

#### CERTIFICATE OF ANALYSIS FOR

# TIN ORE CERTIFIED REFERENCE MATERIAL OREAS 141

Table 1. Certified Va	alues, SD's,	95% Confid	ence and To	lerance Lim	nits for ORE	AS 141.	
Constituent	Certified	SD	95% Cor Lin		95% Tolerance Limits		
	Value		Low	High	Low	High	
Silver, Ag (ppm)	1.58	0.11	1.51	1.65	1.42	1.75	
Arsenic, As (ppm)	789	29	767	812	771	807	
Bismuth, Bi (ppm)	324	29	303	344	314	333	
Copper, Cu (ppm)	2453	98	2387	2518	2407	2499	
Indium, In (ppm)	34	5	29	39	33	35	
Molybdenum, Mo (ppm)	2.28	0.29	2.08	2.49	2.18	2.39	
Lead, Pb (ppm)	59.0	3.8	56.7	61.4	56.0	62.1	
Zinc, Zn (ppm)	3637	178	3502	3771	3554	3719	
Tin via fusion, Sn (ppm)	6061	339	5794	6327	5934	6187	
Tin via PPP, Sn (ppm)	6312	259	5944	6680	6259	6365	

Note - intervals may appear asymmetric due to rounding; "PPP" = pressed powder pellet with X-ray fluorescence.



#### INTRODUCTION

OREAS reference materials are intended to provide a low-cost method of evaluating and improving the quality of analysis of geological samples. To the geologist they provide a means of implementing quality control in analytical data sets generated in exploration from the grass roots level through to prospect evaluation, and in grade control at mining operations. To the analyst they provide an effective means of calibrating analytical equipment, assessing new techniques and routinely monitoring in-house procedures.

#### SOURCE MATERIAL

OREAS 141 is a medium grade Sn oxide ore certified reference material (CRM) prepared by Ore Research & Exploration. The material was sourced from the Doradilla Project located in north central NSW and consists of a large Sn laterite deposit underlain by Sn silicate skarn with potential for copper, nickel, indium and zinc mineralisation. The skarn horizon has a strike length of 16km with zones of oxide, supergene and primary Sn mineralization. Compositionally OREAS 141 is dominated by smectite clay with minor quartz, kaolin and goethite. Sn mineralization occurs as varlamoffite [(Sn,Fe)(O,OH)<sub>2</sub>] with some relict cassiterite. OREAS 141 is one of three tin CRMs prepared from oxide material and characterised for Ag, As, Bi, Cu, In, Mo, Pb, Zn and Sn.

#### COMMINUTION AND HOMOGENISATION PROCEDURES

The material was prepared in the following manner:

- a) drying at 105° C to constant mass;
- b) crushing and screening;
- c) multi-stage milling to 100% minus 35 microns;
- d) final homogenisation;
- e) packaging into 10g units sealed in laminated foil pouches.

## ANALYSIS OF OREAS 141

Ten commercial laboratories participated in the analytical program to characterise Ag, As, Bi, Cu, In, Mo, Pb, Zn and Sn. Their results together with uncorrected means, medians, one sigma standard deviations, relative standard deviations and percent deviation of lab means from the corrected mean of means (PDM<sup>3</sup>) are presented in Tables A2 and A11 (Appendix). The parameter PDM<sup>3</sup> is a measure of laboratory accuracy while the relative standard deviation is an effective measure of analytical precision where homogeneity of the test material has been confirmed. The analytical methods employed by each laboratory are explained, together with other abbreviations used, in Table A1 (Appendix).

Each participating laboratory received 5 samples of 50g each. Each set of subsamples submitted to each laboratory was taken at regular intervals during packaging of the standard in order to maximise their representation. Tin was characterised via fusion methods (sodium peroxide, lithium borate and iodide) with ICP-OES, ICP-MS or AAS finish and via pressed powder pellet with XRF. The other elements were characterised by 4-acid (including HF) digest with ICP-OES, ICP-MS or AAS finish.



Table 1 (above) presents the certified values together with their associated 1SD's, 95% confidence and tolerance limits. Indicative (uncertified) values are provided in Table 2 for the major and trace elements determined by borate fusion XRF (Al<sub>2</sub>O<sub>3</sub> to Zn) and laser ablation with ICP-MS (Ag to Zr) and are the means of duplicate assays from Bureau Veritas, Perth. Table 3 provides performance gate intervals for the certified values based on their associated standard deviations. The summary statistics are also available in Excel format (**OREAS 141 DataPack.xlsx**).

	Table 2. Indicative Values for OREAS 141.   Constituent   Unit   Value   Constituent									
Constituent	Unit	Value	Constituent	Unit	Value	Constituent	Unit	Value		
Laser Ablatic	n ICP-M	S								
Ag	ppm	1.55	Но	ppm	2.35	Sn	ppm	5670		
As	ppm	826	In	ppm	29.7	Sr	ppm	113		
Ba	ppm	249	La	ppm	80	Та	ppm	1.44		
Be	ppm	9.70	Lu	ppm	0.95	Tb	ppm	1.90		
Bi	ppm	325	Mn	wt.%	0.094	Те	ppm	0.40		
Cd	ppm	1.70	Мо	ppm	2.00	Th	ppm	23.4		
Ce	ppm	120	Nb	ppm	15.9	Ti	wt.%	0.489		
Co	ppm	23.7	Nd	ppm	61	TI	ppm	0.50		
Cr	ppm	104	Ni	ppm	50	Tm	ppm	1.05		
Cs	ppm	9.32	Pb	ppm	58	U	ppm	6.31		
Cu	ppm	2375	Pr	ppm	17.1	V	ppm	167		
Dy	ppm	12.2	Rb	ppm	58	W	ppm	47.3		
Er	ppm	7.38	Re	ppm	< 0.01	Y	ppm	78		
Eu	ppm	3.13	Sb	ppm	41.4	Yb	ppm	6.16		
Ga	ppm	27.4	Sc	ppm	19.6	Zn	ppm	3515		
Gd	ppm	11.3	Se	ppm	< 5	Zr	ppm	288		
Hf	ppm	8.95	Sm	ppm	13.2					
Borate Fusio	n XRF									
Al <sub>2</sub> O <sub>3</sub>	wt.%	17.39	Fe <sub>2</sub> O <sub>3</sub>	wt.%	22.73	Pb	ppm	55		
As	ppm	820	K <sub>2</sub> O	wt.%	0.695	SiO <sub>2</sub>	wt.%	41.89		
Ва	ppm	265	MgO	wt.%	0.865	Sn	ppm	5990		
CaO	wt.%	3.39	MnO	wt.%	0.130	SO <sub>3</sub>	wt.%	0.097		
Co	ppm	25.0	Na <sub>2</sub> O	wt.%	0.505	TiO <sub>2</sub>	wt.%	0.835		
Cr	ppm	100	Ni	ppm	60	U	ppm	12.5		
Cu	ppm	2410	$P_2O_5$	wt.%	0.119	Zn	ppm	3500		
Thermogravi	metry									
LOI <sup>1000</sup>	wt.%	9.43								

Table 2. Indicative Values for OREAS 141.

Note: the number of significant figures reported is not a reflection of the level of certainty of stated values. They are instead an artefact of ORE's in-house CRM-specific LIMS.

#### **STATISTICAL EVALUATION OF OREAS 141**

#### **Certified Value and Confidence Intervals**

The certified value is the mean of means of accepted replicate values of accepted participating laboratories computed according to the formulae



$$\overline{x}_i = \frac{1}{n_i} \sum_{j=1}^{n_i} x_{ij}$$
$$\ddot{x} = \frac{1}{p} \sum_{i=1}^{p} \overline{x}_i$$

where

 $x_{ij}$  is the jth result reported by laboratory i; p is the number of participating laboratories;  $n_i$  is the number of results reported by laboratory i;  $\overline{x_i}$  is the mean for laboratory i;  $\ddot{x}$  is the mean of means.

The confidence intervals were obtained by calculation of the variance of the consensus value (mean of means) and reference to Student's-t distribution with degrees of freedom (p-1).

$$\hat{V}(\ddot{x}) = \frac{1}{p(p-1)} \sum_{i=1}^{p} (\bar{x}_i - \ddot{x})^2$$

Confidence Interval = 
$$\ddot{x} \pm t_{1-x/2}(p-1)(\hat{V}(\ddot{x}))^{1/2}$$

where

 $t_{1-x/2}(p-1)$  is the 1-x/2 fractile of the t-distribution with (p-1) degrees of freedom.

The distribution of the values is assumed to be symmetrical about the mean in the calculation of the confidence interval.

The test for rejection of individual outliers from each laboratory data set was primarily based on *z* scores (rejected if  $|z_i| > 2.5$ ) computed from the robust estimators of location and scale, *T* and *S*, respectively, according to the formulae:

$$S = 1.483 \text{ median } / x_j - \text{median } (x_i) / _{j=1....n}$$

$$z_i = \frac{x_i - T}{S}$$

where

*T* is the median value in a data set; *S* is the median of all absolute deviations from the sample median multiplied by 1.483, a correction factor to make the estimator consistent with the usual parameter of a normal distribution.



The z-score test is used in combination with a second method of individual outlier detection that determines the percent deviation of the individual value from the median. Outliers in general are selected on the basis of z-scores > 2.5 and with percent deviations > 1.5%. In certain instances statistician's prerogative has been employed in discriminating outliers.

Each laboratory data set is tested for outlying status based on z-score discrimination and rejected if  $|z_i| > 2.5$ . After individual and lab data set outliers have been eliminated a non-iterative 3 standard deviation filter is applied, with those values lying outside this window also relegated to outlying status.

Individual outliers and, more rarely, laboratory means deemed to be outlying are shown left justified and in bold in the tabulated results (see Appendix) and have been omitted in the determination of certified values.

The magnitude of the confidence interval is inversely proportional to the number of participating laboratories and interlaboratory agreement. It is a measure of the reliability of the certified value, i.e. the narrower the confidence interval the greater the certainty in the certified value. A 95% confidence interval indicates a 95% probability that the interval includes the true value of the analyte under consideration.

#### Statement of Homogeneity

The standard deviation of each laboratory data set includes error due to both the imprecision of the analytical method employed and to possible inhomogeneity of the material analysed. The standard deviation of the pooled individual analyses of all participating laboratories includes error due to the imprecision of each analytical method, to possible inhomogeneity of the material analysed and, in particular, to deficiencies in accuracy of each analytical method.

In determining tolerance intervals that component of error attributable to measurement inaccuracy was eliminated by transformation of the individual results of each data set to a common mean (the uncorrected grand mean) according to the formula

$$x'_{ij} = x_{ij} - \overline{x}_i + \frac{\sum_{i=1}^{p} \sum_{j=1}^{n_i} x_{ij}}{\sum_{i=1}^{p} n_i}$$

where

 $x_{ij}$  is the jth raw result reported by laboratory i;  $x'_{ij}$  is the jth transformed result reported by laboratory i;  $n_i$  is the number of results reported by laboratory i; p is the number of participating laboratories;  $\overline{x}_i$  is the raw mean for laboratory i.

The homogeneity of each constituent was determined from tables of factors for two-sided tolerance limits for normal distributions (ISO 3207) in which



Lower limit is 
$$\ddot{x} - k'_2(n, p, l - \alpha)s''_g$$
  
Upper limit is  $\ddot{x} + k'_2(n, p, l - \alpha)s''_a$ 

where

n is the number of results;  $1-\alpha$  is the confidence level; p is the proportion of results expected within the tolerance limits;  $k'_2$  is the factor for two – sided tolerance limits (m,  $\alpha$  unknown);  $s''_g$  is the corrected grand s tan dard deviation.

The meaning of these tolerance limits may be illustrated for tin by fusion, where 99% of the time at least 95% of subsamples will have concentrations lying between 5934 and 6187 ppm. Put more precisely, this means that if the same number of subsamples were taken and analysed in the same manner repeatedly, 99% of the tolerance intervals so constructed would cover at least 95% of the total population, and 1% of the tolerance intervals would cover less than 95% of the total population (IS0 Guide 35).

The corrected grand standard deviation,  $s_{g}$ , used to compute the tolerance intervals is the weighted means of standard deviations of all data sets for a particular constituent according to the formula:

$$s''_{g} = \frac{\sum_{i=l}^{p} (s_{i}(l - \frac{S_{i}}{s'_{g}}))}{\sum_{i=l}^{p} (l - \frac{S_{i}}{s'_{g}})}$$

where

$$l - (\frac{s_i}{2s'_g})$$
 is the weighting factor for laboratory *i*;

 $s_{g}^{\prime}$  is the grand standard deviation computed from the transformed (i.e. means -

adjusted) results

according to the formula

$$s'_{g} = \left[\frac{\sum_{i=j}^{p} \sum_{j=i}^{n_{i}} (x'_{ij} - \overline{x}'_{i})^{2}}{\sum_{i=l}^{p} n_{i} - l}\right]^{1/2}$$

#### where $\overline{x}'_i$ is the transformed mean for laboratory i

The weighting factors were applied to compensate for the considerable variation in analytical precision amongst participating laboratories. Hence, weighting factors for each data set have been constructed so as to be inversely proportional to the standard deviation of that data set. It should be noted that estimates of tolerance by this method are considered conservative as a significant proportion of the observed variance, even in



those laboratories exhibiting the best analytical precision, can presumably be attributed to measurement error.

#### **Performance Gates**

Performance gates provide an indication of a level of performance that might reasonably be expected from a laboratory being monitored by this CRM in a QA/QC program. They take into account errors attributable to measurement and CRM variability. For an effective CRM the contribution of the latter should be negligible in comparison to measurement errors. Sources of measurement error include inter-lab bias, analytical precision (repeatability) and inter-batch bias (reproducibility).

Two methods have been employed to calculate performance gates. The first method uses the same filtered data set used to determine the certified value, i.e. after removal of all individual, lab dataset (batch) and 3SD outliers. These outliers can only be removed after the absolute homogeneity of the CRM has been independently established, i.e. the outliers must be confidently deemed to be analytical rather than arising from inhomogeneity of the CRM. The standard deviation is then calculated for each analyte from the pooled individual analyses (excluding the INAA data for gold) generated from the certification program.

Table 3 shows performance gates calculated for two and three standard deviations. As a guide these intervals may be regarded as warning or rejection for multiple 2SD outliers, or rejection for individual 3SD outliers in QC monitoring, although their precise application should be at the discretion of the QC manager concerned. A second method utilises a 5% window calculated directly from the certified value. Standard deviation is also shown in relative percent for one, two and three relative standard deviations (1RSD, 2RSD and 3RSD) to facilitate an appreciation of the magnitude of these numbers and a comparison with the 5% window. Caution should be exercised when concentration levels approach lower limits of detection of the analytical methods employed as performance gates calculated from standard deviations tend to be excessively wide whereas those determined by the 5% method are too narrow.

Constituent	Certified		Absolute Standard Deviations					Standard D	eviations	5% window		
	Value	1SD	2SD Low	2SD High	3SD Low	3SD High	1RSD	2RSD	3RSD	Low	High	
Ag (ppm)	1.58	0.11	1.37	1.80	1.26	1.91	6.85%	13.7%	20.5%	1.50	1.66	
As (ppm)	789	29	732	846	704	875	3.62%	7.24%	10.9%	750	829	
Bi (ppm)	324	29	265	382	236	412	9.03%	18.1%	27.1%	308	340	
Cu (ppm)	2453	98	2257	2648	2159	2746	3.99%	7.99%	12.0%	2330	2575	
In (ppm)	34	5	24	44	18	50	15.3%	30.6%	45.9%	32	36	
Mo (ppm)	2.28	0.29	1.71	2.86	1.43	3.14	12.5%	25.1%	37.6%	2.17	2.40	
Pb (ppm)	59.0	3.8	51.4	66.6	47.6	70.4	6.44%	12.9%	19.3%	56.1	62.0	
Zn (ppm)	3637	178	3280	3993	3102	4172	4.90%	9.81%	14.7%	3455	3818	
Sn-fusion (ppm)	6061	339	5383	6738	5044	7077	5.59%	11.2%	16.8%	5758	6364	
Sn-PP (ppm)	6312	259	5794	6830	5534	7090	4.11%	8.21%	12.3%	5996	6628	

#### Table 3. Performance Gates for OREAS 141.

Note - intervals may appear asymmetric due to rounding; "PP" - pressed pellet X-ray fluorescence

## **PARTICIPATING LABORATORIES**

Acme Analytical Laboratories Ltd, Vancouver, BC, Canada Activation Laboratories, Ancaster, ONtario, Canada ALS Chemex, Brisbane, QLD, Australia



ALS Chemex, Vancouver, BC, Canada Genalysis Laboratory Services Pty Ltd, Perth, WA, Australia Intertek Testing Services, Jakarta, Indonesia OMAC Laboratories Ltd, Loughrea, County Galway, Ireland SGS Lakefield Research Ltd, Lakefield, ON, Canada SGS Australia, Perth, WA, Australia Ultra Trace Pty Ltd, Perth, WA, Australia

## PREPARER AND SUPPLIER OF THE REFERENCE MATERIAL

Certified reference material OREAS 141 is prepared, certified and supplied by:



ORE Research & Exploration Pty Ltd	Tel:	+613-9729 0333
37A Hosie Street	Fax:	+613-9729 8338
Bayswater North VIC 3153	Web:	www.ore.com.au
AUSTRALIA	Email:	info@ore.com.au

It is available in unit sizes of 10g (single-use laminated foil pouches).

#### **INTENDED USE**

OREAS 141 is a reference material intended for the following:

- i) for the monitoring of laboratory performance in the analysis of Ag, As, Bi, Cu, In, Mo, Pb, Zn and Sn in geological samples;
- ii) for the calibration of instruments used in the determination of the concentration of Ag, As, Bi, Cu, In, Mo, Pb, Zn and Sn;
- iii) for the verification of analytical methods for Ag, As, Bi, Cu, In, Mo, Pb, Zn and Sn.

#### STABILITY AND STORAGE INSTRUCTIONS

OREAS 141 is a reference material made from tin oxide ore from the Doradilla Project. In its unopened state in the laminated foil pouches and under normal conditions of storage it has a shelf life beyond ten years.

#### INSTRUCTIONS FOR CORRECT USE

The certified values for OREAS 141 refer to the concentration level of Ag, As, Bi, Cu, In, Mo, Pb, Zn and Sn in its packaged state. The CRM should <u>not</u> be dried prior to weighing and analysis.

#### HANDLING INSTRUCTIONS

Fine powders pose a risk to eyes and lungs and therefore standard precautions such as the use of safety glasses and dust masks are advised.



## TRACEABILITY

The analytical samples were selected in a manner to represent the entire batch of prepared CRM. This 'representivity' was maintained in each submitted laboratory sample batch and ensures the user that the data is traceable from sample selection through to the analytical results that underlie the consensus values. Each analytical data set has been validated by its assayer through the inclusion of internal reference materials and QC checks during analysis. The laboratories were chosen on the basis of their competence (from past performance in inter-laboratory programs) for a particular analytical method, analyte or analyte suite, and sample matrix. Most of these laboratories have and maintain ISO 17025 accreditation. The certified and non-certified (indicative) values presented in this report are calculated from the means of accepted data following robust statistical treatment as detailed in this report.

#### LEGAL NOTICE

Ore Research & Exploration Pty Ltd has prepared and statistically evaluated the property values of this reference material to the best of its ability. The Purchaser by receipt hereof releases and indemnifies Ore Research & Exploration Pty Ltd from and against all liability and costs arising from the use of this material and information.

## QMS ACCREDITED

ORE Pty Ltd is accredited to ISO 9001:2008 by Lloyd's Register Quality Assurance Ltd for its quality management system including development, manufacturing, certification and supply of CRMs.





## **CERTIFYING OFFICER**

September, 2008

Craig Hamlyn (B.Sc. Hons - Geology), Technical Manager - ORE P/L

## REFERENCES

ISO Guide 30 (1992), Terms and definitions used in connection with reference materials.

ISO Guide 31 (2000), Reference materials - Contents of certificates and labels.

ISO Guide 3207 (1975), Statistical interpretation of data - Determination of a statistical tolerance interval.

ISO Guide 35 (2006), Certification of reference materials - General and statistical principals.



## APPENDIX

## Analytical Data for OREAS 141



Abbreviation	Explanation
Std.Dev.	one standard deviation
Rel.Std.Dev.	one relative standard deviation (%)
PDM <sup>3</sup>	percent deviation of lab mean from corrected mean of means
NR	not reported
4A	four acid digest (HF-HNO <sub>3</sub> -HClO <sub>4</sub> -HCl)
PF	sodium peroxide fusion
BF	lithium metaborate fusion
IF	iodide fusion
AAS	atomic absorption spectrometry
OES	inductively coupled plasma optical emission spectrometry
MS	inductively coupled plasma mass spectrometry
PPP	pressed powder pellet
XRF	x-ray fluorescence

Table A1. Explanation of abbreviations used in Tables A2 – A11.

Table A2. Results for Ag in OREAS 141 (abbreviations as in Table A1; values in ppm).

		J -						11 /		
Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
No.	А	В	С	D	Е	F	G	Н	1	J
	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*OES
1	1.77	1.00	1.60	1.60	1.50	1.50	1.64	1.70	1.67	2.00
2	1.60	1.50	1.60	1.70	1.50	1.46	1.72	1.60	1.74	2.00
3	1.53	1.50	1.60	1.60	1.50	1.43	1.56	1.70	1.74	1.90
4	1.71	1.50	1.40	1.70	1.50	1.48	1.57	1.60	1.83	2.00
5	1.45	1.50	1.40	1.70	1.40	1.52	1.61	1.60	1.65	2.00
Mean	1.61	1.40	1.52	1.66	1.48	1.48	1.62	1.64	1.73	1.98
Median	1.60	1.50	1.60	1.70	1.50	1.48	1.61	1.60	1.74	2.00
Std.Dev.	0.13	0.22	0.11	0.05	0.04	0.03	0.06	0.05	0.07	0.04
Rel.Std.Dev.	8.07%	16.0%	7.21%	3.30%	3.02%	2.36%	3.98%	3.34%	4.06%	2.26%
PDM <sup>3</sup>	1.91%	-11.5%	-3.91%	4.94%	-6.44%	-6.56%	2.41%	3.68%	9.15%	25.2%

Table A3. Results for As in OREAS 141 (abbreviations as in Table A1; values in ppm).

Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
No.	А	В	С	D	E	F	G	Н	1	J
	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*OES
1	629	782	826	767	832	797	927	840	747	800
2	675	784	831	779	821	783	932	890	739	808
3	682	804	786	783	815	788	866	880	746	803
4	658	792	737	782	818	804	842	890	754	813
5	780	807	738	780	820	791	878	850	738	815
Mean	685	794	784	778	821	793	889	870	745	808
Median	675	792	786	780	820	791	878	880	746	808
Std.Dev.	57	11	46	6	6	8	39	23	7	6
Rel.Std.Dev.	8.32%	1.43%	5.81%	0.83%	0.79%	1.03%	4.41%	2.70%	0.88%	0.79%
PDM <sup>3</sup>	-13.2%	0.58%	-0.71%	-1.40%	4.05%	0.43%	12.6%	10.2%	-5.64%	2.35%



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Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
No.	А	В	С	D	E	F	G	Н	I.	J
	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*OES
1	385	299	364	280	333	319	380	310	314	307
2	359	299	346	287	341	305	377	310	306	315
3	373	300	347	281	355	314	349	320	307	307
4	376	306	307	284	335	312	350	310	307	315
5	374	296	307	289	345	312	358	310	309	312
Mean	373	300	334	284	342	312	363	312	309	311
Median	374	299	346	284	341	312	358	310	307	312
Std.Dev.	9	4	26	4	9	5	15	4	3	4
Rel.Std.Dev.	2.50%	1.22%	7.77%	1.35%	2.57%	1.61%	4.08%	1.43%	0.99%	1.29%
PDM <sup>3</sup>	15.3%	-7.35%	3.25%	-12.2%	5.53%	-3.52%	12.0%	-3.64%	-4.67%	-3.89%

Table A4. Results for Bi in OREAS 141 (abbreviations as in Table A1; values in ppm).

Table A5. Results for Cu in OREAS 141 (abbreviations as in Table A1; values in ppm).

Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
No.	А	В	С	D	E	F	G	Н	1	J
	4A*MS	4A*MS	4A*AAS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*OES
1	2440	2370	2570	1880	2452	2360	2660	2500	2468	2320
2	2500	2430	2520	1890	2489	2290	2680	2500	2459	2390
3	2490	2430	2410	1890	2464	2310	2600	2500	2477	2350
4	2510	2420	2220	1930	2431	2360	2560	2500	2503	2390
5	2290	2440	2270	1890	2459	2370	2610	2500	2489	2360
Mean	2446	2418	2398	1896	2459	2338	2622	2500	2479	2362
Median	2490	2430	2410	1890	2459	2360	2610	2500	2477	2360
Std.Dev.	91	28	152	19	21	36	48	0	17	29
Rel.Std.Dev.	3.73%	1.15%	6.35%	1.03%	0.85%	1.52%	1.84%	0.00%	0.70%	1.25%
PDM <sup>3</sup>	-0.27%	-1.41%	-2.23%	-22.7%	0.27%	-4.67%	6.91%	1.93%	1.09%	-3.69%

Table A6. Results for In in OREAS 141 (abbreviations as in Table A1; values in ppm).

Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
No.	А	В	С	D	E	F	G	Н	1	J
	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	-	-
1	37.70	32.30	46.12	36.80	24.62	33.20	34.80	29.00	NR	NR
2	38.50	31.20	44.97	37.10	25.57	31.90	36.30	29.00	NR	NR
3	37.90	31.70	43.37	36.30	27.41	32.30	34.60	30.00	NR	NR
4	37.90	31.80	40.64	35.70	25.26	32.70	35.00	29.00	NR	NR
5	36.50	31.50	39.42	36.60	25.54	33.30	36.50	29.00	NR	NR
Mean	37.70	31.70	42.90	36.50	25.68	32.68	35.44	29.20		
Median	37.90	31.70	43.37	36.60	25.54	32.70	35.00	29.00		
Std.Dev.	0.73	0.41	2.83	0.53	1.04	0.59	0.89	0.45		
Rel.Std.Dev.	1.95%	1.28%	6.60%	1.46%	4.05%	1.82%	2.51%	1.53%		
PDM <sup>3</sup>	11.0%	-6.65%	26.3%	7.5%	-24.4%	-3.77%	4.36%	-14.0%		



Doplicato	Lah	Lab	Lah	Ìch	Lah	Lah	Lah	Lah	Lah	Lah
Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
No.	A	В	С	D	E	F	G	н	1	J
	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*OES
1	1.60	2.00	2.40	2.50	2.20	2.37	2.38	2.50	2.34	<1
2	2.20	2.00	2.30	2.60	1.90	2.44	2.42	2.50	2.42	<1
3	1.60	2.00	2.20	2.70	2.20	2.34	2.71	2.40	2.36	<1
4	1.60	2.00	2.10	3.10	2.30	2.36	2.52	2.70	2.44	<1
5	2.00	2.00	2.10	2.70	2.10	2.37	2.56	3.30	2.32	<1
Mean	1.80	2.00	2.22	2.72	2.14	2.38	2.52	2.68	2.38	<1
Median	1.60	2.00	2.20	2.70	2.20	2.37	2.52	2.50	2.36	<1
Std.Dev.	0.28	0.00	0.13	0.23	0.15	0.04	0.13	0.36	0.05	
Rel.Std.Dev.	15.7%	0.00%	5.87%	8.38%	7.09%	1.59%	5.15%	13.6%	2.15%	
PDM <sup>3</sup>	-21.2%	-12.5%	-2.84%	19.0%	-6.34%	3.99%	10.2%	17.3%	4.00%	

Table A7. Results for Mo in OREAS 141 (abbreviations as in Table A1; values in ppm).

Table A8. Results for Pb in OREAS 141 (abbreviations as in Table A1; values in ppm).

Deviliante	1 - 1-	1 - 1-	1	L . I.	1 - 1-	L . I	1 - 1	1	L . I	1 - 1-
Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
No.	A	В	С	D	E	F	G	н	l I	J
	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*OES
1	66.2	55.0	65.0	61.0	58.4	59.5	56.2	56.0	54.7	62.0
2	64.5	54.0	63.0	63.0	59.7	56.7	54.5	55.0	55.4	66.0
3	65.0	57.0	66.0	61.0	64.8	57.8	58.5	56.0	54.2	60.0
4	66.1	58.0	56.0	62.0	55.9	58.7	57.7	56.0	57.1	60.0
5	62.2	57.0	55.0	63.0	56.7	59.4	59.9	55.0	53.1	64.0
Mean	64.8	56.2	61.0	62.0	59.1	58.4	57.4	55.6	54.9	62.4
Median	65.0	57.0	63.0	62.0	58.4	58.7	57.7	56.0	54.7	62.0
Std.Dev.	1.6	1.6	5.1	1.0	3.5	1.2	2.1	0.5	1.5	2.6
Rel.Std.Dev.	2.51%	2.92%	8.44%	1.61%	5.94%	2.02%	3.64%	0.99%	2.71%	4.18%
PDM <sup>3</sup>	9.76%	-4.80%	3.33%	5.02%	0.11%	-1.04%	-2.84%	-5.82%	-7.01%	5.70%

Table A9. Results for Zn in OREAS 141 (abbreviations as in Table A1; values in ppm).

Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
No.	А	В	С	D	E	F	G	Н	1	J
	4A*MS	4A*MS	4A*AAS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*MS	4A*OES
1	3040	3550	3600	2860	3675	3540	3990	3900	3621	3550
2	3080	3620	3610	2870	3598	3460	3980	3900	3553	3610
3	3050	3630	3480	2910	3696	3480	3820	3900	3605	3480
4	3080	3600	3180	2920	3596	3560	3790	3700	3602	3590
5	2790	3630	3180	2910	3585	3530	3910	3800	3572	3610
Mean	3008	3606	3410	2894	3630	3514	3898	3840	3591	3568
Median	3050	3620	3480	2910	3598	3530	3910	3900	3602	3590
Std.Dev.	123	34	216	27	51	42	91	89	27	55
Rel.Std.Dev.	4.09%	0.93%	6.34%	0.93%	1.42%	1.20%	2.33%	2.33%	0.76%	1.54%
PDM <sup>3</sup>	-17.3%	-0.84%	-6.23%	-20.4%	-0.18%	-3.37%	7.19%	5.59%	-1.26%	-1.89%



Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	, Lab	Lab	Lab
No.	А	В	С	D	Е	F	G	н	I	J
	PF*OES	PF*MS	PF*MS	BF*XRF	PF*MS	PF*MS	BF*MS	PF*OES	IF*AA/ICP	-
1	6300	6050	5667	6100	6484	6170	5490	5400	6356	NR
2	6320	6130	5742	6000	6779	6010	4820	6000	6290	NR
3	6380	6010	5760	6000	6764	6080	5610	5600	6365	NR
4	6300	5940	5785	6100	6599	6140	5550	5800	6304	NR
5	6300	5880	5798	6100	6664	6130	5590	5800	6424	NR
Mean	6320	6002	5750	6060	6658	6106	5412	5720	6348	
Median	6300	6010	5760	6100	6664	6130	5550	5800	6356	
Std.Dev.	35	97	51	55	122	63	334	228	53	
Rel.Std.Dev.	0.55%	1.61%	0.89%	0.90%	1.83%	1.03%	6.17%	3.99%	0.84%	
PDM <sup>3</sup>	4.28%	-0.97%	-5.12%	-0.01%	9.86%	0.75%	-10.7%	-5.62%	4.74%	

Table A10. Results for Sn via fusion in OREAS 141 (abbreviations as in Table A1; values in ppm).

Table A11. Results for Sn via PPP\*XRF in OREAS 141 (abbreviations as in Table A1; values in ppm).

Replicate	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
No.	А	В	С	D	E	F	G	Н	I I	J
	PPP*XRF	-	PPP*XRF	-	-	PPP*XRF	PPP*XRF	-	-	PPP*XRF
1	6350	NR	6066	NR	NR	6730	6050	NR	NR	6320
2	6340	NR	6007	NR	NR	6780	6070	NR	NR	6330
3	6330	NR	6085	NR	NR	6800	6060	NR	NR	6360
4	6400	NR	6012	NR	NR	6780	6050	NR	NR	6320
5	6320	NR	6038	NR	NR	6900	6070	NR	NR	6360
Mean	6348		6042			6798	6060			6338
Median	6340		6038			6780	6060			6330
Std.Dev.	31		34			63	10			20
Rel.Std.Dev.	0.49%		0.56%			0.92%	0.17%			0.32%
PDM <sup>3</sup>	0.57%		-4.28%			7.70%	-3.99%			0.41%

