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reference materials using EPMA and LA-ICP-MS**

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## INTRODUCTION

Native gold may contain measurable quantities of over 20 trace elements, which could be used for fingerprinting and provenance studies, as well as gaining insight into the physicochemical conditions of gold mineralization. In-situ measurements, using electron probe microanalysis (EPMA) by wavelength dispersive spectrometry (WDS) and laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) techniques, are well suited for trace element studies of gold given the relatively simple sample preparation procedures, low cost, short analysis time, and minimal sample destruction. The success of such studies of gold, however, requires sufficient absolute concentrations of trace elements relative to the detection limits of a given analytical technique. Furthermore, such studies require the development of suitable gold standards for matrix-sensitive calibrations of X-ray spectra (WDS), and ablation (LA-ICP-MS) and secondary ion mass spectrometry (SIMS).

The trace element composition of three synthetic standards (Au-RM-2, NA-Au-30, and NA-Au-31) was studied at microscopic ( $\leq 50\ \mu\text{m}$ ) scale in order to assess their suitability as standard reference materials (SRM) for in-situ, trace element studies of the composition of gold. Electron probe and LA-ICP-MS analyses were undertaken at four Canadian laboratories: Geological Survey of Canada, Queen's University Facility of Isotope Research, Earth and Planetary Materials Analysis Laboratory at the University of Western Ontario, and the Great Lakes Institute for Environmental Research at University of Windsor.

In this data release, we present the results of in-situ trace element characterization of three, high-purity, samples of gold ( $\text{Au} \geq 95\ \text{wt.}\%$ ) with known

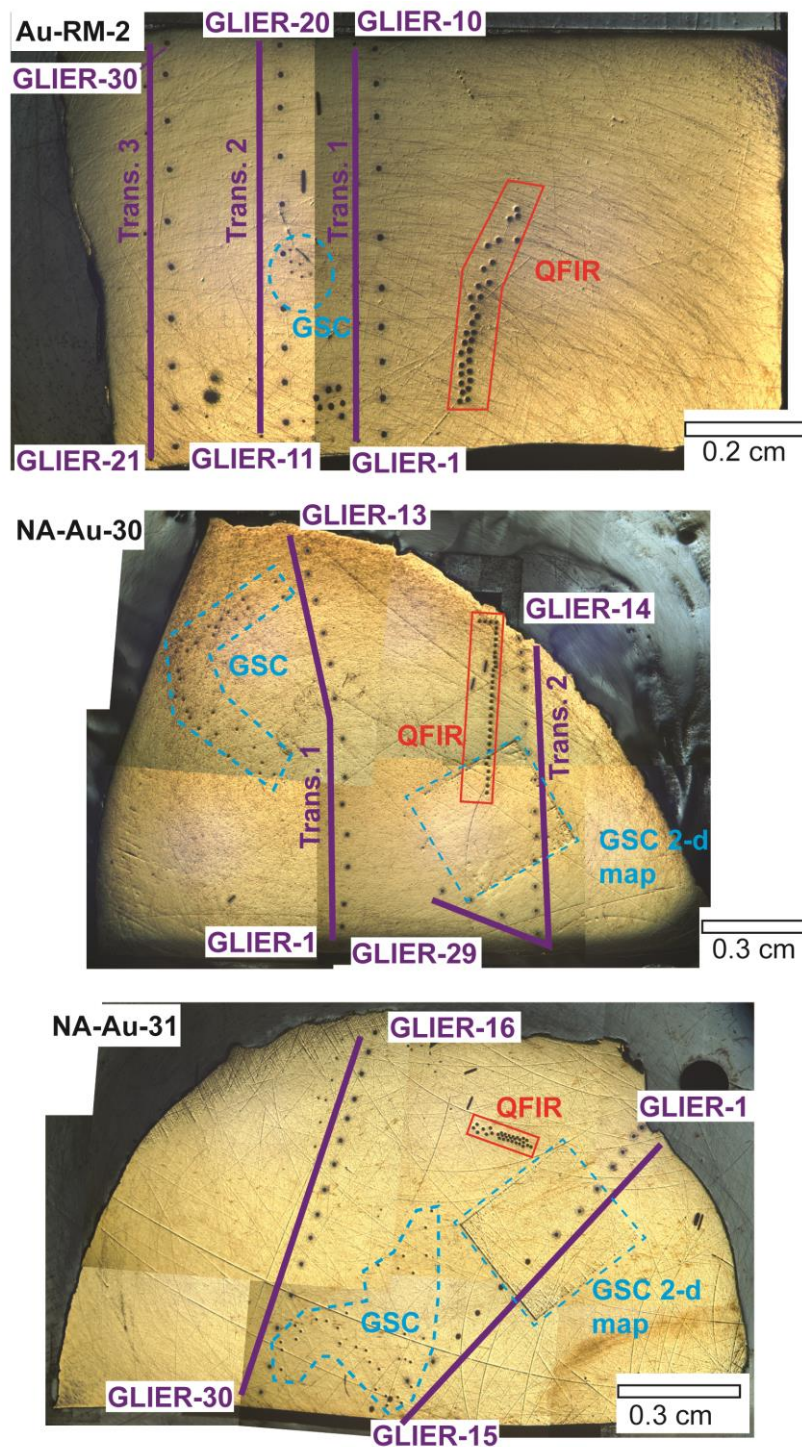
quantities of selected trace elements. The samples, manufactured by two gold refineries to serve as SRM for chemical analysis, have been used previously for calibration of laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS) analyses.

## SAMPLES AND METHODOLOGY

Synthetic samples of high-purity gold (95-99 %; Au-RM-2, NA-Au-30, and NA-Au-31; Fig. 1) were characterized using in-situ analytical techniques (EPMA and LA-ICP-MS). Sample Au-RM-2 is a certified gold standard used by the London Bullion Market Association (LBMA; Murray, 2009). The sample was manufactured by Tanaka Kikiniku Kogyo K.K. (Japan) by spiking molten gold with trace elements, homogenizing the melt, and, using a graphite-mould, cooled rapidly to minimize the segregation of elements. The accepted trace element concentrations for sample Au-RM-2 (Table 1) were determined by averaging multiple analyses of solutions by ICP-optical emission spectrometry (OES) at ten participating analytical facilities. Gold samples NA-Au-30 and NA-Au-31 were synthesized by the Norddeutsche Affinerie AG, now Aurubis AG (Germany), which provided the certified trace element concentrations for the SRMs (Table 1). Kovacs et al. (2009) characterized samples NA-Au-30 and NA-Au-31 by LA-ICP-MS, using both solution and solid calibration modes (Table 1).

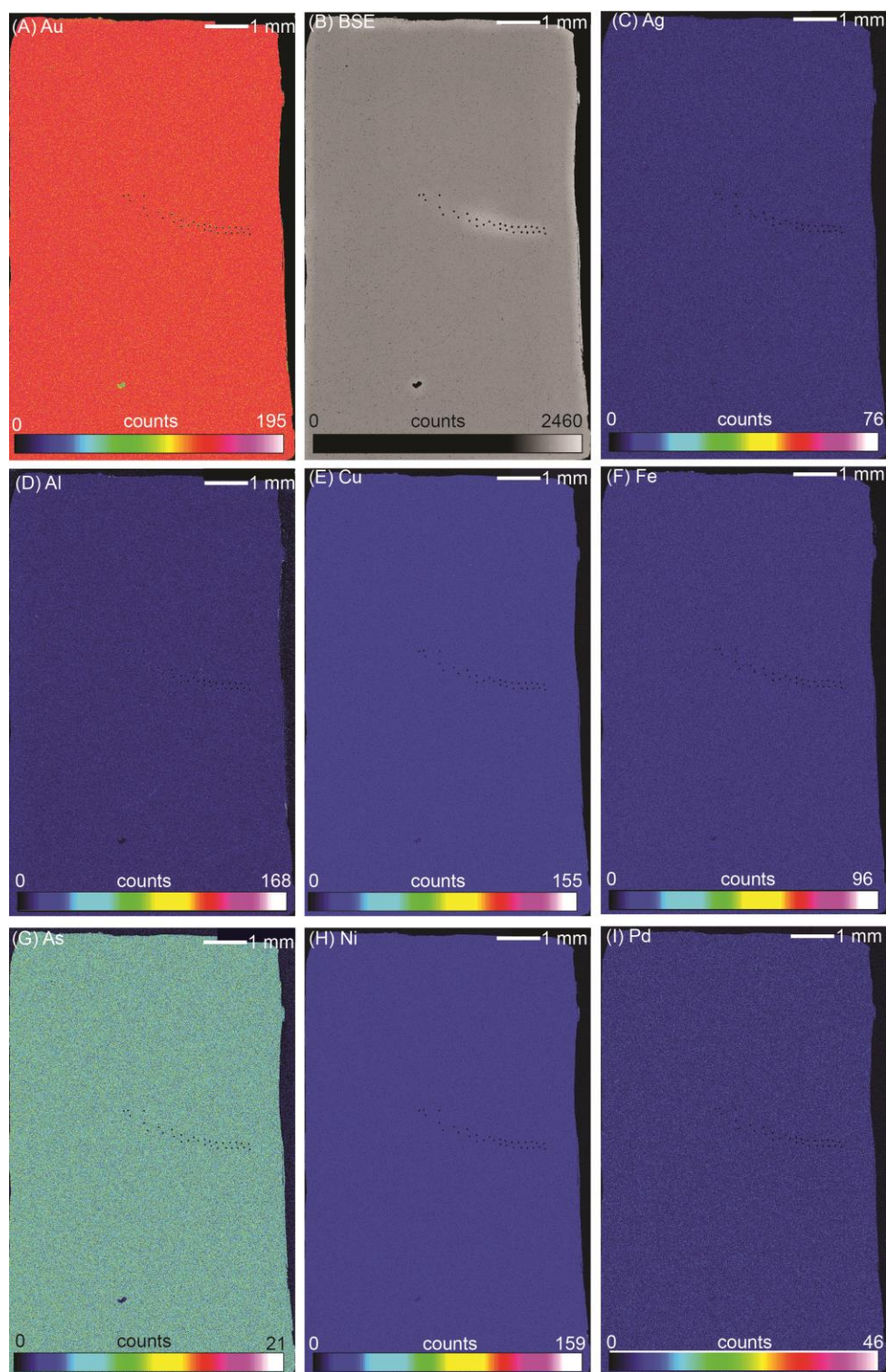
### *Sample Preparation*

Sheets of gold, one to two mm-thick, were mounted in epoxy and the surface of each mount was levelled manually on a polishing lap (Fig. 1). The intermediate polishing steps, using 6, 3, and 1  $\mu\text{m}$  diamond paste were performed by hand. The

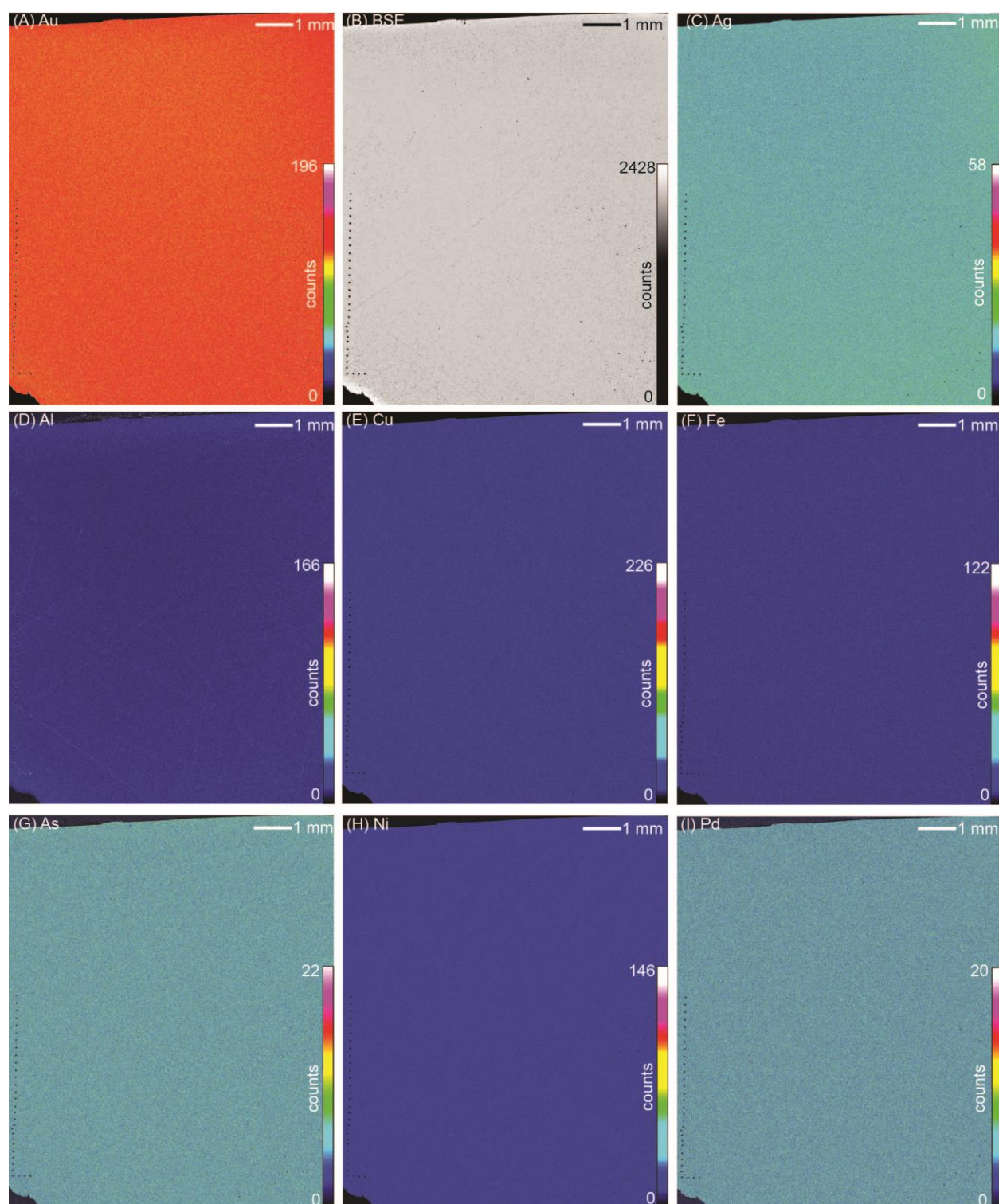


**Figure 1.** Stitched reflected light images of gold standard reference materials Au-RM-2, NA-Au-30, and NA-Au-31. Shown for reference are the locations of analyses obtained at QFIR (red outline), GSC (light blue outline) and GLIER (purple lines). 2-D LA-ICP-MS maps obtained at GSC are shown as light blue squares.





**Figure 2.** Backscatter electron and compositional maps of gold samples Au-RM-2. A) Au; B) BSE; C) Ag; D) Al; E) Cu; F) Fe; G) As; H) Ni; I) Pd.



**Figure 3.** Backscatter electron and compositional maps of gold sample NA-Au-30.





**Figure 4.** Backscatter electron and compositional maps of gold sample NA-Au-31.

**Table 1.** Trace element concentrations of standard reference gold samples.

Z	Element	<u>Au-RM-2<sup>a</sup></u>		<u>NA-Au-30<sup>b</sup></u>				<u>NA-Au-31<sup>b</sup></u>			
		Avg. <sup>a</sup>	Unc. <sup>a</sup>	Avg. <sup>b</sup>	Unc. <sup>b</sup>	Avg. <sup>c</sup>	Unc. <sup>c</sup>	Avg. <sup>b</sup>	Unc. <sup>b</sup>	Avg. <sup>c</sup>	Unc. <sup>c</sup>
12	Mg	9.9	0.9	-	-	-	-	-	-	-	-
13	Al	28.3	1.8	-	-	-	-	-	-	-	-
14	Si	28.0	3.8	-	-	-	-	-	-	-	-
20	Ca	28.0	2.6	-	-	-	-	-	-	-	-
22	Ti	31.6	1.3	-	-	2.28	0.03	-	-	3.96	0.20
24	Cr	27.7	2.2	9	0.3	10.5	0.2	25	-	27.5	0.3
25	Mn	28.2	1.5	7	0.1	7.73	0.19	62	-	62.5	1.6
26	Fe	30.1	2.2	34	0.5	43.4	0.5	806	-	989	8
27	Co	-	-	10	0.1	10.7	0.2	124	-	114	2
28	Ni	29.2	2.6	48	0.9	53.0	0.8	1092	-	1102	8
29	Cu	31.6	2.4	99	2.1	99	-	1062	-	1062	-
30	Zn	31.4	2.3	11	0.6	12.4	0.9	114	-	111	2
33	As	47.1	2.8	43	1.7	45.7	2.2	112	-	106	5
34	Se	37.4	2.8	10	1.7	10.2	1.3	114	-	103	6
45	Rh	39.6	2.4	-	-	-	-	-	-	-	-
46	Pd	29.2	1.3	55	2.8	58.7	0.8	1152	-	1096	24
47	Ag	99.6	5.6	10000	100	9000	1000	54500	-	54000	4000
48	Cd	-	-	10	0.3	11.8	0.5	82	-	104	3
50	Sn	29.4	1.8	50	0.9	53.2	0.8	772	-	1114	6
51	Sb	11.3	1.6	9	0.3	12.1	0.6	102	-	111	2
52	Te	12.0	3.2	10	1.3	11.1	1.5	112	-	106	8
78	Pt	30.2	2.1	58	0.9	68	4.0	1152	-	1119	66
82	Pb	28.9	2.4	9	0.9	11.5	1.5	90	-	108	2
83	Bi	9.7	0.8	9	0.5	11.1	1.2	100	-	110	3

<sup>a</sup>average ICP-OES concentrations determined at 10 laboratories on 25 g aliquots, as reported by Murray (2009). The uncertainty, reported by Murray (2009) has been calculated according to the ISO guide, using the coverage factor value of 2.

<sup>b</sup>Certified concentration values reported by Aurubis AG. The reported uncertainties are 1 S.D.

<sup>c</sup> average of 6 analyses by femtosecond-source LA-ICP-MS using solution calibration, as reported by Kovacs et al. (2009). Copper concentrations reported by the manufacturer and determined by ICP-OES were used as internal standards. The reported uncertainty is 1 S.D.

final polishing step was performed using 0.5  $\mu\text{m}$  Al-oxide powder. Prior to analysis, samples were cleaned with deionised water in an ultrasonic bath and with ethanol.

### *Electron Probe Microanalyses*

Backscatter electron and compositional maps (Au, Ag, Al, As, Cu, Fe, Ni, Pd, and Te; Figs. 2-4) of carbon-coated gold mounts were acquired using a JEOL JXA-8530F



field-emission (FE) electron probe at the Earth and Planetary Materials Analysis laboratory at the University of Western Ontario (London, Ontario). The maps were acquired in wavelength dispersive (WDS) mode, using an excitation voltage of 20 kV, an operating current of 100 nA, and a dwell time of 10 ms per spot. Samples Au-RM-2 and NA-Au-31 were mapped using 5  $\mu\text{m}$  x 5  $\mu\text{m}$  resolution, whereas sample NA-Au-30 was mapped at 5.5  $\mu\text{m}$  x 5.5  $\mu\text{m}$  resolution. Peak positions were calibrated using pure metal standards, except for the As peak position, which was calibrated using a gallium arsenide standard.

The gold samples were analyzed for minor and trace elements (>10 ppm) using a JEOL JXA-8230 electron probe at Queen's University (Kingston, Ontario). Due to the high conductivity of the gold samples and metal standards used in the calibration procedure, the grain mounts were not carbon or gold coated. Instead, copper tape was applied along the edges of the mount. The samples were analyzed by WDS, using an accelerating potential of 20 kV, a beam current of 2500 nA, and a 10  $\mu\text{m}$  defocused beam. High-purity synthetic metals were used as analytical standards. Due to the overall low levels of trace elements and high detection limits, only Au, Ag, Fe, and Ni could be analyzed with confidence in all three samples (Table 2; Figs. 5-8). The concentrations of Au were determined using the  $M\alpha$  peak, whereas the  $K\alpha$  peak was used to determine the concentrations of Fe and Ni. In the case of Ag, the  $L\alpha_2$  peak was used (Fig. 9) and the electron microprobe was operated in differential mode (pulse height analyzer (PHA) on; Fialin et al, 1999) to suppress higher-order reflections of nearby Au X-rays.

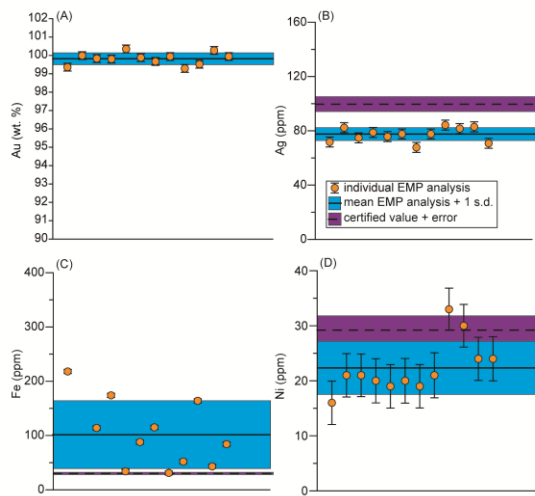
#### *Laser Ablation-Inductively Coupled Plasma-Mass-Spectrometry (LA-ICP-MS) Analyses*

The gold samples were analyzed by LA-ICP-MS at the Geological Survey of Canada (GSC; Ottawa, Ontario), Queen's University, and the University of Windsor (Windsor, Ontario). At the GSC, the samples were analyzed using an Agilent Technologies 7700x Series quadrupole ICP-MS coupled to a Photon Machines Analyte 193 nm Excimer laser ablation system (e.g. Cabri and Jackson, 2011; Lawley et al., 2015). A fast time-resolved analysis data acquisition protocol (peak hopping, 1 point/peak), which provides signal intensity data in counts per second for each mass sweep performed by the mass spectrometer, was used to acquire data on selected isotopes for 38 elements. The samples were ablated for 60 s in spot mode with a 43  $\mu\text{m}$  spot size, energy density of 5.71 J/cm<sup>2</sup>, and the beam operating at 10 Hz frequency. Thirty randomly positioned analyses were performed on each sample. Both glass (NIST610 and GSE-1G) and sulphide (Po726 and Mass-1) reference materials were used for calibration and quality control of LA-ICP-MS analyses. The basaltic glass GSE-1G (Guillong et al., 2005) and polymetallic sulphide Mass-1 (Wilson et al., 2002) are synthetic reference materials certified by the United States Geological Survey (USGS). NIST 610 (Kane, 1998a; 1998b) is a synthetic silicate glass certified by the National Institute of Standards and Technology. Po726 is a synthetic pyrrhotite standard (Sylvester et al., 2005), developed as a reference material for analyses of gold and platinum group elements. The reference glass GSE-1G was used as the primary standard for all elements, except S and the platinum group elements (PGE), using current “preferred” concentration values from the Geological and Environmental Reference Materials (GeoREM) data base

**Table 2.** JEOL JXA-8230 electron microprobe results acquired at QFIR

Analysis	Au (wt.%)	1 s	Ag (ppm)	1 s	Fe (ppm)	1 s	Ni (ppm)	1 s
<i>Au-RM-2</i>								
1	99.36	0.21	71.7	3.7	218	3.7	16	3.9
2	99.99	0.21	82.3	3.7	<i>1,115</i>	<i>3.9</i>	21	3.9
3	99.83	0.21	74.8	3.7	114	3.7	21	3.9
4	99.80	0.21	78.8	3.7	174	3.7	20	4.0
5	100.35	0.21	75.7	3.7	34	3.8	19	4.0
6	99.88	0.21	77.7	3.7	88	3.7	20	4.1
7	99.67	0.21	67.7	3.7	115	3.7	19	3.9
8	99.94	0.21	77.7	3.7	31	3.7	21	4.1
9	99.29	0.21	84.2	3.7	52	3.7	33	3.8
10	99.52	0.21	81.7	3.7	164	3.7	30	3.9
11	100.27	0.21	83.0	3.7	43	3.7	24	3.9
12	99.94	0.21	70.8	3.7	84	3.7	24	4.0
13			77.5	3.7				
14			80.1	3.7				
15			80.7	3.7				
<b>MEAN</b>	<b>99.8</b>		<b>77.6</b>		<b>102</b>		<b>22</b>	
<b>ST. DEV.</b>	<b>0.3</b>		<b>4.8</b>		<b>62</b>		<b>5</b>	
<i>NA-Au-30</i>								
1	98.36	0.21	9,752	36	82	3.7	20	4.0
2	98.42	0.21	9,926	36	74	3.7	18	4.0
3	98.82	0.21	9,784	36	83	3.7	30	3.9
4	98.17	0.21	9,899	36	93	3.7	18	3.8
5	98.07	0.21	9,472	36	96	3.7	13	4.1
6	98.39	0.21	9,969	36	86	3.7	29	3.9
7	98.29	0.21	9,722	36	84	3.7	16	3.9
8	98.50	0.21	9,716	36	87	3.7	13	4.0
9	98.55	0.21	9,761	36	105	3.7	21	4.0
10	98.19	0.21	9,515	36	90	3.7	13	4.0
11	98.29	0.21	9,869	36	90	3.7	18	3.8
12	98.26	0.21	9,667	36	124	3.7	13	4.0
13	98.06	0.21	9,745	36	97	3.7	11	3.9
14	99.07	0.21	9,798	36	79	3.7	30	4.0
15	98.32	0.21	9,601	36	118	3.7	15	3.9
<b>MEAN</b>	<b>98.38</b>		<b>9,746</b>		<b>93</b>		<b>19</b>	
<b>ST. DEV.</b>	<b>0.27</b>		<b>142</b>		<b>14</b>		<b>6</b>	
<i>NA-Au-31</i>								
1	93.83	0.21	54,600	251	832	3.9	855	4.04
2	93.62	0.21	53,800	251	864	3.9	935	4.05
3	93.39	0.21	54,300	250	896	3.9	1,066	4.07
4	93.37	0.21	54,100	250	878	3.9	972	4.05
5	93.73	0.21	54,400	251	858	3.9	939	4.05
6	93.55	0.21	53,400	250	829	3.9	907	4.04
7	93.63	0.21	53,900	250	858	3.9	968	4.05
8	93.85	0.21	52,800	249	<i>731</i>	<i>3.8</i>	<i>710</i>	<i>4.02</i>
9	93.37	0.21	54,700	251	856	3.9	961	4.05
10	93.38	0.21	53,600	250	882	3.9	976	4.05
11	93.64	0.21	54,100	249	884	3.9	1,080	4.06
12	93.73	0.21	55,200	251	902	3.9	1,053	4.06
13	93.49	0.21	54,100	250	871	3.9	991	4.06
14	93.48	0.21	53,400	249	849	3.9	966	4.05
15	93.61	0.21	54,200	250	870	3.9	965	4.06
<b>MEAN</b>	<b>93.56</b>		<b>54,129</b>		<b>866</b>		<b>974</b>	
<b>ST. DEV.</b>	<b>0.15</b>		<b>504</b>		<b>21</b>		<b>61</b>	

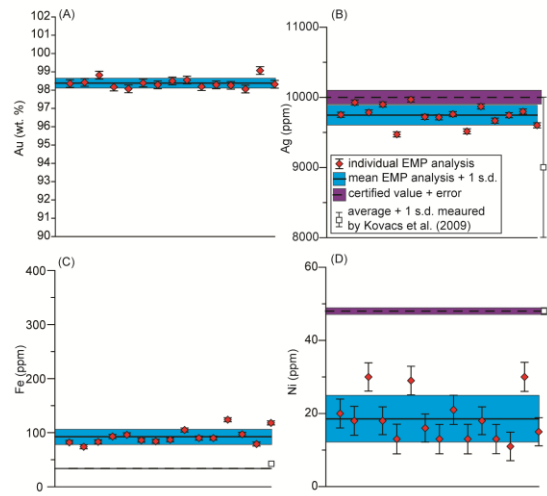
notes: italics - analyses excluded from the mean.



**Figure 5.** Trace element concentrations of Au, Ag, Fe and Ni in Sample Au-RM-2, determined by electron microprobe at QFIR. Data are compared to the certified value (black dashed lines) and uncertainty (purple band), reported by Murray (2009). Orange circles: individual measurements on Au-Rm-2; Blue band: standard deviation of 12 analyses of Au-Rm-2 calculated around the mean (thick black line). A) Au, B) Ag, C) Fe, D) Ni.

(<http://georem.mpch-mainz.gwdg.de>). The PGE and S were calibrated against Po726. Certified Hg concentrations are not available for any of the external standards used in this study; consequently Hg contents of the gold SRMs could not be determined. The difference in ablation yield between the reference standards and the gold samples was corrected by normalization to the concentration of Ag, Ni, and Fe measured by EPMA at Queen's Facility for Isotope Research (QFIR). The normalization to an internal standard value also corrects, to some degree, the matrix effects and signal drift in the ICP-MS.

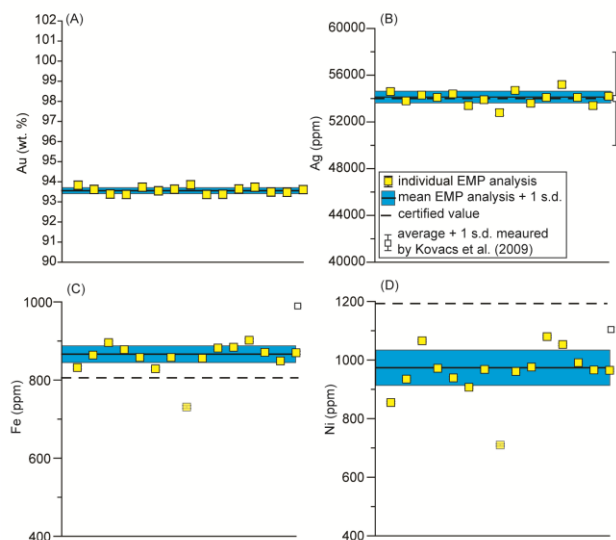
Because of interference between the Pd  $L\beta_1$  peak with the Ag  $L\alpha_2$  peak (Fig. 9), we



**Figure 6.** Trace element concentrations of Au, Ag, Fe and Ni in Sample NA-Au-30, determined by electron microprobe at Queen's Facility for Isotope Research. Data are compared to the certified value (black dashed lines) and uncertainty (purple band), reported by Aurubis AG. Also shown are the values reported by Kovacs et al. (2009; grey square = average concentrations, error bars = 1 s.d.) for NA-Au-30. Red diamonds: individual measurements on NA-Au-30; Blue band: standard deviation of 15 analyses of Au-Rm-2 calculated around the mean (thick black line). A) Au, B) Ag, C) Fe, D) Ni.

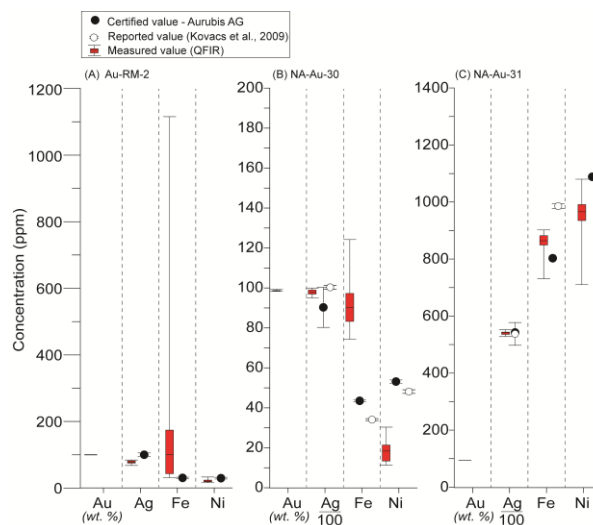
are only moderately confident that the measured Ag concentrations of Pd-rich sample Na-Au-31 ( $1096 \pm 24$  ppm; Kovacs et al., 2009), determined by EPMA, are accurate. Consequently Ni was used as the internal standard for quantification of LA-ICP-MS data for NA-Au-31. Iron concentrations measured by EPMA at QFIR were used for internal standardisation of data calibrated against Po726. The program GLITTER (Griffin et al., 2008), which follows the data processing procedures of Longerich et al. (1996), was used for reduction of LA-ICP-MS data acquired at GSC.





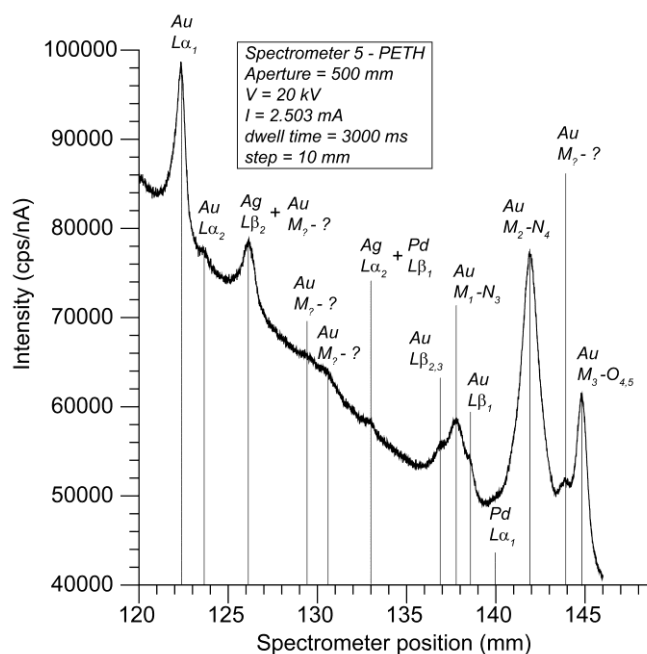
**Figure 7.** Trace element concentrations of Au, Ag, Fe and Ni in Sample NA-u-31, determined by electron microprobe at Queen's Facility for Isotope Research. Data are compared to the certified value (black dashed lines) reported by Aurubis AG. Also shown are the values reported by Kovacs et al. (2009; grey square = average concentrations, error bars = 1 s.d.) for NA-Au-30. Yellow squares: individual measurements on NA-Au-31; Blue band: standard deviation of 15 analyses of NA-Au-31 calculated around the mean (thick black line). A) Au, B) Ag, C) Fe, D) Ni.

In addition to performing spot analyses, the LA-ICP-MS at GSC was used to generate 2-D trace element concentration maps of gold samples NA-Au-30 and NA-Au-31 (Figs. 10 and 11, respectively). The elemental maps, approximately 0.3 cm x 0.3 cm, were obtained using the "line-of-spots" protocol described by Cabri and Jackson (2011). Lines of individual, edge to edge 10  $\mu$ m square spots were ablated to form 2-dimensional maps of trace element distribution. Data were acquired using a fast time-resolved analysis acquisition protocol. Raw signal intensity data were processed using the CONVERT, LAMTRACE and Pixelate spreadsheet programs (Jackson, 2008; Cabri and Jackson, 2011). Data were internally normalised to Ag values determined by EPMA at QFIR, using the  $^{109}\text{Ag}$  isotope.



**Figure 8.** Box and whisker plots of EPMA analyses acquired at QFIR. A) Au-RM-2 compared to certified values of Murray, 2009; B) and C) NA-Au-30 and NA-Au-31, respectively, compared to values reported by AurubisAG and Kovacs et al. (2009). Note that Au is reported in wt.%, and that concentrations of Ag in B) and C) are divided by 100.

Laser ablation-ICP-MS analyses at QFIR were performed on a Finnigan Element 2 HR-ICP-MC coupled to a frequency-quintupled (213 nm) Nd-YAG laser (LUV 213, New Wave-Mercantek, Fremont, California). Thirty randomly positioned analysis pits, ~50  $\mu$ m in diameter, were used to analyze each sample. The samples were ablated for 60 s using energy density of 10.3 J/cm<sup>2</sup>. Isotopes of 30 elements were analyzed in low, medium, and high mass resolution modes; the resolution used for each element considered the potential isobaric interferences, the agreement between measured and certified values of standard reference materials, and the overall smoothness of time-integrated signal.



**Figure 9.** X-ray intensity spectrum of sample Au-RM-2, centered around the Ag  $L\alpha$  peak position on the PETH diffraction crystal. Also shown are the positions of  $L\alpha$  and  $L\beta$  lines for Au, Ag, and Pd, as well as the positions of minor Au M-lines. A minor Au M-line interferes with the Ag  $L\beta$  line; consequently Ag concentrations were determined using the magnitude of the  $L\alpha$  peak. Note that the intensity of the Ag  $L\alpha_2$  peak of Pd-rich sample NA-Au-31 (>300 ppm) may be affected by interference with the Pd  $L\beta_1$  peak. The analytical conditions are summarized in the figure.

Synthetic standard reference glasses NIST 610 and NIST 612 (Kane, 1998a; 1998b) and a gas blank were used for the calibration of LA-ICP-MS analyses of sample AU-RM-2, by calculating best-fit lines for each isotope in each resolution. Analyses of samples NA-Au-30 and NA-Au-31 were calibrated using a gas blank and NIST 612, only. The lines of best fit were determined using the instrument software Element 2 XR. The measured S content of NIST 612 glass (Average  $S_{\text{meas}} \sim 16$  ppm) is significantly lower than the certified value of the NIST 612 reference glass ( $377 \pm 70$ , Jochum et al., 2011), suggesting a poor calibration of S measurements at QFIR. Consequently, concentrations of S in the gold samples could not be determined at QFIR. Similarly, the concentrations of Ir, Os, and Ru, could not be determined due to the low (<0.001 ppm to b.d.l.) concentrations of these elements in the NIST 612 glass. Finally, the concentration of Te in the NIST612 reference glass was not available at the time of analysis (30.9 ppm; Wang and Becker, 2014) and, as a result, Te

was not analyzed at QFIR. Internal standardization, accounting for the difference in ablation yield between the reference standards and the gold samples, was performed using the Ag, Ni, and Fe concentrations determined by EPMA at QFIR.

Laser ablation-ICP-MS analyses at the Great Lakes Institute for Environmental Research (GLIER) at the University of Windsor were performed on an Agilent Technologies 7900 quadrupole ICP-MS coupled to a Photon Machines Excite 193 nm ultra-short pulse (<4 ns) excimer laser ablation system. Thirty spot analyses, defining linear transects, were performed on each sample (Fig. 1). Individual spots were ablated for 60 s, using a 65  $\mu\text{m}$  spot size, energy density of 5.75 J/cm<sup>2</sup>, and the beam operating at 10 Hz frequency. Both silicate glass (NIST610; Kane, 1998a, 1998b) and sulphide (Po725; Sylvester et al., 2005) reference materials were used for calibration of LA-ICP-MS analyses. Like Po726, Po725 is a synthetic pyrrhotite standard, developed as a reference material for analyses of gold

**Table 3.** Trace element concentrations determined by LA-ICP-MS at GSC

Z	Element <sup>a</sup>	Au-RM-2 <sup>b</sup> n = 30			NA-Au-30 <sup>b</sup> n = 30			NA-Au-31 <sup>c</sup> n = 30		
		Mean	Median	+/-1 IQR	Mean	Median	+/-1 IQR	Mean	Median	+/-1 IQR
12	Mg	10.8	10.9	0.7/0.9	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
13	Al	27.4	26.2	4.6/3.1	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
14	Si	84.9	78.3	25.8/15.9	56.4	36.5	64.5/36.5	70.4	82.7	19.9/82.7
16	S <sup>d</sup>	2,655	2,695	328/510	1,999	2,049	185/235	1,070	1,070	198/166
20	Ca	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
22	Ti	30.4	30.5	1.5/1.7	1.9	1.9	0.3/0.2	3.8	3.8	0.3/0.4
23	V	0.15	0.14	0.03/0.04	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
24	Cr	25.6	26.0	0.6/0.5	10.3	10.6	0.5/1.2	26.7	27.0	1.2/1.5
25	Mn	26.1	26.0	0.8/0.3	8.5	8.5	0.1/0.2	59.4	59.3	0.8/0.6
26	Fe	35.7	30.9	1.7/4.5	51.7	48.0	3.2/3.0	937	905	31/11
27	Co	b.d.l.	b.d.l.	-	10.2	10.1	0.1/0.1	98.8	98.8	1.9/1.0
28	Ni	24.1	24.0	0.9/1.3	52.0	52.1	0.5/1.3	<b>974</b>	<b>974</b>	-
29	Cu	31.4	26.7	3.3/1.8	102.9	102.6	2.0/1.5	988	991	7.3/15.8
30	Zn	37.2	36.3	3.8/3.6	17.0	16.1	0.6/0.6	134.4	134.7	2.2/2.7
33	As	33.6	31.1	7.4/3.1	40.4	40.1	1.8/1.6	86.9	87.4	2.9/4.3
34	Se	32.8	28.5	16.9/8.1	9.5	9.6	0.4/1.6	98.3	95.3	16.9/12.1
42	Mo	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
44	Ru <sup>d</sup>	0.04	0.05	0.04/0.03	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
45	Rh <sup>d</sup>	117.4	114.9	21.8/13.7	0.54	0.55	0.07/0.04	6.8	6.9	0.3/0.2
46	Pd <sup>d</sup>	72.3	73.3	11.7/13.5	99.4	102.4	6.3/6.2	826	845	17/40
47	Ag	<b>77.6</b>	<b>77.6</b>	-	<b>9,746</b>	<b>9,746</b>	-	46,984	46,763	1515/898
48	Cd	b.d.l.	b.d.l.	-	11.1	11.1	0.1/0.3	90.2	90.6	1.2/1.7
49	In	0.09	0.08	0.02/0.01	0.18	0.18	0.01/0.01	3.2	3.3	0.0/0.1
50	Sn	19.6	18.7	3.9/1.8	41.7	41.5	1.1/1.1	777	774	14/7
51	Sb	12.3	11.7	2.4/1.7	13.6	13.5	0.6/0.6	128.9	129.2	4.6/3.5
52	Te	12.4	10.2	4.3/3.4	14.9	14.7	0.7/1.0	151.7	151.4	15.9/19.8
74	W	b.d.l.	b.d.l.	-	0.79	0.80	0.06/0.06	1.4	1.3	0.1/0.1
73	Ta	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
75	Re	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
76	Os <sup>d</sup>	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
77	Ir <sup>d</sup>	0.07	0.07	0.02/0.01	0.54	0.56	0.02/0.06	0.31	0.30	0.04/0.03
78	Pt <sup>d</sup>	83.5	86.7	11.7/15.5	123.1	124.7	10.1/4.0	836	854	15/20
80	Hg	n/a	n/a	-	n/a	n/a	-	n/a	n/a	-
81	Tl	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	-
82	Pb	33.6	25.7	7.5/4.6	13.3	12.9	1.2/0.8	132.0	131.1	14.0/15.7
83	Bi	8.7	7.6	3.0/1.9	11.8	11.5	0.8/0.8	120.5	119.0	12.1/11.6

<sup>a</sup>All elements except PGE and S were calibrated using the GSE-1G synthetic silicate glass. Reference sulphide Po726 was used to calibrate the LA-ICP-MS analyses of PGE and S.

<sup>b</sup>Concentrations determined using Ag concentrations, determined by electron probe microanalysis at QFIR, as internal standards.

<sup>c</sup>Concentrations determined using Ni concentrations, determined by electron probe microanalysis at QFIR, as internal standards.

<sup>d</sup>Concentrations of S and PGE determined using Fe concentrations, determined by electron probe microanalysis at QFIR, as internal standards.



**Table 4.** Trace element concentrations determined by LA-ICP-MS at QFIR

Z	Element <sup>a</sup>	Au-RM-2 <sup>b</sup> n = 30			NA-Au-30 <sup>b</sup> n = 28			NA-Au-31 <sup>c</sup> n = 29		
		Mean	Median	+/- IQR	Mean	Median	+/- IQR	Mean	Median	+/- IQR
12	Mg	23.0	22.6	5.1/4.2	262	20.0	15.1/10.6	5.1	4.5	3.2/1.6
13	Al	42.3	43.6	3.1/8.3	20.7	19.7	7.5/6.3	13.7	13.5	4.8/4.3
14	Si	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
16	S	n/a	n/a	-	n/a	n/a	-	n/a	n/a	-
20	Ca	35.0	35.3	15.0/14.2	b.d.l.	b.d.l.	b.d.l.	48.2	16.1	47.9/16.1
22	Ti	45.3	44.9	5.5/2.6	11.8	11.7	2.1/2.0	11.0	11.2	1.4/2.2
23	V	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
24	Cr	27.6	26.9	2.6/1.4	11.0	11.6	3.2/5.7	32.5	32.3	1.2/1.4
25	Mn	29.7	29.2	1.3/1.9	5.6	8.8	0.6/8.7	71.4	71.0	1.5/1.2
26	Fe	113.2	112.4	28.3/39.4	194.9	178.3	55.8/24.6	1,938	1,939	91/75
27	Co	b.d.l.	b.d.l.	-	7.2	9.1	1.9/6.6	110.0	109.7	1.7/75.4
28	Ni	22.3	21.5	3.6/2.1	43.7	45.5	2.4/5.2	<b>974</b>	<b>974</b>	-
29	Cu	26.2	25.3	3.5/1.5	96.1	99.1	4.2/9.6	1,062	1,064	23/22
30	Zn	42.6	42.9	4.2/5.0	12.2	13.3	4.8/6.4	144.2	135.5	16.4/7.5
33	As	59.1	58.8	15.8/8.0	90.4	90.8	8.3/7.7	154.6	148.2	24.3/9.1
34	Se	51.4	53.5	10.3/21.0	20.5	18.1	12.5/6.8	182.4	175.7	35.2/22.4
42	Mo	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
44	Ru	n/a	n/a	-	n/a	n/a	-	n/a	n/a	-
45	Rh	26.5	25.7	3.6/2.9	0.19	0.17	0.09/0.06	6.4	6.7	0.4/1.6
46	Pd	8.1	8.1	0.8/1.3	18.7	19.0	1.7/2.1	330.8	313.8	48.0/17.4
47	Ag	<b>77.6</b>	<b>77.6</b>	-	<b>9,764</b>	<b>9,746</b>	-	45,338	43,606	5,601/3.0
48	Cd	b.d.l.	b.d.l.	-	16.3	16.0	3.6/2.2	148.8	148.7	10.1/9.6
49	In	b.d.l.	b.d.l.	-	0.5	0.5	0.2/0.5	4.1	4.0	0.7/0.4
50	Sn	21.3	21.1	4.5/6.6	41.4	43.1	6.1/8.8	934	940	31/56
51	Sb	10.8	10.4	2.2/2.1	11.0	11.3	1.3/2.2	116.6	116.1	7.4/5.7
52	Te	n/a	n/a	-	n/a	n/a	-	n/a	n/a	-
74	W	b.d.l.	b.d.l.	-	0.6	0.5	0.7/0.5	b.d.l.	b.d.l.	-
73	Ta	0.86	1.2	0.3/1.2	2.0	0.13	4.2/0.13	b.d.l.	b.d.l.	-
75	Re	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	-
76	Os	n/a	n/a	-	n/a	n/a	-	n/a	n/a	-
77	Ir	n/a	n/a	-	n/a	n/a	-	n/a	n/a	-
78	Pt	24.2	22.6	3.6/1.7	51.7	52.6	1.9/5.1	851	847	19/19
80	Hg	n/a	n/a	-	n/a	n/a	-	n/a	n/a	-
81	Tl	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
82	Pb	30.8	27.3	9.2/6.7	12.3	13.7	2.1/6.1	131.3	127.0	12.4/8.8
83	Bi	7.5	5.5	5.2/2.5	7.4	10.7	1.9/10.7	123.7	121.5	9.4/9.0

<sup>a</sup>All elements were calibrated using the NIST610 and NIST612 synthetic silicate glasses<sup>b</sup>Concentrations determined using Ag concentrations, determined by electron microprobe analysis at QFIR, as internal standards.<sup>c</sup>Concentrations determined using Ni concentrations, determined by electron microprobe analysis at QFIR, as internal standards.

**Table 5.** Trace element concentrations determined by LA-ICP-MS at GLIER

Z	Element <sup>a</sup>	Au-RM-2 <sup>b</sup> n = 30			NA-Au-30 <sup>b</sup> n = 29			NA-Au-31 <sup>c</sup> n = 30		
		Mean	Median	+/-1IQR	Mean	Median	+/-1 IQR	Mean	Median	+/-1 IQR
12	Mg	7.4	7.4	0.7/0.6	1.0	0.7	1.0/0.2	0.93	0.20	0.18/0.12
13	Al	32.3	30.4	5.3/3.0	15.7	11.4	6.3/4.1	50.6	10.5	0.53/0.44
14	Si	87.2	86.4	43.2/55.4	82.0	80.7	48.0/49.9	223	105	107/64
16	S	926.2	838.4	392/281	1106	927	289/115	1578	478	428/61
20	Ca	25.2	24.3	6.6/8.7	4.7	4.7	2.9/4.2	11.5	3.3	7.5/3.3
22	Ti	21.0	21.8	0.9/1.6	1.2	1.2	0.3/0.6	3.2	2.7	0.5/0.8
23	V	0.10	0.11	0.01/0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	-
24	Cr	19.6	20.4	0.8/0.7	11.5	11.0	1.6/0.7	22.9	21.1	1.7/2.0
25	Mn	20.5	21.2	0.6/1.1	5.5	7.0	0.3/3.6	43.6	45.5	5.2/8.4
26	Fe	21.2	21.1	1.7/1.6	31.2	36.3	2.5/12.8	652	709	62/144
27	Co	b.d.l.	b.d.l.	-	7.5	9.1	0.3/3.7	87.7	90.2	4.6/7.8
28	Ni	21.0	21.0	1.2/1.2	40.6	46.0	1.6/13.5	<b>974</b>	<b>974</b>	-
29	Cu	23.8	23.7	1.6/1.0	89.4	94.6	2.0/13.3	1119	1055	92/55
30	Zn	36.5	36.1	3.7/3.1	17.4	16.4	2.4/0.6	306	180	62/29
33	As	47.9	45.7	11.1/7.3	63.6	64.4	2.0/3.3	209	170	41/16
34	Se	45.1	43.5	15.4/13.3	14.1	14.4	0.9/1.7	402	233	78/41
42	Mo	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
44	Ru	0.05	0.05	0.03/0.02	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
45	Rh	143.0	134.5	27.6/7.0	0.61	0.61	0.04/0.05	8.4	8.6	0.3/0.4
46	Pd	87.6	84.3	13.7/8.5	129	117	19/6	1168	1075	204/94
47	Ag	<b>77.6</b>	<b>77.6</b>	-	<b>9,746</b>	<b>9,746</b>	-	70,012	53,789	10,675/5,548
48	Cd	b.d.l.	b.d.l.	-	18.4	17.4	3.1/0.9	361	187	69/28
49	In	0.08	0.08	0.01/0.01	0.16	0.17	0.02/0.05	3.2	3.4	0.1/0.4
50	Sn	21.6	21.1	4.5/3.1	40.5	47.7	2.9/18.9	851	908	48/110
51	Sb	10.1	10.2	1.9/1.9	11.3	11.7	1.0/2.1	142	134	15/5
52	Te	14.7	13.9	4.4/4.4	16.7	16.7	1.9/1.5	343	213	60/30
74	W	b.d.l.	b.d.l.	-	0.47	0.57	0.06/0.30	1.2	1.1	0.2/0.2
73	Ta	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
75	Re	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
76	Os	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-
77	Ir	0.08	0.07	0.02/0.01	0.50	0.53	0.03/0.08	0.24	0.27	0.02/0.06
78	Pt	107	102	19/7	143	145	8/13	1057	1138	61/89
80	Hg	-	-	-	-	-	-	-	-	-
81	Tl	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	-	0.11	0.005	0.003/0.002
82	Pb	27.9	28.8	5.4/7.8	12.7	12.6	1.3/0.9	194	147	27/13
83	Bi	9.9	19.1	2.3/2.8	13.4	13.4	1.3/1.5	250	166	43/23

<sup>a</sup>All elements except PGE and S were calibrated using the NIST610 synthetic silicate glass. Reference sulphide Po725 was used to calibrate the LA-ICP-MS analyses of PGE and S.

<sup>a</sup>Concentrations determined using Ag concentrations, determined by electron microprobe analysis at QFIR, as internal standards.

<sup>b</sup>Concentrations determined using Ni concentrations, determined by electron microprobe analysis at QFIR, as internal standards.

and platinum group elements. The trace element contents of the three gold samples were internally normalized using the same elements and values as in the LA-ICP-MS studies described above. The LA-ICP-MS data, acquired at GLIER, were processed using a customized Excel<sup>TM</sup> spread sheet supplied by J. Chapman (GSC) and developed by S. Gilbert (University of Tasmania) and D. Layton-Matthews (Queen's University).

## DATA INTEGRITY

### *Electron Probe Microanalysis*

Spatial variation in the distribution of trace elements in samples Au-RM-2, NA-Au-30, and NA-Au-31 is shown in Figures 2-4. Backscatter images of all three samples indicate incomplete removal of micron-scale diamond grains, which were inadvertently embedded during polishing (Figs. 2B, 3B, and 4B). Consequently, care was taken to avoid diamond inclusions during spot analyses.

Quantitative WDS spot analyses (Table 2) suggest that all three samples are more heterogeneous with respect to minor elements (Fig. 5-8) than previously reported (Table 1; Murray, 2009; Kovacs et al., 2009). Concentrations of Cu, although measurable in all samples, were consistently higher than those reported by Murray (2009) and cited by Kovacs et al. (2009), and were not quantified due to suspected inability to accurately measure Cu by EPMA at QFIR. Sample NA-Au-31 yielded the highest concentrations of Ag ( $54,129 \pm 504$  ppm), in good agreement with the certified value ( $54,500$  ppm) and the concentration reported by Kovacs et al. (2009;  $54,000 \pm 4,000$  ppm). The agreement between the measured and certified Ag concentrations suggests that

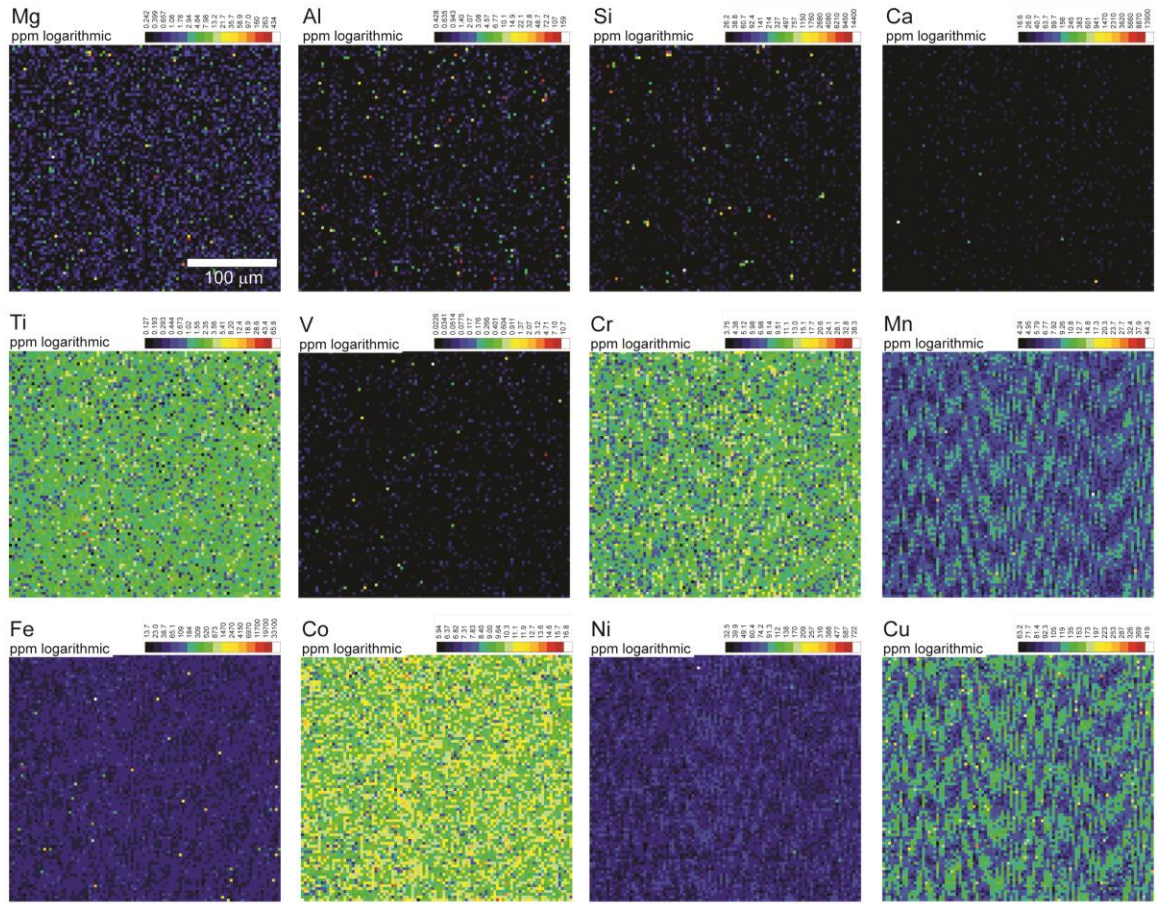
interference on the Ag  $L\alpha_2$  peak, resulting from the high Pd content of NA-Au-31 (Fig. 9), did not significantly affect the Ag measurements. Overall, concentrations of Ag, Fe, and Ni, determined by EPMA at QFIR, do not show systematic deviations from the certified values suggesting that differences between measured and certified are not due to poor calibration.

### *Laser-Inductively-Coupled-Mass-Spectrometry (LA-ICP-MS) Analyses*

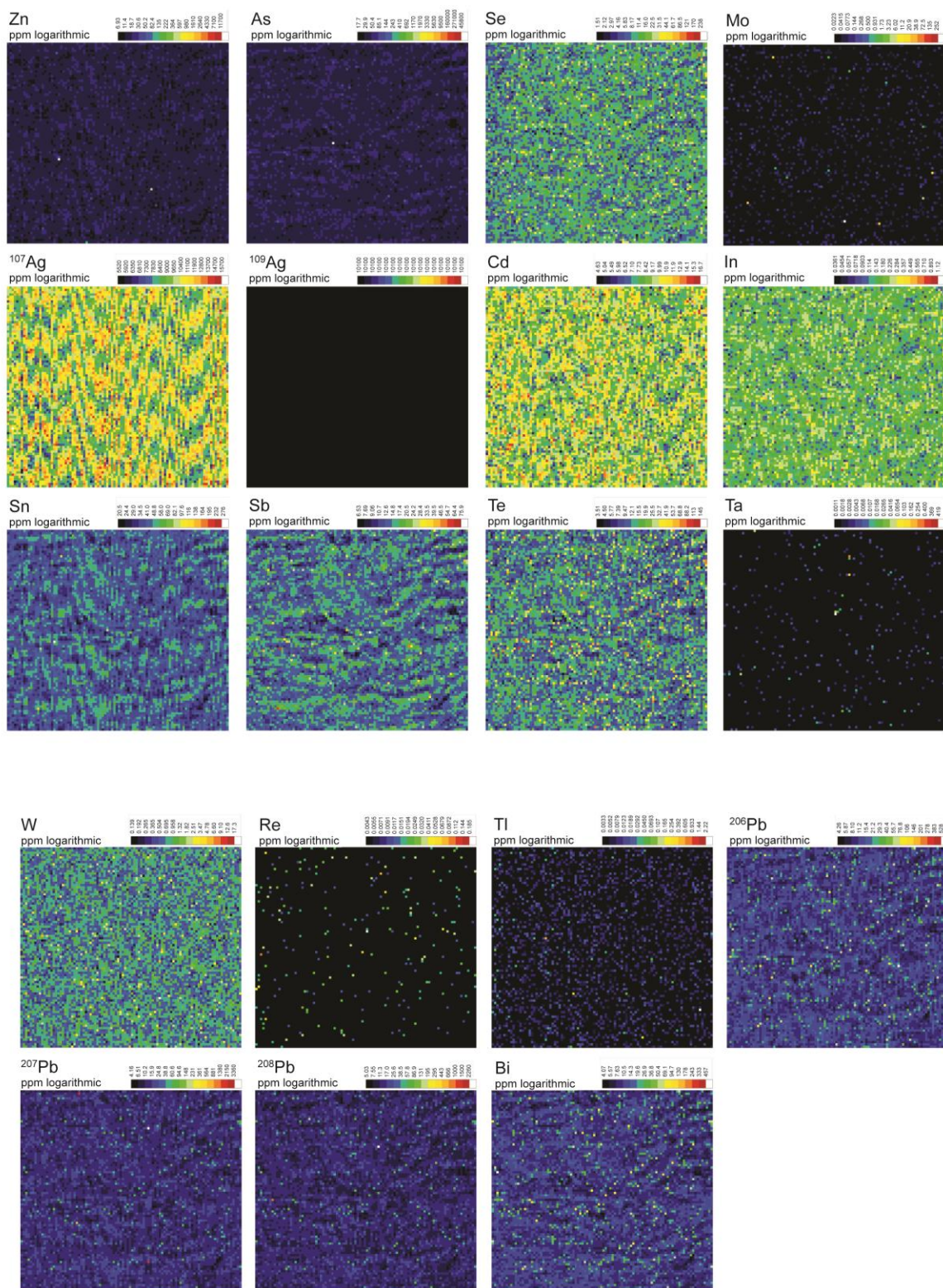
#### Element concentration maps

The element concentration maps, acquired at the GSC, are shown in Figs. 10 and 11 (NA-Au-30 and NA-Au-31, respectively). Maps of elements Mg, Al, Si, Ca, V, Mo, Ta, Re, and Tl in sample NA-Au-30 indicate low concentrations near or below the detection limit. Maps of Mn, Cu, Sn, and importantly Ag, as determined from  $^{107}\text{Ag}$  (the isotope of silver not used for internal normalization) show distinct wavy patterns. These are considered to be largely analytical artefacts produced by signal aliasing from the interplay of systematic fluctuations in signal intensities, related to pulsing of the laser (10Hz), and the sampling interval of the mass spectrometer (0.499 s per mass sweep). In contrast, other elemental maps of sample NA-Au-30 show good evidence for compositional heterogeneity that cannot be ascribed to aliasing effects. All three isotopes of Pb (206-208) show anomalously Pb-rich ( $\leq 100$  ppm) "pixels" occurring in the same spot, which significantly exceed the average background concentrations ( $\leq 15$  ppm). Similar brightly coloured "pixels" are seen in the maps of Fe and Bi, indicating micrometer-scale heterogeneity with respect to these elements.



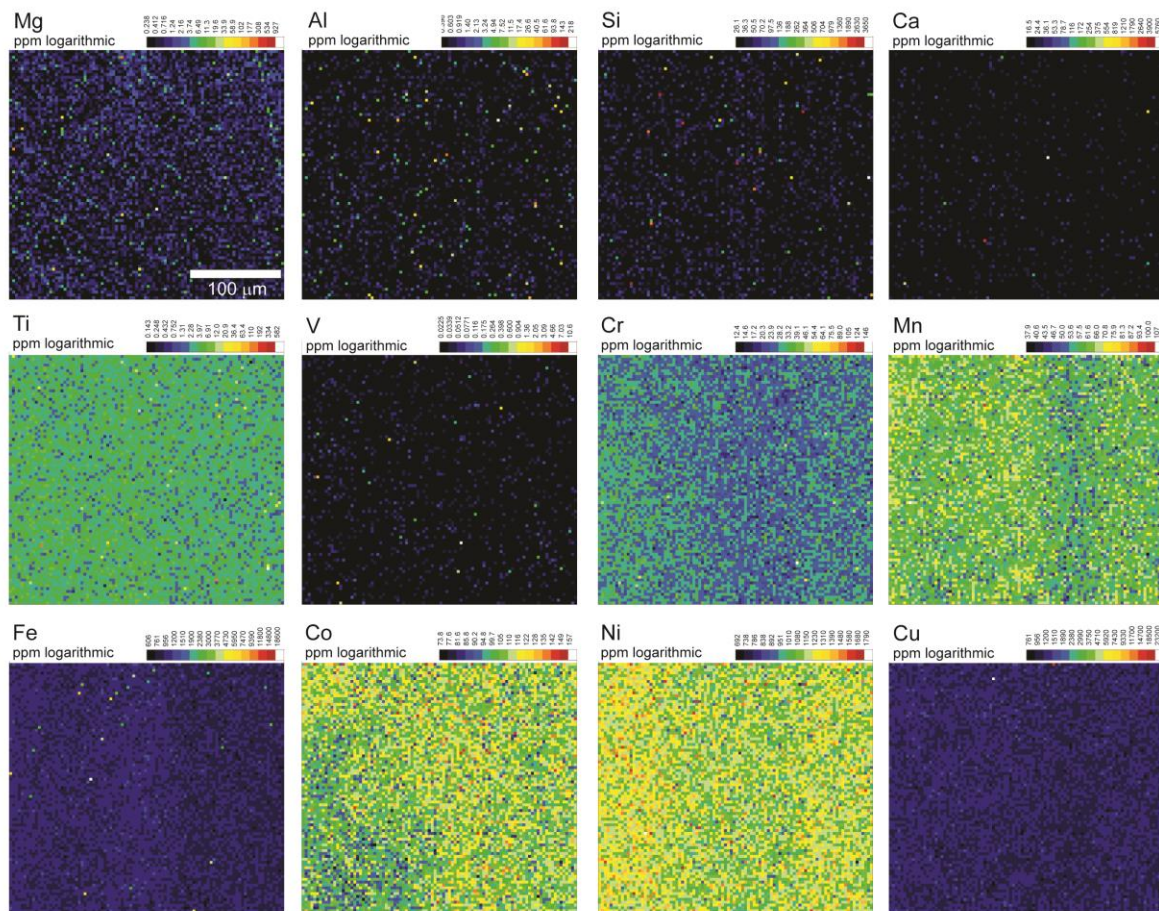


**Figure 10.** Element concentration maps for a 0.3 cm x 0.3 cm area within sample NA-Au-30. Data acquired as lines of 10 μm spots. Concentrations are in ppm metal.



*Figure 10. continued*





**Figure 11.** Element concentration maps for a 0.3 cm x 0.3 cm area within sample NA-Au-31. Data acquired as lines of 10 μm spots. Concentrations are in ppm metal.



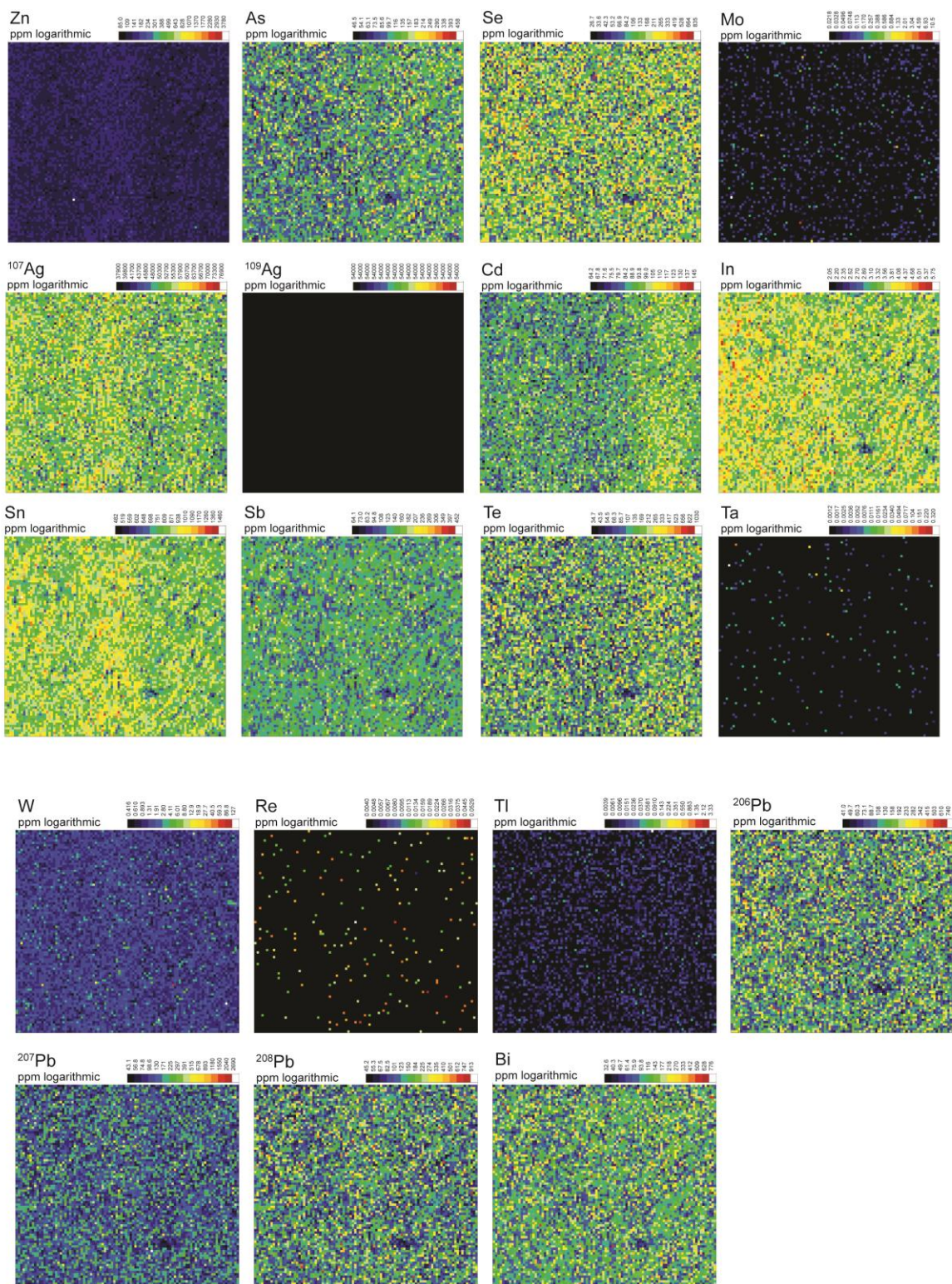


Figure 11. continued

Magnesium, Al, Si, Ca, V, Mo, Ta, Re, and Tl elemental maps of sample NA-Au-31 (Fig. 11) are all characterized by "cold" colours, indicating low concentrations of these elements near or below the detection limit. The distribution of Mn, Cd, Sn, and to lesser extent As, Ti, Fe, Te define two bands oriented parallel to the length of each map, which are also observed in the map of  $^{107}\text{Ag}$ . These bands are interpreted as analytical artefacts, related to acquisition of data along 16 north-south oriented transects, separated by analyses of standard materials. Each line of analyses is thus affected by the analyses of standards immediately before and after. Sample heterogeneity, however, is evident in the compositional maps of As, Se, In, Sn, Sb, Te, Pb and Bi, where a cluster of dark "pixels" in the lower right-hand quadrant of the each map indicates an  $\sim 20\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$  area of relatively low concentrations of these elements.

#### LA-ICP-MS analyses

The results of LA-ICP-MS analyses are presented in Tables 3-5 and Fig. 12. In addition to the elements that could not be measured due to poor calibration, the concentrations of Mo, Re, Tl, and V were found to be below the detection limit in all three samples, by all three labs. The concentrations of Rh, Pd, and Pt, determined at GSC and GLIER, are significantly higher than the certified values. The discrepancy in PGE concentrations may result from the use of synthetic sulphides as calibration standards and Fe, as measured by EPMA at QFIR ( $102 \pm 62\text{ ppm}$ , rather than the certified value of  $30.1 \pm 2.2\text{ ppm}$ ). In contrast, at QFIR the PGE were calibrated against NIST glasses and internally normalized to Ag concentrations. The concentrations of Fe, Mg, and Ti, measured at QFIR are significantly higher than the concentrations measured at GSC or GLIER.

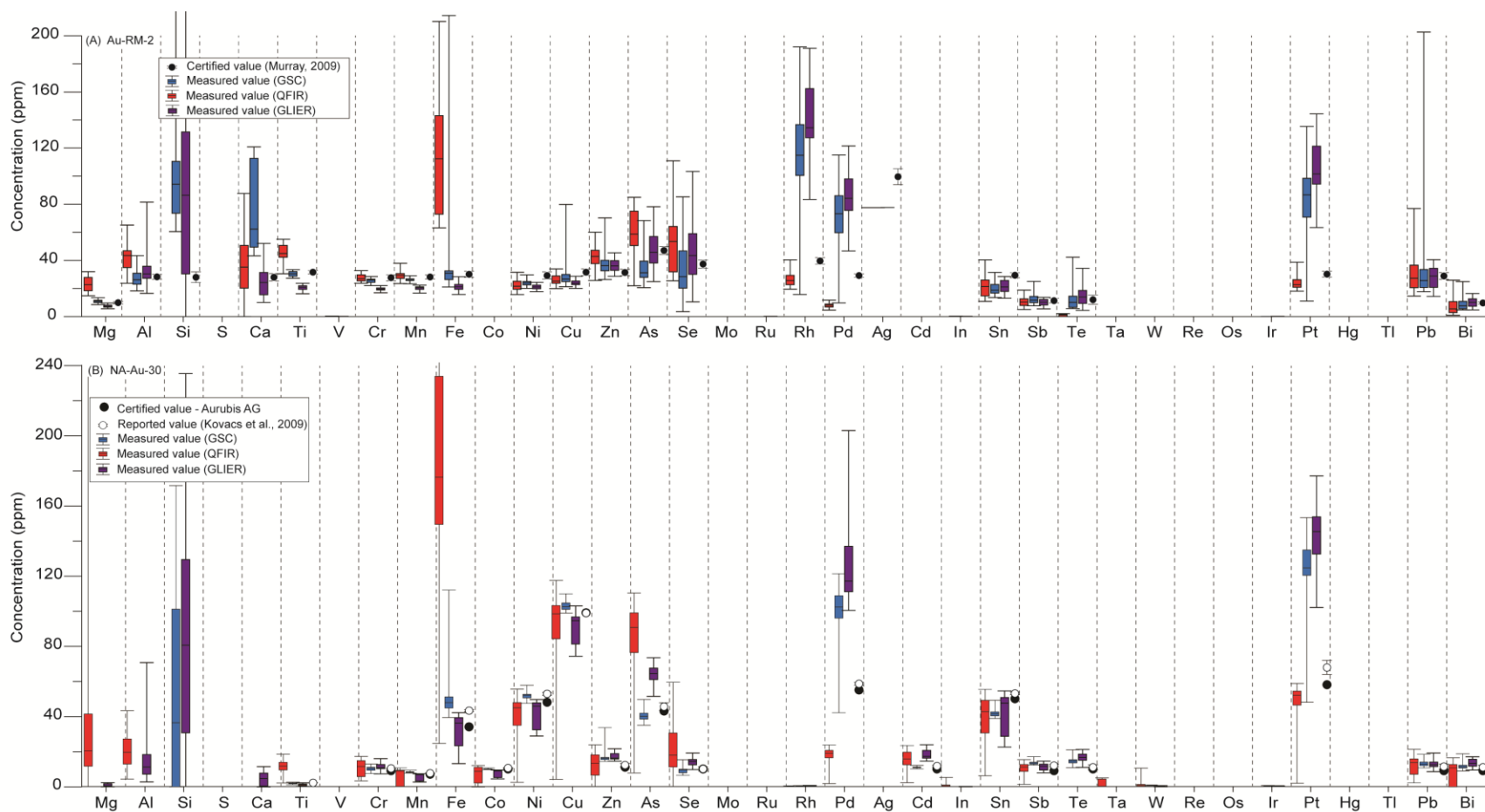
The differences in measured Fe concentrations arise from the poor calibration of Fe at QFIR as indicated by the poor agreement between measured and certified values of NIST 610 and NIST 612 synthetic glasses. In contrast, the measured concentrations of Ti and Mg in the NIST glasses agree with the certified values within 20 %.

#### DATA

Complete EPMA and LA-ICP-MS data for individual spot analyses is provided in electronic appendices A1-A4.

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**Figure 12.** Box and whisker plots of LA-ICP-MS analyses (red: QFIR; blue: GSC; blue). A) Au-RM-2 compared to certified values of Murray, 2009; B) NA-Au-30 compared to values reported by Aurubis AG and Kovacs et al. (2009); and C) NA-Au-31. Note the breaks in ordinate axis in C).



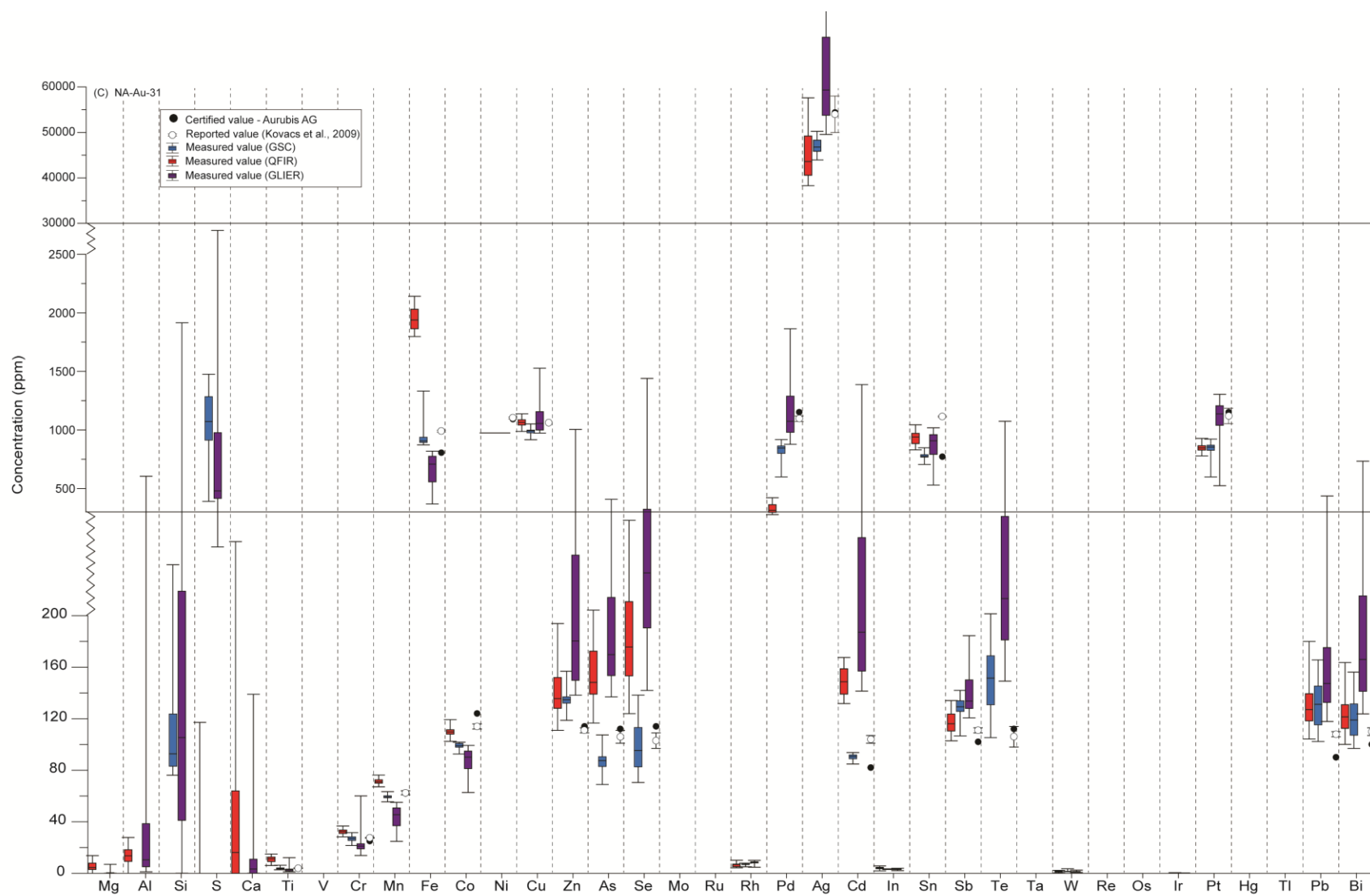


Figure 12. continued

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