Supplementary Table 1† Spectral interferences on Ru, Rh and Pd in LA-ICP-MS PGE analysis.

Interferences		**Ru**			**Rh**	**Pd**		
		99	101	102	103	105	106	108
Argide	**Co**	$^{59}\mathrm{Co}^{40}\mathrm{Ar}^{+}$ (99.60*)						
	Ni		$^{61}\mathrm{Ni}^{40}\mathrm{Ar}^{+}$ (1.13)	$^{62}\mathrm{Ni}^{40}\mathrm{Ar}^{+}$ (3.58)				
	Cu	$^{63}\mathrm{Cu}^{36}\mathrm{Ar}$ (0.23)	$^{65}\mathrm{Cu}^{36}\mathrm{Ar}^{+}$ (0.10)		$^{63}\mathrm{Cu}^{40}\mathrm{Ar}^{+}$ (68.89)	$^{65}\mathrm{Cu}^{40}\mathrm{Ar}^{+}$ (30.71)		
	Zn				$^{67}\mathrm{Zn}^{36}\mathrm{Ar}^{+}$ (0.01)		$^{66}\mathrm{Zn}^{40}\mathrm{Ar}^{+}$ (27.70)	$^{68}\mathrm{Zn}^{40}\mathrm{Ar}^{+}$ (18.72)
Isobaric				$^{102}\mathrm{Pd}^{+}$ (1.02)			$^{106}\mathrm{Cd}^{+}$ (1.20)	$^{108}\mathrm{Cd}^{+}$ (0.90)
Doubly Charged		$^{198}\mathrm{Hg}^{++}$ (10.02) $^{198}\mathrm{Pt}^{++}$ (7.20)	$^{202}\mathrm{Hg}^{++}$ (29.80)	$^{204}\mathrm{Hg}^{++}$ (6.85) $^{204}\mathrm{Pb}^{++}$ (1.40)	$^{206}\mathrm{Pb}^{++}$ (24.10)			
Oxide			$^{85}\mathrm{Rb}^{16}\mathrm{O}^{+}$ (72.44)	$^{86}\mathrm{Sr}^{16}\mathrm{O}^{+}$ (9.84) $^{88}\mathrm{Sr}^{14}\mathrm{O}^{+}$ (82.28) $^{90}\mathrm{Zr}^{12}\mathrm{O}^{+}$ (50.88)	$^{85}\mathrm{Rb}^{18}\mathrm{O}^{+}$ (0.14) $^{87}\mathrm{Rb}^{16}\mathrm{O}^{+}$ (27.77) $^{87}\mathrm{Sr}^{16}\mathrm{O}^{+}$ (6.98)	$^{89}\mathrm{Y}^{16}\mathrm{O}^{+}$ (99.76)	$^{88}\mathrm{Sr}^{18}\mathrm{O}^{+}$ (16.52) $^{90}\mathrm{Zr}^{16}\mathrm{O}^{+}$ (51.30)	$^{90}\mathrm{Zr}^{18}\mathrm{O}^{+}$ (10.30) $^{92}\mathrm{Zr}^{16}\mathrm{O}^{+}$ (17.17) $^{92}\mathrm{Mo}^{16}\mathrm{O}^{+}$ (14.77)
Hydride		$^{98}\mathrm{Mo}^{1}\mathrm{H}^{+}$ (24.13)	$^{100}\mathrm{Mo}^{1}\mathrm{H}^{+}$ (9.63) $^{100}\mathrm{Ru}^{1}\mathrm{H}^{+}$ (12.60)	$^{101}\mathrm{Ru}^{1}\mathrm{H}^{+}$ (17.00)	$^{102}\mathrm{Ru}^{1}\mathrm{H}^{+}$ (31.6) $^{102}\mathrm{Pd}^{1}\mathrm{H}^{+}$ (1.02)	$^{104}\mathrm{Ru}^{1}\mathrm{H}^{+}$ (18.70) $^{104}\mathrm{Pd}^{1}\mathrm{H}^{+}$ (11.14)	$^{105}\mathrm{Pd}^{1}\mathrm{H}^{+}$ (22.60)	$^{107}\mathrm{Ag}^{1}\mathrm{H}^{+}$ (51.75)
Hydroxide				$^{85}\mathrm{Rb}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$ (71.98)	$^{86}\mathrm{Sr}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$ (9.84)	$^{88}\mathrm{Sr}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$ (82.37)	$^{89}\mathrm{Y}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$ (99.70)	
Nitride		$^{85}\mathrm{Rb}^{14}\mathrm{N}^{+}$ (27.53)	$^{87}\mathrm{Rb}^{14}\mathrm{N}^{+}$ (27.73) $^{87}\mathrm{Sr}^{14}\mathrm{N}^{+}$ (6.97)	$^{87}\mathrm{Rb}^{15}\mathrm{N}^{+}$ (0.10)	$^{88}\mathrm{Sr}^{15}\mathrm{N}^{+}$ (0.30) $^{89}\mathrm{Y}^{14}\mathrm{N}^{+}$ (99.60)	$^{90}\mathrm{Zr}^{15}\mathrm{N}^{+}$ (0.19) $^{91}\mathrm{Zr}^{14}\mathrm{N}^{+}$ (11.18)	$^{92}\mathrm{Mo}^{14}\mathrm{N}^{+}$ (17.13) $^{92}\mathrm{Zr}^{14}\mathrm{N}^{+}$ (99.60)	$^{94}\mathrm{Zr}^{14}\mathrm{N}^{+}$ (17.33)
Others		$^{64}\mathrm{Zn}^{35}\mathrm{Cl}^{+}$ (36.82) $^{87}\mathrm{Sr}^{12}\mathrm{C}^{+}$ (6.92)	$^{66}\mathrm{Zn}^{35}\mathrm{Cl}^{+}$ (21.1) $^{88}\mathrm{Sr}^{13}\mathrm{C}^{+}$ (0.91) $^{89}\mathrm{Y}^{12}\mathrm{C}^{+}$ (98.90)	$^{94}\mathrm{Zr}^{12}\mathrm{C}^{+}$ (4.88) $^{89}\mathrm{Y}^{13}\mathrm{C}^{+}$ (1.10) $^{65}\mathrm{Cu}^{37}\mathrm{Cl}^{+}$ (75.01) $^{67}\mathrm{Zn}^{35}\mathrm{Cl}^{+}$ (31.07)	$^{66}\mathrm{Zn}^{37}\mathrm{Cl}^{+}$ (6.76) $^{91}\mathrm{Zr}^{12}\mathrm{C}^{+}$ (11.10) $^{90}\mathrm{Zr}^{13}\mathrm{C}^{+}$ (0.57)	$^{93}\mathrm{Nb}^{12}\mathrm{C}^{+}$ (98.90) $^{92}\mathrm{Mo}^{13}\mathrm{C}^{+}$ (0.16) $^{68}\mathrm{Zn}^{37}\mathrm{Cl}^{+}$ (45.55)	$^{94}\mathrm{Zr}^{12}\mathrm{C}^{+}$ (17.21)	$^{96}\mathrm{Ru}^{12}\mathrm{C}^{+}$ (5.46) $^{96}\mathrm{Mo}^{12}\mathrm{C}^{+}$ (16.52)

*: Abundance in %.

Supplementary Table 2† Summary of reported limits of detection (LOD) for ^{103}Rh and ^{105}Pd and CuAr contributions in LA-ICP-MS PGE analysis of chalcopyrite.

Published Applications	ICP-MS	Collision and Reaction Cell Gas	Laser Ablation System	Wave Length (nm)	Repetition Rate (Hz)	Energy Output (mJ pulse^{-1})	Spot Size (µm)	Scan Mode	Internal Standard	LOD (ng g^{-1})		CuAr Contribution (µg g^{-1})		CuAr Interference Correction
										^{103}Rh	^{105}Pd	^{103}Rh	^{105}Pd	
Alard et al., 2000[2]	Perkin Sciex ELAN 6000	-	Nd:YAG	266	4	0.5	40 - 60	Spot	-	24[a] 107[b]	39[a*] 320[b*]	-	-	-
Ballhaus et al., 2000[4]	VG Plasma QuaPQ2	-	Lamda Physik Lex 120I ArF	266	10	-	70	Line	-	10s	10s	-	-	No correction
Smith et al., 2014[5]	Thermo X Series 2	No	New Wave UV	213	10	6[f]	30	Line	^{33}S	-	-	-	-	Linear correlation[d]
Cabri et al., 2003[8]	VG Plasma Quad2S	No	Nd:YAG	266	10	0.3	35 - 40	Spot	^{34}S	< 100	< 100	-	-	Sylvester (2001)[53]
Barnes et al., 2006[15]	Thermo X7	7% H_2 + He	Nd:YAG	213	20	0.4	80	Spot	^{34}S	19 ± 49 (1sd)[c]	110 ± 40 (1sd)[c]	-	-	Linear correlation[d]
Godel et al., 2007[16]	Thermo X7	7% H_2 + He	Nd:YAG	213	20	0.8	80	Spot	^{34}S	60	350	2	2	Linear correlation[d]
Holwell et al., 2007[17]	Thermo X Series	no	New Wave UV	213	10	0.3	40	Spot	^{33}S	11	34[*]	-	-	Linear correlation[d]
Godel et al., 2008[18]	Thermo X7	7% H_2 + He	Nd:YAG	213	20	0.3	80	Spot	^{34}S	-	-	0.5	0.5	Linear correlation[d]
Hutchinson et al., 2008[19]	Thermo X Series	No	NewWave UV	213	10	0.35	40	Spot	^{33}S	-	-	-	-	-
Holwell et al., 2010[20]	Thermo X Series	No	NewWave UV	213	10	0.35	40	Spot	-	-		-	-	No correction
Dare et al., 2010[21]	Thermo X7	-	Nd:YAG	213	10	0.3	80	Spot	^{57}Fe	121[c]	293[c]	-	-	Linear correlation[d]
Holwell et al., 2011[22]	Thermo X Series	No	New Wave UV	213	10	0.35	30 - 55	Spot	^{33}S	11	34	-	-	-
Dare et al., 2011[23]	Thermo X7	-	Nd:YAG	213	10	0.3	80	Spot	^{57}Fe	-	-	-	-	-
Piña et al., 2012[24]	Thermo X7	-	Nd:YAG	213	10	0.8	80	Spot	^{57}Fe	-	-	-	-	-
Osbahr et al., 2013[25]	Agilent 7500i	-	New Wave UP	193	15	1.62[f]	35 - 50	Spot	S	-	-	4 - 5	6 - 8	Linear correlation[d]
Prichard et al., 2013[26]	Thermo X Series	No	NewWave UV	213	10	-	30	Line	^{33}S	100	-	-	-	Linear correlation[d]
Huminicki et al., 2008[27]	-	-	-	-	-	-	-	-	-	-	-	-	-	Sylvester (2001)[53]
Lorand et al., 2001[28]	Perkin Sciex ELAN 6000	-	Nd:YAG	266	4	0.5	40 - 60	Spot	-	24[a]	36[a*]	-	-	Linear correlation[e]
Guillong et al., 2011[35]	Agilent 7500 Agilent 7700 Thermo X7 PE 6100 DRC	No	NewWave UV New Wave UP Resonetics M50 ArF Geolas ArF	193 213	10	-	40	Spot	Cu	-	-	1.5 - 36	4.0 - 92	Linear correlation[e]
Cox et al., 2010[36]	Thermo X7	7% H_2 + He	Nd:YAG	213	-	-	80	Spot	-	< 100	< 100	-	-	No correction

[a]: LOD using He as a carrier gas; [b]: LOD using Ar carrier gas only; [c]: calculated based on the equation LOD = 3 x $(BC)^{1/2}$ x C/I, where BC is background count rate in counts s^{-1} ($CuFeS_2$ blank), I is counts s^{-1} and C is a content of Rh or Pd from a calibration standard, and sd is standard deviation; [d]: linear correlation between CuAr and Cu signal using Cu-rich synthetic standard; [e]: linear correlation between CuAr and Cu signal using pure Cu metal standard; [f]: Fluence in J cm^{-2}; *: LOD for Pd but not specify which Pd isotope; -: Unknown.

Supplementary Table 3† Synthetic and natural Cu-rich mineral samples used for PGE analyses by SN-ICP-MS and LA-ICP-MS.

Sources/Location	Material		Sample Name	Cu (%)*
GSC, Canada	Synthetic sulphide	Cubanite (Cbn, $CuFe_2S_3$)	OSP6	24.17
		Mooihoekite (Mh, $Cu_9Fe_9S_{16}$)	OSP7	35.87
		Bornite (Bn, Cu_5FeS_4)	OSP9	62.19
Creighton mine (footwall), Sudbury Ni-Cu camp, Ontario, Canada	Natural sulphide	Chalcopyrite (Ccp, $CuFeS_2$)	CNMC CRG-1902	34.52
Cavnic, Romania			CMNMC 31802	33.77
French Creek Mine, Pennsylvania, USA			CMNMC 31805	34.46
Sherritt-Gordon Mine, Manitoba, Canada			CMNMC 31819	34.57
Magma Mine, Superior, Arizona, USA			CMNMC 57165	34.61
Pima, Tucson, Arizona, USA			CMNMC 57199	34.55
Ani Mine, Akita, Japan			CMNMC 80822	34.61
Leeds Tp., Mégantic Co., Québec, Canada		Bornite (Bn, Cu_5FeS_4)	CMNMC 42116	63.31
Harvey Hill Mine, Québec, Canada			CMNMC 58944	62.99

*: EMPA data.

Table 4† Laser ablation systems operating and data acquisition parameters.

Manufacturer	**Teledyne Photon Machines**	**ESI NWR**
Model	ArF Excimer G2	Nd:YAG Solid State
Type of sample cell	Fast washout two-volume HelEx II	Two-volume
Wavelengths (nm)	193	213
Frequency (Hz)	10	10
Pulse width (ns)	< 5	4
Fluence (J cm^{-2})	3.78 - 4.25	1.66 - 3.80
Spot size (μm)	10, 20, 30, 40, 50, 65 and 110	110
Scan mode	Line and spot	Line and spot
Line scan speed (μm s^{-1})	1	3
He Carrier gas flow rate (L min^{-1})	MFC-1: 0.6; MFC-2: 0.4	0.7

Table 5† ICP-MS operating and data acquisition parameters.

Analysis Type		**LA-ICP-MS**				**SN-ICP-MS**			
Laboratory		GSC Canada		Agilent Technologies Canada Inc.				CANMET Canada	
Agilent ICP-MS model		7700x		8900x MS/MS		8800x MS/MS			
Sampling depth (mm)		6.5		8.0		8.0		5.9 - 8	
Ar carrier gas flow rate (L min^{-1})		1.02 - 1.04		0.9		1.05		1.05	
Collision mode only	Scan type	On-mass				On-mass			
	Gas type	No gas	He			He		He	
	Gas flow rate (mL min^{-1})	0	1, 2, 3, 4, 5, 6, 7, 8, 9			6		6	
	Octopole bias (V)	-5.8	-18			-18		-24	
	Octp RF (V)	200	200			200		200	
	KED (V)		5			5		7	
Collision and reaction mode	Scan type			On-mass and Mass-shift					
	Gas type			He	NH_3	He	NH_3	He	NH_3
	Gas flow rate (mL min^{-1})			1	0, 0.1, 0.2, 0.3, 0.4, 0.5	2	0.3	1	0.2 - 0.3
	Octopole bias (V)			-5		-4		-6	
	Octp RF (V)			180		140		170	
	KED (V)			-7		-7		-9	

Table 5† continued.

Analysis Type	**LA-ICP-MS**		**SN-ICP-MS**	
Data acquisition mode	Time resolved analysis		Spectrum	
Scan mode	Peak hopping			
Isotopes monitored (On-mass)	^{29}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{34}S, ^{42}Ca, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{62}Ni, ^{63}Cu,^{65}Cu, ^{66}Zn, ^{68}Zn, ^{75}As, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{99}Ru, ^{101}Ru, ^{102}Ru, ^{103}Rh, ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{109}Ag, ^{111}Cd, ^{189}Os, ^{193}Ir, ^{195}Pt, ^{197}Au, ^{202}Hg, ^{206}Pb, ^{208}Pb	^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{34}S, ^{39}K, ^{42}Ca, ^{57}Fe, ^{59}Co, ^{60}N, ^{62}Ni, ^{63}Cu, ^{65}Cu, ^{66}Zn, ^{68}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{99}Ru, ^{101}Ru, ^{102}Ru, ^{103}Rh, ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{109}Ag, ^{111}Cd, ^{175}Lu, ^{177}Hf, ^{189}Os, ^{191}Ir, ^{193}Ir,^{195}Pt, ^{197}Au, ^{198}Pt, ^{206}Pb	^{99}Ru, ^{101}Ru, ^{102}Ru,^{103}Rh, ^{105}Pd, ^{106}Pd, ^{107}Ag, ^{108}Pd, ^{109}Ag, ^{111}Cd, ^{191}Ir, ^{193}Ir, ^{195}Pt, ^{197}Au, ^{198}Pt	^{59}Co, ^{60}Ni, ^{62}Ni. ^{66}Zn, ^{68}Zn, ^{69}Ga, ^{71}Ga, ^{72}Ge, ^{73}Ge, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{99}Ru, ^{101}Ru, ^{102}Ru, ^{103}Rh, ^{105}Pd, ^{106}Pd, ^{107}Ag, ^{108}Pd, ^{109}Ag, ^{111}Cd, ^{140}Ce, ^{173}Yb, ^{175}Lu, ^{177}Hf, ^{181}Ta, ^{182}W, ^{188}Os, ^{191}Ir, ^{193}Ir, ^{195}Pt, ^{197}Au, ^{198}Pt, ^{205}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{209}Bi
Isotope monitored (Mass-shift)		^{197}Au → ^{231}Au	^{103}Rh → ^{171}Rh ^{195}Pt → ^{229}Pt ^{197}Au → ^{231}Au	^{103}Rh → ^{171}Rh ^{188}Os → ^{203}Os ^{189}Os → ^{204}Os ^{191}Ir → ^{206}Ir ^{193}Ir → ^{208}Ir ^{195}Pt → ^{229}Pt ^{197}Au → ^{231}Au ^{198}Pt → ^{232}Pt
Dwell time per isotope	50 ms (Rh); 30 ms (Pd); 10 ms (other PGE, Ag and Au); 3 - 10 ms (majors and other traces)	50 ms (Rh); 30 ms (Pd); 15 ms (Cd); 10 ms (Co, Ni, Zn, other PGE, Ag and Au); 5 ms (S, Fe, Cu and Pb); 3 ms (other traces); 1 - 2 ms (majors)	80 ms (Rh, Pd); 20 ms (other PGE, Ag and Au)	1 s (Rh, Pd and Cd); 0.4 s (others)

Supplementary Table 6† Background equivalent contents (BECs, ng g^{-1}) in Zn, Rb, Sr, Y, Zr and Mo (100 µg g^{-1}) and Cu (700 to 1000 µg g^{-1}) matrix blank using 8800x SN-ICP-MS/MS in He collision gas and NH_3/He reaction gas mode.

Element	**Rh**				**Pd**							
Isotope	**103**				**105**				**106**		**108**	
Collision and Reaction Gas Mode	**[He]**		**[NH_3/He]**		**[He]**		**[NH_3/He]**		**[NH_3/He]**			
	Mean	**SD[a]**	**Mean**	**SD[a]**	**Mean**	**SD[a]**	**Mean**	**SD[a]**	**Mean**	**SD[a]**	**Mean**	**SD[a]**
Zn (n = 6)	0.0035	0.0029	0.00037	0.000031	0.0026	0.00017	0.0031	0.00028	0.0032	0.00028	0.0030	0.00025
Rb (n = 6)	0.0007	0.00014	0.00077	0.00015	0.0018	0.00056	0.0018	0.00029	0.0022	0.00039	0.0019	0.00026
Sr (n = 6)	0.0060	0.0018	0.0538	0.0017	0.102	0.0061	2.15	0.0339	0.0053	0.00060	0.0063	0.0040
Y (n = 6)	0.0031	0.00016	0.0028	0.00021	15.76	1.36	5.46	0.191	1.44	0.088	0.0053	0.0008
Zr (n = 6)	0.0018	0.00068	0.0014	0.00046	0.0032	0.00045	0.0110	0.00057	5.85	0.299	2.08	0.101
Nb (n = 6)	0.00090	0.00024	0.00072	0.00012	0.00075	0.00010	0.0014	0.00018	0.0013	0.00012	0.0041	0.00013
Mo (n = 6)	0.0025	0.0016	0.0018	0.0010	0.0028	0.0008	0.0028	0.00071	0.0037	0.00040	0.046	0.0010
Ag (n = 6)	0.0014	0.000057	0.0015	0.000059	0.0022	0.0012	0.0028	0.0013	0.0024	0.00080	0.0021	0.0010
Pb (n = 6)	6.26	0.212	0.00052	0.00012	0.0031	0.0004	0.0035	0.0008	0.0033	0.00081	0.0034	0.00032
700 Cu[b] (n = 15)	0.00238	0.00006	0.00040	0.0001	0.0062	0.0005	0.00040	0.0003	0.00133	0.0004	0.00122	0.0003
1000 Cu[c] (n = 15)	0.0046	0.0011	0.00030	0.0002	0.0108	0.0028	0.00030	0.0004	0.00125	0.0008	0.00144	0.0005

[a]: standard deviation; [b]: 700 µg g^{-1} Cu; [c]: 1000 µg g^{-1} Cu; n**:** number of analysis.

Supplementary Table 7† Element content (in µg g^{-1}) of Mass-1determined using 7700x LA-ICP-MS and 8900x LA-ICP-MS/MS at spot size of 110 µm.

Analysis Mode	Items	Co	Ni	Cu	Zn	Mo	Ag	Cd	Os	Ir	Pt	Au	Pb
Information value (GeoRem 2002, compiled value[56])	Mean	67	71 - 102	134000	210000	61	67	70	0.031	64	62	47	67 - 80
7700x LA-ICP-MS No gas mode	Mean	66	161	118298	183034	57	54	29	0.006	75	68	45	77
	SD^a	1.9	62	5603	9487	1.3	1.5	5	0.004	1.8	1.7	2.6	4
	RSD (%)	3	39	5	5	2.3	3	17	78	2.4	3	6	6
	n	38	38	38	38	38	38	38	38	38	38	38	38
	Rel. Diff. (%)^b	-2	86	-12	-13	-6	-20	-58	-82	18	10	-5	4.01
7700x LA-ICP-MS He collision gas mode (He = 5 mL min^{-1})	Mean	73	136	99765	196846	58	55	27	0.007	68	62	46	76
	SD^a	6	43	14988	24118	2.30	1.5	5	0.006	3	3	5.99	2.58
	RSD (%)	8	31	15	12	4	3	17	83	4	5	13	3
	n	23	23	23	23	23	23	23	20	23	23	23	23
	Rel. Diff. (%)^b	9	57	-26	-6	-5	-17	-62	-78	7	0.1	-5	-3.8
8900x LA-ICP-MS/MS No gas mode	Mean					60	65	37	0.0026	65	58	54	81
	SD^a					0.5	0.3	2.8	0.0009	1.4	2.8	2.4	0.6
	RSD (%)					0.8	0.5	8	34	2.2	5	4	0.7
	n					2	2	2	5	6	6	6	2
	Rel. Diff. (%)^b					-1	-2	-47	-92	2	-6	15	11
8900x LA-ICP-MS/MS NH_3/He reaction gas mode (NH_3/He = 0.3 mL min^{-1})	Mean	70	103	145444	265441	60	73	49	0.0104	64	58	54	86
	SD^a	1.9	1.8	3513	9575	1.5	1.7	6	0.013	0.9	2.5	3	2.2
	RSD (%)	3	1.7	2.4	4	2.5	2.3	11	122	1.4	4	6	3
	n	7	7	7	7	7	7	7	8	11	11	11	7
	Rel. Diff. (%)^b	4	19	9	26	-1	9	-30	-67	1	-5	16	16

^{a}: standard deviation; ^{b}: the relative difference of element value determined by LA-ICP-MS against the value obtained by SN-ICP-MS; n**:** number of analysis.

Supplementary Table 8† Element content (in µg g^{-1}) of PGE-1B using 7700x LA-ICP-MS and 8900x LA-ICP-MS/MS at spot size of 110 µm, and 8800x SN-ICP-MS/MS analysis.

Analysis Mode	Items	Ru	Rh	Pd	Os	Ir	Pt	Au
8800x SN-ICP-MS/MS NH$_3$/He reaction gas mode	Mean	233	257	263	72.6	135	196	367
	SD[a]	5	6	4	9	6	4	5
	RSD (%)	2.2	2.2	1.4	12	4	1.9	1.4
	n	40	40	60	20	60	40	18
7700x LA-ICP-MS No gas mode	Mean	235	252	244	115	159	196	332
	SD[a]	14	17	13	31	23	14	20
	RSD (%)	6	7	5	27	14	7	6
	n	38	38	38	38	38	38	38
	Rel. Diff. (%)[b]	2	-2	-7	58	18	-0.1	-10
7700x LA-ICP-MS He collision gas mode (He = 5 mL min^{-1})	Mean	247	250	253	106	159	202	320
	SD[a]	9	7	10	21	8	9	7
	RSD (%)	3	3	4	20	5	5	2
	n	30	30	30	30	30	30	30
	Rel. Diff. (%)[b]	7	-2.7	-4	46	18	3	-13
8900x LA-ICP-MS/MS No gas mode	Mean	222	213	229	77	147	175	259
	SD[a]	6	8	3	17	14	2.3	5
	RSD (%)	2.5	4.0	1.0	22.0	10.0	1.0	2.0
	n	4	4	4	3	4	4	4
	Rel. Diff. (%)[b]	-4	-17	-13	6	9	-11	-29
8900x LA-ICP-MS/MS NH$_3$/He reaction gas mode (NH$_3$/He = 0.3 mL min^{-1})	Mean	219	213	223	91.4	148	180	267
	SD[a]	1.7	4	4	20	12	5	6
	RSD (%)	1.0	2.0	2.0	22.0	8.0	3.0	2.0
	n	6	6	6	6	6	6	6
	Rel. Diff. (%)[b]	-5	-17	-15	26	10	-8	-27

[a]: standard deviation; [b]: the relative difference of element value determined by LA-ICP-MS against the value obtained by SN-ICP-MS; n**:** number of analysis.

Supplementary Table 9† PGE content (ng g^{-1}) determined using 8800x SN-ICP-MS/MS from this study vs. certified or recommended values (± 95% confidence intervals) for geological reference material PTM-1a[58].

Element	**PTM-1a**				
	Certified	**This Study**	**n**	**RSD (%)**	**Rel. Diff. (%)[b]**
Ru	700 ± 400[a]	695	44	8	-0.8
Rh	940 ± 90[a]	967	30	7	3.0
Pd	10070 ± 410	10200	89	8	1.3
Ir	350 ± 90[a]	375	66	11	7.0
Pt	7290 ± 220	7027	59	11	3.6
Au	3300 ± 200	3536	33	11	2.2

[a]: provisional values;[58] b: the relative difference of element value determined by LA-ICP-MS against the value obtained by SN-ICP-MS; n**:** number of analysis.

Supplementary Table 10† Precision and accuracy in analyzing 0.1, 1 and 10 ng g^{-1} PGE in 1000 µg g^{-1} Cu matrix determined using 8800x SN-ICP-MS/MS.

Element	**0.1 ng g^{-1} PGE**				**1 ng g^{-1} PGE**				**10 ng g^{-1} PGE**			
	Measured	**n**	**RSD (%)**	**Rel. Diff. (%)[a]**	**Measured**	**n**	**RSD (%)**	**Rel. Diff. (%)[a]**	**Measured**	**n**	**RSD (%)**	**Rel. Diff. (%)[a]**
Ru	0.088	5	9	-12	0.93	5	2.1	-7.0	9.4	5	2.6	-6.0
Rh	0.087	5	4	-13	0.91	5	4	-9.0	9.3	5	4	-8.0
^{105}Pd	0.111	5	8%	11	0.93	5	3	-7.0	9.2	5	3	-9.0
^{106}Pd	0.111	5	5	11	0.92	5	4	-8.0	9.2	5	3	-8.0
^{108}Pd	0.108	5	6	8	0.93	5	3	-7.0	9.2	5	2.3	-8.0
Os	0.098	5	11	-1.6	1.03	5	4	2.7	9.8	5	2.2	-1.6
Ir	0.119	5	6	19	1.24	5	3	24	12	5	2.0	21
Pt	0.106	5	4	6.0	1.10	5	1.8	10	11	5	1.5	10
Au	0.108	5	4	8.0	1.09	5	2.9	9.0	11	5	1.7	7.0

[a]: the relative differences between measured contents and theoretical values (based on gravimetric dilutions of stock solutions); n**:** number of analysis.

Supplementary Table 11† PGE content (ng g^{-1}) for synthetic chalcopyrite and bornite determined using 7700x LA-ICP-MS analysis.

Sample	**Item**	**Rh**	**Rh**[a]	**Rh**[b]	**^{105}Pd**	**^{105}Pd**[a]	**^{105}Pd**[b]	**^{106}Pd**	**^{108}Pd**
OSP6	Mean	94	28	< 50	306	144	113	112	117
	SD[c]	14	0.7		23	26	12	11	12
	RSD (%)	15	2.6		8	18	11	10	10
	n	12	2	12	12	11	10	12	12
	Rel. Diff. (%)[d]	5913	1679		244	62	27	27	34
OSP7	Mean	161	42	49	481	214	201	204	184
	SD[c]	17	11		41	40	33	32	37
	RSD (%)	11	25		9	19	17	16	20
	n	8	4	1	8	7	7	8	8
	Rel. Diff. (%)[d]	6655	1663	1977	150	11	5	6	-5
OSP9	Mean	243	76	69	739	255	332	333	323
	SD[c]	56	20	21	139	18	100	100	83
	RSD (%)	23	26	31	19	7	30	30	26
	n	12	5	5	12	5	12	12	12
	Rel. Diff. (%)[d]	5731	1737	1568	187	-0.9	29	30	26

[a]: CuAr^{+} interference correction on ^{103}Rh^{+} and ^{105}Pd^{+} is based on the linear correlation between Cu^{+} and CuAr^{+}; [b]: CuAr^{+} interference correction on ^{103}Rh^{+} and ^{105}Pd^{+} is based on the Paul Sylvester (2002),[53] and Cd interference correction but no ZnAr correction was applied; [c]: standard deviation; [d]: the relative differences between measured contents and theoretical values (based on gravimetric dilutions of stock solutions); n**:** number of analysis.