Supplementary Materials: Selenium and other trace element mobility in waste products and weathered sediments at Parys Mountain copper mine, Anglesey, UK

Liam A. Bullock, John Parnell, Magali Perez, Joerg Feldmann and Joseph G. Armstrong

Table S1. Trace element content of natural bedrock, soils and water run-off at Parys Mountain mining district. World average soil, crust, stream sediment and stream water compositions also shown (Salminen et al. [46] and references therein).

Natural deposits	As (ppm)	Au (ppm)	Bi (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	S (%)	Sb (ppm)	Se (ppm)	Te (ppm)	TOC (%)	pH
Sulphidic bedrock (ppm/%)																		
Pyritic ore	495	0.3	35.0	0.3	95.6	<LOD	543	14.7	0.9	1.9	2.6	148.5	18.6	10.1	59.2	1.50	0.02	-
Pyritic ore	474	0.3	33.9	0.3	87.3	<LOD	523	14.2	0.9	1.7	2.1	142.5	18.6	9.8	64.4	1.54	0.02	-
Pyritic ore	467	0.3	33.4	0.2	85.9	<LOD	509	14.3	0.9	1.7	2.0	142.5	18.6	9.3	60.9	1.56	0.02	-
Pyritic ore	467	0.3	33.7	0.3	85.4	<LOD	520	14.6	0.9	1.6	2.0	143	18.6	9.4	60.8	1.51	0.02	-
Weathering soil																		
Clay (ponded yellow)	1030	0.5	105.5	2.1	18.7	4	1050	14.9	3.5	26.1	1.9	9990	2.8	72.3	48.8	0.26	2.3	-
Clay (ponded yellow)	1000	0.4	92.3	2.0	3.1	3	1010	15.1	3.0	25.4	2.1	9300	2.6	78.3	47.4	0.27	2.3	-
Clay (ponded yellow)	918	0.4	87.5	1.9	2.5	3	973	13.9	2.9	23.1	1.8	8850	2.5	66.7	48.9	0.28	2.3	-
Clay (ponded yellow)	902	0.4	87.6	1.8	2.5	3	947	14.1	3.0	23.9	1.9	8980	2.5	66.6	49.3	0.30	2.3	-
Soil (yellow)	249	<LOD	26.5	0.0	24.8	<LOD	951	6.4	0.0	7.2	0.3	192	0.3	8.6	15.9	0.08	0.1	-
Soil (yellow)	295	<LOD	31.4	0.3	17.9	2	862	5.2	0.2	9.6	2.7	1040	0.5	25.8	10.5	0.19	0.1	
Soil (yellow)	175	<LOD	17.2	0.5	28.4	3	626	7.0	0.1	6.6	24.2	696	0.3	23.4	6.5	0.12	0.1	-
Soil (yellow)	175.5	<LOD	17.1	0.5	27.4	3	627	7.0	0.1	6.6	23.8	692	0.3	23.0	6.7	0.12	0.1	-
Water run-off (µg·L⁻¹)																		
Ochre 2	0.66 ± 0.03	<LOD	<LOD	<LOD	0.11 ± 0.05	0.43 ± 0.17	-	-	<LOD	0.09 ± 0.02	2.24 ± 0.36	<LOD	-	0.07 ± 0.02	0.24 ± 0.06	<LOD	-	6.6
Ochre 3	3.12 ± 0.52	<LOD	<LOD	<LOD	2.49 ± 0.01	<LOD	-	-	<LOD	<LOD	2.31 ± 0.03	14.6 ± 3.6	-	<LOD	<LOD	<LOD	-	6.0
Ochre 4	27.9 ± 1.51	<LOD	0.10 ± 0.05	99.3 ± 7.1	255 ± 14	10.4 ± 0.51	-	-	<LOD	0.09 ± 0.01	101 ± 5	10.19 ± 0.60	-	0.07 ± 0.01	2.52 ± 1.01	<LOD	-	2.5
World averages																		
Soils (ppm/%)	5.0	0.0	0.3	0.3	10	80	25	5	0.05	1.2	20	17	0.02	0.5	0.3	0.01	-	-
Cont. crust (ppm/%)	5.7	0.01	0.2	0.1	15	73	28	5	0.05	0.6	34	17	0.01	0.7	0.1	0.03	-	-
Stream sediment (ppm/%)	6.0	-	-	0.3	8.0	42	15.5	2.8	0.04	0.6	18.5	36.3	0.1	0.6	-	-	-	-
Stream water (µg·L⁻¹)	2.0	-	0.05	0.2	0.3	0.4	7.0	40	-	1.0	2.5	0.05	0.0007	0.1	0.2	0.01	-	-

Hyphen (-) depicts element not measured. Lower levels of detection (LOD) (whole rock): As (0.1 ppm), Au (0.2 ppm), Bi (0.01 ppm), Cd (0.01 ppm), Co (0.1 ppm), Cr (1 ppm), Cu (0.2 ppm), Fe (0.01%), Hg (0.01 ppm), Mo (0.05 ppm), Ni (0.2 ppm), Pb (0.2 ppm), S (0.01%), Sb (0.05 ppm), Se (0.2 ppm), Te (0.01 ppm), W (0.05 ppm). Lower levels of detection (water): As (0.15 µg·L⁻¹), Au (0.04 µg·L⁻¹), Bi (0.05 µg·L⁻¹), Cd (0.13 µg·L⁻¹), Cr (0.13 µg·L⁻¹), Hg (0.16 µg·L⁻¹), Mo (0.01 µg·L⁻¹), Ni (0.52 µg·L⁻¹), Pb (0.31 µg·L⁻¹), Sb (0.02 µg·L⁻¹), Se (0.20 µg·L⁻¹), Te (0.06 µg·L⁻¹), W (0.07 µg·L⁻¹). Hyphen (-) depicts element not measured. Lower levels of detection (LOD) (whole

rock): As (0.1 ppm), Au (0.2 ppm), Bi (0.01 ppm), Cd (0.01 ppm), Co (0.1 ppm), Cr (1 ppm), Cu (0.2 ppm), Fe (0.01%), Hg (0.01 ppm), Mo (0.05 ppm), Ni (0.2 ppm), Pb (0.2 ppm), S (0.01%), Sb (0.05 ppm), Se (0.2 ppm), Te (0.01 ppm), W (0.05 ppm). Lower levels of detection (water): As (0.15 µg·L⁻¹), Au (0.04 µg·L⁻¹), Bi (0.05 µg·L⁻¹), Cd (0.13 µg·L⁻¹), Cr (0.13 µg·L⁻¹), Hg (0.16 µg·L⁻¹), Mo (0.01 µg·L⁻¹), Ni (0.52 µg·L⁻¹), Pb (0.31 µg·L⁻¹), Sb (0.02 µg·L⁻¹), Se (0.20 µg·L⁻¹), Te (0.06 µg·L⁻¹), W (0.07 µg·L⁻¹).

Table S2. Trace element concentrations of mine waste smelt deposits, ochre sediments and mine water associated with the Parys Mountain mining district.

Mine waste deposits	As (ppm)	Au (ppm)	Bi (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	S (%)	Sb (ppm)	Se (ppm)	Te (ppm)	TOC (%)	pH
							Smelt (ppm/%)											
RMS	48.9	<LOD	19.1	0.4	29.7	2	854	2.7	0.9	2.3	0.8	3850	1.7	13.1	29.6	0.02	0.2	-
RMS	41.2	<LOD	17.2	0.3	27.8	2	815	2.6	0.9	2.0	0.9	3750	1.7	12.3	26.6	0.03	0.2	-
RMS	45.9	<LOD	16.4	0.3	27.6	2	943	2.8	0.9	2.1	0.8	3840	1.8	13.0	29.8	0.03	0.1	-
RWSS	1005	0.6	161.5	2.9	35.3	3	435	14.4	40.8	21.9	2.7	7150	0.8	242	140.0	0.72	0.8	-
RWSS	972	1.0	212.0	5.3	6.3	1	411	15.5	61.7	23.0	2.5	12450	0.8	326	159.5	0.96	0.8	-
RWSS	953	1.2	227.0	5.0	6.3	2	400	16.5	71.6	23.5	2.8	14150	0.8	341	162.0	0.93	0.8	-
RWSS	1040	0.8	230.0	5.2	6.3	2	415	16.6	69.7	24.5	2.9	13600	0.8	351	173.0	0.84	0.8	-
							Ochre sediment (ppm/%)											
Ochre 1	60.9	<LOD	3.4	0.1	1.9	8	338	8.4	0.1	2.1	3.5	449	0.3	2.8	1.6	0.09	3.6	-
Ochre 1	71.8	<LOD	3.9	0.1	2.2	10	356	9.0	0.2	2.5	5.6	570	0.4	3.7	2.2	0.09	3.5	-
Ochre 2	437	<LOD	1.9	0.8	1.3	31	3510	39.8	0.5	12.5	7.2	159	0.6	13.2	7.3	0.13	4.0	-
Ochre 2	619	<LOD	2.9	1.7	1.7	110	7140	39.1	0.5	24.8	13.7	220	0.6	20.4	12.3	0.22	3.9	-
Ochre 3	465	<LOD	1.9	1.0	1.3	42	4000	40.4	0.3	14.4	8.2	187	0.5	14.6	8.8	0.16	3.3	-
Ochre 3	586	<LOD	2.6	1.5	1.7	85	6240	40.5	0.4	21.0	12.5	215	0.6	18.4	11.7	0.20	3.4	-
Ochre 4	1520	<LOD	14.2	<LOD	1.5	5	1150	44.6	0.5	23.8	4.2	1385	2.3	28.4	32.6	0.18	2.5	-
Ochre 4	1590	<LOD	16.0	0.2	1.2	4	1110	44.8	0.6	26.2	2.6	1190	2.4	24.2	37.2	0.21	2.5	-
							Mine water (µg·L⁻¹)											
Underground pool (µg·L⁻¹)	1113 ± 107	<LOD	<LOD	88.7 ± 11.1	247 ± 36	116 ± 18	-	-	<LOD	2.49 ± 0.33	151 ± 21	<LOD	-	0.89 ± 0.12	55.6 ± 4.9	0.19 ± 0.05	-	2.3

Table S3. Calculated error for whole rock (rock, sediments, soils) for ICP-MS, based on certified and achieved values for certified reference materials.

Ref. material	Analysis	As (ppm)	Au (ppm)	Bi (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Hg (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	S (ppm)	Sb (ppm)	Se (ppm)	Te (ppm)
GEOMS-03	Certified value	622	0.3	0.4	0.3	12.0	72	133	4.1	0.7	3.2	54.6	6.2	0.04	11.7	2.3	0.11
	Value achieved	609	0.3	0.3	0.3	11.4	71	133	4.1	0.7	3.2	51.2	6.4	0.03	12.9	2.2	0.12
		613	0.3	0.3	0.3	11.5	73	131	4.0	0.7	3.3	52.7	7.1	0.04	12.4	2.7	0.09
		620	0.4	0.3	0.3	11.4	72	132	4.0	0.7	3.3	52.3	4.8	0.04	12.3	2.4	0.12
		610	0.3	0.3	0.3	11.5	72	131	4.0	0.7	3.0	53.6	4.6	0.03	12.0	2.4	0.11
MRGeo08	Certified value	32.2	<0.2	0.7	2.2	19.5	94	648	3.8	0.07	14.6	687	1040	0.33	3.0	1.2	0.03
	Value achieved	32.5	<0.2	0.7	2.4	19.1	92	646	3.6	0.06	14.6	708	1070	0.31	3.5	1.4	0.02
		31.5	<0.2	0.7	2.2	19.1	94	633	3.6	0.07	14.3	695	1080	0.31	3.4	1.8	0.02
		34.4	<0.2	0.7	2.2	18.2	92	634	3.6	0.09	14.4	709	1070	0.31	3.6	1.8	0.01
		33.5	<0.2	0.7	2.2	17.4	92	638	3.6	0.07	14.2	700	1080	0.29	3.1	1.8	0.02
OGGeo08	Certified value	112	<0.2	10.1	20.5	89.1	72	7720	4.7	0.5	844	7730	6530	2.58	22.0	11.3	0.18
	Value achieved	117.5	0.07	10.6	19.2	94.6	81	8460	5.2	0.5	886	8890	7310	2.70	22.1	10.7	0.15
		118.5	0.07	10.4	18.4	95.4	82	8380	4.9	0.5	907	8540	7260	2.80	21.2	11.8	0.17
		118	<0.2	10.5	18.8	96.8	81	8410	5.0	0.5	903	8620	7240	2.79	20.8	11.1	0.16
		121	<0.2	11.2	19.4	98.0	82	8480	5.0	0.5	901	8640	7230	2.78	21.8	11.4	0.16
GBM908-10	Certified value	55	0.5	1.2	1.8	15.4	21	3630	2.6	0.02	62.9	2255	2065	0.37	1.4	0.9	0.05
	Value achieved	57.4	0.6	1.1	1.7	14.5	22	3630	2.6	0.01	61.5	2180	2050	0.37	1.3	1.2	0.05
		57.5	0.4	1.2	1.8	15.3	21	3530	2.6	0.03	68.3	2210	2070	0.36	1.3	0.9	0.04
		54.4	0.4	1.1	1.7	14.6	22	3650	2.7	0.01	61.9	2240	2090	0.38	1.3	0.9	0.04
		54.8	0.4	1.2	1.8	14.3	22	3650	2.6	0.01	60.6	2260	2070	0.38	1.5	0.9	0.04
		57.3	0.4	1.1	1.7	14.9	23	3570	2.6	0.01	63.5	2250	2090	0.38	1.3	0.8	0.03
Average achieved																	
GEOMS-03		613.0	0.3	0.3	0.3	11.5	72	131.3	4.0	0.7	3.2	52.5	5.7	0.0	12.4	2.4	0.1
MRGeo08		33.0	-	0.7	2.3	18.5	92.5	637.8	3.6	0.1	14.4	703.0	1075.0	0.3	3.4	1.7	0.0
OGGeo08		118.8	0.1	10.7	19.0	96.2	81.5	8432.5	5.0	0.5	899.3	8672.5	7260.0	2.8	21.5	11.3	0.2
GBM908-10		56.3	0.4	1.2	1.7	14.7	22	3606.0	2.6	0.0	63.2	2228.0	2074.0	0.4	1.3	0.9	0.0
Error																	
GEOMS-03		1.4	-10.0	15.4	3.8	4.6	0.0	1.3	1.0	7.1	0.6	4.0	6.9	12.5	-5.8	-5.4	0.0
MRGeo08		-2.4	-	4.5	-2.0	5.6	1.6	1.6	4.4	-3.6	1.5	-2.3	-3.3	7.6	-13.9	-41.7	41.7
OGGeo08		-6.0	-	-5.3	7.3	-8.0	-13.2	-9.2	-6.7	12.7	-6.5	-12.2	-11.2	-7.3	2.4	0.4	11.1
GBM908-10		-2.3	12.0	0.9	3.1	4.4	-4.8	0.7	-1.4	-60.0	-0.4	1.2	-0.4	-1.1	7.6	-4.4	20.0
ERROR (%)		-2	1	4	3	2	-4	-1	-1	-11	-1	-2	-2	3	-2	-13	18

Table S4. ICP-MS instrument settings used for water sample analysis.

Parameter	Value	
RF power	1550 W	
Carrier gas	1.14 L min^{-1}	
Sample depth	8.0 mm	
Spray chamber temperature	2 °C	
Nebulizer	Microflow	
Nebulizer pump	0.1 rps	
Sampler and skimmer cones	Nickel	
Gas in the reaction/collision cell	Helium (4.3 mL min^{-1})	Hydrogen (3.5 mL min^{-1})
Mass monitored for the different	^{52}Cr, ^{59}Co, ^{72}Ge, ^{60}Ni, ^{95}Mo, ^{111}Cd, ^{121}Sn, ^{125}Te, ^{126}Te, ^{201}Hg, ^{208}Pb, ^{209}Bi	^{75}As, ^{77}Se, ^{78}Se, ^{197}Au

Table S5. Correlation coefficients for all trace elements, and significance of a correlation coefficient (determined by t-test confidence level of linear relationships in Microsoft Excel) between Au vs. Bi, Cd, Hg, Ni, Pb, S, Se and Te. Statistically significant correlation coefficients: $P < 0.05$.

Element	As	Au	Bi	Cd	Co	Cr	Cu	Fe	Hg	Mo	Ni	Pb	S	Sb	Se	Te	TOC
As	1.00																
Au	0.60	1.00															
Bi	0.50	0.93	1.00														
Cd	0.60	0.93	0.93	1.00													
Co	-0.27	-0.58	-0.13	-0.35	1.00												
Cr	-0.07	-0.77	-0.35	-0.08	-0.36	1.00											
Cu	0.01	-0.43	-0.34	-0.03	-0.33	0.97	1.00										
Fe	0.57	0.81	-0.16	0.11	-0.34	0.60	0.67	1.00									
Hg	0.39	0.94	0.93	0.92	-0.17	-0.22	-0.24	-0.06	1.00								
Mo	0.85	0.56	0.54	0.70	-0.61	0.19	0.30	0.54	0.43	1.00							
Ni	-0.23	0.68	-0.29	-0.11	-0.14	0.37	0.36	0.16	-0.17	-0.03	1.00						
Pb	0.49	0.79	0.91	0.87	-0.33	-0.41	-0.31	-0.20	0.77	0.61	-0.33	1.00					
S	-0.04	-0.65	-0.12	-0.28	0.91	-0.32	-0.23	-0.09	-0.19	-0.43	-0.26	-0.28	1.00				
Sb	0.47	0.93	0.97	0.95	-0.23	-0.25	-0.24	-0.05	0.99	0.53	-0.17	0.84	-0.23	1.00			
Se	0.50	0.87	0.94	0.85	0.10	-0.31	-0.35	-0.09	0.92	0.40	-0.35	0.77	0.11	0.93	1.00		
Te	0.17	-0.17	0.36	0.21	0.77	-0.16	-0.28	-0.07	0.33	-0.16	-0.27	0.10	0.85	0.29	0.57	1.00	
TOC	0.25	0.02	-0.22	0.03	-0.67	0.59	0.60	0.66	-0.19	0.45	0.12	-0.08	-0.41	-0.15	-0.33	-0.45	1.00

Significance of correlation coefficient

P value (Au vs Se)	0.00005
P value (Au vs Te)	0.04738
P value (Au vs Pb)	0.00048
P value (Au vs Ni)	0.0000000002
P value (Au vs Sb)	0.00386
P value (Au vs Hg)	0.01573
P value (Au vs Bi)	0.00020
P value (Au vs Cd)	0.00214
P value (Au vs S)	0.00945