

G-Probe 25b — an International Proficiency Test for Microanalytical Laboratories — Report on Round 25b (Speleothem, KCSp-1NP, Nanoparticulate powder pellet) / December 2021

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Abstract

Results are presented for Round 25b of the G-Probe Proficiency Testing programme for microanalytical laboratories, organised by the International Association of Geoanalysts (IAG). The test material distributed in this round of G-Probe was the speleothem nano-particulate powder pellet, KCSp-1NP, prepared at Kiel University. This is the first time that a carbonate material in the form of a nano-particulate powder pellet has been the subject of G-Probe. As well as offering an innovation and new opportunities in proficiency testing, use of this carbonate nano-pellet also presents some new challenges and unfamiliar obstacles, e.g., the very low mass fractions of many trace elements in speleothem carbonate material and the porosity of the powder pellets. In this report, the data contributed by 25 laboratories are listed, together with an assessment of consensus values as composition location estimators, consequent *z*-scores and a series of charts that show the distribution of contributed results and reveal the overall performance of participating laboratories. Assigned values were conferred for 8 elements, and provisional values for a further 8, out of 61 elements reported. However, for 16 of those elements, an insufficient number of laboratories reported results to allow data distributions to be formally assessed.

Introduction

This twenty-fifth round of G-Probe, the international proficiency testing programme for microanalytical laboratories, was conducted in a similar manner to recent rounds. The programme is organised by the IAG and is conducted in a manner that conforms with the recently published G-Probe Protocol (IAG, 2020).

To accommodate difficulties encountered with shipments and delays in laboratory readiness due to the Coronavirus pandemic, the original deadline for submission of results for this round was extended by several weeks with the benefit that 25 laboratories reported their results. All data submitted were processed using the online system, which also provided the automated sections of this report. The overall aim of the programme is to provide participating laboratories with *z*-score information for their reported measurement results so that each laboratory can decide whether the quality of their data is satisfactory in relation both to the G-Probe fitnessfor-purpose criterion and to the results submitted by other laboratories contributing to the round. In circumstances where *z*-scores are unsatisfactory, a participating laboratory is encouraged to investigate its procedures for unsuspected analytical bias and to take corrective action if it appears justified. The programme is designed to be part of the routine quality assurance procedures employed by microanalytical geochemistry laboratories.

G-Probe Steering Committee:

D. Garbe-Schönberg (principal organiser and producer of powder pellets), P.C. Webb (results coordinator and website administrator), P.J. Potts (results reviewer), J. Woodhead (supplier of original material), M. Thompson (statistical advisor), C.J.B. Gowing (distribution coordinator), L. Danyushevsky, R. Mertz-Kraus and A. Kronz (analytical advisors).

Timetable for Round 25b of G-Probe:

Distribution of test material: June 2021 Results submission deadline: 6th October 2021 Release of report: December 2021

G-Probe 25b Test Material details

The speleothem starting material for this test sample originated from a Pliocene calcitic speleothem sampled from shallow caves beneath the arid Nullarbor plain of South Australia (Woodhead et al., 2019) and was supplied by Jon Woodhead of the University of Melbourne, Australia. This sample was chosen as a first attempt to provide a potential carbonate reference material with concentration profiles similar to many real-world materials, especially those typically encountered by the palaeoclimate research community. For analysis of such materials the commonly employed NIST glasses can prove problematic as calibrants - not only because of the potential for matrix-related complexity - but also the fact that some elements of immediate interest (e.g., Mg) are only present at trace level in NIST glasses. A pure calcite speleothem (with no obvious detrital contamination) was chosen in order to provide a relatively homogeneous starting product and, from several hundred potential candidates, this particular sample was chosen because of its optimal levels of Mg, Sr, U and Ba.

The sample was first pulverized at the University of Melbourne and then further processed to an ultra-fine grain size at Kiel University following a modified wetmilling protocol with high-energy ball mills as detailed in Garbe-Schönberg and Müller (2014). In total, about 200 g original powder was processed with 30 individually milled batches. Participants were alerted to the fact that the nano-particulate materials of this pellet are hygroscopic and were advised to store the pellet in a desiccator and/or under vacuum. They were also advised that many trace elements are at very low mass fractions in this material so that special attention should be paid to the limits of detection of the procedure used. One pellet was distributed to each participant.

For homogeneity testing following ISO Guide 35:2017 (ISO, 2017) subsets of 10 pellets were distributed to 4 international laboratories for analysis of 10 points per pellet by LA-ICP-MS to assess between-pellet heterogeneity. In addition, one pellet was analysed at 100 points for estimating within-pellet microheterogeneity. All 30 batches of nano-powder were analysed for Sr/Ca and Mg/Ca ratios by ICP-OES, and 28 batches by solution ICP-MS for bulk composition at the University of Kiel. After careful assessment of all these homogeneity data, the speleothem "nano-pellets" were considered suitable for use in this proficiency test.

Submission of results

For G-Probe 25b, participants were instructed to apply their routine measurement procedures to provide one measurement result for the nano-particulate powder pellet representative of its average composition (Result A), however, 5 laboratories provided two measurements, results A and B.

A total of 708 measurement results, submitted by 25 laboratories, are listed in Table 1. Where results A and B were provided, the average was used for the subsequent data assessment. Of the resultant 604 individual values reported for 61 analytes, 557 values were by LA-ICP-MS from 22 laboratories, 26 by EPMA from 5 laboratories, and one laboratory provided 21 values without defining its method.

Target values and results summary

Robust statistical procedures were used to derive a consensus value from the contributed data for each elemental component in the test material. These procedures included the evaluation of the Huber robust mean, the median for the dataset and a mode derived from a kernel density distribution as detailed by Thompson (2017). Evaluations of appropriate consensus values involved a critical assessment of distributions of results from ordered sequential charts for each analyte. Consensus values were credited with assigned status on the basis that:

- (i) sufficient laboratories had contributed data for estimating a measurand (usually a minimum of 15);
- (ii) visual assessment gave confidence that a substantial proportion of the results distribution was symmetrically disposed about the consensus;
- (iii) the ratio of the uncertainty in the location estimate to the target precision (as defined below) was an acceptably small value; and
- (iv) where possible, an evaluation of measurement results by procedure was judged to provide no clear evidence of procedural bias among the measurement results from which the consensus was derived.

Where these criteria were nearly, but not fully met, measurands were credited with 'provisional' rather than 'assigned' status. Instances of provisional status were identified because either:

- (i) a smaller number of results (less than 15 but more than 8) contributed to the consensus, or
- (ii) the results were unduly dispersed in relation to the target precision (*H*_a, see below), or
- (iii) the distribution of results was significantly skewed
 (but not severely enough to preclude the recognition of a clear consensus), or
- (iv) procedural bias was identified in some of the contributed data but a target value could nevertheless be recognised based on the most coherent part of the overall data distribution conforming approximately to a random sample from a normal distribution.

Where data were either insufficient in number, or the distribution was too variable or too highly skewed for the confident estimation of a consensus to provide *z*-scores, data distributions are presented 'for information' only.

The resulting consensus values credited with assigned or provisional status were those judged to be the best available estimates of the true composition of the test material and therefore suitable for use as target values for proficiency testing. It should be noted, however, that in many cases, these estimates are derived from a single analytical method. Data distributions for those analytes given assigned or provisional status are presented in Figure 1, and those for which no status could be conferred are shown for information in Figure 2. Measurement results in the Figure 1 and 2 data distribution plots are presented in order of increasing magnitude and identified according to laboratory code. Data symbols are coded by colour and shape according to the method of measurement. The majority of results were obtained by LA-ICP-MS, and for a limited number of major elements and S by EPMA.

For trace elements there is no option other than to make assessments based on LA-ICP-MS data, and therefore concerns about the possibility of single method bias, noted above, must be kept in mind and the outcomes should be regarded with caution in the reflection of true values. Nevertheless, the derived consensus values represent the best that currently can be obtained and therefore are considered appropriate for the purposes of this proficiency test.

Several laboratories in this round required values of a major element oxide for internal standardisation of LA-ICP-MS data. Laboratories coded E2, E13, E16, E23, E31, E32 and E45 were instructed that estimates of CaO could be based on stoichiometry. Inspection of the results provided by these participants showed no detectable evidence that the use of these values had been responsible for any significant bias in datasets. However, three laboratories (E22, E25, E46) appear to have reported and possibly used the CaCO₃ mass fraction instead of the corresponding CaO value for standardisation purposes and therefore their results are always anomalous.

Table 2 lists assigned and provisional values for one major component and 15 trace elements in G-Probe 25b (KCSp-1NP). Data distribution charts for the 16 measurands that were judged to have satisfactory distributions for consensus values to be conferred with assigned or provisional status are shown in Figure 1. These are: Al₂O₃*, As*, Ba, Ce*, Cu, Ga*, La*, Li*, Mn, Ni*, Pb*, Sr, U, V, Y, and Zr. Of these, values of the 8 analytes marked '*' were credited with provisional status for reasons given above.

Data distribution plots for the 30 analytes: SiO_2 , TiO_2 , Fe_2O_3T , MgO, CaO, Na_2O , K_2O , P_2O_5 , B, Co, Dy, Er, Eu,

Gd, Ge, Hf, Ho, Lu, Nb, Nd, Pr, Rb, S, Sc, Sm, Ta, Th, W, Yb and Zn are plotted in Figure 2 for information only, as the data were either insufficient in number, or the data distribution was too highly dispersed or too highly skewed for the confident estimation of a consensus for provision of *z*-scores. Approximate values for many of these elements are included in supplementary Table 0.1 for reasons outlined below.

Relatively few analytes could be credited with assigned or provisional status (compared with "normal" G-Probe rounds using silicate rock test materials), mainly because many trace elements were present at very low mass fractions which fell below the detection limits of the techniques employed. Therefore, this test material was more challenging than usual both for analysts and for the estimation of appropriate consensus values. Where few data are available there is a great deal of uncertainty attached to any value that might be considered plausible. Table 0.1 lists potential values, tentatively estimated, where normal assessment is not possible on account of too few data, or data that is generally too variable. It is considered that such approximations can provide some guidance for analysts to judge whether their results are broadly within the range of values derived by other participants. However, it is not justified to report uncertainties in these cases. Although the listed values for TiO₂, Dy, Er, Hf, Nb, Pr, W and Yb and possibly Nd, Sc and Th could be regarded as the more credible based on their data distributions, there was insufficient data to make any positive assessment.

Observations

Test materials presented as pressed powder pellets have been used in previous G-Probe rounds e.g., GP-4 (carbonate MACS-3), GP-10 (phosphate MAPS-4), GP-20 (ultra-milled basalt glass GSD-2G-NP), and this is a strategy for presenting materials that cannot be prepared as homogenous glasses or minerals. However, powder pellets are characterized by some porosity that may challenge analysis by EPMA. This issue, along with the presence of the carbonate matrix may be a cause for systematically low CaO in EPMA results, whereas other EPMA results for major elements e.g., SiO₂, MgO were compatible with LA-ICP-MS results. With vanishingly small quantities of many of the constituents of this test material, it is not altogether surprising that fewer measurands than usual could be credited with a defined status. However, it was disappointing that results were not more coherent for many constituents, especially some components apparently present in comfortably measurable mass fractions such as SiO₂, MgO and Na₂O, and trace elements such as B, Cr, Sc and Zn, and therefore that they could not be assessed more positively. A significant number of "high tails" have been observed, especially in data distributions for Fe₂O₃ and P₂O₅, though the consequence for plots in Table 2 is for such data to be missing as it plots outside the limits of the graph. The general tendency for an appreciable number of measurement results to be too high in this round led to frequent use of the mode as the most appropriate estimator of central tendency.

Impurities from small inclusions were detected in some of the pellets during the homogeneity pre-tests. Such anomalies can be easily detected and excluded from data integration during post-processing of LA-ICP-MS data prior to submission. Indeed, no comparable anomalies in TiO₂, Fe₂O₃, Ce, Cr, Ga, Mo, Ni, Pb, Sc, W, Zn, and Zr data were detected in the distributions of contributed data.

Some preliminary data from ICP-MS bulk analysis of 28 batches of nano-powder are provided in Table 0.2. The molar ratio for Sr/Ca of 0.861 mmol/mol as determined during this round compares to 0.838 mmol/mol derived from bulk analysis of 30 batches of nano-powder by ICP-OES, and a Mg/Ca molar ratio of 34.7 mmol/mol compares well with 35.3 mmol/mol from bulk ICP-OES data. These bulk analyses also confirmed excellent homogeneity of Sr/Ca and Mg/Ca between all 30 batches of nano-particulate powder with values within 0.5 %RSD (2SD). The Ba/Ca molar ratio of 9.44 µmol/mol from this round compares to 9.87 µmol/mol in the bulk data and the U/Pb molar ratio of 170 reproduced exactly the same value as in the preliminary solution bulk data by ICP-MS. However, the database for bulk composition of KCSp-1NP is too small for a valid comparison with values from this G-Probe round.

Z-score analysis

Assessment of submitted results followed the strategy adopted in recent rounds of G-Probe (Wilson et al. 2019; Wilson et al. 2020; Garbe-Schönberg et al. 2021) and detailed in the G-Probe protocol (IAG, 2020). Based on an assessment of the variation of measurement results in earlier rounds, and in order to provide sufficient discrimination for the proficiency test to be helpful to participating laboratories, the fitness for purpose criterion applied throughout was provided by the modified Horwitz function:

$$H_a = k X_a^{0.8495}$$

where H_a is the standard deviation for proficiency, also referred to as the target precision, for each measurand; X_a , represented as a mass fraction, is the best estimate of the true composition, also known as the 'target value' (and may be credited with assigned or provisional status). The factor k = 0.01, which is regarded as appropriate for laboratories working to a 'pure geochemistry' standard of performance, where analytical results are designed for geochemical research and where care is taken to provide data of high precision and accuracy, sometimes at the expense of a reduced sample throughput rate.

Z-scores were calculated for the average measurement result submitted by each laboratory from:

$$z = [X - X_a] / H_a$$

where X is the (average) measurement result submitted, X_a is the target value (assigned and provisional) and H_a is the target precision (all as mass fractions).

Z-score values for results submitted to G-Probe 25b are listed in Table 3. *Z*-scores derived from provisional values of measurands are shown in italics.

Participating laboratories are invited to assess their performance using the following criteria:

Z-score results in the range -2 < z < 2 are considered to be 'satisfactory' (in the sense that no action is called for by the participant). If the z-score for any element falls outside this range, especially if it is outside the range -3 < z < 3, laboratories are advised to examine their procedures and, if necessary, take action to ensure that their determinations are not subject to unsuspected analytical bias.

Should a participating laboratory decide that this performance standard is not appropriate for assessment of their measurement results, they are invited to recalculate their *z*-scores by substituting the appropriate value of the standard deviation for proficiency testing, H_a , into the equation for the calculation of *z*-scores (i.e. $z = [X - X_a] / H_a$). Adoption of such an approach should include a justification as to why an amended value of H_a is more appropriate for assessment of their data.

Overall performance

A summary of the overall performance of individual laboratories for this round is plotted in multiple *z*-score charts in Figure 3. In these charts, the *z*-score performance for each element is distinguished by symbols that make it easy to identify whether the measurements results were satisfactory or gave *z*-scores that exceeded the action limits. This chart is designed to help individual laboratories judge their overall performance in this proficiency test. Note, however, that participants should always review their *z*-scores in accordance with their own fitness-forpurpose criteria.

Participation in future rounds

The benefit from proficiency testing arises from regular participation and laboratories are invited to contribute to Round 26 of G-Probe, the test samples for which will be distributed in spring 2022.

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References

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ADDENDUM — IMPORTANT NOTICE TO ANALYSTS

Change in uncertainty estimation for medians:

Note that in 2020 a change was made to the algorithm for estimating the uncertainty of median values compared to that used in previous rounds of G-Probe. The revised procedure was implemented for the first time for round 24 (G-Probe 24). As described in the new G-Probe protocol (IAG, 2020), median uncertainties are now increased by a factor of 1.2533. Therefore, when comparing uncertainties from this and future rounds with those from rounds previous to Round 24, those uncertainty values previously reported for medians should be increased by this factor.

 Table 0.1 Potential values, tentatively estimated, for analytes that were reported in insufficient numbers or were generally too variably disposed for formal assessment.

	Potential value (g 100g ⁻¹)	Number of laboratories reporting		Potential value (mg kg ^{.1})	Number of laboratories reporting
SiO ₂	0.80	21	Gd	0.0013	5
TiO₂	0.000063	8	Hf	0.0011	7
Fe ₂ O ₃ T	0.005	18	Но	0.00027	6
MgO	1.33	21	Lu	0.00015	4
CaO	54.1	17	Nb	0.0021	6
Na ₂ O	0.063	18	Nd	0.0023	7
K ₂ O	0.0017	13	Pr	0.00058	7
	(mg kg ⁻¹)		Rb	0.022	13
В	2.8	14	Sc	0.14	10
Со	0.029	14	Sm	0.00076	4
Dy	0.00098	7	Th	0.00058	8
Er	0.001	7	Yb	0.001	7

 Table 0.2 Preliminary bulk analysis data for selected elements from homogeneity pre-tests by solution ICP-MS (medians of 28 batches of nano-powder).

	Median value	2 SD
TiO	0.000064	0.000032
AI2O3	0.00061	0.0000072
Fe₂O₃T	0.00063	0.00009
	(mg kg ⁻¹)	(mg kg ⁻¹)
As	0.65	0.068
В	0.9	0.36
Ва	13	0.5
Со	0.05	0.020
Cr	0.06	0.026
Cu	3.5	0.6
Li	0.14	0.07
Mn	0.28	0.04
Ni	0.8	0.12
Pb	0.02	0.0014
Rb	0.029	0.005
Sc	0.4	0.06
Sr	736	21

	Median value	2 SD
	(mg kg ⁻)	(mg kg⁻¹)
U	3.4	0.11
v	0.14	0.026
W	0.017	0.0012
Y	0.017	0.0014
REEs		
La	0.0044	0.0022
Се	0.0086	0.0052
Pr	0.0009	0.0004
Nd	0.0033	0.0012
Sm	0.0011	0.00018
Gd	0.0015	0.00026
Tb	0.0002	0.00002
Dy	0.0012	0.00012
Но	0.0003	0.00002
Er	0.0010	0.00014
Tm	0.0002	0.00004
Yb	0.0011	0.00014

Lab C	ada	F2A	F2B	F3A	F3B	E5A	E5B	F8A	F8B	F11A	F11B	F13A	F13B
SiO2	a 100a-1	0.95		LUA	202	0.874	0.9	0.7404	200	0 75/18/033	2110	0.747	2100
3102	g 100g	0.95				0.074	0.9	0.7404		0.734104933		0.747	
1102	g 100g					0.0045	0.0014	0.000520		0.0000001		0.00024	
A1203	g 100g	0.14				0.0015	0.0014	0.000530		0.000729		0.00074	
Fe2031	g 100g	0.14				1 502	1 570	1.229		0.00017		0.00537	
MgO	g 100g -	1.51				1.563	1.579	1.328		1.343526231		1.5	
CaU	g 100g-1	55.04				53.38	53.35	0.0504		0.0770		56.03	
Nazo	g 100g-1	0.06				0.065	0.064	0.0581		0.0778		0.0014	
K20	g 100g-1	0.04				0.0018	0.0016	0.00111		0.00334		0.0014	
P205	g 100g-'	0.01						0.00385		0.00322		0.00472	
Ag	mg kg ⁻ '							0.00413		4 555404500		10	
AS	mg kg ⁻ '							1.47		1.555194506		1.3	
Au	mg kg ⁻ '					4.04	0.00	0.00		0.500044044		0.40	
в	mg kg ⁻¹	40.55		10		4.61	2.99	2.88		2.599644314		3.46	
Ва	mg kg ⁻¹	12.55		12		13.42	13.91	12.2		12.38031868		12.32	
Be	mg kg⁻¹							0.0151					
Ві	mg kg ⁻¹					00.40							
Br	mg kg⁻¹					30.13	28						
Ce	mg kg ⁻¹	0.01		0.008				0.00594		0.00782			
CI	mg kg ⁻¹					175.4	93.5						
Co	mg kg ⁻¹	0.24				10		0.0284		0.0304			
Cr	mg kg ⁻¹	0.16				4.2	1.97	0.0905		0.0881			
Cs	mg kg ⁻¹					0.015	0.011						
Cu	mg kg ⁻¹	5.01		4.94		4.71	4.82	4.483		4.553296609		3.44	
Dy	mg kg ⁻¹			0.002				0.000797		0.000946			
Er	mg kg ⁻¹			0.001				0.000774		0.000739			
Eu	mg kg ⁻¹							0.000583		0.00149			
Ga	mg kg ⁻¹	0.02						0.0207		0.0229			
Gd	mg kg ⁻¹			0.002				0.00067					
Ge	mg kg ⁻¹	0.02				0.436	0.45						
Hf	mg kg ⁻¹			0.001				0.00106		0.00113			
Но	mg kg ⁻¹							0.000216		0.000286			
In	mg kg ⁻¹												
La	mg kg ⁻¹			0.004				0.00302		0.00308			
Li	mg kg ⁻¹							0.1176		0.133305934			
Lu	mg kg ⁻¹							0.000112					
Mn	mg kg ⁻¹	0.25						0.2406		0.290731909		0.27	
Мо	mg kg ⁻¹									0.00237			
Nb	mg kg ⁻¹							0.002		0.00191			
Nd	mg kg ⁻¹			0.004				0.00195		0.00267			
Ni	mg kg ⁻¹	0.94		1.28		1.57	2.3	0.9145		0.998147352		1.04	
Pb	mg kg ⁻¹	0.02		0.055		0.021	0.033	0.017		0.0208		0.036	
Pd	mg kg ⁻¹												
Pr	mg kg ⁻¹			0.001				0.000588		0.000715			
Rb	mg kg ⁻¹	0.02		0.025				0.0172		0.0501			
Re	mg kg ⁻¹												
S	mg kg ⁻¹												
Sb	mg kg ⁻¹												
Sc	mg kg ⁻¹	0.13								U.149385777		ļ	
Se	mg kg ⁻¹	0.55										ļ	
Sm	mg kg ⁻¹			0.001									
Sn	mg kg ⁻¹	0.11						0.025		0.0492			
Sr	mg kg ⁻¹	750.3		641		745	731	656.1		693.7784294		723.88	
Та	mg kg ⁻¹							0.000153		0.000249			
Tb	mg kg ⁻¹							0.000134					
Th	mg kg-1			0.001		0.0015	0.001	0.000589		0.00058		ļ	
ті	mg kg-1	0.01						0.00446				ļ	
Tm	mg kg ⁻¹							0.000125					
U	mg kg ⁻¹	3.57		3.42		3.54	3.38	3.056		3.196244351		3.4	
v	mg kg ⁻¹	0.16		0.161		0.14	0.4	0.1304		0.147435376		0.133	
w	mg kg ⁻¹	0.01						0.011					
Y	mg kg ⁻¹	0.02		0.017				0.0154		0.0225		0.013	
Yb	mg kg ⁻¹			0.001				0.000653		0.00106			
Zn	mg kg ⁻¹	0.3				0.643	0.559	0.2065		0.200127043			
Zr	mg kg ⁻¹	0.26		0.246		0.271	0.211	0.2301		0.24493791		0.24	

LabLobLubL						E 46 D		E 40 D			F 00.4	5005		
dod open	Lab C	ode	E14A	E14B	E15A	E15B	E16A	E16B	E22A	E22B	E23A	E23B	E24A	E24B
IndexImage <th< td=""><td>SiO2</td><td>g 100g-1</td><td>0.757</td><td></td><td>0.728</td><td></td><td>0.87</td><td></td><td>1.501</td><td>1.418</td><td>0.968</td><td></td><td>0.851</td><td></td></th<>	SiO2	g 100g-1	0.757		0.728		0.87		1.501	1.418	0.968		0.851	
Aboo end b <t< td=""><td>TiO2</td><td>g 100g-1</td><td></td><td></td><td>0.00006</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<>	TiO2	g 100g-1			0.00006									
reactorreactor00<	AI2O3	g 100g-1			0.00068				0.001	0.001	0.00064			
Heg inse inse <th< td=""><td>Fe2O3T</td><td>g 100g-1</td><td></td><td></td><td>0.0082</td><td></td><td></td><td></td><td>0.01</td><td>0.013</td><td>0.0033</td><td></td><td></td><td></td></th<>	Fe2O3T	g 100g-1			0.0082				0.01	0.013	0.0033			
Ca09.90°9.10°9	MgO	g 100g-1	1.45		1.384		1.36		2.739	3.7735			1.379	
Na200.98°0.0720.0880.0280.0230.020.0500P3050.99°0.99°0.0270.080.080.080.080.070.080.0	CaO	g 100g-1	51.48		54.99				93.623	93.622			51.691	
indi	Na2O	g 100g-1			0.0723		0.06		0.126	0.124				
P205	К20	g 100g-1			0.00034		0.001		0.02	0.03				
Agmayma	P2O5	g 100g-1			0.00273		0.008		0.07	0.06	0.0092			
AndmayNo1.3701.44NoNoNoNoNoBmay1.551.3701.2360.442.3052.3052.1301.220NoNoBmay1.550.1351.202.3052.1301.220NoNoNoBmay0.0128NoNoNoNoNoNoNoNoNoBmay0.0128NoNoNoNoNoNoNoNoNoBmay0.0128NoNoNoNoNoNoNoNoNoBmay0.0084NoN	Aa	mg kg-1												
new new <td>As</td> <td>ma ka-1</td> <td></td> <td></td> <td>1.379</td> <td></td> <td>1.54</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	As	ma ka-1			1.379		1.54							
nnn	Au	ma ka-1												
BasNo.11.551.2312.82.3362.131912.2812.8BasAver10.012812.82.131912.2812.812.8BasAver0.01280.0128111111BasAver10.00180.0040.060.160.007111BasAver0.00500.0080.0830.120.0771111CaAver0.1640.0080.0080.0120.07711111CaAver0.01690.070.0370.030.03711<	B	ma ka-1			2 2 2 2		6.04							
adiamay1.0.31.0.31.0.02.0.3002.0.3002.0.3000.0.001.0.01.0.0Bimay11	B	ing kg	11 55		12.550		12.6		22.265	21 210	10.06			
Bit Note: Note: Note: Note: Note: Note:	ва	mg kg	11.55		13.5		12.0		23.305	21.319	12.20			
Bit max max max max max max max Ca max ⁻¹ max 0.0000 0.0004 0.10 0.11 0.000 0.000 Ca max ⁻¹ 0.0000 0.0004 0.010 0.017 0.000 0.000 Ca max ⁻¹ 0.0100 0.003 0.012 0.007 1.01 0.010 Ca max ⁻¹ 0.0000 0.007 1.01 0.007 0.000 0.007 Ca max ⁻¹ 0.0000000 0.007 0.000 0.007 0.000 0.007 Ca max ⁻¹ 0.0000000 0.007 0.000 0.007 0.000 0.007 Ca max ⁻¹ 0.0000000 0.000 0.000 0.000 0.000 0.000 Ca max ⁻¹ 0.0000000 0.000 0.000 0.000 0.000 0.000 Ca max ⁻¹ 0.0000000 0.0000 0.0000 0.0000 0.0000 0.0000 Ca max ⁻¹ 0.0000000 0.00000 0.0000 0.0000 0.0000 0.0000 Ca max ⁻¹ 0.0000000 0.00000 0.0000 0.00000 0.0000 Ca	Be	mg kg ⁻¹			0.0126									
Brmay-May-	Ві	mg kg-1									-			
Comww'0.00600.00640.160.160.160.06NGamww'0.1440.0380.0120.087NNNGamww'0.1440.0380.0120.0571.013.07NNGamww'0.001090.070.0570.087NNNNGamww'0.0000854.730.0090.077NNNNFmww'0.0000850.010.007NNNNNGamww'0.0000850.010.007NNNNNGamww'0.0000850.010.0030.03NNNNNGamww'0.0000850.020.0380.037NN <td>Br</td> <td>mg kg⁻¹</td> <td></td>	Br	mg kg ⁻¹												
Clmyw'000	Ce	mg kg ⁻¹			0.00606		0.0064		0.16	0.14	0.006			
Comays0.1440.0830.0830.1120.087maysmaysGamays'0.010190.070.0571.013.1070.015Gamays'0.001990.050.051.010.0570.050.01Dymays'0.0008854.730.00070.0070.0210.001Eumays'0.00089570.0030.0030.0230.0230.023Eumays'0.002970.0280.0390.0330.0230.023Gamays'0.0007730.0280.0050.0370.0230.02Gamays'0.0007730.0280.0050.0050.000.005Hemays'0.000770.0280.00020.0050.000.001Inmays'0.000170.0280.0090.0050.000.001Inmays'0.000170.0280.0090.0050.000.00Inmays'0.000180.0030.0020.0050.000.00Inmays'0.000180.0130.0200.0020.000.00Inmays'0.00180.0130.0120.0110.0110.011Inmays'0.01670.0120.0110.0110.0110.011Inmays'0.01680.0220.0220.0210.0110.011Inmays'0.01680.0220.0210.0210.0110.011	CI	mg kg-1												
CrmaysLL0.72.0371.103.107LMMCamays4.584.964.730.0550.050.050.050.07LLL <td>Co</td> <td>mg kg-1</td> <td>0.184</td> <td></td> <td>0.0363</td> <td></td> <td>0.083</td> <td></td> <td>0.112</td> <td>0.087</td> <td></td> <td></td> <td></td> <td></td>	Co	mg kg-1	0.184		0.0363		0.083		0.112	0.087				
ComayerA.98A.996MMO.05MMMMDymayer4.88A.996A.73MMMMMMDymayer4.800.000865M0.0010.007MMMMBrmayer0.0008537M0.00280.0030.003MMMMCamayer0.002770.0280.0330.023MMMMMCamayer0.000770.0280.0330.023MMM	Cr	mg kg ⁻¹					0.7		2.037	1.01	3.107			
Cu male" 4.58 4.59 4.73 male male male male Dy male" 0.000986 0.007 0.007 male male Er male" 0.000986 0.01 0.007 male male Ga male" 0.000986 0.027 0.028 0.039 0.037 0.023 male Ga male" 0.000773 0.028 0.039 0.037 0.023 male Ga male" 0.000773 0.028 0.039 0.037 0.022 male male Ga male" 0.000773 0.028 0.002 0.002 male mal	Cs	mg kg ⁻¹			0.00169				0.05	0.05				
Dymain mainNo0.000985No0.0000.007NoNoNoErmain0.00098570.0210.0030.0030.0030.0030.003Eumain0.0029770.0280.0390.0370.0230.015Gomain0.0007730.0280.0150.0120.011Gomain0.0007730.0240.0150.0120.011Gomain0.001070.00060.0050.0210.011Hemain0.001070.00080.0050.0020.002Hemain0.0000750.0030.0020.0020.002Lamain0.000360.0050.0050.005Lamain0.003260.00390.0060.0050.002Lumain0.010140.0120.0220.0020.001Momain0.001640.0150.0120.0280.001Ndmain0.001640.0160.0150.0110.011Ndmain0.001640.0160.0110.0110.011Ndmain0.001640.0110.0110.0110.011Ndmain0.001671.42.1431.5411.244Pdmain0.01870.0220.0140.0110.011Pdmain0.005520.0220.0640.0310.024Pdmain0.005520.0220.0640	Cu	mg kg-1	4.58		4.956		4.73							
Fr makr Image Image <thimage< th=""> Image Imag</thimage<>	Dy	mg kg-1			0.000985				0.009	0.007				
Eu matrix No 0.0037 No 0.003 No No No Ga matrix 0.000773 0.028 0.039 0.037 0.023 No Ga matrix 0.000773 No 0.015 0.012 No No Ga matrix 0.000770 No 0.006 0.002 No No H matrix 0.000170 No 0.0002 0.002 No No Ho matrix 0.0000170 No 0.0002 0.002 No No In matrix 0.0000170 No 0.002 0.002 No No In matrix 0.0000150 0.13 0.162 0.022 No No In matrix 0.0271 0.274 0.22 No 0.0267 No Mo matrix 0.00188 0.012 0.012 No No Ma matrix 0.00177 <	Er	mg kg-1			0.000986				0.01	0.007				
Ga maker Image 0.0279 0.028 0.039 0.037 0.023 Image Gd maker' 0.000773 0.0179 0.0254 0.023 Image Ga maker' 0.00107 0.002 0.005 0.02 0.023 H maker' 0.000075 0.002 0.002 0.002 0.002 In maker' 0.000073 0.0039 0.006 0.005 Image Image Ia maker' 0.000073 0.0039 0.006 0.005 Image Image Ia maker' 0.000250 0.0039 0.006 0.005 Image Image <thimage< th=""> Image Image</thimage<>	Eu	mg kg-1			0.000537				0.004	0.003				
Constraint Constraint <thconstraint< th=""> Constraint Constrai</thconstraint<>	Ga	ma ka-1			0.0279		0.028		0.039	0.037	0.023			
Construct Construct <t< td=""><td>Gd</td><td>ma ka-1</td><td></td><td></td><td>0.000773</td><td></td><td>0.020</td><td></td><td>0.015</td><td>0.007</td><td>0.020</td><td></td><td></td><td></td></t<>	Gd	ma ka-1			0.000773		0.020		0.015	0.007	0.020			
Constraint Constraint <thconstraint< th=""> Constraint Constra</thconstraint<>	Go	ma ka-1			0.000110				0.0170	0.012				
m module 0 0.00000 0.00000	Ge	mg kg-1			0.00107				0.006	0.204				
no mode mode <thm< td=""><td></td><td>ing kg</td><td></td><td></td><td>0.00107</td><td></td><td></td><td></td><td>0.000</td><td>0.003</td><td></td><td></td><td></td><td></td></thm<>		ing kg			0.00107				0.000	0.003				
Inmaigrage	но	mg kg			0.000515				0.002	0.002				
La majar 0.00026 0.0009 0.006 0.005 0.001 0.0015 0.012 0.011 0 0 0.005 0.005 0.012 0.011 0 0 0.005 0.005 0.012 0.011 0 0 0 0 0 0 0.016 0.017 0 <	lin	mg kg ⁻¹								0.005				
Lims kg*ms kg* <td>La</td> <td>mg kg⁻¹</td> <td></td> <td></td> <td>0.00326</td> <td></td> <td>0.0039</td> <td></td> <td>0.006</td> <td>0.005</td> <td></td> <td></td> <td></td> <td></td>	La	mg kg ⁻¹			0.00326		0.0039		0.006	0.005				
Lums/gr0.2470.2740.2740.22CC0.0020.0020.007CCC <t< td=""><td>Li</td><td>mg kg-1</td><td></td><td></td><td>0.1305</td><td></td><td>0.13</td><td></td><td>0.162</td><td>0.228</td><td></td><td></td><td></td><td></td></t<>	Li	mg kg-1			0.1305		0.13		0.162	0.228				
Mnmg/su*0.2470.2740.22110.26711Momg/su*0.001640.0120.0150.0120011Nbmg/su*0.001840.00290.0100.0110.0120.01101Ndmg/su*1.170.00291.40.0120.0111111Pbmg/su*1.170.01871.42.1431.5811.214111Pdmg/su*0.001870.0120.00310.03211111Pdmg/su*0.0005520.0220.00540.0480.0311111Remg/su*0.005520.0220.0540.0480.031111147.4Sbmg/su*1.431.54111 <t< td=""><td>Lu</td><td>mg kg⁻¹</td><td></td><td></td><td></td><td></td><td></td><td></td><td>0.002</td><td>0.002</td><td></td><td></td><td></td><td></td></t<>	Lu	mg kg ⁻¹							0.002	0.002				
Mo ms/gr 0.00184 0.001 0.015 0.015 0.015 0.015 0.015 Nd mg/gr 0.00188 0.001 0.011 0.011 0.011 0.011 Nd mg/gr 1.177 0.00258 0.012 0.011 1.24 0.001 0.011 Ni mg/gr 1.177 0.017 1.4 2.143 1.81 1.24 0.01 1.01 Pd mg/gr 0.017 0.017 0.033 0.032 0.01 1.01 1.01 Pd mg/gr 0.000552 0.022 0.054 0.048 0.031 0.02 1.01 1.0	Mn	mg kg-1	0.247		0.274		0.22				0.267			
Nb mg kgr 0.00188 0.015 0.012 0.015 0.012 0.011 0.0011 Nd mg kgr ¹ 1.177 0.00259 0.011 0.012 0.011 0.011 0.011 Ph mg kgr ¹ 1.177 0.0187 1.4 2.143 1.581 1.214 0.011 0.011 0.011 Pd mg kgr ¹ 0.0187 0.012 0.031 0.032 0.001 0.011 0.011 0.011 Pd mg kgr ¹ 0.000552 0.022 0.054 0.048 0.031 0.02 0.011 0.001 0.011 Re mg kgr ¹ 0.00255 0.022 0.054 0.048 0.031 0.011 0.011 0.011 So mg kgr ¹ 1432 0.00255 0.022 0.054 0.048 0.031 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 <td>Мо</td> <td>mg kg-1</td> <td></td> <td></td> <td>0.00164</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	Мо	mg kg-1			0.00164									
Ndms/ms/ms/ms/ms/ms/ms/ms/ms/ms/ms/ms/ms/m	Nb	mg kg ⁻¹			0.00188				0.015	0.012				
Nimake"1.177Image of the second seco	Nd	mg kg-1			0.00259				0.012	0.011				
Pbmb br' mb kr'Image0.0187Image0.0310.032ImageImageImagePdmb kr'Image0.00187Image <td>Ni</td> <td>mg kg-1</td> <td>1.177</td> <td></td> <td></td> <td></td> <td>1.4</td> <td></td> <td>2.143</td> <td>1.581</td> <td>1.214</td> <td></td> <td></td> <td></td>	Ni	mg kg-1	1.177				1.4		2.143	1.581	1.214			
Pd mg kg ⁻¹ I I <thi< th=""> I <thi< td=""><td>Pb</td><td>mg kg-1</td><td></td><td></td><td>0.0187</td><td></td><td></td><td></td><td>0.031</td><td>0.032</td><td></td><td></td><td></td><td></td></thi<></thi<>	Pb	mg kg-1			0.0187				0.031	0.032				
Pr mg kg ⁻¹ 0.000552 0.02 0.003 0.002 1 1 1 Rb mg kg ⁻¹ 1 0.0255 0.022 0.054 0.048 0.031 1 1 Re mg kg ⁻¹ 1432 1 <th1< th=""> <th1< th=""> 1 <th< td=""><td>Pd</td><td>mg kg-1</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></th<></th1<></th1<>	Pd	mg kg-1												
Rb mg kgri L 0.0255 0.022 0.054 0.048 0.031 L L Re mg kgri L <thl< th=""> <thl< th=""> L</thl<></thl<>	Pr	mg kg-1			0.000552				0.003	0.002				
Re mg kg ⁻¹ 1432 Image of the second se	Rb	mg kg-1			0.0255		0.022		0.054	0.048	0.031			
S mg/kg ⁻¹ 1432 Image of the second s	Re	mg kg-1												
Sb mg kg ⁻¹ mg kg ⁻¹ 0.1644 0.028 0.12 0.093 max max Sc mg kg ⁻¹ 0.1644 0.028 0.12 0.093 max max Se mg kg ⁻¹ 0.000522 0.028 0.12 0.093 max max Sm mg kg ⁻¹ 0.000522 0.016 0.11 max max Sn mg kg ⁻¹ 0.000522 0.23 max max max max max Sr mg kg ⁻¹ 0.000546 0.23 max max 684.5 max Ta mg kg ⁻¹ 0.000546 0.002 0.002 0.002 0.002 0.002 0.002 0.002 max max Th mg kg ⁻¹ 0.000523 0.002 0.002 0.002 0.002 0.002 max max Tm mg kg ⁻¹ 0.000523 0.168 0.002 0.002 0.002 max max max max <	s	mg kg ⁻¹	1432										1474.4	
Sc mg kg ⁻¹ 0.1644 0.028 0.12 0.093 Image: Constraint of the second seco	Sb	mg kg-1	t										· · ·	
Se mg kg ⁻¹ 0.000522 0.012 0.012 0.000 0.013 0 0 Sm mg kg ⁻¹ 0.000522 0.016 0.013 0 0 0 Sn mg kg ⁻¹ 0.000522 0.016 0.016 0.013 0 0 Sn mg kg ⁻¹ 661 739.3 722 1228.266 1223.298 719.8 684.5 Ta mg kg ⁻¹ 0.000546 0.002 0	Sc	mg kg-1			0.1644		0.028		0.12	0.093				
Sm mg kg ⁻¹ 0.000522 0.016 0.013 Sn mg kg ⁻¹ 0.000522 0.23	Se	mg ka-1												
Image of the second s	Sm	ma ka-1			0.000522				0.016	0.013				
Sin Ingrag Constraint Constraint <t< td=""><td>9m</td><td>mg kg-1</td><td></td><td></td><td>0.000322</td><td></td><td>0.23</td><td></td><td>0.010</td><td>0.013</td><td></td><td></td><td></td><td></td></t<>	9m	mg kg-1			0.000322		0.23		0.010	0.013				
sin ing ng 001 7.39.3 7.22 1228.296 719.6 684.5 Ta mg kg ⁻¹ 0.000546 0.002 0.001 0.001 0.001 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.001 0.001 0.001 0.001 0.001 0.002 0.002 0.002 0.002 0.002 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.011 0.001 0.011 0.016 0.011 0.0016 0.011 0.004 <t< td=""><td></td><td>mg kg 1</td><td>661</td><td></td><td>720.2</td><td></td><td>700</td><td></td><td>1000 000</td><td>1222 200</td><td>710.9</td><td></td><td>694 5</td><td></td></t<>		mg kg 1	661		720.2		700		1000 000	1222 200	710.9		694 5	
Ia mg kg ⁻¹ 0.00240 0.002 0.003 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.011 0.011 0.016 0.013 0.024 0.016 0.012 0.011 0.011 0.011 0.012 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.016 0.011 0.016 0.011 0.001 0.016 0.011 0.016 0.011 0.016 0.011 0.016 0.011 0.016 0.011 0.016 0.011 0.016 0.011 0.011 0.011 0.011	31 To	ing kg ⁻	001		138.3		122		1220.200	1223.290	119.0		004.0	
ID Ing kg ⁻¹ ID ID <thid< th=""> ID</thid<>	ть	mg Kg			0.000546				0.002	0.002				
In mg kg ⁻¹ 0.000523 0.002 0.001 0.002 0.001 0.001 0.003 0.012 0.011 0.001 0.011 0.001 0.011 0.001 0.011 0.011 0.016 0.011 0.016 0.011 0.011 0.011 0.011 0.011	(1) 	mg kg ⁻¹							0.002	0.002			L	
TI mg kg ⁻¹ <	In	mg kg ⁻¹			0.000523				0.002	0.002			ļ	
Tm mg kg ⁻¹ M M 0.002 0.002 0.002 M M M U mg kg ⁻¹ 3.092 3.437 3.61 7.084 5.981 3.415 M M V mg kg ⁻¹ 0.15 0.1635 0.16 0.323 0.273 0.151 M M W mg kg ⁻¹ 0.0114 M M 0.012 M M Y mg kg ⁻¹ 0.018 0.0191 0.016 0.033 0.024 0.016 M M Yb mg kg ⁻¹ 0.018 0.0191 0.016 0.033 0.024 0.016 M M Yb mg kg ⁻¹ 0.018 0.0191 0.016 0.011 0.008 M<	ті	mg kg ⁻¹											ļ	
U mg kg ⁻¹ 3.092 3.437 3.61 7.084 5.981 3.415 Image: Constraint of the state of the sta	Tm	mg kg-1							0.002	0.002				
V mg kg ⁻¹ 0.15 0.1635 0.16 0.323 0.273 0.151 W mg kg ⁻¹ 0.0114 0.016 0.323 0.273 0.151 Y mg kg ⁻¹ 0.0114 0.012 Y mg kg ⁻¹ 0.0191 0.016 0.033 0.024 0.016 Yb mg kg ⁻¹ 0.00983 0.016 0.011 0.008 Zn mg kg ⁻¹ 0.256 1.28 gr 0.232 0.265 0.25 0.491 0.347 0.233	U	mg kg ⁻¹	3.092		3.437		3.61		7.084	5.981	3.415			
W mg kg ⁻¹ 0.0114 Image: Constraint of the system of	v	mg kg ⁻¹	0.15		0.1635		0.16		0.323	0.273	0.151			
Y mg kg ⁻¹ 0.018 0.0191 0.016 0.033 0.024 0.016 0 Yb mg kg ⁻¹ 0.000983 0.011 0.008 0 0 Zn mg kg ⁻¹ 0.256 1.28 Zr mg kg ⁻¹ 0.232 0.265 0.25 0.491 0.347 0.233	w	mg kg ⁻¹			0.0114						0.012			
Yb mg kg ⁻¹ 0.000983 0.011 0.008 0 0 Zn mg kg ⁻¹ 0.256 1.28 0 0 0 0 0 0 Zr mg kg ⁻¹ 0.232 0.265 0.25 0.491 0.347 0.233 0	Y	mg kg ⁻¹	0.018		0.0191		0.016		0.033	0.024	0.016			
Zn mg kg ⁻¹ 0.256 1.28	Yb	mg kg-1			0.000983				0.011	0.008				
Zr mg kg ⁻¹ 0.232 0.265 0.25 0.491 0.347 0.233	Zn	mg kg-1			0.256		1.28							
	Zr	mg kg ⁻¹	0.232		0.265		0.25		0.491	0.347	0.233			

		E25A	ESER	ESCA	ESER	E24.A	E24B	E22A	ESOR	E25A	ESER	E40A	EAOP
Lab Co	ode	E25A	E29B	E26A	E26B	E31A	ESIB	E32A	E32B	E35A	E35B	E40A	E40B
SiO2	g 100g ⁻¹	3.23		0.81	0.76			0.7988		0.82		0.6653	
TiO2	g 100g ⁻¹	0.74						0.000065		0.007			
AI2O3	g 100g-1	0.01						0.000732		0.01		0.000053	
Fe2O3T	g 100g ⁻¹	0.046		0.06	0.06			0.00471		0.01		0.00071	
MgO	g 100g ⁻¹	3.47		1.33	1.37			1.546		1.45		1.26	
CaO	g 100g-1	92		53.86	54.66					51.2			
Na2O	g 100g-1	0.18		0.06	0.04			0.0728		0.06		0.067	
K2O	g 100g-1	0.074						0.00168		0.003			
P2O5	g 100g-1	0.09						0.00332		0.009			
Ag	mg kg ⁻¹	0.44											
As	mg kg ⁻¹			1.22	1.68	1.61							
Au	mg kg ⁻¹												
B	ma ka-1			6.39	5.56	2.52						2.933163465	
Ba	ma ka-1	32.7		12.51	12.07	12.5		13.4				12 71167843	
Bo	ma ka-1	02.1		12.01	12.01	12.0		10.1					
De Di	ma ka-1	0.071											
Di	ing kg	0.071											
Br	mg kg	0.04						0.000					
Ce	mg kg ⁻¹	0.21						0.009					
CI	mg kg ⁻¹												
Co	mg kg-1	1.33		0.11	0.11	0.019		0.027					
Cr	mg kg ⁻¹	7.3				1.24				62			
Cs	mg kg-1	0.13											
Cu	mg kg-1	13.2		4.74	4.94	4.66		4.924				4.814878638	
Dy	mg kg ⁻¹	0.35											
Er	mg kg ⁻¹	0.25											
Eu	mg kg ⁻¹	0.18											
Ga	mg kg ⁻¹	1.24		0.03	0.03	0.024							
Gd	mg kg ⁻¹	0.4											
Ge	mg kg ⁻¹			0.04	0.04								
Hf	mg kg ⁻¹	0.25											
Но	mg kg ⁻¹	0.11											
In	mg kg ⁻¹												
La	mg kg ⁻¹	0.16						0.004					
Li	mg kg ⁻¹			0.13	0.14	0.167		0.14				0.145893952	
	ma ka-1	0.081			-								
Mn	ma ka-1	0.0008						0.29		70		0.273179504	
Mo	ma ka-1												
Nb	ma ka-1	0.38											
Nd	ma ka-1	0.00											
NU NI	mg kg-1	6.90		1.00	1.00	1.02		1		76			
Dh	mg kg-1	0.09		1.09	1.09	0.062		0.010		70		0.0152	
PU	ing kg	0.25				0.002		0.019				0.0155	
Pa	mg kg ⁻¹	0.40				0.071							
Pr	mg kg ⁻¹	0.12		0.04									
Rb	mg kg ⁻¹	0.69		0.01	0.02	0.083		0.028					
Ke	mg kg ⁻¹				4007								
s	mg kg-1			1196.96	1088.33								
Sb	mg kg-1	0.29											
Sc	mg kg-1	6.75		0.09	0.16	0.051							
Se	mg kg-1					0.297							
Sm	mg kg-1	0.36											
Sn	mg kg-1	0.68											
Sr	mg kg-1	18900		715.72	690.93	748		737				721.4056547	
Та	mg kg-1	0.09											
Tb	mg kg-1	0.088											
Th	mg kg-1	0.082											
ті	mg kg-1	0.11											
Tm	mg kg-1	0.091											
U	mg kg-1	7.61		3.49	3.56	3.42		3.22				3.37050933	
v	mg kg-1	3.82		0.17	0.17	0.148		0.141				0.156589668	
w	mg kg-1	0.32						0,011					
Y	ma ka-1	0.46		0.01	0.01	0.014		0.015				0.0147	
Yh	ma ka-1	0.75		0.01	0.01	5.514		0.010				0.0177	
7n	ma ka-1	11.2		0.53	0.33	0 365		0.258					
7.	a **9	1.02		0.20	0.00	0.000		0.240				0.233060023	
<u></u>	ing Kg 1	1.00	1	0.20	0.24	0.220		0.242			1	0.200909932	

Lab C	ada	F41A	F41B	F42A	F42B	F43A	F43B	E45A	F45B	F46A	F46B	E50A	E50B
SiO2	a 100a-1	0.657	2410	L-72/1	LHED	0.317	LTOD	Litor	2400	1 11	Lind	0.859	0.86
TiO2	g 100g	0.00067				0.0005				1.11		0.000	0.00
AI2O3	g 100g	0.000000		0.000688		0.00003							
Fe203T	g 100g-1	0.00070		0.0115		0.00001				0.02		0.016	0.016
MaO	g 100g-1	1.2		1.24		0.817				2.84		1 31	1 309
CaO	g 100g-1			54.6		37.6				95.73		53 108	53 108
Na2O	g 100g			0.0643		0.0539				0.1		0.062	0.062
K20	g 100g-1	0.0017		0.00139		0.0000				0.1		0.002	0.002
P205	g 100g-1	0.0056		0.00305		0.0021				0.01			
Ag	ma ka-1	0.0000		0.00000		0.0021				0.01			
As	ma ka-1	1.59								1.88			
Δυ	ma ka-1												
B	ma ka-1	23		5.84		12		2 71	2 65				
Ba	ma ka-1	13.7		12.2		9.46		14.9	15.05	27.55		12.31	12.39
Be	ma ka-1									0.03			
Bi	ma ka-1												
Br	ma ka-1												
Ce	mg kg ⁻¹					0.0054							
ci	mg kg ⁻¹												
Co	mg kg ⁻¹					0.021				1.84			
Cr	mg kg ⁻¹			0.943									
Cs	mg kg ⁻¹												
Cu	mg kg ⁻¹	5.1		4.48		3.8		4.5	4.7			4.41	4.39
Dv	mg kg ⁻¹					0.0007							
Er	mg kg ⁻¹					0.0015							
Eu	mg kg ⁻¹												
Ga	mg kg ⁻¹					0.138				0.04			
Gd	mg kg ⁻¹												
Ge	mg kg ⁻¹												
Hf	mg kg ⁻¹					0.00094							
Но	mg kg ⁻¹					0.00025							
In	mg kg ⁻¹												
La	mg kg-1					0.0026							
Li	mg kg ⁻¹	0.3								0.14			
Lu	mg kg-1					0.00015							
Mn	mg kg ⁻¹	0.47		0.237		0.25		0.27	0.28				
Мо	mg kg ⁻¹												
Nb	mg kg-1					0.0021							
Nd	mg kg-1					0.0016							
Ni	mg kg ⁻¹	1		1.22		0.69				3.23		1.13	1.11
Pb	mg kg ⁻¹	0.03		0.0215		0.022							
Pd	mg kg ⁻¹												
Pr	mg kg-1					0.00056							
Rb	mg kg-1	0.067											
Re	mg kg ⁻¹												
s	mg kg ⁻¹					1300							
Sb	mg kg-1												
Sc	mg kg-1									0.27			
Se	mg kg ⁻¹												
Sm	mg kg ⁻¹												
Sn	mg kg ⁻¹	<u></u>		007		051		700.0	770.0	4550.55		700.0	746.4
Sr	mg kg ⁻¹	/11		685		651		789.9	779.6	1558.55		708.2	710.1
Т	mg kg ⁻¹	├ ───┤											
(1) (T)	mg kg ⁻¹					0.000.10							
l in	mg kg ⁻¹	├ ───┤				0.00043							
	mg kg ⁻¹	├ ──┤											
I m	mg kg-1	4.05		2.10				2.04	2.00	5.00		2.00	2.04
	mg kg ⁻¹	4.05		3.18		2.8		3.24	3.28	5.38		3.29	3.24
V	mg kg ⁻¹	0.174		0.15		0.12		0.13	U.14				
vv	mg kg ⁻¹					0.010							
T Vh	mg kg ⁻¹	├ ───┤				0.016							
01	mg kg ⁻¹	0.00				0.0009							
Zn	mg kg-1	0.38		0.010		0.05				0.12			
∠r	mg kg ⁻¹	0.276		0.249		0.25				0.46			

Lab C		E51A	E51D	1	i								
	Jue	LUIA	LUID	-	-	-	-	-	-	-	-	-	_
SiO2	g 100g ⁻¹	0.668											
TiO2	g 100g-1												
AI2O3	g 100g-1	0.00068											
Fe2O3T	g 100g-1	0.088											
MaO	g 100g-1	1.21											
	a 100a-1	51.18											
Naco	g 100g	0.05											
Nazo	g roog .	0.05											
K2O	g 100g ⁻¹	0.0017											
P2O5	g 100g-1												
Ag	mg kg ⁻¹												
As	mg kg ⁻¹												
Au	mg kg ⁻¹												
B	ma ka-1	5 46											
Ba	ma ka-1	11.3											
Da	ing kg	11.5											
ве	mg kg⁻'												
Bi	mg kg ⁻¹												
Br	mg kg ⁻¹												
Ce	mg kg ⁻¹												
CI	mg kg-1												
Co	mg kg-1	0.17											
Cr	ma ka-1												
 Co	a **9												
CS	mg kg	4.07											
cu	mg kg ⁻¹	4.07											
Dy	mg kg ⁻¹												
Er	mg kg ⁻¹												
Eu	mg kg ⁻¹												
Ga	mg kg ⁻¹												
Gd	mg kg ⁻¹												
Go	ma ka-1												
	ma ka-1												
пі ··	iliy ky												
но	mg kg⁻'												
In	mg kg ⁻¹												
La	mg kg ⁻¹												
Li	mg kg ⁻¹												
Lu	mg kg ⁻¹												
Mn	mg kg ⁻¹	0.25											
Мо	mg kg ⁻¹												
Nb	ma ka-1												
Nd	ma ka-1												
Nu	ing kg	4.40											
NI	mg kg⁻'	1.13											
Pb	mg kg ⁻¹												
Pd	mg kg ⁻¹												
Pr	mg kg ⁻¹												
Rb	mg kg-1												
Re	mg kg-1												
s	mg kg-1			İ									
Sh	ma ka-1	<u> </u>											
80	ma ka-1	0 167											
0.	ing Ng	0.107											
Se	mg kg ⁻¹												
Sm	mg kg ⁻¹												
Sn	mg kg ⁻¹												
Sr	mg kg ⁻¹	661											
Та	mg kg ⁻¹												
Tb	mg kg-1												
Th	ma ka-1												
 TI	a **9												
	ing Kg '												
Im	mg kg-1												
U	mg kg-1	2.98											
v	mg kg-1	0.124											
w	mg kg-1												
Y	mg kg-1	0.018											
Yb	mg ka-1	-											
Zn	ma ka-1												
		0.077											
۲Ľ	mg kg ⁻¹	U.3//		1									

	Designated Value	Uncertainty of designated value	Horwitz Quality	Horwitz Target Precision	Uncertainty/ Target Precision	Number of reported results	Robust Mean of results	Robust SD of results	Median of results	Status of designated value	Type of designated value
	X _{pt}	u(<i>x_{pt}</i>)	k x 0.01	σ_{pt}	u(x _{pt})/σ _{pt}	п					
	g 100g-1	g 100g-1		g 100g-1			g 100g ⁻¹	g 100g-1	g 100g-1		
AI2O3	0.0007086	0.0000369	1	0.00004221	0.8741	15	0.000809	0.0002811	0.000732	Provisional	Mode
	mg kg⁻¹	mg kg-1		mg kg-1			mg kg-1	mg kg-1	mg kg-1		
As	1.513	0.04267	1	0.1137	0.3752	9	1.513	0.128	1.54	Provisional	Robust Mean
Ва	12.34	0.0902	1	0.676	0.1334	23	12.82	1.174	12.5	Assigned	Mode
Ce	0.007823	0.001021	1	0.001298	0.7865	11	0.00804	0.002579	0.007823	Provisional	Median
Cu	4.695	0.09224	1	0.2975	0.31	20	4.677	0.3357	4.695	Assigned	Median
Ga	0.024	0.00166	1	0.003365	0.4933	12	0.03058	0.01045	0.02795	Provisional	Mode
La	0.00354	0.00036	1	0.000662	0.5438	9	0.003882	0.00113	0.0039	Provisional	Mode
Li	0.135	0.00502	1	0.0146	0.3439	11	0.145	0.022	0.14	Provisional	Mode
Mn	0.261	0.012	1	0.02555	0.4696	17	0.2628	0.02969	0.267	Assigned	Mode
Ni	1.09	0.0604	1	0.08606	0.7018	21	1.278	0.4373	1.13	Provisional	Mode
Pb	0.02	0.00169	1	0.002882	0.5864	15	0.02767	0.01185	0.022	Provisional	Mode
Sr	717.7	10.49	1	21.34	0.4915	24	717.7	51.38	720.6	Assigned	Robust Mean
U	3.32	0.0442	1	0.2217	0.1994	23	3.405	0.3153	3.415	Assigned	Mode
v	0.151	0.005068	1	0.01605	0.3157	21	0.1541	0.02165	0.151	Assigned	Median
Y	0.016	0.0009013	1	0.002385	0.378	17	0.01716	0.003665	0.016	Assigned	Median
Zr	0.2435	0.00379	1	0.02409	0.1573	21	0.2533	0.02294	0.249	Assigned	Mode

Table 3 - G-Probe 25b Z-scores for Calcitic speleothem	, KCSp-1NP	Pellet. 06/10/2027
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Lab Code	E2	E3	E5	E8	E11	E13	E14	E15	E16	E22	E23	E24	E25
AI2O3: 1	*	*	17.56	-4.09	0.49	0.74	*	-0.68	*	6.90	-1.63	*	220.11
As: 1	*	*	*	-0.38	0.37	-1.88	*	-1.18	0.23	*	*	*	*
Ba: 1	0.32	-0.50	1.97	-0.20	0.07	-0.02	-1.16	1.72	0.39	14.80	-0.11	*	30.13
Ce: 1	1.68	0.14	*	-1.45	0.00	*	*	-1.36	-1.10	109.50	-1.40	*	155.71
Cu: 1	1.06	0.82	0.24	-0.71	-0.48	-4.22	-0.39	0.88	0.12	*	*	*	28.58
Ga: 1	-1.19	*	*	-0.98	-0.33	*	*	1.16	1.19	4.16	-0.30	*	361.36
La: 1	*	0.69	*	-0.79	-0.70	*	*	-0.42	0.54	2.96	*	*	236.33
Li: 1	*	*	*	-1.19	-0.12	*	*	-0.31	-0.34	4.11	*	*	*
Mn: 1	-0.43	*	*	-0.80	1.16	0.35	-0.55	0.51	-1.60	*	0.23	*	-10.18
Ni: 1	-1.74	2.21	9.82	-2.04	-1.07	-0.58	1.01	*	3.60	8.97	1.44	*	67.40
Pb: 1	0.00	12.14	2.43	-1.04	0.26	5.55	*	-0.45	*	3.99	*	*	79.80
Sr: 1	1.53	-3.60	0.95	-2.89	-1.12	0.29	-2.66	1.01	0.20	23.81	0.10	-1.56	852.13
U: 1	1.13	0.45	0.63	-1.19	-0.56	0.36	-1.03	0.53	1.31	14.49	0.43	*	19.35
V: 1	0.56	0.62	7.41	-1.28	-0.22	-1.12	-0.06	0.78	0.56	9.16	0.00	*	228.56
Y: 1	1.68	0.42	*	-0.24	2.74	-1.26	0.84	1.28	0.00	5.24	0.00	*	186.20
Zr: 1	0.68	0.10	-0.10	-0.56	0.06	-0.15	-0.48	0.89	0.27	7.29	-0.44	*	34.72

Table 3 - G-Probe 25b Z-scores for Calcitic speleothem	, KCSp-1NP Pellet.	06/10/2021
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Lab Code	E26	E31	E32	E35	E40	E41	E42	E43	E45	E46	E50	E51	
AI2O3: 1	*	*	0.55	220.11	-15.53	1.22	-0.49	3.82	*	*	*	-0.68	
As: 1	-0.56	0.85	*	*	*	0.67	*	*	*	3.22	*	*	
Ba: 1	-0.07	0.24	1.58	*	0.56	2.02	-0.20	-4.25	3.91	22.51	0.02	-1.53	
Ce: 1	*	*	0.91	*	*	*	*	-1.87	*	*	*	*	
Cu: 1	0.49	-0.12	0.77	*	0.40	1.36	-0.72	-3.01	-0.32	*	-0.99	-2.10	
Ga: 1	1.78	0.00	*	*	*	*	*	33.88	*	4.75	*	*	
La: 1	*	*	0.69	*	*	*	*	-1.42	*	*	*	*	
Li: 1	0.00	2.19	0.34	*	0.75	11.30	*	*	*	0.34	*	*	
Mn: 1	*	*	1.13	2729.23	0.48	8.18	-0.94	-0.43	0.55	*	*	-0.43	
Ni: 1	0.00	-0.81	-1.05	870.45	*	-1.05	1.51	-4.65	*	24.87	0.35	0.46	
Pb: 1	*	14.57	-0.35	*	-1.64	3.47	0.52	0.69	*	*	*	*	
Sr: 1	-0.68	1.42	0.90	*	0.17	-0.32	-1.53	-3.13	3.14	39.41	-0.40	-2.66	
U: 1	0.92	0.45	-0.45	*	0.23	3.29	-0.63	-2.35	-0.27	9.29	-0.25	-1.53	
V: 1	1.18	-0.19	-0.62	*	0.35	1.43	-0.06	-1.93	-1.00	*	*	-1.68	
Y: 1	-2.52	-0.84	-0.42	*	-0.54	*	*	0.00	*	*	*	0.84	
Zr: 1	0.27	-0.73	-0.06	*	-0.40	1.35	0.23	0.27	*	8.99	*	5.54	







Figure 1: G-Probe 25b - Calcitic speleothem, KCSp-1NP Pellet. Data distribution charts for elements for which values were assigned or provisional values given for guidance. Horizontal lines show the limits for -2<z<2 where the z-score is derived according to the Quality specified.



















Figure 2: G-Probe 25b - Calcitic speleothem, KCSp-1NP Pellet. Data distribution charts provided for information only for elements for which values could not be credited with assigned or provisional status.



Figure 3: G-Probe 25b - Calcitic speleothem, KCSp-1NP Pellet. Multiple z-score charts for laboratories participating in the G-Probe 25b round. Symbols indicate whether or not an elemental result complies with the -2<z+2 criteria (see key).