39	9.26	-38359.54	2.32	(-67745, -8974)	(2.053, 2.597)	Quantitative
	Dried	102	0.25	0.68	182437.59	0.36	0.26	141342.44	-14.77	8.95	-43470.33	2.82	(-85923, -1018)	(2.427, 3.205)	Qualitative
	Vessel	102	0.14	0.72	325437.00	0.20	0.15	260328.75	-49.17	10.50	-78703.31	4.39	(-139664, -17743)	(3.828, 4.946)	Quantitative
	Ground	102	0.14	0.85	318958.24	0.20	0.15	275607.52	-47.19	1.01	-41431.88	4.17	(-80100, -2763)	(3.816, 4.526)	Quantitative
	Ignited	102	0.14	0.85	329506.66	0.20	0.14	286489.88	-50.43	2.10	-34098.08	4.21	(-72876, 4680)	(3.855, 4.567)	Quantitative
Fe	Raw	102	1.40	0.66	39750.62	2.15	0.74	30182.14	0.48	17.33	7913.17	0.74	(-6023, 21849)	(0.631, 0.849)	Qualitative
	Sieved	99	1.53	0.72	36853.44	2.38	0.78	27176.68	0.57	8.45	4688.81	0.77	(-7786, 17163)	(0.67, 0.865)	Quantitative
	Dried	102	1.97	0.80	28192.05	3.03	0.89	20204.24	0.74	8.98	5599.59	1.00	(-7374, 18573)	(0.898, 1.1)	Quantitative
	Vessel	102	1.94	0.82	28736.13	2.97	0.88	21603.57	0.73	8.99	7488.60	1.03	(-4914, 19891)	(0.935, 1.128)	Quantitative
	Ground	102	0.68	0.88	81495.87	1.05	0.60	71253.52	-1.17	1.36	-4578.30	1.61	(-19966, 10809)	(1.494, 1.734)	Quantitative
	Ignited	102	0.56	0.88	99007.85	0.86	0.52	87527.17	-2.20	1.76	-1506.48	1.73	(-17836, 14823)	(1.606, 1.861)	Quantitative

Figure S5. Regression plots of pXRF measurements before and after drying samples (n=102) collected from an iron slag heap in Teesside, UK pXRF. OLS regression (black solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (circles); soil matrix (triangle); surface samples (red); subsurface samples (blue).

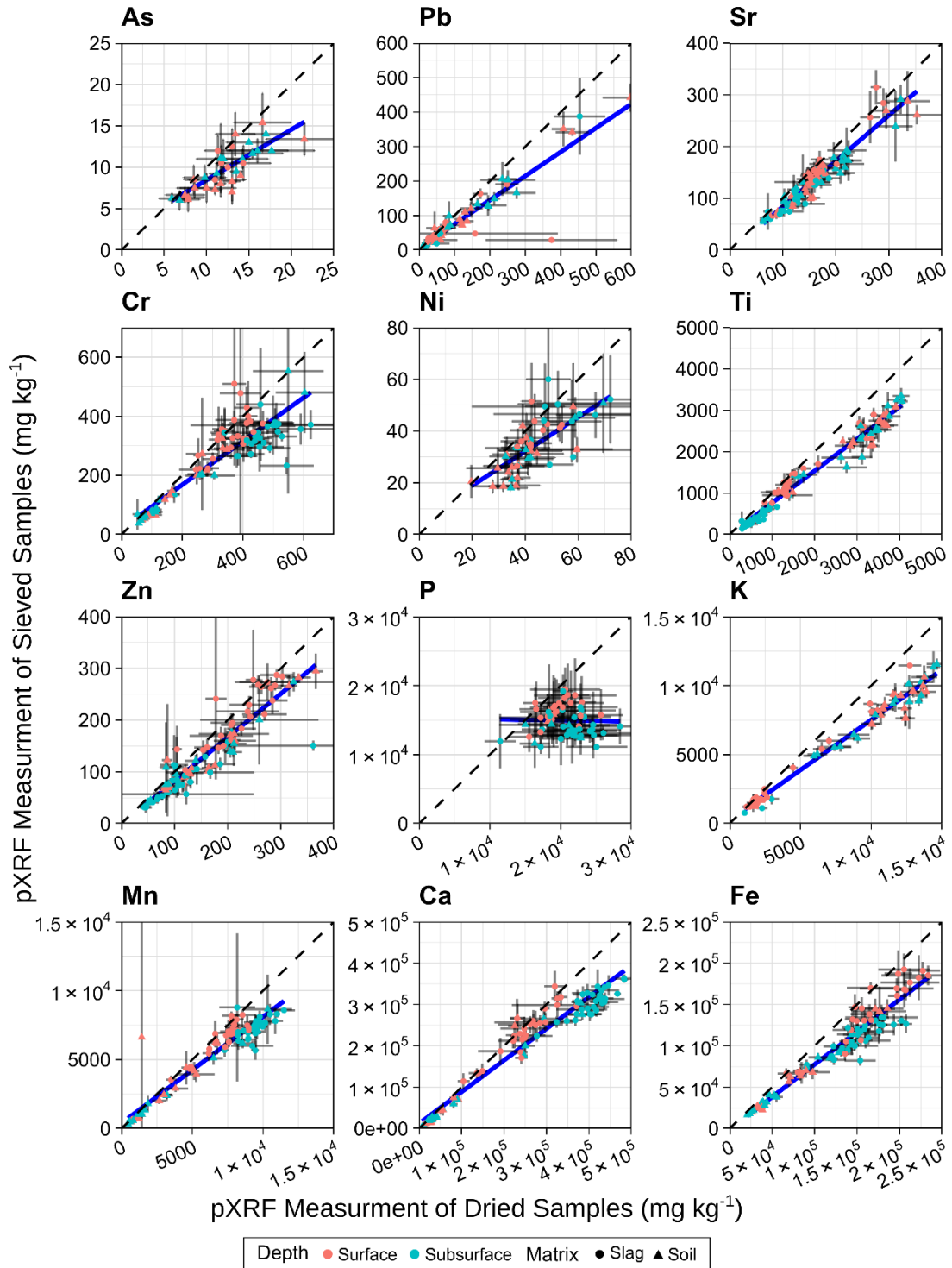
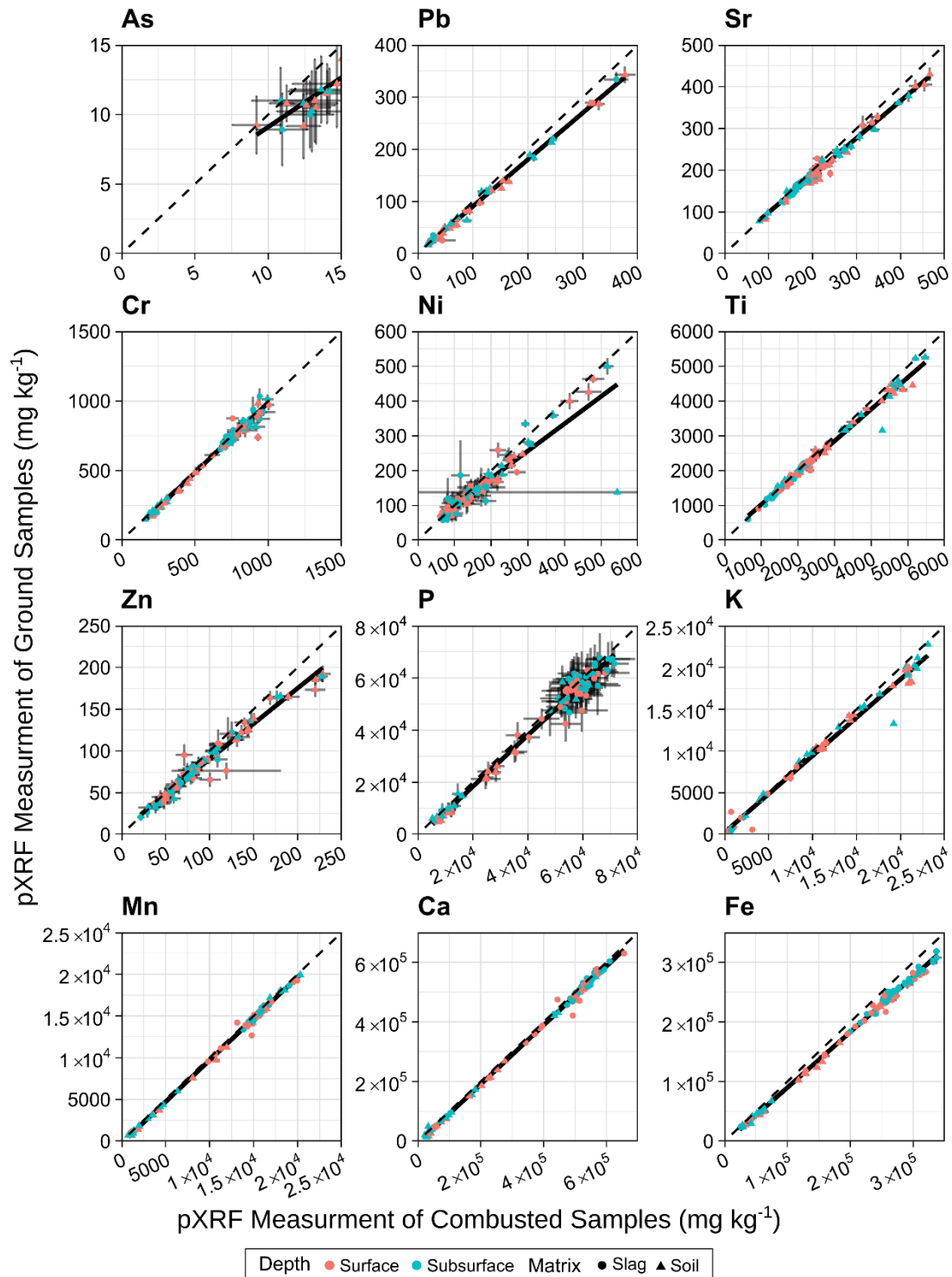


Figure S6. Regression plots of pXRF measurements before and after combusting samples (n=102) collected from an iron slag heap in Teesside, UK. pXRF. OLS regression (black solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (circles); soil matrix (triangle); surface samples (red); subsurface samples (blue).



Tabel S4. Additional summary statistics of ordinary least squared regression on pXRF measurements before and after drying / igniting of samples (n=102). n is the number of samples above pXRF LOD; residual prediction deviation (RPD); Person's correlation coefficient squared (r^2); ratio of performance to inter-quartile Distance (RPIQ); Lin's concordance correlation coefficient (r_c); mean absolute error (MAE); coefficient of determination (R^2); relative standard deviation (RSD).

Processing Step	element	n	RDD	r^2	RMSE	RPIQ	r_c	MAE	R^2	Intercept	Slope	Intercept 95% CI	Slope 95% CI
Drying	As	57	1.090	0.647	3.2	1.346	0.589	2.5	0.132	2.3	0.611	(0, 4)	(0.446, 0.776)
	Pb	94	2.174	0.859	51.4	1.611	0.867	24.3	0.786	5.5	0.698	(-4, 15)	(0.635, 0.76)
	Sr	105	1.974	0.903	29.4	1.759	0.873	24.2	0.741	-4.8	0.885	(-15, 5)	(0.826, 0.943)
	Cr	106	1.740	0.822	92.4	3.250	0.816	69.1	0.666	20.5	0.738	(-4, 45)	(0.667, 0.809)
	Ni	116	0.900	0.499	12.3	1.065	0.515	10.2	-0.259	5.7	0.663	(-3, 14)	(0.474, 0.851)
	Ti	106	2.266	0.968	544.7	4.284	0.888	435.9	0.803	-8.7	0.773	(-73, 55)	(0.745, 0.802)
	Zn	100	1.966	0.850	41.8	2.859	0.866	32.3	0.738	-2.1	0.844	(-16, 11)	(0.769, 0.919)
	P	110	0.457	0.001	6768.6	0.636	-0.007	5692.7	-3.884	15281.4	-0.016	(11450, 19113)	(-0.2, 0.168)
	K	81	2.113	0.975	2324.3	4.410	0.866	1823.6	0.773	249.9	0.727	(-7, 507)	(0.698, 0.755)
	Mn	106	2.223	0.907	1548.4	3.953	0.884	1171.4	0.796	388.1	0.772	(28, 748)	(0.721, 0.823)
	Ca	105	2.511	0.948	62726.1	5.237	0.906	44887.0	0.840	12114.8	0.765	(2064, 22165)	(0.729, 0.801)
	Fe	105	1.929	0.939	32102.8	3.473	0.853	26605.2	0.728	-1049.7	0.785	(-6444, 4344)	(0.745, 0.826)
Igniting	As	57	0.861	0.550	2.3	0.826	0.509	2.0	-0.420	2.0	0.711	(-2, 6)	(0.392, 1.03)
	Pb	94	6.723	0.995	14.1	7.031	0.988	9.3	0.978	1.0	0.897	(-1, 3)	(0.881, 0.913)
	Sr	105	4.053	0.981	17.5	2.542	0.967	13.7	0.939	9.7	0.891	(4, 15)	(0.867, 0.916)
	Cr	106	7.222	0.984	36.0	14.404	0.990	24.6	0.981	-18.9	1.007	(-36, -1)	(0.982, 1.033)
	Ni	116	2.086	0.794	47.4	2.055	0.871	22.8	0.768	20.8	0.785	(5, 37)	(0.705, 0.866)
	Ti	106	6.104	0.985	193.1	6.038	0.985	114.5	0.973	107.8	0.915	(48, 168)	(0.892, 0.937)
	Zn	100	3.567	0.965	13.2	4.021	0.955	9.0	0.921	5.3	0.849	(2, 9)	(0.815, 0.883)
	P	110	5.965	0.980	3691.0	11.170	0.986	2935.7	0.972	-1346.7	0.985	(-2740, 47)	(0.956, 1.013)
	K	81	5.849	0.982	1345.2	12.469	0.984	820.3	0.970	248.5	0.918	(-234, 731)	(0.883, 0.952)
	Mn	106	13.486	0.997	441.5	18.322	0.997	344.1	0.994	-264.1	0.996	(-405, -123)	(0.985, 1.007)
	Ca	105	13.422	0.997	15653.7	24.247	0.997	12611.0	0.994	-7300.4	0.990	(-11790, -2810)	(0.98, 1)
	Fe	105	5.401	0.997	18919.8	10.795	0.982	16897.2	0.965	-3113.3	0.931	(-5192, -1034)	(0.921, 0.94)