Reference Material Data Sheet

IAG UoK Loess

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Description of the reference material

The loess sample was collected and prepared as a candidate reference material under the direction of H.U. Kasper, University of Cologne, Germany. The sample was collected from Nussloch, 10 km South of Heidelberg and 3 km East of the upper Rhine Graben, Germany (49° 19′ N, 8° 43′ E) and 217 m above sea level. The basement of the loess consists of Middle Triassic limestone and dolomite ('Muschelkalk'). The main section comprises 16 m thick loess deposits from the Würmian. The sample was collected from the upper Würmian loess which was deposited as part of the last glacial - interglacial cycle, 15,000 - 20,000 a BP. Examination of this sample indicates that the main mineralogical components are quartz, feldspar, carbonate phases, mica, clay minerals and iron-rich minerals. The sample also contains accessory zircon, rutile, tourmaline, anatase, brookite, garnet, epidote and amphibole.

The sample was tested for homogeneity by selecting at random ten packets (16 for trace elements) of the sample prepared for distribution. Duplicate test portions from each packet were analysed by WDXRF at the Open University (Milton Keynes). For the elements for which values could be assigned, homogeneity was considered to be satisfactory for use in the GeoPT13 round of the IAG's proficiency testing programme (see the ***Appendix*** *for an assessment of the homogeneity results).*

Characterisation as a reference material

This material is characterised as a reference material using results from GeoPT13/2003 round of the International Association of Geoanalysts' GeoPT proficiency testing scheme. The Proficiency Testing Steering Committee for this round was Prof. M. Thompson (statistician), Prof. P.J. Potts (results coordinator) Dr S.R.N. Chenery, Dr P.C. Webb and Dr H.U. Kasper. The GeoPT13 report was published on the International Association of Geoanalysts web site (http://www.geoanalyst.org/index.php/proficiency-testing-proficiency-testing/geopt-programme/previous-rounds).

Intended use

This reference material is designed for use by laboratories measuring the major and trace element mass fractions in silicate rocks and similar materials for the calibration of a measurement system, the assessment of a measurement procedure, assigning values to other materials, and quality control. Note that the material may be used only for a single purpose in the same measurement process. For example, it must not be used for calibration and method validation at the same time.

Minimum sample size

On the basis of the homogeneity results and an assessment of the methods used to contribute results to the GeoPT13 round, the minimum sample size recommended for use as a test portion is 0.2 g.

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Reference values

Measurand	Reference value	Uncertainty (expanded)	p		Measurand	Reference value	Uncertainty (expanded)	p
	g/100 g	*g/100 g*				*mg/kg*	*mg/kg*	
SiO_2	53.30	0.13	68		**Ho**	0.86	0.06	33
TiO_2	0.422	0.006	74		**La**	25.8	0.6	53
Al_2O_3	6.15	0.03	70		**Li**	21.7	0.8	22
Fe_2O_3T	2.09	0.02	79		**Lu**	0.39	0.03	34
MnO	0.064	0.002	73		**Mo**	1.29	0.07	26
MgO	2.94	0.03	70		**Nb**	8.45	0.31	53
CaO	16.32	0.07	77		**Nd**	24.4	0.6	43
Na_2O	1.07	0.02	70		**Ni**	42.6	1.6	62
K_2O	1.35	0.02	74		**Pb**	11.4	0.3	53
P_2O_5	0.127	0.003	67		**Pr**	6.3	0.1	34
CO_2	14.94	0.15	19		**Rb**	51.1	0.9	65
LOI	16.03	0.03	59		**Sb**	0.58	0.03	23
	mg/kg	*mg/kg*			**Sm**	4.99	0.15	39
Ba	201	4	69		**Sr**	279	4	72
Be	1.06	0.04	16		**Ta**	0.76	0.11	26
Ce	52.6	1.0	56		**Tb**	0.70	0.03	36
Co	5.8	0.3	54		**Th**	8.12	0.25	55
Cs	2.68	0.06	35		**Tl**	0.34	0.02	13
Cu	11.3	0.8	59		**Tm**	0.38	0.04	28
Dy	4.10	0.45	34		**U**	2.80	0.20	46
Er	2.45	0.15	32		**Y**	24.0	1.5	60
Eu	0.89	0.03	37		**Yb**	2.49	0.04	39
Ga	6.98	0.34	38		**Zn**	34.4	1.1	64
Gd	4.40	0.12	32		**Zr**	312	9	64

Reference values *are the GeoPT assigned values obtained from a re-assessment using robust statistical analysis of results originally submitted to the GeoPT13 round. This reassessment took into account more recent experience of GeoPT data evaluation. Values are reported on a dried basis.*

Uncertainties *are the robust standard deviation of the mean or median or mode of the assigned value expanded by a coverage factor of two, and rounded up.*

Fe_2O_3T *is the total iron expressed measured as Fe_2O_3,* ***LOI*** *is the loss on ignition, nominally determined by heating a test portion to 1050 °C for 2 hours;* ***p*** *is the number of independent data sets.*

Period of validity

Provided the storage and handling conditions are met, this reference material is not expected to deteriorate with time. On exposure to air, the material may absorb moisture, and instructions for handling must be followed.

Storage information

Store in a sealed container in a cool dry environment.

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Information values

Measurand	Information value	Uncertainty (expanded)	p		Measurand	Information value	Uncertainty (expanded)	p
	g/100 g	*g/100 g*				*mg/kg*	*mg/kg*	
Fe(II)O	0.76	0.04	18		**Hf**	9.6	1.0	37
	mg/kg	*mg/kg*			**Sc**	5.7	0.3	40
As	6.7	0.7	34		**Sn**	1.6	0.2	17
Bi	0.13	0.02	11		**V**	37	2	58
Cd	0.11	0.02	20		**W**	1.4	0.3	16
Cr	106	5	66					

Information values *are mainly 'provisional' values derived from the GeoPT13 dataset following a re-assessment of source data originally submitted to the GeoPT13 round. This reassessment took into account more recent experience of GeoPT data evaluation, together with the opportunity to select median or mode values as information values, when justified by the data distribution. These data are provided for information purposes only and* ***not*** *for the calibration of methods or the assessment of data. Results are reports on a dried basis.*

Uncertainties *are the robust standard deviation of the median expanded by a coverage factor of two, and rounded up.*

Fe(II)O *is the mass fraction (g/100g) of ferrous iron;* ***p*** *is the number of independent data sets.*

Instructions for handling

Before any measurements are made, every portion of the test sample must be dried at 105 ± 5 °C for at least 2 hours. Avoid contamination and cross-contamination of the test material.

Assessment of reference values

The reference values were determined as 'consensus' values based on the statistical location of the participants' results in the GeoPT13 round. This location was determined as a robust mean if the distribution of results was unimodal and, outliers aside, close to symmetrical. If a slight asymmetry was apparent in a unimodal distribution, the median was chosen as an alternative. If a noteworthy skew was apparent and an objective explanation for the outcome was forthcoming, the mode of the results might be used. In other circumstances, usually when the number of valid results contributing to the location was less than 15 or their dispersion was unusually great, no reference value was assigned, although values may be reported as information values. These judgements were made by the IAG Proficiency Testing Steering Committee.

Metrological traceability

Traceability was not formally demonstrated for this reference material. However, traceability could be demonstrated by the use of certified reference materials as calibrators or for performance assessment by the laboratories participating in this round and by the fact that some participating laboratories were formally accredited (although none of this information was recorded during the GeoPT13 round). Furthermore, traceability is implied by the overall consensus between datasets for individual elements/oxides submitted by laboratories that contributed to the GeoPT programme.

Reference to reference material characterisation report

Further details of the procedures used, the results, their statistical analysis and assessment, on which the property values listed in this certificate are based, can be found in the GeoPT13 report (http://www.geoanalyst.org/index.php/proficiency-testing-proficiency-testing/geopt-programme/previous-rounds).

Safety information

Silicate powders containing mineral can cause harm especially if inhaled or in contact with the skin. User organisations must undertake a health and safety risk assessment and ensure that the appropriate procedures are followed in the handling and use of this material. Further details are available on the relevant Material Safety Data Sheet.

Legal notice – terms and conditions

1. The IAG shall not be liable to the user of this material for loss (whether direct or indirect) of profits, business, anticipated savings or reputation or for any indirect or consequential loss or damage whatsoever even if previously advised thereof and whether arising from negligence, breach of these Terms and Conditions or howsoever occurring.

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Revisions

Any revisions to this reference material data sheet will made available on the IAGeo Ltd web site (www.iageo.com).

Acknowledgements

Peter Webb and Thomas Meisel are gratefully acknowledged for undertaking a re-assessment of the GeoPT13 data set and for other contributions to this data sheet.

Approvals

This reference material information sheet was approved on behalf of the Certification and Reference Material Committee of the International Association of Geoanalysts.

Name *Philip J. Potts* **Position** *Chair of IAG Certification and Reference Material Committee* **Date** **26th February 2017**

Appendix - GeoPT13 Homogeneity Report

Homogeneity testing was based on analysis of duplicate test portions taken from each of 16 packets, which had been selected at random from the batch that had been prepared for distribution. These samples were analysed in duplicate by WD-XRF at the Open University for the major and minor elements. Results of the evaluation of homogeneity data are listed in Tables H1 and H2. In a typical homogeneity test, the classical criterion is that elemental results 'pass' the F-test after a randomised repeated experiment. However, that is not appropriate for proficiency testing, since the Harmonised Protocol requires merely that variation between distributed units should have an insignificant effect on the interpretation of proficiency testing results. If the analytical variance is particularly small, the F-test may detect a significant level of between packet variation that is, in fact, inconsequential in relation to the expected variation among the results from participating laboratories. To address this need, the Harmonised Protocol specifies that the ratio of the sampling standard deviation to the target standard deviation should be less than 0.3. Elements that pass this criterion are considered to be 'sufficiently homogeneous'. However, detailed evaluation of the Harmonised Protocol has shown that this procedure is unduly prone to the rejection of material that is, in fact, satisfactory. This tendency can be eliminated by a statistically sound procedure described by Fearn and Thompson (Analyst, 2001, 126, 1414-1417). This revised procedure is used in the GeoPT programme to assess 'sufficient homogeneity'. A further problem can arise when the precision of the analytical method used in the homogeneity test is too poor to detect reliably the required level of sufficient homogeneity. This requirement in the analysis of data is also taken into account in the new test. To provide a valid test for 'sufficient homogeneity', the data on which the test is based must be collected according to a strictly executed randomised design. Deviation from strict randomness can inadvertently occur, so all data used in GeoPT are tested for a range of 'pathological' features that might invalidate the test. The outcomes of all these tests are shown in Tables H1 and H2. 'Data test' looks for 'pathological features' in the data. 'Analytical precision' checks that the results meet a suitable level of precision. 'Harmonised Protocol' indicates whether the material is sufficiently homogeneous according to that

procedure. 'Fearn-Thompson test' indicates whether the distributed units are sufficiently homogeneous according to the procedure adopted by GeoPT. Closer examination of the results shows that there was a small but significant trend in the LOI data, probably caused by the absorption of moisture after the samples had been dried and were awaiting weighing, but before they had been ignited. Despite the relatively small range between maximum and minimum values in this trend, the LOI data is not considered to be fit for purpose for proficiency testing, so no conclusions on the homogeneity of this element can be drawn from these data. In the case of Cu, the analysed concentration is about three times the detection limit of the XRF technique, and may not, therefore, be of satisfactory precision for homogeneity testing. In any case, Cu was one of the elements that could not be given an assigned value, because of the unsatisfactory distribution of data submitted by participating laboratories, and in consequence, no z-scores are presented for this element in this report. (Note: following a reassessment of the data submitted to this GeoPT round, it was decided that the original assessment of the Cu data had been influenced by the poor sensitivity of contributed XRF data as was experienced in homogeneity testing and that the presence of a clear consensus in combination with the symmetrical distribution of data justified the assignment of a reference value for this element). Note that the precision of XRF data is also an issue in the analysed values for a number of elements where concentrations are close to the XRF detection limit. The overall conclusion of this homogeneity evaluation is that the loess sample is suitable for the GeoPT13 proficiency testing round, noting that a technique of better detection limit capability would have provided better data for some trace elements from which a more comprehensive evaluation of homogeneity could have been made.

Table H1 Results of homogeneity testing on the WD-XRF major element data and LOI.

Analyte	***Data test***	***Analytical precision***	***Harmonised Protocol test***	***Fearn-Thompson test***
SiO2	*OK*	*OK*	*OK*	*OK*
TiO2	*OK*	*	*SIG*	*OK*
Al2O3	*OK*	*	*OK*	*OK*
Fe2O3	*OK*	*OK*	*OK*	*OK*
MnO	*OK*	*OK*	*OK*	*OK*
MgO	*OK*	*OK*	*OK*	*OK*
CaO	*OK*	*	*OK*	*OK*
LOI	*TREND*	*OK*	*SIG*	*SIG*
Cr	*OK*	*OK*	*OK*	*OK*
Ni	*OK*	*OK*	*OK*	*OK*

** Analytical standard deviation in the homogeneity test exceeds the ideal limit*

SIG Deviation from 'sufficient homogeneity' detected at the 95% level of confidence.

Table H2 Results of homogeneity testing on the WD-XRF trace element data.

Measurand	***Data test***	***Analytical precision***	***Harmonised Protocol test***	***Fearn-Thompson test***
Sr	*OK*	*	*OK*	*OK*
Zr	*OK*	*	*SIG*	*OK*
Ba	*OK*	*	*OK*	*OK*
Sc	*OK*	*	*OK*	*OK*
V	*OK*	*	*OK*	*OK*
Cr	*OK*	*	*OK*	*OK*
Co	*OK*	*OK*	*OK*	*OK*
Ni	*BIAS*			
Cu	*OK*	*	*SIG*	*SIG*
Zn	*OUTLIER*			
As	*OK*	*OK*	*OK*	*OK*
S	*OK*	*	*SIG*	*OK*
TiO2	*OK*	*	*OK*	*OK*
Fe2O3	*OK*	*OK*	*OK*	*OK*

** Analytical standard deviation in the homogeneity test exceeds the ideal limit*

SIG Deviation from 'sufficient homogeneity' detected at the 95% level of confidence.