

G-Probe 28 – an International Proficiency Test for Microanalytical Laboratories Report on Round 28 (Fossil coral, KCp-1NP, Nano-particulate powder pellet) / January 2024

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Abstract

Results are presented for Round 28 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 a fossil coral from the Chagos Archipelago, prepared as a nano-particulate powder pellet, KCp-1NP, at Kiel University. In this report, the data contributed by 27 laboratories are listed, together with an assessment of consensus values as composition location estimators, consequent z-scores, and a series of charts showing the distribution of contributed results that reveal the overall performance of participating laboratories. Assigned values were conferred for 5 elements, and provisional values for a further 10 out of 63 elements reported. To assist in the future characterisation of materials of this type, the mass fraction ranges within which the true values are expected to lie are listed for a further 13 elements. However, insufficient numbers of results were reported for a further 35 elements for their status to be assessed.

Introduction

This twenty-eighth 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 conforms with the published G-Probe Protocol (IAG, 2020).

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 this 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), P.C. Webb (results coordinator and website administrator),
P.J. Potts (results reviewer), M. Thompson (statistical advisor), C.J.B. Gowing (distribution coordinator),
L. Danyushevsky, R. Mertz-Kraus and A. Kronz (analytical advisors).

Timetable for Round 28 of G-Probe:

Distribution of test material: March 2023 Results submission deadline: 6th September 2023 Release of report: January 2024

G-Probe 28 test material details

The starting material for this test sample originated from a fossil coral boulder collected from Eagle Island in the Chagos Archipelago (Sample E5 in Leupold et al., 2021). A section of the fossil Porites sp. was cut as a flat slice and further characterized by SEM and 2-D XRD to avoid regions with secondary diagenetic overprint. U/Th dating revealed ages around 1700 AD. A sub-sample was then further processed with thorough cleaning with dilute hydrogen peroxide and ultrapure water. A total of ~180 grams of original material was ultra-milled in 22, 14, and 14 individual batches of 3 - 4 g, using a high-energy ball mill (Fritsch Pulverisette 7 Premium) furnished with agate milling gear. The resulting batches were unified as slurries, re-homogenized by shaking, and freeze-dried. The dry nano-particulate powder was re-homogenized and then pelletized to tablets of 13 mm OD. Details of the procedure are outlined in Garbe-Schönberg and Müller (2014).

For homogeneity testing following the IAG G-Probe Protocol (IAG, 2020), 10 pellets were analysed with 10 points per pellet by LA-ICP-MS at 60 µm spot size to assess both within-pellet and between-pellet heterogeneity. After careful assessment of all homogeneity data, the KCp-1NP nano-particulate powder pellets were considered suitable for use as test materials. However, participants should not assume that their individual pellet is sufficiently homogeneous for their particular analytical procedure. A material can be sufficiently homogeneous at the selected beam size / spatial resolution for some analytes and not for others. Participants were alerted to the fact that nanoparticulate materials are hygroscopic and were advised to store the pellet in a desiccator and/or under vacuum.

Submission of results

For G-Probe 28, participants were instructed to apply their routine measurement procedures to provide one measurement result per analyte for the nanoparticulate powder pellet representative of its average composition (Result A), however, 5 laboratories provided two measurements, results A and B.

A total of 701 measurement results, submitted by 27 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 584 individual values reported for 63 analytes, 547 values were by LA-ICP-MS from 24 laboratories, 6 by EPMA from two laboratories, 3 by μ -XRF from one laboratory and 28 by an unspecified method by two laboratories.

Note that the automated output captions provided for Tables 1 and 2, and Figures 1, 2 and 3, refer to this round as G-Probe 28z to distinguish the data handling employed in this round where only CaO is quoted as an oxide mass fraction in g/100 g. Other 'major' elements usually reported as oxides are quoted in this round in elemental form in terms of mg/kg.

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 for each dataset of the Huber robust mean, the median or a mode derived from a kernel density distribution as detailed by Thompson (2017). Evaluations of 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 of sigmoidal plots gave confidence that a substantial proportion of the results from which the consensus was estimated 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 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'.

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. By far the majority of results were obtained by LA-ICP-MS, and for a limited number of elements by EPMA and μ -XRF.

For most 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 in principle 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 are, therefore, 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 J1, J28, J31, J41, J51, J57, J62 and J63 were provided with information that the CaO content should be about 56 g/100 g. 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.

Table 2 lists assigned and provisional values for one major component (CaO) and 14 trace elements in G-Probe 28 (KCp-1NP). Data distribution charts for these 15 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: CaO*, B*, Ba, Ce*, Co*, Cu, Li*, Mg*, Mn*, Na*, Pb, Sr, U, V* and Y*. Of these, values of the 10 analytes marked '*' were credited with provisional status for reasons given above.

Data distribution plots for the 26 analytes: Al, As, Be, Cd, Cr, Cs, Dy, Er, Fe, Ga, K, La, Mo, Nb, Nd, Ni, P, Pr, Rb, Sc, Si. Sn, Ti, W, Zn and Zr are plotted in Figure 2 for information only, as the data were either insufficient in number, or the data distribution were too highly dispersed or too highly skewed for the confident estimation of a consensus for provision of *z*-scores. Ranges within which values of some of these elements are most likely to occur are given in supplementary Table 0.1 for reasons outlined below.

Observations

In evaluating the overall performance of measurement results submitted to this G-Probe 28 round, remarkably coherent results are noted for Ba, Cu and U, with slightly less well aligned data for Pb and Sr. In addition, a substantial proportion of coherent results were provided for Ca, Ce, Mg, V and Y. However, data distributions of Co and Li were more difficult to assess as their form is bimodal with no criteria for judging which mode (or neither) would provide the most useful estimate. As a result, only provisional status could be conferred. With particular reference to measurement results for calcium, it is noteworthy that four laboratories provided values that are clear outliers, almost certainly because they reported Ca data in the form of CaCO₃ values rather than CaO as requested.

Data distributions for many other elements are disappointing, either because insufficient numbers of results were reported or their distribution lacks a clearly identifiable consensus. In these circumstances, it is not possible to provide a consensus estimator using the normal G-Probe criteria. Accepting that the microanalysis of carbonates is a challenging and developing area of endeavour, data in Table 0.1 provides guidance as to the compositional range within which the true value of each of these measurands is thought most likely to fall, noting that significant further work would be required to confirm this proposition.

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 (X) from:

$z = [X - X_a] / H_a$

where X_a is the target value (assigned or provisional) and H_a is the target precision (all as mass fractions).

Z-score values for results submitted to G-Probe 28 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.

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 GP-25b (speleothem KCSp-1NP). This is a strategy for presenting materials that cannot be prepared as homogenous glasses or minerals. However, powder pellets are characterized by some porosity and moisture content and cannot be polished with wet polishing techniques. This may represent challenges for measurements by EPMA and SEM.

Participation in future rounds

The benefit from proficiency testing arises from regular participation and laboratories are invited to contribute to Rounds 29 (Mica glass) and 30 (Limestone) of G-Probe, the test samples for which will be distributed in spring 2024.

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APPENDIX

Table 0.1 Ranges within which true values are thought most likely to fall for analytes that were reported in insufficient numbers or results were generally too variably disposed for formal assessment of assigned or provisional values.

	Lower limit of probable value (mg kg ⁻¹)	Upper limit of probable value (mg kg ⁻¹)	Number of laboratories reporting
AI	4.9	8.5	17
Cr	0.52	1.7	19
Ga	0.016	0.28	8
к	82	140	15
La	0.0035	0.01	10
Ni	0.22	0.57	17
Р	10	32	12
Rb	0.14	0.44	18
Si	2200	3900	20
Sn	0.12	0.33	7
Ті	0.3	0.55	10
Zn	0.39	1.2	13
Zr	0.006	0.1	10

Lab Q		11.6	14 12	12.4	128	110.0	1108	111.0	144 B	1154	1150	121 A	1248
Lab Co		JIA	318	JJA	338	50.0	3108	52.5	JIIB	JIJA	3136	321A	J21B
CaU	g 100g-'			00		53.6		53.5		95		0.00	87.06
Ag	mg kg ⁻¹												
AI	mg kg ⁻¹					6.01		5.687				1994.32	2005.84
As	mg kg ⁻¹					0.357							
В	mg kg ⁻¹							48.742		52.1			
Ва	mg kg ⁻¹	6.01		6.23		5.98		5.572		10.9		496.58	489.75
Be	mg kg ⁻¹	0.17											
Bi	mg kg-1												
Cd	mg kg ⁻¹					0.014							
Ce	mg kg ⁻¹	0.063				0.0086		0.104					
CI	ma ka-1											2409 45	2492 51
C.	ma ka-1	0.45				0.303		0.411		0.5		2100110	2102.01
Cr.	ma ka-1	1.64				0.000		1 505		1.37		1630.45	1508.87
	mg kg-1	0.03				0.741		0.005		1.07		1030.43	1330.07
CS	ilig kg	0.03				10		0.095					
Cu	mg kg ^{-,}	1.5				1.3		1.20					
Dy	mg kg ⁻¹	0.021				0.0018							
Er	mg kg ⁻¹	0.013				0.0013							
Eu	mg kg ⁻¹	0.031						0.116					
F	mg kg ⁻¹												
Fe	mg kg ⁻¹					31.4				147		8505.76	9140.42
Ga	mg kg ⁻¹	0.07						0.281				2.11	2.34
Gd	mg kg ⁻¹	0.021						0.386					
Ge	mg kg ⁻¹							0.493					
Hf	mg kg ⁻¹	0.02						0.307					
Но	mg kg ⁻¹	0.013						0.07					
In	mg kg-1												
к	mg kg ⁻¹	123		6.1		95.4		113.65		218		536.41	498.64
La	mg kg ⁻¹	0.047				0.0045		0.078					
11	ma ka-1	0.65		0.57		0.514		0.79		1.6			
1.0	ma ka-1	0.013						0.061					
Ma	ma ka ⁻¹			01/1 37		1079		930.24		1663		2840.53	2031.85
Mn	ma ka-1	1.04		014.07		0.472		0.487		1000	-	72.33	79.12
Mo	ma ka-1	0.07				0.972		0.407				72.55	73.12
No	ma ka-1	3955		1113.3		4611				7/17			
Na	ing kg	3033		4443.3		4011				7417			
ND	mg kg	0.04				0.0007							
Na	mg kg	0.035				0.0037		0.702				00.47	10.04
	mg kg ⁻ '	0.93				0.280		0.793				20.47	18.34
Р	mg kg ⁻¹	71				11.67		28.991					
Pb	mg kg ⁻¹	0.12		0.12		0.095		0.234					
Pr	mg kg ⁻¹	0.032											
Rb	mg kg ⁻¹	0.44				0.178				0.67		1.09	1.11
Rh	mg kg ⁻¹												
s	mg kg ⁻¹											4113.48	4182.94
Sb	mg kg ⁻¹												
Sc	mg kg ⁻¹	0.21											
Si	mg kg-1	3830		1473		2800				9405			
Sm	mg kg ⁻¹	0.045											
Sn	mg kg ⁻¹					0.136							
Sr	mg kg ⁻¹	7193		7371.8		7948		7411.331		13758	1	5706.91	5576.49
Та	mg kg ⁻¹	0.03											
ТЬ	ma ka-1	0.016											
Те	ma ka-1												
ть	ma ka-1	0.01											
т:	ma ka-1	0.01				0 202		2 204				12 05	44.07
	mg kg 1	0.04				0.302		2.204				42.00	44.27
	mg Kg ⁻	0.01											
Im	mg kg ⁻¹	0.012		L	L						ļ	ļ	
U	mg kg ⁻¹	2.5		ļ	ļ	2.26		2.516		4.27	ļ		
v	mg kg ⁻¹					0.058		0.124				5.64	5.98
w	mg kg ⁻¹	0.07				0.0088							
Y	mg kg ⁻¹	0.095				0.034		0.087				1.22	1.32
Yb	mg kg ⁻¹	0.02				0.0011							
Zn	mg kg ⁻¹	1.12				0.537		1.478				2.97	2.95
Zr	mg kg ⁻¹	0.39										2128.41	2058.14

Lab Co	odo	.1224	.122B	.1234	.123B	.1284	.128B	.131A	.131B	.1324	.132B	.1334	.133B
	5ue	522A	54.7	06.24	3230	3204	3200	551A	3315	552A	5525	5554	3335
CaO	g 100g-'	94.7	54.7	96.34				55.4		55.50631534	55.69911562	55	
Ag	mg kg ⁻¹									0.0198	0.0169		
AI	mg kg ⁻¹					8.273492244		0.34		8.60032139	8.221391817		
As	mg kg ⁻¹					0.0829				0.128811606	0.0738		
В	mg kg ⁻¹	42.1	39.6			47.20288429				48.17333462	48.50892627		
Ва	mg kg ⁻¹	5.75	5.73	9.58		5.971136898		4.66		5.467621242	5.527265378	5.72	
Be	mg kg ⁻¹	2.04	1.68							0.011	0.0025		
Bi	ma ka-1									0.00072	0.0011		
C4	ma ka-1									0.0106	0.0104		
Cu Cu	mg kg			0.01		0.00000				0.0100	0.0194		
Ce	mg kg			0.01		0.00889				0.00982	0.00999		
CI	mg kg ⁻¹												
Co	mg kg ⁻¹	0.933	1.37	0.6		0.325748476				0.416717672	0.415774087		
Cr	mg kg ⁻¹	2.22	4.04	5.52		1.626370308		0.55		2.283505848	2.249627865		
Cs	mg kg ⁻¹									0.00726			
Cu	mg kg ⁻¹	1.33	1.42	5.17		1.376190083				1.562352101	1.56488677	1.04	
Dy	mg kg ⁻¹									0.00728	0.00128		
Er	mg kg ⁻¹									0.00293			
Eu	mg kg ⁻¹												
F	ma ka-1							42.6		133 7248946	172 7218307		
	ma ka-1			60.96		66 31227059		200		31 58226207	31 48312522	81.0	
C -	ing Ng			00.00		00.31227038		209	L	0.040	0.0470	01.9	
Ga	mg kg ⁻¹					├ ───┤				0.016	0.0172		
Gd	mg kg ⁻¹												
Ge	mg kg ⁻¹									0.036	0.0151		
Hf	mg kg ⁻¹												
Но	mg kg ⁻¹												
In	mg kg ⁻¹									0.00147	0.00119		
к	mg kg ⁻¹			137.51		117.9097953		1.39		106.8922209	107.785063		
La	mg kg ⁻¹	0.007	0.008	0.01		0.00522				0.0051	0.00486		
11	ma ka-1	0.359	0 201	0.61		0.61874626				0 594601055	0 617484732	0.47	
<u>-</u>	ma ka-1	0.000	0.201	0.01		0.01011020				0.001001000	0.011101102	0.11	
Lu Ma	mg kg			1004		4057.000407		1001		770 0000000	004.0450470	001	
Mg	ing kg			1004		1037.002427		1001		772.9620060	024.0155476	921	
Mn	mg kg⁻'			0.89		0.537825252		10.9		0.621802974	0.529355348		
Мо	mg kg ⁻¹									0.0332	0.0382		
Na	mg kg ⁻¹			7002		4073.865733				3794.07721	3996.545192	2770	
Nb	mg kg ⁻¹									0.0038	0.00393		
Nd	mg kg ⁻¹									0.00475	0.00627		
Ni	mg kg ⁻¹	0.776	0.349	13.89		0.282512634				0.379241122	0.365168989	0.4	
Р	mg kg ⁻¹			31.65		27.92259807				9.739298775	11.52274955		
Pb	mg kg ⁻¹	0.079	0.1			0.108652526				0.10383022	0.100471834	0.076	
Pr	ma ka-1		-			0.00115				0.000768	0.00148		
Ph	ma ka-1	0 144	0.163	0.26		0.333386215				0 371385647	0.372309047	0.27	
Dh.	ma hart	0.144	0.100	0.20		0.000000210				0.0225	0.0207	0.21	
Rii	ing Kg							045		0.0333	0.0307		
8	mg kg ⁻ '							940					
Sb	mg kg ⁻¹									0.0121	0.00838		
Sc	mg kg ⁻¹					0.0244				0.0774	0.0845		
Si	mg kg-1	2993	2884	4268		3117.446463		410		2715.948949	2787.899862	2202	
Sm	mg kg ⁻¹									0.000903	0.00000273		
Sn	mg kg-1									0.147775176	0.153629559		
Sr	mg kg ⁻¹	7338	7312	12561		7912.399714		232		7442.881955	7427.048503	7739	
Та	mg kg-1									0.00111	0.00161		
ть	mg kg ⁻¹												
Те	ma ka-1									0.017	0.00316		
ть	ma ka-1									0.01	0.0013		
т:	mg lumi					0.41004005				0.001	0.0013		
	mg Kg ⁻ '		L			0.41094805				0.302991001	0.345057346		<u> </u>
<u> </u>	mg kg ⁻¹					↓ ↓				0.00386	0.00148		
Tm	mg kg-1					ļļ							
U	mg kg-1	2.25	2.28	3.64		2.529144865		0.82		2.519326387	2.499182802	1.97	
v	mg kg-1	0.069	0.067	0.1		0.0607				0.0661	0.0641		
w	mg kg-1									0.0142	0.0155		
Y	mg kg-1			0.23		0.0422				0.0453	0.0422	0.038	
Yb	mg kg-1					1 1							
Zn	ma ka-1	0.812	0.921			0.548334811				0 558715236	0 555955927	0.39	
7.	ma ka-1	0.012	0.021	0.1		0.00033				0.00084	0.00005	0.00	
1 <u>4</u> 1	ing Ng			0.1		0.00933				0.00904	0.00900		

		19.44	10.45	105.4	1055	107.4	1070		1405	144.4	1445	1.00	1405
Lab Co	ode	J34A	J34B	J35A	J35B	J3/A	J3/B	J40A	J40B	J41A	J41B	J46A	J46B
CaO	g 100g ⁻¹	54.298		56		54.251		95.63					
Ag	mg kg ⁻¹					0.019							
AI	mg kg ⁻¹	4.9395		5		7.488				8.425		7.214	
As	mg kg ⁻¹					0.061				0.124			
P	ma ka-1					26.748		63.1		45.93		30.44	
B	ing ing	5 0202		0.05		5 002		00.1		40.005		5.552	
Ва	mg kg ⁻¹	5.8393		6.05		5.893		11		6.025		5.553	
Be	mg kg ⁻¹					0.022							
Bi	mg kg ⁻¹												
Cd	mg kg ⁻¹					0.015							
Ce	mg kg ⁻¹	0.0064				0.012				0.011			
CI	ma ka-1												
0.		0.4454		0.21		0.202				0.426		0.471	
C0	iliy ky	0.4434		0.31		0.302				0.420		0.471	
Cr	mg kg ⁻¹	1.0236				0.701				0.577		0.523	
Cs	mg kg ⁻¹					0.002							
Cu	mg kg ⁻¹	1.4112		1.34		1.399				1.452		1.552	
Dy	mg kg ⁻¹												
Fr	ma ka-1												
Eu	ma ka-1												
	ma lund											<u> </u>	
	mg Kg ⁻											l	
Fe	mg kg-1	0.5153		83.13		46.331		1199		30.14		ļ	
Ga	mg kg-1			0.24		0.016				0.018			
Gd	mg kg-1												
Ge	mg kg ⁻¹												
Hf	mg kg ⁻¹												
Но	ma ka-1												
	mg kg												
In	mg kg ·											ļ	
к	mg kg ⁻¹	97.051		92.93		112.527							
La	mg kg ⁻¹	0.0045											
Li	mg kg ⁻¹	0.4166		0.42		0.634		0.7		0.61		0.573	
Lu	mg kg ⁻¹												
Ma	ma ka-1	849 24		932 75		936 977		1492		947 4		866.3	
Mp	ma ka-1	0.3064		002.10		0.564		1102		0.556		0.402	
Ma	mg kg	0.3304				0.004				0.000		0.432	
MO	mg kg ^{-,}					0.024							
Na	mg kg ⁻¹	4014.4		4432.16		4016.857		7166					
Nb	mg kg ⁻¹												
Nd	mg kg ⁻¹												
Ni	mg kg ⁻¹	1.357		0.22		0.28				0.389		0.523	
Р	mg kg ⁻¹	53.855				14.53				16.91		13.59	
Ph	ma ka-1	0.0863		0.1		0 109		0.13		0 118		0.109	
D-		0.0000		0.1		0.100		0.10		0.110		0.100	
	iliy ky	0.4050		0.45		0.07						0.075	
Rb	mg kg ⁻¹	0.1656		0.15		0.37				0.36		0.375	
Rh	mg kg ⁻¹												
S	mg kg ⁻¹	817.69											
Sb	mg kg-1	0.1173				0.014							
Sc	mg kg-1					0.029							
Si	mg kg-1	2409.9		2843.17		2731.548		5095		3727.5		İ	
Sm	ma ka-1											<u> </u>	
0	ma lund					0.247						<u> </u>	
	ing Kg 1	7000 0		7000 50		0.247		47704		7005 1	ļ	7407	ļ
Sr	mg kg ⁻¹	7663.6		7930.58		7618.503		1794		7985.1		/427	
Та	mg kg ⁻¹												
Tb	mg kg-1												
Te	mg kg-1												
Th	mg kg-1											1	
ті	ma ka-1					0.53/				0.48		0.533	
т.	maluert					0.004				0.40		0.000	
<u> </u>	ing Kg 1	ļ									ļ	<u> </u>	ļ
Im	mg kg-1											ļ	
U	mg kg-1	2.1728		2.46		2.309		4		2.466		2.295	
v	mg kg-1					0.064				0.068			
w	mg kg-1					0.024							
Y	mg ka-1	0.0325				0.039		1		0.041		1	
vh.	ma ka-1	0.0020				0.000				0.071		<u> </u>	
7-	ing Ng	0 7000				0.510				0.057		 	
Zn	mg kg-1	0.7002				0.516				0.657		L	
Zr	mg kg ⁻¹					0.013				0.017	1	I	1

		154.4	1540	1544	1540	1574	1670	150.4	1500	150.4	ICOD	100.4	ICOD
Lab Co	ode	J51A	J51B	J54A	J54B	J5/A	J5/B	J58A	J28B	J59A	128B	J60A	J60B
CaO	g 100g-1							54.4	54.11	53.42		54.412	54.194
Ag	mg kg ⁻¹									0.0229			
AI	mg kg ⁻¹	11.129		5.01		5.32		16.2	16.6	4.947			
As	mg kg ⁻¹												
В	mg kg ⁻¹			40.34		55.7		32.9	34.5	44.87			
Ва	mg kg ⁻¹	5.855		5.78		4.85		5.8	5.66	5.248			
Be	ma ka-1									0.00695			
Bi	ma ka ⁻¹												
C4	ma ka-1									0.1299			
Co	ma ka-1			0.006				0.012	0.022	0.0091			
Ce Cl	mg kg			0.000				0.013	0.022	0.0001			
	ing kg	0.4050		0.00				0.740	0.070	223.0			
0	mg kg ·	0.4959		0.29				0.718	0.676	0.3164			
Cr	mg kg ⁻¹	3.155		0.69				2.87	3.32	0.7104			
Cs	mg kg ⁻¹									0.00164			
Cu	mg kg ⁻¹	1.446		1.24				3.89	3.39	1.298			
Dy	mg kg ⁻¹									0.00153			
Er	mg kg ⁻¹									0.00113			
Eu	mg kg ⁻¹									0.00031			
F	mg kg-1												
Fe	mg kg ⁻¹	552.768		40.4				2050	1879	22.46		95.4	143.3
Ga	mg kg-1			0.68									
Gd	mg kg ⁻¹												
Ge	mg kg ⁻¹												
Hf	ma ka-1												
Но	ma ka-1									0.000342			
In	ma ka ⁻¹									0.000042			
	ma ka ⁻¹							323	205	82.47			
	ma ka-1			0.0035				323	233	0.00408			
La	nig kg	0 4121		0.0033		0.4291				0.00408			
LI	mg kg	0.4131		0.43		0.4201				0.4179			
LU	mg kg ⁻ '	4000.004							050	0.000091			740.0
Mg	mg kg ⁻¹	1003.684		992		888		934	953	927.8		614	/12.8
Mn	mg kg ⁻¹					0.3689		0.753	0.719	0.3855		153.1	134.8
Мо	mg kg ⁻¹									0.0211			
Na	mg kg ⁻¹	4253.879		3827				4364	4378	3919			
Nb	mg kg ⁻¹			0.00156						0.00131			
Nd	mg kg ⁻¹									0.00362			
Ni	mg kg ⁻¹			0.25				11.5	9	0.3544			
Р	mg kg ⁻¹	28.239						26.7	27.2				
Pb	mg kg ⁻¹			0.1		0.0982		0.836	0.668	0.0863			
Pr	mg kg ⁻¹									0.000803			
Rb	mg kg ⁻¹			0.16				0.428	0.404	0.141			
Rh	mg kg ⁻¹												
s	mg kg ⁻¹												
Sh	ma ka ⁻¹												
Sc	ma ka-1							0.652	0.575				
si	ma ka-1	2730 201		2774				4771	4882	3640			
Sm	ma ka-1	2100.201		2114						0.000855			
0.11 0.1	mg lung			0.40				1.00	0.70	0.000000			
31	ing Kg	7075 500		0.12		7004		1.00	0.79	0.2400		5744.0	E750
ər	rng kg"	10/5.502		0/49		/021		/612	7693	/21/		5/44.2	5750
Та	mg kg ⁻¹												
Tb	mg kg ⁻¹									0.000187			
Te	mg kg ⁻¹												
Th	mg kg ⁻¹									0.00033			
Ті	mg kg ⁻¹	1.283								0.304			
ТІ	mg kg ⁻¹												
Tm	mg kg-1									0.000102			
U	mg kg-1	2.441		2.39		2.41		2.34	2.26	2.162			
v	mg kg ⁻¹			0.05						0.0526			
w	mg kg-1									0.0081			
Y	mg ka-1	0.049		0.044				0.139	0.126	0.0387			
Yh	ma ka-1	5.0.0	-	5.5.4				550	520	0.00082			
7n	ma ka-1							3 75	37	0.86460			
7.	ma ka-1	<u> </u>		0.0076				0.102	0.025	0.00403			
1 <u>~</u> 1	ing Ng		1	0.0070				0.102	0.030	0.00021		1	

Lab C	odo	.1624	.162B	.1634	.163B	.1644	.164B	i .		_		_	_
Lab Co	50e	502A	3020	303A	3036	304A	3040	-	-	-	-	-	-
CaU	g toog	34.5											
Ag	mg kg ⁻¹	0.00											
AI	mg kg ⁻¹	6.09											
As	mg kg ⁻¹												
В	mg kg ⁻¹	45.08				35.2							
Ва	mg kg ⁻¹	5.89				6.21							
Be	mg kg ⁻¹												
Bi	mg kg-1												
Cd	mg kg ⁻¹												
Ce	mg kg ⁻¹												
CI	mg kg ⁻¹												
Co	mg kg ⁻¹												
Cr	mg kg ⁻¹	3.9											
Cs	mg kg ⁻¹												
Cu	mg kg ⁻¹	1.35				1.48							
Dy	mg kg ⁻¹												
Er	mg kg ⁻¹												
Eu	mg kg ⁻¹												
F	mg kg ⁻¹												
Fe	mg kg ⁻¹												
Ga	ma ka-1												
Gd	ma ka-1												
Gu	mg kg-1												
Ge	ing kg												
HT	mg kg 1												
но	mg kg												
In	mg kg ⁻¹												
ĸ	mg kg ⁻¹												
La	mg kg ⁻¹												
Li	mg kg ⁻¹			0.379		0.6							
Lu	mg kg ⁻¹												
Mg	mg kg-1	888.18		1044.7		856							
Mn	mg kg-1			0.552									
Мо	mg kg ⁻¹												
Na	mg kg ⁻¹	3666.37											
Nb	mg kg ⁻¹												
Nd	mg kg-1												
Ni	mg kg-1												
Р	mg kg ⁻¹												
Pb	mg kg ⁻¹	0.1		0.084		0.1							
Pr	mg kg ⁻¹												
Rb	mg kg ⁻¹					0.342							
Rh	mg kg ⁻¹												
s	ma ka-1												
Sb	mg ka-1												
Sc	mg ka-1												
Si	mg ka-1			2195.1									
Sm	ma ka-1			2.00.1									
Sn	ma ka-1	033											
e.	9 N9	7505.05		7083 /		7200							
та Та	ma ka-1	1000.00		1000.4		1200							
	ma ka-1					-							
10 To	mg Kg ⁻¹												
10	mg kg=1												
I N	mg kg ⁻¹												
<u>n</u>	mg kg-1												
П	mg kg-1												
Tm	mg kg-1												
U	mg kg ⁻¹	2.42		1.804		2.53							
v	mg kg ⁻¹												
w	mg kg-1												
Y	mg kg-1	0.04		0.041									
Yb	mg kg-1												
Zn	mg kg-1												
Zr	mg kg-1												
L													

Table 2 - G-Probe 28z Designated	values and statistical summary	for Fossil Coral, KCp-1NP Pellet.

	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		
CaO	54.3	0.295	1	0.5953	0.4955	18	55.49	2.004	54.85	Provisional	Mode
	mg kg ⁻¹	mg kg-1		mg kg-1			mg kg-1	mg kg-1	mg kg-1		
в	45.08	2.274	1	2.033	1.119	15	44.42	8.224	45.08	Provisional	Median
Ва	5.89	0.06318	1	0.3608	0.1751	25	5.902	0.4483	5.89	Assigned	Median
Ce	0.009576	0.00119	1	0.001542	0.7718	12	0.01133	0.004961	0.009951	Provisional	Mode
Co	0.426	0.04518	1	0.03874	1.166	17	0.4286	0.1222	0.426	Provisional	Median
Cu	1.399	0.0422	1	0.1064	0.3967	19	1.41	0.1327	1.399	Assigned	Median
Li	0.5402	0.02882	1	0.0474	0.6081	22	0.5402	0.1352	0.5715	Provisional	Robust Mean
Mg	930.2	13.8	1	26.6	0.5189	25	965.7	119.1	937	Provisional	Mode
Mn	0.486	0.0393	1	0.04333	0.907	17	0.6745	0.3089	0.556	Provisional	Mode
Na	4074	133.9	1	93.26	1.436	17	4229	531.9	4074	Provisional	Median
Pb	0.1	0.004258	1	0.01131	0.3764	21	0.1046	0.01739	0.1	Assigned	Median
Sr	7435	108.7	1	155.5	0.6993	27	7479	542.9	7435	Assigned	Median
U	2.415	0.04362	1	0.1692	0.2579	24	2.385	0.2171	2.415	Assigned	Median
v	0.063	0.00384	1	0.007639	0.5027	11	0.073	0.02353	0.06512	Provisional	Mode
Y	0.041	0.0015	1	0.005303	0.2828	17	0.0573	0.03046	0.04218	Provisional	Mode

Lab Code	J1	J3	J10	J11	J15	J21	J22	J23	J28	J31	J32	J33	J34
CaO: 1	*	2.85	-1.18	-1.35	68.36	53.80	0.67	70.61	*	1.84	2.18	1.17	-0.01
B: 1	*	*	*	1.80	3.45	*	-2.08	*	1.04	*	1.60	*	*
Ba: 1	0.33	0.94	0.25	-0.88	13.89	1350.71	-0.42	10.23	0.22	-3.41	-1.09	-0.47	-0.14
Ce: 1	34.65	*	-0.63	61.24	*	*	*	0.28	-0.44	*	0.21	*	-2.06
Co: 1	0.62	*	-3.17	-0.39	1.91	*	18.73	4.49	-2.59	*	-0.25	*	0.50
Cu: 1	0.95	*	-0.93	-1.12	*	*	-0.23	35.45	-0.21	*	1.55	-3.37	0.11
Li: 1	2.32	0.63	-0.55	5.27	22.36	*	-5.49	1.47	1.66	*	1.39	-1.48	-2.61
Mg: 1	*	-0.60	5.59	0.00	27.55	73.54	*	27.59	4.77	2.66	-4.94	-0.35	-3.05
Mn: 1	12.79	*	-0.32	0.02	*	1736.41	*	9.32	1.20	240.34	2.07	*	-2.07
Na: 1	-2.35	3.96	5.76	*	35.85	*	*	31.40	0.00	*	-1.91	-13.98	-0.64
Pb: 1	1.77	1.77	-0.44	11.85	*	*	-0.93	*	0.76	*	0.19	-2.12	-1.21
Sr: 1	-1.56	-0.41	3.30	-0.15	40.67	-11.53	-0.71	32.97	3.07	-46.33	-0.00	1.96	1.47
U: 1	0.50	*	-0.92	0.60	10.97	*	-0.89	7.24	0.67	-9.43	0.56	-2.63	-1.43
V: 1	*	*	-0.65	7.99	*	752.32	0.65	4.84	-0.31	*	0.28	*	*
Y: 1	10.18	*	-1.32	8.67	*	231.74	*	35.64	0.22	*	0.51	-0.57	-1.60

Table 3 - G-Probe 2	87 7.scores for	Fossil Coral	KCn-1NP Pellet	06/09/2023
		1 00011 00141,	Rop-Intronet.	00,00,2020

Lab Code	J35	J37	J40	J41	J46	J51	J54	J57	J58	J59	J60	J62	J63
CaO: 1	2.85	-0.09	69.42	*	*	*	*	*	-0.08	-1.48	0.00	0.33	*
B: 1	*	-9.02	8.87	0.42	-2.77	*	-2.33	5.22	-5.60	-0.10	*	0.00	*
Ba: 1	0.44	0.01	14.16	0.37	-0.93	-0.10	-0.30	-2.88	-0.44	-1.78	*	0.00	*
Ce: 1	*	1.57	*	0.92	*	*	-2.32	*	5.14	-0.96	*	*	*
Co: 1	-2.99	-3.20	*	0.00	1.16	1.80	-3.51	*	6.99	-2.83	*	*	*
Cu: 1	-0.55	0.00	*	0.50	1.44	0.44	-1.49	*	21.07	-0.95	*	-0.46	*
Li: 1	-2.54	1.98	3.37	1.47	0.69	-2.68	-2.32	-2.36	*	-2.58	*	*	-3.40
Mg: 1	0.09	0.25	21.12	0.65	-2.40	2.76	2.32	-1.59	0.50	-0.09	-10.03	-1.58	4.30
Mn: 1	*	1.80	*	1.62	0.14	*	*	-2.70	5.77	-2.32	3310.95	*	1.52
Na: 1	3.84	-0.61	33.16	*	*	1.93	-2.65	*	3.19	-1.66	*	-4.37	*
Pb: 1	0.00	0.80	2.65	1.59	0.80	*	0.00	-0.16	57.64	-1.21	*	0.00	-1.41
Sr: 1	3.19	1.18	66.63	3.54	-0.05	1.55	-4.41	-2.66	1.40	-1.40	-10.86	0.46	-2.26
U: 1	0.27	-0.63	9.37	0.30	-0.71	0.15	-0.15	-0.03	-0.68	-1.50	*	0.03	-3.61
V: 1	*	0.13	*	0.65	*	*	-1.70	*	*	-1.36	*	*	*
Y: 1	*	-0.38	*	0.00	*	1.51	0.57	*	17.25	-0.43	*	-0.19	0.00

Table 3 - G-Probe 28z Z-scores for Fossil Coral, KCp-1NP Pellet. 06/09/2023

Lab Code	J64
CaO: 1	*
B: 1	-4.86
Ba: 1	0.89
Ce: 1	*
Co: 1	*
Cu: 1	0.76
Li: 1	1.26
Mg: 1	-2.79
Mn: 1	*
Na: 1	*
Pb: 1	0.00
Sr: 1	-1.51
U: 1	0.68
V: 1	*
Y: 1	*









Figure 1: G-Probe 28z - Fossil Coral, KCp-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 28z - Fossil Coral, KCp-1NP Pellet. Data distribution charts provided for information only for elements for which values could not be credited with assigned or provisional status.

	۲	J3	J10	11L	J15	J21	J22	J23	J28	J31	J32	J33	J34	J35	J37	J40	J41	J46	J51	J54	J57	J58	J59	J60	J62	J63	J64			
Y			•	•		•		•	•		٠	•	•		•		•		•	•		•	•		•	•				
V			٠			•	•		٠		٠				•		•			•			•							
U	•		•	٠			•		•	•	٠	•	•	٠	•		•	•	•	•	•	•	٠		•	▼	•			
Sr	•	٠		٠		▼	•			•	٠	٠	•		•			•	•	▼	•	٠	٠	•	•	•	•			
Pb	•	•	•				•		•		٠	•	•	٠	•		•	•		•	•		٠		•	•	•			
Na	•								•		٠	•	•		•				•	•			٠		▼					
Mn			•	•					•				•		•		•	•			•		•			•				
Mg		•		٠							•	٠	•	•	•		•	•			•	•	•	•	•		•			
Li		٠	٠				▼	٠	٠		٠	٠	•	•	•		٠	•	•	•	•		•			•	•			No data
Cu	•		•	٠			•		•		٠	•	•	٠	•		•	•	•	•			٠		•		•		•	z < -3
Co	•		•	٠	•				•		٠		•	•	•		•	•	•	▼			•						•	-3 < z < -2
Ce			•					٠	•		٠		•		•		•			•			٠						•	OK
Ва	•	•	•	•			•		•	•	•	•	•	•	•		•	•	•	•	•	•	•		•		•			2<2<3
В				•			•		•		•				•		•	•		•		•	•		•		•			2-0
CaO			•	•			•			•		•	•		•							•	•	•	•					7 > 3

Figure 3: G-Probe 28z - Fossil Coral, KCp-1NP Pellet. Multiple z-score charts for laboratories participating in the G-Probe 28z round. Symbols indicate whether or not an elemental result complies with the -2<z<+2 criteria (see key).