Supplementary material

Propagation of errors on the signal due to blank correction

With n standing for the total number of counts per second (cps × dwell time × number of cycles) for a particular element, mass balance conservation reads:

$$n = n_{meas} - n_{blk}$$

Clearly, the uncertainties depend on the sample/blank ratio. Using logarithms to take the large dynamic range into account, differentiating and taking expectations:

$$\frac{\sigma_n^2}{n^2} = \frac{\sigma_{meas}^2}{(n_{meas} - n_{blk})^2} + \frac{\sigma_{blk}^2}{(n_{meas} - n_{blk})^2}$$

where σ^2 stands for variance. A more explicit expression is:

$$\frac{\sigma_n^2}{n^2} = f_{meas}^2 \times \frac{\sigma_{meas}^2}{n_{meas}^2} + f_{blk}^2 \times \frac{\sigma_{blk}^2}{n_{blk}^2}$$

where the amplification factors f are defined as:

$$f_{meas} = \frac{n_{meas}}{n_{meas} - n_{blk}} \quad \text{and} \quad f_{blk} = \frac{n_{blk}}{n_{meas} - n_{blk}}$$

These formulas produce the desired results that (1) when $n_{meas} \gg n_{blk}$, $f_{blk} \to 0$, and $\sigma_n/n \to \sigma_{meas}/n_{meas}$ and (2) when $n_{meas} \to n_{blk}$, $f_{blk} \to \infty$, and $\sigma_n/n \to \infty$. For a 3-sigma interval and assuming that $\sigma_{meas} < \sigma_{blank}$, standard formulae for the limit of detection (*https://media.iupac.org/publications/analytical_compendium/*) can be retrieved.

Table S1. Standard solutions used in this work

Level	Concentration (ng/mL)	Volume (mL)	Standard concentration (µg/L)	Required volume (mL)
Std 1	0.1	10	100	0.01
Std 2	0.5	10	100	0.05
Std 3	1	10	100	0.1
Std 4	2	10	100	0.2
Std 5	10	10	100	1

Isotopes monitored

^{63}Cu (STD), ^{63}Cu (KED), ^{65}Cu (STD), ^{65}Cu (KED), ^{99}Ru (STD), ^{99}Ru (KED), ^{100}Ru (STD), ^{100}Ru (KED), ^{101}Ru (STD), ^{101}Ru (KED), ^{103}Rh (STD), ^{103}Rh (KED), ^{105}Pd (STD), ^{105}Pd (KED), ^{106}Pd (STD), ^{106}Pd (KED), ^{107}Ag (STD), ^{107}Ag (KED), ^{108}Pd (STD), ^{108}Pd (KED), ^{109}Ag (STD), ^{109}Ag (KED), ^{115}In (STD), ^{115}In (KED), ^{186}Os (STD), ^{186}Os (KED), ^{188}Os (STD), ^{188}Os (KED), ^{191}Ir (STD), ^{191}Ir (KED), ^{193}Ir (STD), ^{193}Ir (KED), ^{194}Pt (STD), ^{194}Pt (KED), ^{195}Pt (STD), ^{195}Pt (KED), ^{196}Pt (STD), ^{196}Pt (KED), ^{197}Au (STD), ^{197}Au (KED), ^{204}Pb (STD), ^{204}Pb (KED), ^{206}Pb (STD), ^{206}Pb (KED), ^{207}Pb (STD), ^{207}Pb (KED), ^{208}Pb (STD), ^{208}Pb (KED).

Table S2. Matrix of isotopic abundances (in percent) used for calculating the potential contribution of argides and Mo between mass 92 and mass 116 of argides and Mo to the PGE signal

Mass	$Fe^{40}Ar$	$Co^{40}Ar$	$Ni^{40}Ar$	$Cu^{40}Ar$	$Zn^{40}Ar$	Mo	Ru	Rh	Pd	Ag	Cd
92						14.836					
94						9.2466					
95						15.92					
96	91.75					16.676	5.54				
97	2.119					9.5551					
98	0.282		68.08			24.133	1.87				
99		100					12.76				
100			26.22			9.6335	12.6				
101			1.14				17.06				
102			3.635				31.55		1.02		
103				69.17				100			
104			0.926		48.63		18.62		11.14		
105				30.83					22.33		
106					27.9				27.33		1.25
107					4.1					51.839	
108					18.75				26.46		0.89
109										48.161	
110									11.72		12.49
111											12.8
112											24.13
113											12.22
114											28.73
116											7.49

Table S3. Description of the samples analyzed (see ref 24-26)

coin	Type	Province	group	Mint	Dates
Gil 01	owl	Attica	1	Athens	
Gil 01 R	owl	Attica	1	Athens	
Gil 02	owl	Attica	1	Athens	
Gil 03	owl	Attica	1	Athens	
Gr1	owl	Attica	1	Athens	393-300 BC
P421	owl	Attica	1	Athens	454-404 BC
Dr b		Ionia	2	Istros	
Gil 06			2	Rhodes	200-101 BC
P284		Ionia	2	Ionia	
P288		Ionia	2	Lesbos	400-350 BC
P355	alexander	Ionia	2	Colophon	323-318
P356	alexander	Ionia	2	Colophon	310-301 BC
P417	alexander	Ionia	2	Colophon	323-319 BC
P419	alexander	Ionia	2	Colophon	323-319 BC
P420	alexander	Ionia	2	Colophon	323-319 BC
Alex II b	alexander	Macedonia H	3	Pella	336-323 BC
Alex III b	alexander	Macedonia H	3	Pella	
Hemi 2	Hemidrachm	Macedonia	3	Macedonia	400-200 BC
P272	alexander	Macedonia H	3	Pella	
P285	Tetrobol	Macedonia	3	Macedonia	
P338	Demetrios	Macedonia H	3	Pella	
P363	alexander	Macedonia H	3	Pella	323-317 BC
P364	alexander	Macedonia H	3	Pella	323-317 BC
Alex I b	alexander	Thrace	4	Abydos	320-297 BC
Gil 09		Thrace	4	Abdera	365-245 BC
Gil 10		Thrace	4	Thasos	520-490 BC
P271		Thrace	4	Apollonia Pontika	500-200 BC
P273	Lion	Thrace	4	Chersonesos	
P274	Lion	Thrace	4	Chersonesos	
P289		Thrace	4	Byzantion	387-340 BC
P290		Thrace	4	Thrace	386-338 BC
P294	alexander	Thrace	4	Abydos	350-325
P297		Mysia	4	Kyzikos	390-341 BC
P301		Mysia	4	Kyzikos	
P314	Lion	Thrace	4	Chersonesos	400-338 BC
P316		Thrace	4	Thasos	404-355 BC
P317		Thrace	4	Thasos	525-480 BC
P318		Thrace	4	Chersonesos	400-338 BC
P321		Mysia	4	Kyzikos	525-475 BC
P337	alexander	Thrace	4	Thrace	299-298 BC
P416	alexander	Troas	4	Abydos	310-301 BC

P418	alexander	Troas	4	Abydos	310-301 BC
Pont 1		Thrace	4	Apollonia Pontika	500-200 BC
Pont 2 b		Thrace	4	Apollonia Pontika	500-200 BC
Pont 3 b		Thrace	4	Apollonia Pontika	500-200 BC
Gil 08		Cilicia	5	Cilicia	400-301 BC
P292		Lycia	5	Lycia	167-88 BC
CW22	Athena	Thessaly	6	Pharsalos	450-400 BC
CW34	Athena	Thessaly	6	Pharsalos	
P291		Thessaly	6	Magnesia	350-325 BC
P313		Peloponnese	8	Argos	480-430 BC
Gil 04		Sicily	9	Gela	498-480 BC
P277	Siglos	Persia	10	Persia	
PAR 2 b		Parthia	10	Ecbatana	
R118 b	Licinius Crassus	Rome	11	Narbo	118 BC
R121 b	Plutia	Rome	11	Rome	121 BC
R90 b	Lucretia	Rome	11	Rome	136 BC
All 1	Horse	Gaul	12	Allobroges	
Es03	Henri IV	Spain	12	Jaen	
Fr 2	Louis XI	France	12	Rouen	
GAU	Togirix	Gaul	12	Sequanes	
Es23	Philip V	Mexico	13	Mexico	
Es29	Philip V	Mexico	13	Mexico	
M5	Philip II	Mexico	13	Mexico	
Poto D	Charles III	Peru	14	Potosi	1760 AD
Poto E	Philip IV-Charles II	Peru	14	Potosi	1660-1670
Poto F	Ferdinand VI	Peru	14	Potosi	1750 AD
P374	karshapana Magadha	India	15	India	550-461 BC
P375	Annuruddha-Nagadasaka	India	15	India	445-413 BC
P389	Early ¼ shatamana	India	15	India	c. 600-500 BC
P390	Early ¼ shatamana	India	15	India	c. 600-500 BC
P393	Early ¼ shatamana	India	15	India	c. 600-500 BC

Table S4. Pb and Ag isotopic data from ref 24-26.

coin	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Tmod (Ma)	mu	kappa	ε_{109Ag} ×10,000
Gil 01	18.8408	15.6947	38.9034	62	9.892	3.887	0.03
Gil 01 R	18.8408	15.6947	38.9034	62	9.892	3.887	0.03
Gil 02	18.8555	15.6978	38.8960	57	9.901	3.876	-0.53
Gil 03	18.8511	15.6968	38.8998	58	9.897	3.88	-0.47
Gr1	18.8580	15.7010	38.9140	61	9.912	3.884	-0.15
P421	18.8577	15.6927	38.8614	45	9.881	3.855	
Dr b	18.7720	15.6840	38.8760	92	9.863	3.913	-0.29
Gil 06	18.8613	15.6892	38.8526	36	9.867	3.847	-0.41
P284	18.7513	15.6896	38.8178	118	9.889	3.899	-2.87
P288	18.7826	15.6886	38.8545	93	9.879	3.898	
P355	18.8069	15.6932	38.9462	84	9.892	3.93	-0.03
P356	18.8084	15.6937	38.9275	84	9.894	3.919	-0.48
P417	18.8710	15.7097	38.9038	69	9.943	3.874	
P419	18.8750	15.7465	39.0090	137	10.085	3.936	
P420	18.7504	15.6800	38.8442	100	9.852	3.91	
Alex II b	18.8240	15.7100	39.0060	104	9.954	3.954	0.3
Alex III b	18.8040	15.6770	38.9310	54	9.83	3.918	-0.17
Hemi 2	18.8110	15.6870	38.8840	69	9.867	3.894	-0.16
P272	18.5824	15.6736	38.7175	212	9.861	3.952	-0.23
P285	18.7579	15.6728	38.8653	80	9.823	3.913	0.65
P338	18.7542	15.6711	38.7868	79	9.817	3.875	-0.86
P363	18.8073	15.6897	38.9310	77	9.878	3.921	-0.97
P364	18.7928	15.6829	38.8996	74	9.855	3.912	-0.92
Alex I b	18.7830	15.6880	38.8810	91	9.877	3.862	-0.23
Gil 09	18.7642	15.6963	38.9420	121	9.912	3.956	-2.72
Gil 10	18.8090	15.6872	38.9195	70	9.869	3.913	
P271	18.7607	15.6835	38.8329	99	9.863	3.899	-0.40
P273	18.8366	15.6886	38.8357	53	9.869	3.854	-0.32
P274	18.7490	15.6875	38.8754	116	9.881	3.929	-1.07
P289	18.4547	15.6734	38.6082	305	9.889	3.979	-0.34
P290	18.7445	15.6850	38.8495	114	9.872	3.918	-0.58
P294	18.7140	15.6867	38.7751	140	9.885	3.901	0.03
P297	18.7184	15.6801	38.7772	124	9.858	3.896	-0.58
P301	18.7517	15.6766	38.8614	92	9.839	3.916	-0.60
P314	18.5760	15.6704	38.6270	210	9.85	3.908	-1.30
P316	18.3546	15.6437	38.3836	323	9.795	3.916	-0.30

P317	18.7460	15.6748	38.8597	93	9.833	3.919	0.54
P318	18.6349	15.6651	38.7133	157	9.817	3.912	-1.04
P321	18.7169	15.6785	38.7859	122	9.853	3.901	-0.69
P337	18.7759	15.6658	38.8496	53	9.792	3.891	0.17
P416	19.2647	15.7273	39.0638	-188	9.945	3.721	
P418	19.2875	15.7695	39.2154	-119	10.099	3.793	
Pont 1	18.8520	15.6970	38.8940	58	9.898	3.877	-0.09
Pont 2 b	18.7110	15.6850	38.9160	139	9.879	3.973	-0.48
Pont 3 b	18.8210	15.6810	38.9650	49	9.842	3.926	0.34
Gil 08	18.7189	15.6816	38.8872	126	9.864	3.952	-0.51
P292	18.5627	15.6735	38.7331	226	9.865	3.973	-0.91
CW22	18.842	15.695	38.900	61	9.892	3.885	
CW34							
P291	18.7974	15.6950	38.8976	94	9.901	3.912	-0.09
P313	18.8136	15.6941	38.8537	80	9.894	3.88	-0.50
Gil 04	18.8160	15.6895	38.8193	70	9.876	3.859	0.36
P277	18.7709	15.6836	38.8414	92	9.862	3.897	-0.55
PAR 2 b	18.5480	15.6710	38.7140	232	9.859	3.972	-0.58
R118 b	18.1770	15.6630	38.3490	489	9.919	4.025	-0.96
R121 b	18.4970	15.6740	38.7430	275	9.882	4.022	0.06
R90 b	18.6640	15.6910	38.9010	185	9.912	3.998	-0.69
All 1	18.6680	15.6830	38.9560	167	9.88	4.021	-0.52
Es03	18.3170	15.6450	38.4080	353	9.809	3.955	-0.13
Fr 2	18.3820	15.6370	38.4140	290	9.762	3.912	-0.12
GAU	18.7220	15.6840	39.0130	129	9.873	4.015	-0.58
Es23	18.7290	15.6430	38.6610	42	9.714	3.818	0.63
Es29	18.7380	15.6370	38.6420	23	9.689	3.801	0.86
M5	18.7170	15.6440	38.6650	53	9.72	3.828	0.69
Poto D	18.3190	15.6500	38.4890	361	9.829	3.999	1.55
Poto E	18.6320	15.6700	38.8960	168	9.837	4.01	0.76
Poto F	18.4600	15.6690	38.6960	293	9.871	4.02	3.26
P374	18.0430	15.7045	37.9072	657	10.133	3.883	
P375	18.3919	15.7436	38.3463	477	10.188	3.905	
P389	19.2336	15.7312	40.1451	-157	9.964	4.246	
P390	19.3170	15.7389	40.1725	-203	9.98	4.207	
P393	19.5297	15.7382	40.5651	-365	9.949	4.248	

Table S5. PGE and Au results listed in ng measured for the sake of comparison with blanks. Concentrations may be derived by dividing the amount measured (in ng, corrected for blank) by sample weight.

coin	m (g)	Ru	Os	Rh	Ir	Pd	Pt	Au (ng)
Gil 01	0.2285	0.03	0.82	56.47	3.46	53.29	31.68	181076
Gil 01 R	0.2285	0.07	0.99	63.53	3.68	53.23	35.05	430532
Gil 02	0.1538	0.04	0.00	76.16	2.19	53.11	46.56	85308
Gil 03	0.2290	0.05	0.00	59.35	1.73	108.09	311.51	102438
Gr1	0.1801	0.00	0.00	9.43	0.81	69.16	45.07	151684
P421	0.1963	0.00	0.28	110.70	6.55	53.27	20.12	65525
Dr b	0.1577	0.39	0.00	12.32	5.26	32.99	39.01	454381
Gil 06	0.1215	0.00	0.00	49.56	0.78	131.90	232.08	1769202
P284	0.0915	1.94	1.14	31.93	38.57	73.77	113.47	696558
P288	0.1174	0.80	0.55	8.13	14.00	122.55	177.02	777143
P355	0.3353	0.00	5.49	67.98	0.09	62.77	19.84	794471
P356	0.2471	0.00	0.00	77.42	0.06	14.90	11.07	1576050
P417	0.1753	0.27	1.23	23.38	86.72	139.44	287.98	1833028
P419	0.2100	0.01	0.00	46.63	2.81	21.41	30.84	719251
P420	0.1735	0.09	0.03	10.65	2.09	147.59	222.60	1402293
Alex II b	0.2707	0.00	0.00	55.89	0.55	40.45	38.12	1226518
Alex III b	0.3092	0.01	0.00	30.59	4.73	327.23	583.59	3346105
Hemi 2	0.0859	2.83	1.37	11.30	9.61	62.74	93.97	1182933
P272	0.1385	0.10	0.00	0.69	0.57	275.35	351.66	1510333
P285	0.2566	0.00	0.00	73.96	0.02	23.04	17.10	133785
P338	0.2510	0.07	0.00	80.20	2.25	243.20	776.81	2887679
P363	0.3276	0.32	0.00	43.24	18.61	285.77	382.47	2767440
P364	0.3315	0.00	0.00	54.64	0.00	33.99	30.14	1839881
Alex I b	0.2544	0.00	0.00	89.10	1.92	223.85	406.67	1466861
Gil 09	0.1538	0.00	0.00	28.90	0.13	51.40	15.78	4497641
Gil 10	0.1465	0.09	0.00	33.31	2.52	41.01	27.42	426828
P271	0.1058	0.03	0.00	4.05	1.15	25.74	23.33	397837
P273	0.1760	0.87	1.90	24.64	12.24	186.54	190.82	2097814
P274	0.1813	0.21	0.00	10.18	2.86	60.67	47.69	1500215
P289	0.1975	0.12	0.20	9.57	2.09	76.01	83.48	1954265
P290	0.1172	0.43	0.06	9.45	3.97	44.02	45.75	716191
P294	0.1244	2.73	0.24	9.02	24.68	56.24	70.18	3835909
P297	0.1547	0.25	1.12	19.96	12.48	321.85	483.24	2798173
P301	0.1145	0.13	0.13	5.33	3.33	54.98	45.85	541820
P314	0.2955	0.06	0.00	25.27	1.97	60.88	41.41	362523
P316	0.2424	0.00	0.00	5.00	3.53	83.98	60.88	899326
P317	0.2107	0.00	0.00	76.71	0.13	5.53	6.34	73587
P318	0.2435	0.83	0.00	34.98	17.67	71.98	85.50	1299857
P321	0.1939	0.00	0.02	0.87	0.50	33.40	46.55	831794
P337	0.3431	0.00	0.00	24.43	0.69	79.18	62.44	1635133

P416	0.1749	0.00	1.33	11.29	0.54	127.21	232.80	1865795
P418	0.2057	0.00	0.04	7.13	0.68	218.79	330.45	2801045
Pont 1	0.2770	0.01	0.00	63.30	2.13	274.77	138.04	1040963
Pont 2 b	0.2024	0.00	0.00	18.98	5.76	62.92	87.40	109806
Pont 3 b	0.2075	0.00	0.00	38.34	0.64	37.93	15.13	185701
Gil 08	0.0455	0.05	8.20	2.76	0.53	37.09	25.31	434198
P292	0.1012	0.02	0.00	7.92	0.66	80.59	57.24	842732
CW22	0.1645	0.11	0.00	6.25	0.01	9.54	3.82	144218
CW34	0.1866	1.08	0.49	33.43	24.34	173.76	166.89	522134
P291	0.2568	5.02	0.00	70.06	168.49	143.73	244.63	2080538
P313	0.2727	0.00	0.00	127.99	2.64	82.15	34.25	94832
Gil 04	0.1130	0.01	0.38	3.63	0.10	57.25	62.85	898108
P277	0.2567	0.05	0.00	5.94	5.92	172.04	230.41	866360
PAR 2 b	0.1214	0.17	0.00	14.26	1.67	171.90	121.66	1054096
R118 b	0.1955	0.00	0.00	7.88	0.22	157.17	75.07	2475195
R121 b	0.1889	0.00	0.00	7.40	0.00	237.93	113.38	492555
R90 b	0.1961	0.35	0.00	27.90	18.26	171.40	207.03	1573589
All 1	0.2728	0.03	0.07	21.98	1.27	176.01	82.81	1600563
Es03	0.0957	0.33	0.00	13.47	0.10	28.17	8.69	30144
Fr 2	0.0957	0.01	0.00	2.04	0.02	3.22	1.25	29864
GAU	0.2773	0.04	0.00	32.05	2.62	316.91	187.76	2748746
Es23	0.2072	0.00	0.58	3.47	0.06	100.21	19.99	50471
Es29	0.1832	0.01	0.02	2.53	0.00	14.45	6.14	23970
M5	0.1900	0.05	0.00	16.98	0.01	13.40	4.50	41131
Poto D	0.1661	0.01	0.05	1.10	0.00	1.22	0.13	n.d.
Poto E	0.1504	0.00	0.00	0.42	0.00	0.40	0.00	n.d.
Poto F	0.1659	0.00	0.02	6.11	0.00	1.46	0.51	n.d.
P374	0.2322	7.59	3.27	89.24	69.17	374.94	823.47	3913775
P375	0.2128	2.03	5.89	31.74	19.44	112.35	228.92	2672401
P389	0.1889	3.62	0.84	52.85	51.25	308.43	437.29	2274993
P390	0.1682	1.25	0.73	38.58	18.80	167.75	201.95	1897340
P393	0.1741	0.30	5.21	19.28	57.66	327.15	564.77	2453034

Table S6. Slopes of the regression lines in log-log plots for PGEs and Au (independent variable as rows and dependent variables as columns). Monte-Carlo propagated 1-sigma errors are given in parentheses. These slopes allow the ranges of variation to be compared and relative solid-liquid fractionation to be assessed. In order to preserve symmetry upon exchange of dependent and independent variables, the least-square straight-lines were calculated from the sum of squared orthogonal distances of each point to the line. Data missing or below the detection level were disregarded.

	Ru	**Os**	**Rh**	**Ir**	**Pd**	**Pt**	**Au**
Ru	1	0.3 (0.0)	0.20 (0.02)	0.87 (0.05)	0.25 (0.00)	0.38 (0.00)	0.24 (0.00)
Os	3.14 (0.30)	1	0.09 (0.05)	0.06 (0.37)	0.18 (0.01)	0.24 (0.00)	0.16 (0.00)
Rh	4.89 (0.37)	11 (109)	1	4.1 (9.4)	-1.64 (2.00)	11.6 (211.)	-0.68 (0.25)
Ir	1.15 (0.07)	16.6 (41.5)	0.24 (0.27)	1	0.27 (0.02)	0.39 (0.05)	0.29 (0.01)
Pd	3.94 (0.03)	5.58 (0.22)	-0.61 (2.63)	3.70 (0.41)	1	1.71 (0.49)	0.26 (0.12)
Pt	2.60 (0.02)	4.16 (0.04)	0.09 (261)	2.56 (0.53)	0.58 (0.21)	1	0.62 (0.00)
Au	4.25 (0.01)	6.39 (0.01)	-1.47 (4.34)	3.46 (0.12)	3.9 (66.2)	1.60 (0.01)	1