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Trace Element Analysis of Natural Gold by Laser Ablation ICP-MS: A Combined External/Internal Standardisation Approach

Tom E. **McCandless** (1), Mark E. **Baker** (2) and Joaquin **Ruiz** (1)

(1) Centre for Mineral Resources, Department of Geosciences, University of Arizona Tucson, Arizona USA 85721
(2) Department of Geosciences, University of Arizona Tucson, Arizona USA 85721

For the trace element analysis of gold by laser ablation ICP-MS, external calibration samples of differing matrix composition have been used in previous studies. Data presented here suggest that even for calibration samples and unknowns with closely-matched matrices, discrepancies arise due to variations in the coupling behaviour of the laser with the sample at different power deliveries, and can lead to erroneous trace element determinations. Internal standardisation for gold is complicated because Au and Ag, the most common major elements, do not have minor isotopes that can be used as internal standards. This problem was overcome for natural gold samples by using an external calibration sample only for the major elements Au and Ag, then defocussing the ion path and using ^{107}Ag in each sample as an internal standard against which µg g^{-1} levels of Te, Sb, Hg, Bi, and Cu were determined. The results suggest that trace elements can occupy lattice sites in gold rather than occurring only as micro-inclusions of other phases. The analytical approach taken here may be used in trace element analysis where adequate external calibration samples are not readily available.

La méthode de calibration externe par échantillon ayant des matrices de compositions différentes a été utilisée antérieurement pour le dosage de l'or par ablation laser couplée à un ICP-MS. Les résultats présentés ici montrent que même dans le cas de calibrations par étalons ayant des matrices très proches de celles des échantillons, des différences se produisent, dues à des variations du comportement de couplage entre laser et échantillon pour des puissances restituées différentes et peut conduire à des déterminations en éléments en trace faussées. La standardisation interne pour l'or est difficile car l'or et l'argent, éléments majeurs les plus importants, n'ont pas d'isotopes mineurs pouvant etre utilisés comme standards internes. Ce problème a été résolu, pour les échantillons d'or naturels, en utilisant un standard externe uniquement pour les éléments majeurs Au et Ag, puis en défocalisant le faisceau d'ions et en utilisant ^{107}Ag de chaque échantillon comme standard interne permettant de determiner des concentrations de Te, Sb, Hg, Bi et Cu à des niveaux de l'ordre du µg g^{-1}. Les résultats suggèrent que les éléments en trace peuvent occuper des sites dans les réseaux cristallins de l'or de préference à des micro-inclusions d'autres phases. L'approche analytique adoptée ici peut être utilisée pour d'autres analyses d'éléments en trace quand des échantillons adéquats de calibration externe ne sont pas disponibles.

Inductively coupled plasma-mass spectrometry (ICP-MS) has been a popular method of geochemical analysis because of the wide range of elements that can be routinely detected to sub ng g^{-1} levels. Two drawbacks of solution ICP-MS are the time required for sample preparation and the fact that small-scale spatial variations within individual samples cannot be resolved. Laser ablation ICP-MS overcomes both problems by allowing for rapid, *in situ* analysis of small volumes of solid material, allowing for trace element (Arrowsmith 1987, Imai 1990, Jackson *et al.* 1992, Pearce *et al.* 1992, Jarvis and Williams 1993, Perkins *et al.* 1993, Fryer *et al.* 1995, van de Weijer *et al.* 1992, Ludden *et al.* 1995 and Perkins *et al.* 1992) and isotopic (Feng *et al.* 1993 and Christensen *et al.* 1995) discrimination at the sub-millimetre scale. The use of

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external standards in laser ablation ICP-MS has been of limited success (Perkins *et al.* 1991, Kogan *et al.* 1994, Bea *et al.* 1994, Cromwell and Arrowsmith 1995 and Fend 1994) because the volume of material ablated is dependent on the physical and chemical matrix of the solid. Calibration samples with matrices that differ from the unknowns can lead to erroneous results in quantitative analysis. Thus, the primary challenge of laser ablation ICP-MS is to find adequate methods of standardisation for quantitative analysis. Past approaches include standard addition to powdered or fused samples (Pearce *et al.* 1992, Perkins *et al.* 1991 and Fedorowich *et al.* 1993) or using a standard solution run into the torch in tandem with the products of ablation (Cromwell and Arrowsmith 1995). The least problematic approach is internal standardisation i.e., using a minor isotope of a major element within the sample for which the concentration is independently known, to quantify results (Imai 1990, Jarvis and Williams 1993, Fryer *et al.* 1995, Van de Weijer *et al.* 1992, Ludden *et al.* 1995, Bea *et al.* 1994, Fedorowich *et al.* 1993, Westgate *et al.* 1994, Jenner *et al.* 1993 and Horn *et al.* 1994). Internal standardisation is at present the most popular method, as problems with matrix matching between calibration samples and unknowns is eliminated (van de Weijer *et al.* 1992, Morrison *et al.* 1995, Norman *et al.* 1996 and Perkins *et al.* this volume), although selective fractionation of trace elements in sulfides has been noted for lasers operating in the IR (Watling *et al.* 1995).

A variety of external calibration samples are readily available for trace element analysis of gold by LA-ICP-MS, and have been used with limited success under carefully controlled conditions (Kogan *et al.* 1994). However, our results suggest that external standardisation for quantitative analysis of gold can lead to erroneous results even in cases where calibration sample and unknown matrices are nearly identical.

Using internal standardisation as an alternative method of quantification for gold is complicated by the fact that silver is the next most common element (Boyle, 1979 and Watling *et al.* 1994); Au is monoisotopic and the ^{107}Ag and ^{109}Ag masses are too abundant to be conveniently measured on electron multiplier detectors required for trace element detection. To overcome this problem, Au and Ag in natural gold samples were measured on a Faraday detector using an external calibration sample, then the ion optics were slightly defocused, and the ^{107}Ag mass was measured on the multiplier detector, and used as an internal standard against which Cu, Sb, Te, Hg, and Bi concentrations were determined.

Instrumentation

Laser ablation systems

Two laser ablation systems were used in this study. The Finnigan-MAT System 266™ Nd:YAG laser operates at a wavelength of 1064 nm which is frequency quadrupled to 266 nm. The UV wavelength region was chosen because of the improved energy absorption characteristics in materials such as halite, quartz, and gold. The laser operates in Q-switched mode at pulse rates of 1-12 Hz, delivering a maximum energy of about 5 mJ per pulse at 266 nm. Real time ablation monitoring was achieved with the use of a solid state CCD video camera and a colour monitor. The ablation chamber consists of a sealed 150 ml cylindrical pyrex housing with a UV transparent quartz glass top. Openings in the side of the sample ablation chamber were used for the introduction and exhaust of an argon carrier gas.

The second laser ablation system used in this study was constructed at the University of Arizona and utilizes a Big Sky™ model CFR200 compact, frequency quadrupled (266 nm) Nd:YAG laser. To remove beam aberrations and achieve a small and uniform ablation spot, the output beam from the laser is filtered to a low order gaussian by focussing the beam through a 400 μm diameter pinhole. The filtered beam is collimated and injected into a microscope where it is focused to a small spot on the sample surface by a reflecting Scharzschild microscope objective (Ealing™ 15x). A visible spotting beam (650 nm) is created by a diode laser (Unidata™) directed along the optical axis of the microscope with the aid of a 50/50 visible beam splitter. A dielectric high reflector is used to introduce the UV laser beam into the microscope, which is designed to reflect 266 nm light at 45° and allow for the transmission of visible light from the diode laser along the optical axis of the microscope. Both the diode and UV laser beams are brought to focus on the sample in the same plane. A video camera system is attached to the microscope 10x Huygens-type eyepiece for real time ablation monitoring. The sample chamber is a ~ 5 ml volume with bellows-shaped pyrex sides and a flat quartz top which is parallel to the sample surface. The chamber has a 0.8 mm internal diameter (ID) entry port for introduction of the Ar carrier gas and a 4.0 mm ID exhaust port for the gas and ablated material. The exhaust port leading to the ICP is located along the blunt end of the chamber. The design allows for complete mixing of ablated material with argon before transport to the ICP, and is similar to an in-line mixing chamber (Norman *et al.* 1996).

Mass spectrometry

For this study, a Finnigan-MAT SOLA™ ICP-MS was used. In contrast to most laser ICP-MS configurations, the SOLA™ uses a dual gas flow system in which a solution is introduced into the ICP through peristaltic pumping and aspiration with argon through a concentric nebuliser. The ablated sample material is carried by an argon gas flow along a second line and mixes with aspirated water just prior to introduction into the plasma. This configuration reduces background and improves signal stability for the SOLA. Ions pass through a sample, skimmer, and accelerator cone, the latter producing a cross-over of the ion beam before introduction into the ion optics. The ion optics consist of x-y deflectors, focus, y-steer and phase matching lenses. Ions are then passed through a conventional quadrupole mass filter to the detectors. A DC Faraday detector is used for ion beams greater than 10^6 ions s^{-1} (0.1-1 $\mu g\ g^{-1}$), and the scanning electron multiplier (SEM) detector is the preferred detector for ion beams in the 10^2 - 10^6 ions s^{-1} range (~ 1-100 ng g^{-1}).

External standards and trace elements in natural gold

A previous study reported trace element data for gold using external calibration samples that suggested that results were not dependent on identically matrix-matched calibration samples and unknowns (Hogan et al. 1994). In the present study, trace element intensities appear to be sensitive to subtle matrix differences between the unknown and calibration sample, even when major element compositions do not differ drastically. An experiment to demonstrate this sensitivity was config-ured in the following manner.

The concentration (C) of an element in a sample is related to the known concentration of a calibration sample by the following expression:

$$C_{unknown} = \frac{(C_{calibration}) \times (I_{unknown})}{(I_{calibration})}$$

where I is the intensity of the element minus the background (in counts s^{-1}). If no bias exists between unknown and calibration sample, reducing the output power of the laser will reduce the intensities for a given element in both unknown and calibration sample, but the ratio of unknown intensity to calibration sample intensity should not vary. If there is a difference in the coupling behaviour of the laser between unknown and calibration sample, that difference will manifest itself with changes in the power setting of the laser, and the $I_{unknown}/I_{calibration}$ ratio will vary.

Three samples of natural gold from the Sixteen to One Mine, California, were analysed against an in-house gold calibration sample. The calibration sample is from a gold pour at the Sixteen to One Mine, in which Au and Ag were independently determined by microprobe and fire assay (Table 2). Conditions were held constant for the Finnigan-MAT System 266™

Table 1.
Typical operating conditions for the instrumentation used in this study. All instrumentation is located at the Keck Trace Element Laboratory at the University of Arizona

System 266 UV Laser	
Laser operating mode	Q-switched
Repetition rate	2 Hz
Flashlamp pump energy (at head)	8.5 V
	8.2 V
Power delivery at sample (maximum)	4 mJ/pulse
Ablation pit size	20 μm diameter
Focus condition	focus on surface
Ablation chamber argon flow rate	0.300 l min^{-1}
Big Sky UV Laser	
Laser operating mode	Q-switched
Repetition rate	20 Hz
Flashlamp pump energy (at head)	10.6 V
	9.5 V
Power delivery at sample (maximum)	20 mJ/pulse
Ablation pit size	20 μm diameter
Focus condition	focus on surface
Ablation chamber argon flow rate	0.300 l min^{-1}
SOLA ICP-MS	
Nebuliser flow rate	0.627 l min^{-1}
Quadrupole resolution	37
Ion optics (potentiometer settings)	
X deflection	6.58
Y deflection	3.92
Y steer	6.85
Match	9.50
Focus (Faraday)	7.74
(Multiplier)	5.00
Acquisition mode	peak scan
Mass resolution	16 channels amu^{-1}
Faraday scanning conditions	1 scan, 4 passes
SEM scanning conditions (defocused)	1 scan, 8 passes
Acquisition time (Faraday)	10 s
(Multiplier)	10 s
Dwell time (Faraday)	64 ms
(Multiplier)	16 ms

Table 2.
Comparison of values for the 1621 gold calibration sample, using fire assay, electron microprobe, and laser ICP-MS. Values are in % m/m

	assay (n=2)	σ	probe (n=10)	σ	laser (n=39)	σ
Au	85.3	0.50	85.5	0.20	84.8	2.10
Ag	13.1	0.50	14.5	0.10	15.2	2.10

Nd:YAG, except for power output, which was operated at two different settings (measured at the laser head; Table 1). The $I_{unknown}/I_{calibration}$ ratios for Hg, Cu, Sb and Te demonstrate significant differences, that vary consistently as a function of power setting (Figure 1A,B).

The procedure was repeated for the University of Arizona laser system, with conditions held constant except for the power output (Table 1). Differences in $I_{unknown}/I_{calibration}$ were again noted for trace elements in the gold samples at different power settings that are greater than the 2σ uncertainty for the analyses (Figure 1C,D). Note also that the relative difference of the $I_{unknown}/I_{calibration}$ ratio tends to be consistent between samples for both laser systems (Figure 1). The results suggest that, regardless of the laser system used, subtle differences in the coupling behaviour of UV lasers between noble metal calibration samples and unknowns can occur, leading to erroneous results for trace element determinations in gold. The differences may be due to elemental fractionation in the ablation process, which has been previously observed for trace elements in other minerals (Hager 1989, Ruiz *et al.* 1995, Outridge *et al.* 1996, Caetano *et al.* 1996 and Watling *et al.* 1995).

Combined external/internal standardisation of gold

Gold typically contains only Au and Ag in the weight percent range, though some exceptional samples have high Hg, Bi, or Cu contents (Boyle 1979

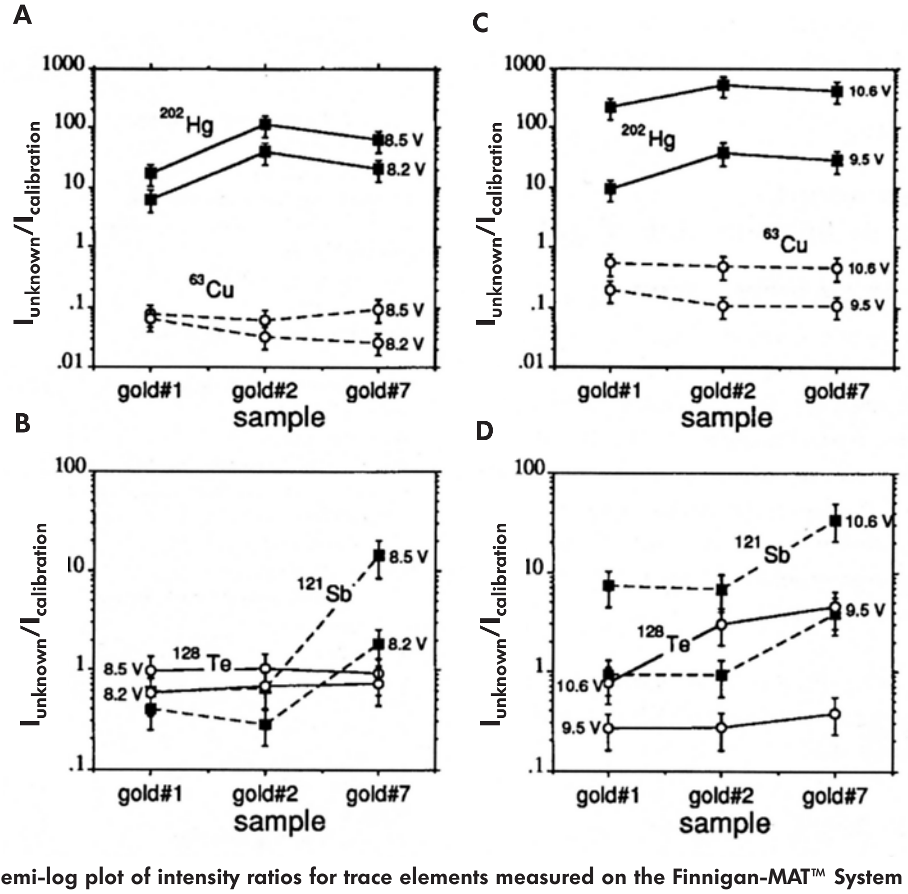

Figure 1. (A,B) Semi-log plot of intensity ratios for trace elements measured on the Finnigan-MAT™ System 266™, with all parameters held constant except power of the laser head which was operated at 8.2 V and 8.5 V. (C,D) Similar plots for the University of Arizona laser, which incorporates a Big Sky™ CFR200 head operating at 10.6 V and 9.5 V. Error bars are set at 2σ = 40%, which is the largest variation observed in the average of any set of analyses.

and Watling *et al.* 1994). We took advantage of this simple mineralogy and determined the major and trace element composition of several natural gold samples in the following manner. The in-house 1621 gold calibration sample was used to determine Au and Ag contents in the unknown samples. External standardisation is a reasonable approach for the major elements Au and Ag because the biases observed for trace elements (Figure 1) are not appreciable for Au and Ag. The ion beam was then defocused so that the ^{107}Ag mass produced an intensity of ~ 800,000 counts s^{-1} that could be measured on the multiplier. A new spot is then selected for ablation, as near to the first ablation point as possible. The ^{107}Ag, ^{63}Cu, ^{128}Te, ^{121}Sb, ^{202}Hg, and ^{210}Bi masses are then measured on the multiplier, and the ^{107}Ag mass is used as an internal standard against which concentrations of Hg, Cu, Sb, Te and Bi are determined. These elements were selected because previous laser ablation studies suggested that their ionisation and ablation efficiencies are nearly similar (Fryer et al. 1995). Mass bias is introduced when the ion beam is defocused, which was corrected for by analysing several noble metal reference samples under focused and defocused conditions. Defocussing also leads to a reduction in sensitivity, which for the elements of this study limited results to a detection limit of ~ 4 μg g$^{-1.}$

Major and trace element compositions are compiled in Table 3. The data represent the average of at least four ablation points for Au and Ag, and at least three ablation points for the trace elements. In every case, ablation points for trace element analysis were obtained as close as possible to the points for major elements. The System 266™ laser was used,

Table 3.
Typical analyses for gold samples from the Sixteen to One Mine. Data are averages of at least four points for both Au and Ag concentrations and for the trace elements. Trace element uncertainties vary from 5-35% (1σ) due to heterogeneous distribution in the gold samples

sample	gold#1	gold#2	gold#3	gold#4	gold#5	gold#6
% m/m						
Au	80.95	75.62	76.90	81.90	74.98	80.90
Ag	17.75	22.33	21.92	16.37	22.79	17.10
σ	0.50	0.40	2.20	0.50	2.10	3.60
μg g^{-1}						
Cu	8123	5720	2385	685	2877	242
Sb	740	63	11	191	72	33
Te	≤4	≤4	134	75	121	49
Hg	3011	10480	1792	7268	12300	9974
Bi	61	89	93	116	191	257

sample	gold#7	gold#8	gold#9	gold#10	gold#26	gold#33
% m/m						
Au	78.69	76.67	82.26	77.65	80.66	85.21
Ag	19.68	21.68	16.62	21.29	16.36	14.46
σ	1.20	2.80	2.40	1.80	2.90	0.20
μg g^{-1}						
Cu	963	222	1464	4266	159	2100
Sb	150	4	162	32	46	37
Te	36	30	105	≤4	‹ 4	10
Hg	6208	6523	1149	631	19902	1200
Bi	33	36	≤4	81	89	≤4

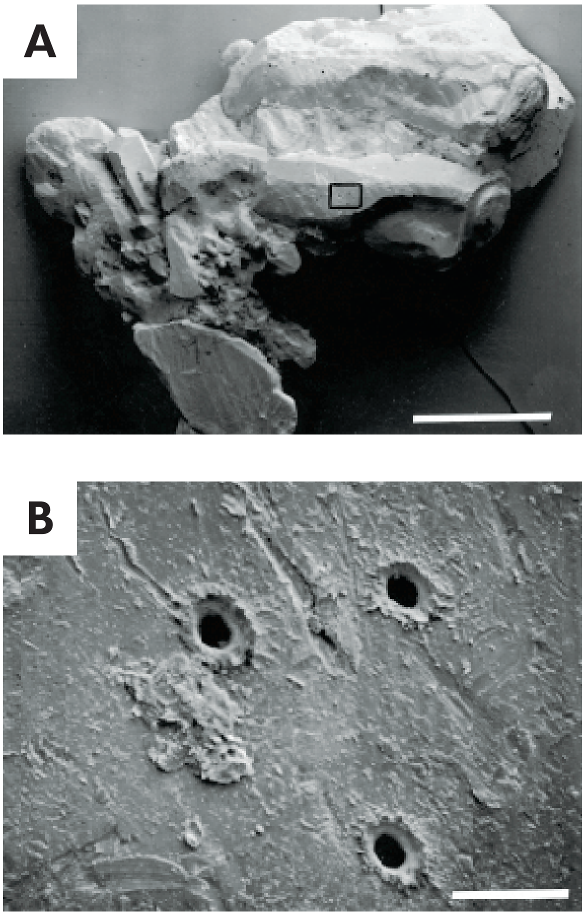

Figure 2. (A) Gold with euhedral quartz intergrowths. Ablation pits can be seen on the upper and central portions of the gold. Scale 2 mm. (B) Close-up of the right central part of the gold sample. The System 266 laser operates in the ultraviolet range and couples better with materials in which transition elements are lacking, as indicated by the well-formed ablation pits. Scale 100 μm.

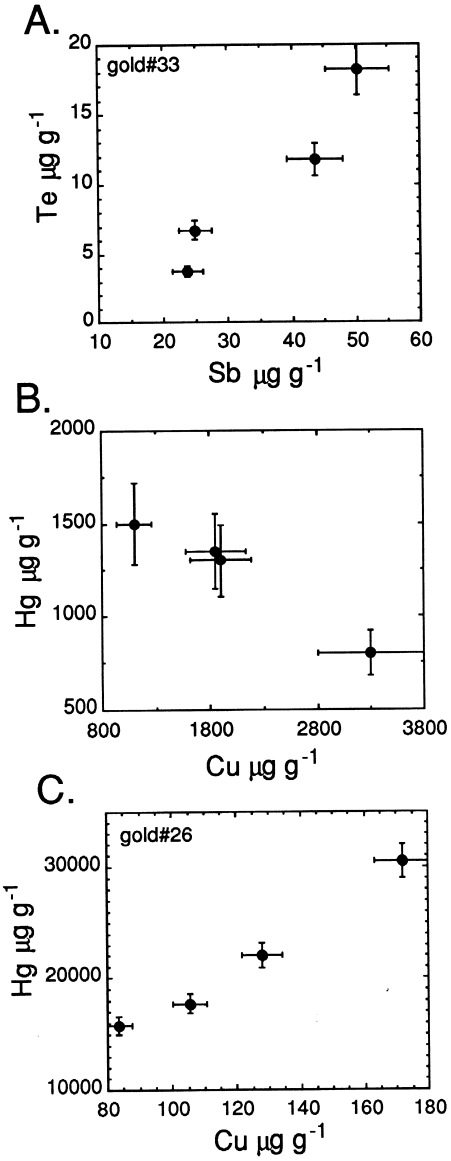

Figure 3. Trace element correlations for (A) Te with Sb and (B) Cu with Hg in gold#33, and (C) Cu with Hg for gold#26. Uncertainties in Hg, Cu, Te, and Sb for each analysis point are ±15% (1σ) assumed from instrumental reproducibility of glass standard NIST SRM 612 (see text for discussion).

and analyses were performed on flat areas of the gold grains to ensure consistent pit volume and geometry with each analysis (Figure 2).

Results

Compositions of natural gold from the Sixteen to One Mine range from 74.98-82.26% m/m Au, and 14.46-22.79% m/m Ag, respectively. Hg is the most abundant trace element, with concentrations reaching the weight percent level (631-19902 µg g^{-1}), followed by Cu (159-8123 µg g^{-1}). Other trace elements range from ≤4 µg g^{-1} to 740 µg g^{-1} (Table 3).

For some samples in which trace elements were consistently above detection limits, correlations between individual ablation points could be recognised (Figure 3). Each ablation point represents a single scan consisting of eight passes through the selected masses, and SOLA software does not calculate statistical uncertainties for single scans. Repeatability of the gold calibration sample is roughly +2% (Table 2), whereas a maximum of +15% is obtained for the NIST glasses. Uncertainties of +15% are therefore estimated for data plotted in Figure 3, which are believed to represent a reasonable maximum instrumental uncertainty for the individual data points.

In gold sample #33, tellurium correlates positively with Sb (Figure 3A), and Cu correlates negatively with Hg (Figure 3B). In contrast, Hg exhibits a positive correlation with Cu in gold #26 (Figure 3C). Micro-inclusions of sulfides and tellurides were rarely encountered during ablation, and would inevitably trip the multiplier due to signal intensities exceeding 10^6 ions s^{-1}. It is unlikely therefore, that the linear correlations observed in Figure 3 are due to fortuitous analysis of micro-inclusions in the gold. The strongly linear relations instead support previous speculations that trace elements can occupy lattice sites in gold (Boyle 1979 and Watling *et al.* 1994), rather than being present only as isolated micro-inclusions of sulphide or telluride minerals. Laser ablation ICP-MS has revealed the reverse to be true, i.e. that gold occurs as micro-inclusions in other sulfides (Chenery *et al.* 1995). The measurement of trace elements in gold can have practical implications. For example, trace element patterns in detrital gold recovered in stream gravels may help identify primary hosts for the gold, and help to optimise exploration models.

Conclusions

The analysis approach for laser ablation ICP-MS taken in this study can be applied to studies of samples where major elements with independently known composition are available, but whose isotopes are not within the range of a multiplier detector. With the SOLA™ ICP-MS, the addition of a Faraday detector allowed major element compositions to be determined directly by laser ablation ICP-MS. However, laser ablation

ICP-MS systems with only multiplier detectors can also be utilized if the concentration of a major element in the sample is determined independently. Defocussing introduces a mass bias, which can be corrected for, and compromises sensitivity, which in this study limited results to concentrations greater than 4 μg g^{-1}.

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References

Arrowsmith P. (1987)
Laser ablation of solids for elemental analysis by inductively coupled plasma-mass spectrometry. **Analytical Chemistry, 59,** 1437-1444.

Bea F. , Pereira M.D. and Stroh A. (1994)
Mineral/leucosome trace-element partitioning in a peraluminous migmatite (a laser ablation ICP-MS study). **Chemical Geology, 117,** 291-312.

Boyle R.W. (1979)
The geochemistry of gold and its deposits. **Geological Survey of Canada Bulletin 280,** 584pp.

Caetano M. , Mao X. and Russo R.E. (1996)
Laser ablation solid sampling: vertical spatial emission intensity profiles in inductively coupled plasma. **Spectrochimica Acta, 51B,** 1473-1485.

Chenery S. , Cook J.M. , Styles M. and Cameron E.M. (1995)
Determination of the three-dimensional distributions of precious metals in sulfide minerals by laser ablation microprobe inductively coupled plasma-mass spectrometry (LAM-ICP-MS). **Chemical Geology, 124,** 55-65.

Christensen J.N. , Halliday A.N. , Lee D.C. and Hall C.M. (1995)
In situ Sr isotopic analysis by laser ablation. **Earth and Planetary Science Letters, 136,** 79-85.

Cromwell E.F. and Arrowsmith P. (1995)
Semiquantitative analysis with laser ablation inductively coupled plasma-mass spectrometry. **Analytical Chemistry, 67,** 131-138.

Fedorowich J.S. , Richards J.P. , Jain J.C. , Kerrich R. and Fan J. (1993)
A rapid method for REE and trace element analysis using laser sampling ICP-MS on direct fusion whole-rock glasses. **Chemical Geology, 106,** 229-249.

Feng R. (1994)
In situ trace element determination of carbonates by laser probe inductively coupled plasma-mass spectrometry using nonmatrix matched standardisation. **Geochimica et Cosmochimica Acta, 58,** 1616-1623.

Feng R. , Machado N. and Ludden J. (1993)
Lead geochronology of zircon by laser probe inductively coupled plasma-mass spectrometry. **Geochimica et Cosmochimica Acta, 57,** 3479-3486.

Fryer B.J. , Jackson S.E. and Longerich H.P. (1993)
The application of laser ablation microprobe inductively coupled plasma-mass spectrometry (LAM-ICP-MS) to *in situ* (U)-Pb geochronology. **Chemical Geology, 109,** 1-8.

Fryer B.J. , Jackson S.E. and Longerich H.P. (1995)
The design, operation and role of the laser ablation microprobe coupled with an inductively coupled plasma-mass spectrometer (LAM-ICP-MS) in the Earth sciences. **The Canadian Mineralogist, 33,** 303-312.

Hager J.W. (1989)
Relative elemental responses for laser ablation inductively coupled plasma-mass spectrometry. **Analytical Chemistry, 61,** 1243-1248.

Horn I. , Foley S.F. , Jackson S.E. and Jenner G.A. (1994)
Experimentally determined partitioning of high field strength- and selected transition elements between spinel and basaltic melt. **Chemical Geology, 117,** 193-218.

Imai N. (1990)
Quantitative analysis of original and powdered rocks and mineral inclusions by laser ablation inductively coupled plasma-mass spectrometry. **Analytica Chimica Acta, 235,** 381-391.

Jackson S.E. , Longerich H.P. , Dunning G.R. and Fryer B.J. (1992)
The application of laser ablation microprobe inductively coupled mass spectrometry (LAM-ICP-MS) to *in situ* trace element determinations in minerals. **The Canadian Mineralogist, 30,** 1049-1064.

Jarvis K.E. and Williams J.G. (1993)
Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS): a rapid technique for the direct, quantitative determination of major, trace and rare elements in geological samples. **Chemical Geology, 106,** 251-262.

Jenner G.A. , Foley S.F. , Jackson S.E. , Green T.H. , Fryer B.J. and Longerich H.P. (1993)
Determination of partition coefficients for trace elements in high pressure-temperature experimental run products by laser ablation microprobe inductively coupled plasma-mass spectrometry (LAM-ICP-MS). **Geochimica et Cosmochimica Acta, 57,** 5099-5103.

Klemme S. , van der Laan S.R. , Foley S.F. and Guenther D. (1995)
Experimentally determined trace and minor element partitioning between clinopyroxene and carbonatite melt under upper mantle conditions. **Earth and Planetary Science Letters, 133,** 439-448.

Kogan V.V. , Hinds M.W. and Ramendik G.I. (1994)
The direct determination of trace metals in gold silver materials by laser ablation inductively coupled plasma-mass spectrometry without matrix matched standards. **Spectrochimica Acta, 49B,** 333-343.

references

Ludden J.N. , Feng R. , Gauthier G. , Stix J. , Lang S. , Francis D. , Machado N. and Wu G. (1995)
Applications of LAM-ICP-MS to analysis of minerals. Canadian Mineralogist, 33, 419-434.

McCandless T.E. , Ruiz J. and Adair B.I. (1994)
Platinum group mineralisation in the Bushveld Complex: a combined QEM-SEM and LA-ICP-MS study. Mineralogical Magazine, 58A, 579-580.

Morrison C.A. , Lambert D.D. , Morrison R.J.S. , Ahlers W.W. and Nicholls I.A. (1995)
Laser ablation inductively coupled plasma-mass spectrometry: an investigation of elemental responses and matrix effects in the analysis of geostandard materials. Chemical Geology, 119, 13-29.

Norman M.D. , Pearson N.J. , Sharma A. and Griffin W.L. (1996)
Quantitative analysis of trace elements in geological materials by laser ablation ICP-MS: instrumental operating conditions and calibration values of NIST glasses. Geostandards Newsletter, 20, 247-261.

Outridge P.M. , Doherty W. and Gregoire D.C. (1996)
The formation of trace element-enriched particulates during laser ablation of refractory materials. Spectrochimica Acta, 51B, 1451-1462.

Pearce N.J.G. , Perkins W.T. , Abell I. , Duller G.A.T. and Fuge R. (1992)
Mineral microanalysis by laser ablation inductively coupled plasma-mass spectrometry. Journal of Analytical Atomic Spectrometry, 7, 53-57.

Perkins W.T. , Fuge R. and Pearce N.J.G. (1991)
Quantitative analysis of trace elements in carbonates using laser ablation inductively coupled plasma-mass spectrometry. Journal of Analytical Atomic Spectrometry, 6, 445-449.

Perkins W.T. , Pearce N.J.G. and Fuge R. (1992)
Analysis of zircon by laser ablation and solution inductively coupled plasma-mass spectrometry. Journal of Analytical Atomic Spectrometry, 7, 611-616.

Perkins W.T. , Pearce N.J.G. and Jeffries T.E. (1993)
Laser ablation inductively coupled plasma-mass spectrometry; a new technique for the determination of trace and ultra-trace elements in silicates. Geochimica et Cosmochimica Act, 57, 475-482.

Ruiz J. , McCandless T.E. and Murray J. (1995)
Effect of laser, wavelength, power density and repetition rate on ablated ejecta. Terra Nova, 7, 343.

van de Weijer P. , Baeten W.L. , Bekkers M.H.J. and Vullings P.J.M.G. (1992)
Fast semiquantitative survey analysis of solids by laser ablation inductively coupled plasma-mass spectrometry. Journal of Analytical Atomic Spectrometry, 7, 599-603.

Watling R.J. , Herbert H.K. , Delev D. and Abell I.D. (1994)
Gold fingerprinting by laser ablation inductively coupled plasma-mass spectrometry. Spectrochimica Acta, 49B, 205-219.

Watling R.J. , Herbert H.K. and Abell I.D. (1995)
The application of laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) to the analysis of selected sulfide minerals. Chemical Geology, 124, 67-81.

Westgate J.A. , Perkins W.T. , Fuge R. , Pearce N.J.G. and Wintle A.G. (1994)
Trace element analysis of volcanic glass shards by laser ablation inductively coupled plasma-mass spectrometry; application to tephrochronological studies. Applied Geochemistry, 9, 323-335.