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CERTIFICATE OF ANALYSIS FOR

MANGANESE ORE
CERTIFIED REFERENCE MATERIAL
OREAS 171

Table 1. Certified Values, SDs, 95% Confidence and Tolerance Limits for OREAS 171.

Constituent	Certified Value	1SD	95% Confidence Limits		95% Tolerance Limits	
			Low	High	Low	High
Borate Fusion XRF						
Al_2O_3, Aluminium(III) oxide (wt.%)	7.32	0.123	7.25	7.39	7.23	7.40
BaO, Barium oxide (wt.%)	0.247	0.011	0.241	0.253	0.239	0.254
CaO, Calcium oxide (wt.%)	0.081	0.007	0.078	0.084	IND	IND
Fe, Iron (wt.%)	3.66	0.034	3.64	3.68	3.63	3.69
K_2O, Potassium oxide (wt.%)	2.05	0.030	2.04	2.07	2.04	2.07
MgO, Magnesium oxide (wt.%)	0.217	0.016	0.208	0.226	0.204	0.231
Mn, Manganese (wt.%)	35.10	0.167	35.02	35.18	34.84	35.36
Na_2O, Sodium oxide (wt.%)	0.236	0.015	0.227	0.244	0.226	0.245
P, Phosphorus (ppm)	663	24	648	677	647	678
SiO_2, Silicon dioxide (wt.%)	24.82	0.170	24.74	24.90	24.59	25.05
TiO_2, Titanium dioxide (wt.%)	0.336	0.009	0.331	0.341	0.326	0.345
V_2O_5, Vanadium(V) oxide (ppm)	418	45	386	450	402	433
Thermogravimetry						
LOI^{1000} (wt.%)	10.54	0.148	10.45	10.63	10.48	10.59

SI unit equivalents: ppm, parts per million ≡ mg/kg ≡ µg/g ≡ 0.0001 wt.% ≡ 1000 ppb, parts per billion.
Note: intervals may appear asymmetric due to rounding.

Table 2. Indicative Values for OREAS 171.

Constituent	Unit	Value	Constituent	Unit	Value	Constituent	Unit	Value
Borate Fusion XRF								
Cr_2O_3	ppm	*133*	Pb	ppm	*< 50*	SnO_2	ppm	*12.7*
Cu	ppm	*42.5*	S	ppm	*49.5*	SO_3	wt.%	*47.28*
Laser Ablation ICP-MS								
Ag	ppm	*0.100*	Hf	ppb	*3140*	Sn	ppm	*1.80*
As	ppm	*47.1*	Ho	ppb	*2165*	Sr	ppm	*244*
Ba	ppm	*2015*	In	ppm	*0.050*	Ta	ppb	*515*
Be	ppm	*3.40*	La	ppm	*76*	Tb	ppb	*2050*
Bi	ppm	*0.30*	Lu	ppb	*725*	Te	ppb	*200*
Cd	ppm	*0.45*	Mo	ppm	*12.6*	Th	ppm	*7.33*
Ce	ppm	*154*	Nb	ppm	*7.69*	Tl	ppm	*1.20*
Co	ppm	*122*	Nd	ppm	*78*	Tm	ppb	*805*
Cr	ppm	*34.5*	Ni	ppm	*72*	U	ppm	*2.69*
Cs	ppm	*2.16*	Pb	wt.%	*0.003*	V	ppm	*233*
Cu	ppm	*84*	Pr	ppm	*20.6*	W	ppm	*3.88*
Dy	ppm	*11.3*	Rb	ppm	*57*	Y	ppm	*44.3*
Er	ppm	*5.84*	Re	ppb	*< 10*	Yb	ppb	*5135*
Eu	ppb	*3780*	Sb	ppm	*2.40*	Zn	ppm	*120*
Ga	ppm	*< 10*	Sc	ppm	*13.1*	Zr	ppm	*106*
Gd	ppm	*13.4*	Se	ppm	*< 5*			
Ge	ppb	*925*	Sm	ppm	*16.7*			

SI unit equivalents: ppm, parts per million ≡ mg/kg ≡ µg/g ≡ 0.0001 wt.% ≡ 1000 ppb, parts per billion.
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.

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.

OREAS reference materials enable users to successfully achieve process control of these tasks because the observed variance from repeated analysis has its origin almost exclusively in the analytical process rather than the reference material itself.

SOURCE MATERIALS

OREAS 171 is a supergene manganese ore matrix-matched certified reference material (MMCRM) prepared and certified by Ore Research & Exploration Pty Ltd. The material was sourced from the Groote Eylandt Mining Company Pty Ltd (GEMCO) Mn deposit which is hosted within a shallow dipping Lower Cretaceous sedimentary rock unit. Groote Eylandt is in the Gulf of Carpentaria off the coast of Australia’s Northern Territory. A portion (22%) of barren siltstone sourced from a quarry north of Melbourne, Australia was added to lower the grade. OREAS 171 is one of a suite of four Mn ore MMCRMs certified by borate fusion XRF covering a Mn grade range of 35-46%.

COMMINUTION AND HOMOGENISATION PROCEDURES

The material constituting OREAS 171 was prepared in the following manner:

- Drying to constant mass at 105°C (Mn ore and barren siltstone);
- Crushing and milling to 98% minus 75 microns (Mn ore and barren siltstone);
- Sieving at 150 microns (Mn ore and barren siltstone);
- Blending the ore component with barren siltstone in appropriate proportions to achieve the desired grades;
- Packaging in 10g units sealed in laminated foil pouches and 1kg units in plastic jars.

ANALYTICAL PROGRAM

Fourteen commercial analytical laboratories participated in the program to characterise the elements reported in Table 1 using lithium borate fusion with x-ray fluorescence. LOI was determined at 1000°C using thermogravimetry. Table 2 shows indicative values for a number of additional elements where data was provided but insufficient for certification (further explained in the ‘Statistical Analysis’ section). The approximate trace element composition of OREAS 171 in this table are the means of duplicate assays from one laboratory.

All analytes were requested to be reported on a dry basis and manganese content to be determined by direct measurement XRF, not by closure to 100%, or any other assumed total.

For the round robin program eight 200g test units were taken at predetermined intervals during the bagging stage, immediately following final blending, and are considered representative of the entire 242kg batch. To maximise representation, the six samples received by each laboratory were obtained by taking one 10g subsample from each of six of the eight available test units. Results, together with uncorrected means, medians, standard deviations, relative standard deviations and percent deviation of lab means from the corrected mean of means (PDM[3]) are presented in the certification data file for this CRM (**OREAS 171 DataPack-2.0.181213_172810.xlsx**).

STATISTICAL ANALYSIS

Certified Values, Standard Deviations, Confidence and Tolerance Limits have been determined for each analytical method following removal of individual and laboratory outliers (see Tables 1). Certified Values are the mean of means after outlier filtering. The 95% Confidence Limit 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. It should not be used as a control limit for laboratory performance.

Indicative (uncertified) values (Table 2) are provided for trace elements determined by laser ablation with ICP-MS (Ag to Zr) and are the means of duplicate assays from Bureau Veritas, Perth. Additional indicative values by fusion XRF are provided where i) the number of laboratories reporting a particular analyte is insufficient (< 5) to support certification; ii) inter-laboratory consensus is poor; or iii) a significant proportion of results are outlying or reported as less than detection limits.

Standard Deviation values (1SDs) are reported in Table 1 and 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 uncertainty and CRM variability. For an effective CRM the contribution of the latter should be negligible in comparison to measurement errors. The Standard Deviation values include all sources of measurement uncertainty: between-lab variance, within-run variance (precision errors) and CRM variability. The SD for each analyte's certified value is calculated from the same filtered data set used to determine the certified value, i.e. after removal of all individual, lab dataset (batch) and 3SD outliers (single iteration). 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 accepted analyses generated from the certification program.

In the application of SD's in monitoring performance it is important to note that not all laboratories function at the same level of proficiency and that different methods in use at a particular laboratory have differing levels of precision. Each laboratory has its own inherent SD (for a specific concentration level and analyte-method pair) based on the analytical process and this SD is not directly related to the round robin program.

The majority of data generated in the round robin program was produced by a selection of world class laboratories. The SD's thus generated are more constrained than those that would be produced across a randomly selected group of laboratories. To produce more generally achievable SD's the 'pooled' SD's provided in this report include inter-lab bias. This 'one size fits all' approach may require revision at the discretion of the QC manager concerned following careful scrutiny of QC control charts.

Performance Gates in Table 3 are 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.

Table 3. Performance Gates for OREAS 171.

Constituent	Certified Value	Absolute Standard Deviations					Relative Standard Deviations			5% window	
		1SD	2SD Low	2SD High	3SD Low	3SD High	1RSD	2RSD	3RSD	Low	High
Borate Fusion XRF											
Al_2O_3, wt.%	7.32	0.123	7.07	7.57	6.95	7.69	1.68%	3.37%	5.05%	6.95	7.69
BaO, wt.%	0.247	0.011	0.224	0.269	0.213	0.280	4.52%	9.04%	13.57%	0.234	0.259
CaO, wt.%	0.081	0.007	0.067	0.095	0.060	0.102	8.50%	17.00%	25.49%	0.077	0.085
Fe, wt.%	3.66	0.034	3.59	3.73	3.56	3.76	0.94%	1.87%	2.81%	3.48	3.84
K_2O, wt.%	2.05	0.030	1.99	2.11	1.97	2.14	1.44%	2.88%	4.32%	1.95	2.16
MgO, wt.%	0.217	0.016	0.186	0.249	0.170	0.265	7.31%	14.62%	21.93%	0.206	0.228
Mn, wt.%	35.10	0.167	34.77	35.44	34.60	35.60	0.48%	0.95%	1.43%	33.35	36.86
Na_2O, wt.%	0.236	0.015	0.207	0.265	0.192	0.279	6.16%	12.33%	18.49%	0.224	0.247
P, ppm	663	24	614	711	589	736	3.68%	7.37%	11.05%	629	696
SiO_2, wt.%	24.82	0.170	24.48	25.16	24.31	25.33	0.68%	1.37%	2.05%	23.58	26.06
TiO_2, wt.%	0.336	0.009	0.317	0.354	0.308	0.364	2.77%	5.55%	8.32%	0.319	0.353
V_2O_5, ppm	418	45	327	509	282	554	10.85%	21.69%	32.54%	397	439
Thermogravimetry											
LOI^{1000}, wt.%	10.54	0.148	10.24	10.84	10.09	10.98	1.41%	2.82%	4.23%	10.01	11.07

SI unit equivalents: ppm, parts per million ≡ mg/kg ≡ µg/g ≡ 0.0001 wt.% ≡ 1000 ppb, parts per billion.
Note: intervals may appear asymmetric due to rounding

Tolerance Limits (ISO Guide 3207) were determined using an analysis of precision errors method and are considered a conservative estimate of true homogeneity. The meaning of tolerance limits may be illustrated for manganese (Mn), where 99% of the time (1-α=0.99) at least 95% of subsamples (ρ=0.95) will have concentrations lying between 34.84 and 35.36 wt.%. 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 (ISO Guide 35).

Based on the statistical analysis of the results of the inter-laboratory certification program it can be concluded that OREAS 171 is fit-for-purpose as a certified reference material (see ‘Intended Use’ below).

PARTICIPATING LABORATORIES

1. ALS, Brisbane, QLD, Australia
2. ALS, Johannesburg, South Africa
3. ALS, Vancouver, BC, Canada
4. Bureau Veritas Geoanalytical, Adelaide, SA, Australia
5. Bureau Veritas Geoanalytical, Cardiff, NSW, Australia
6. Bureau Veritas (Ultra Trace) Geoanalytical, Perth, WA, Australia
7. Intertek Genalysis, Perth, WA, Australia
8. Intertek Minerals (IMI), Jakarta, Indonesia
9. Intertek Testing Services, Darwin, NT, Australia
10. LCT, Sao Paulo, Sao Paulo, Brazil
11. SGS Geosol Laboratorios Ltda, Vespasiano, Minas Gerais, Brazil
12. SGS Lakefield Research Ltd, Lakefield, Ontario, Canada
13. SGS South Africa Pty Ltd, Booysens, Gauteng, South Africa

PREPARER AND SUPPLIER OF THE REFERENCE MATERIAL

Reference material OREAS 171 has been prepared, certified and is supplied by:

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It is available in 10g units in single-use laminated foil pouches and in 1kg units in plastic jars.

INTENDED USE

OREAS 171 is intended for the following uses:

- For the monitoring of laboratory performance in the analysis of analytes reported in Table 1 in geological samples;
- For the verification of analytical methods for analytes reported in Table 1;
- For the calibration of instruments used in the determination of the concentration of analytes reported in Table 1.

STABILITY AND STORAGE INSTRUCTIONS

OREAS 171 is an oxidised reference material and is stable in the laminated foil pouches. Under normal conditions of storage it has a shelf life beyond ten years.

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.

INSTRUCTIONS FOR CORRECT USE

The certified values for lithium borate fusion XRF and for LOI are on a dry basis. This requires the removal of hygroscopic moisture by drying in air to constant mass at 105°C. If the reference material is not dried prior to analysis, the certified values should be corrected to the moisture-bearing basis.

METROLOGICAL 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 undertaken by ORE Pty Ltd) for a particular analytical method, analyte or analyte suite, and sample matrix. Most of these laboratories have and maintain ISO 17025 accreditation. The certified values presented in this report are calculated from the means of accepted data following robust statistical treatment as detailed in this report.

Guide ISO/TR 16476:2016, section 5.3.1 describes metrological traceability in reference materials as it pertains to the transformation of the measurand. In this section it states, *"Although the determination of the property value itself can be made traceable to appropriate units through, for example, calibration of the measurement equipment used, steps like the transformation of the sample from one physical (chemical) state to another cannot. Such transformations may only be compared with a reference (when available), or among themselves. For some transformations, reference methods have been defined and may be used in certification projects to evaluate the uncertainty associated with such a transformation. In other cases,* ***only a comparison among different laboratories using the same method is possible. In this case, certification takes place on the basis of agreement among independent measurement results*** *(see ISO Guide 35:2006, Clause 10)."*

COMMUTABILITY

The measurements of the results that underlie the certified values contained in this report were undertaken by methods involving pre-treatment (digestion/fusion) of the sample. This served to reduce the sample to a simple and well understood form permitting calibration using simple solutions of the CRM. Due to these methods being well understood and highly effective, commutability is not an issue for this CRM. All OREAS CRMs are sourced from natural ore minerals meaning they will display similar behaviour as routine 'field' samples in the relevant measurement process. Care should be taken to ensure 'matrix matching' as close as practically achievable. The matrix and mineralisation style of the

CRM is described in the ‘Source Material’ section and users should select appropriate CRMs matching these attributes to their field samples.

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.

DOCUMENT HISTORY

Revision No	Date	Changes applied
1	3rd Sep, 2018	Added major and trace element characterisation.
0	7th Aug, 2012	First publication.

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

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

REFERENCES

ISO Guide 30 (2015), Terms and definitions used in connection with reference materials.

ISO Guide 31 (2015), Reference materials – Contents of certificates and labels.

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

ISO Guide 35 (2017), Certification of reference materials - General and statistical principals.