

# **GEOPT13 - AN INTERNATIONAL PROFICIENCY TEST FOR ANALYTICAL GEOCHEMISTRY LABORATORIES - REPORT ON ROUND 13 / July 2003 (Köln Loess)**

**Philip J. Potts<sup>1\*</sup>, Michael Thompson<sup>2</sup>, Simon R.N. Chenery<sup>3</sup>, Peter C. Webb<sup>1</sup>  
and H. Uwe Kasper<sup>4</sup>**

<sup>1</sup>Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK.

<sup>2</sup>Department of Chemistry, Birkbeck College, Gordon House, London, WC1H 0PP, UK.

<sup>3</sup>British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK.

<sup>4</sup>Geologisches Institut, Universität zu Köln, Zülpicher Str 49a, D-50674 Köln, Germany.

\*Corresponding author: e-mail p.j.potts@open.ac.uk

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## **Abstract**

Results are presented for GeoPT13, round thirteen of the GeoPT international proficiency testing programme for analytical geochemistry laboratories. The sample distributed for this round was Köln Loess, a sample collected and prepared as a candidate reference material by the University of Cologne, Germany. In this report, contributed data are listed, together with an assessment of assigned values, z-scores and charts showing both the distribution of contributed results and the overall performance of participating laboratories.

## **Introduction**

This thirteenth round of the international proficiency testing programme, GeoPT13, was conducted in a similar manner to earlier rounds. The programme is designed to be part of the routine quality assurance scheme of analytical geochemistry laboratories. The trial involves distributing a sample of established homogeneity to participating laboratories, which are required to analyse the sample using a well-characterised technique or techniques operated under

routine analytical conditions. Results are then tabulated by the organisers and z-scores calculated by comparing each analysed result submitted with the value assigned to be the best estimate of the true composition. These assigned values were estimated by robust statistical analysis of all the contributed data. By examining the magnitude of the z-score, participating laboratories can decide whether the quality of their data is satisfactory in relation to both their chosen fitness-for-purpose criteria and results submitted by all the other laboratories contributing to the round, and choose to take corrective action if this appears justified.

Full details of the programme have been included in reports of previous rounds, the current publication status of which is listed in Appendix 1. More specifically, the procedures followed in this round comply with the protocol published for conducting the GeoPT series of proficiency tests (see [www.geoanalyst.org](http://www.geoanalyst.org)). In this report, therefore, only the features of the present round are included and readers interested in further details are invited to

review the GeoPT protocol and previously published reports.

**Steering Committee for Round 13:** M. Thompson (Chair), P.J. Potts (Secretary), S.R.N. Chinery, P.C. Webb and H.U. Kasper

**Sample:** 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 ( $49^{\circ} 19' \text{N}$ ,  $8^{\circ} 43' \text{E}$  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 WD-XRF at the OU. For the elements for which values could be assigned, homogeneity was considered to be satisfactory for use in the GeoPT13 round. An analysis of the results with additional comments is listed in Appendix 2.

#### **Timetable for GeoPT13:**

Distribution of sample: March 2003.

Deadline for submission of analytical results: 15th May 2003.

Distribution of draft report: July 2003

#### **Submission of results**

Results submitted by the eighty-nine laboratories that participated in this round are listed in Table 1. Note that laboratory N49 requested that the results submitted by this laboratory should be withdrawn, and that laboratories N88 and N89 submitted their data too late for the results to be included in the assessment of assigned values.

#### **Assigned values**

Following procedures described in earlier rounds, a robust statistical procedure was used to derive assigned value concentrations [ $X_a$ ], these being judged to be the best estimates of the true composition of this sample. Data in Table 2 lists assigned values for 12 majors and 41 trace elements (of which 6 are provisional values). Values were assigned on the basis that: (i) sufficient laboratories had contributed data for an element, (ii) the statistical assessment gave confidence that the results showed a central portion approximating to a normal distribution. Part of this assessment involved examining a bar chart for each element to judge the distribution of results. Bar charts for elements shown in Figure 1 were judged to have satisfactory or provisional distributions, namely:

$\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3\text{T}$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{CO}_2$ , LOI, As, Ba, Be, Bi, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Li, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, Tl, Tm, U, V, W, Y, Yb and Zn. Note that of these, Hf, Mo, Sc, Ta, V, and W were assigned provisional values.

Charts in Figure 2 show distribution data for elements that were not judged to be sufficiently satisfactory in the statistical analysis to assign values. In the present round, values could not be assigned to the following elements, despite the availability of sufficient analytical results:

$\text{FeO}$ ,  $\text{H}_2\text{O}^+$ , Ag, Cd, F, Ge, Hg, S, Sn, and Zr.

For other elements that are not included in either of these two lists, insufficient data was reported to allow any assessment to be made.

The most common reasons for elements failing the assessment of assigned values were as follows:

- (i) Insufficient number of contributed results.
- (ii) Results showing a strong positive skew in the frequency distribution diagram, sometimes with an indication of multi-modality.
- (iii) A robust mean clearly different from the mode, which makes the determination of a consensus impracticable.
- (iv) A very wide distribution of results as judged by the robust standard deviation value so that no matter where the consensus was placed, most of the participants would receive an 'unsatisfactory' classification if z-scores were calculated.

### Z-score analysis

As in previous rounds, laboratories were invited to choose one of two performance standards against which their analytical results would be judged:

**Data quality 1** 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.

**Data quality 2** for laboratories working to an 'applied geochemistry' standard of performance, where, although precision and accuracy are still important, the main objective is to provide results on large numbers of samples collected as part of geochemical mapping projects or geochemical exploration programmes.

The target standard deviation ( $H_a$ ) for each element assessed was calculated from a modified version of the Horwitz function as follows:

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

Where  $X_a$  is the concentration of the element expressed as a *fraction*, and the factor  $k = 0.01$  for

pure geochemistry labs and  $k=0.02$  for applied geochemistry labs.

Z-scores were calculated for each elemental result submitted by each laboratory from:

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

where

$X$  is the contributed result,  $X_a$  is the assigned value and  $H_a$  is the target standard deviation.

Z-score results are listed in Table 3 and participating laboratories are invited to assess their performance using the following criterion:

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, contributing laboratories are advised to examine their procedures to ensure that determinations are not subject to unsuspected analytical bias.

### Overall performance

A summary of the overall performance of individual laboratories in this round is plotted in Figure 3 as a multiple z-score chart. In this chart, the z-score performance for each element is distinguished by symbols that make it simple to identify whether the results were satisfactory or gave z-scores that exceeded the action limits. This chart is designed to help individual laboratories to judge their overall performance in this proficiency testing round.

The statistical interpretation of results from this proficiency testing round suggests that this loess sample caused unexpected difficulties, almost certainly caused by the unsuspected presence of zircon (Uwe Kasper, pers. comm.). The bar chart for Zr indicates a non-normal distribution of results with a small but significant number of laboratories underestimating the Zr content. One contributing factor may be the use of simple acid digestion procedures that have not completely dissolved the zircon. Another could be additional sampling uncertainty associated with the relatively small mass of test portion used by some techniques. The bar

chart for Hf, an element often associated with Zr, also shows a small but significant number of laboratories reporting low results, possibly for the same reasons. However, in the instance of Hf, it was judged that there was sufficient consensus in these data to report a provisional value.

### **Participation in future rounds**

The benefit from proficiency testing arises from regular participation and laboratories are invited to contribute to the GeoPT14 round, the sample for which will be distributed during September 2003.

### **Acknowledgments**

The authors thank Liz Lomas (OU) for valued secretarial assistance with the production of this report. The GeoPT programme is organised on behalf of the International Association of Geoanalysts.

## **Appendix 1**

### **Publication status of proficiency testing reports**

#### **GeoPT1**

Thompson M., Potts P.J., Kane J.S. and Webb P.C. (1996)

GeoPT1. International proficiency test for analytical geochemistry laboratories - Report on round 1. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 20, 295-325.

#### **GeoPT2**

Thompson M., Potts P.J., Kane J.S., Webb P.C. and Watson, J.S. (1998)

GeoPT2. International proficiency test for analytical geochemistry laboratories - Report on round 2. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 22 127-156.

#### **GeoPT3**

Thompson M., Potts P.J., Kane J.S. and Chappell B.W. (1999a)

GeoPT3. International proficiency test for analytical geochemistry laboratories - Report on round 3. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 23, 87-121.

#### **GeoPT4**

Thompson M., Potts P.J., Kane J.S., Webb P.C. and Watson J.S. (1999b)

GeoPT4. International proficiency test for analytical geochemistry laboratories - Report on round 4. Published in the electronic version of Geostandards Newsletter: The Journal of Geostandards and Geoanalysis (Summer 2000).

#### **GeoPT5**

Thompson M., Potts P.J., Kane J.S., and Wilson S. (1999c)

GeoPT5. International proficiency test for analytical geochemistry laboratories - Report on round 5. Published in the electronic version of Geostandards Newsletter: The Journal of Geostandards and Geoanalysis (Summer 2000).

#### **GeoPT6**

Potts P.J., Thompson M., Kane J.S., Webb P.C. and Carignan J. (2000)

GEOPT6 - an international proficiency test for analytical geochemistry laboratories - report on round 6 (OU-3: Nanhoron microgranite) and 6A (CAL-S: CRPG limestone). International Association of Geoanalysts: Unpublished report.

#### **GeoPT7**

Potts P.J., Thompson M., Kane J.S., and Petrov L.L. (2000)

GEOPT7 - an international proficiency test for analytical geochemistry laboratories - report on round 7 (GBPG-1 Garnet-biotite plagiogneiss). International Association of Geoanalysts: Unpublished report.

#### **GeoPT8**

Potts P.J., Thompson M., Kane J.S., Webb, P.C. and Watson J.S. (2000)

GEOPT8 - an international proficiency test for analytical geochemistry laboratories - report on round 8 / February 2001 (OU-4 Penmaenmawr microdiorite). International Association of Geoanalysts: Unpublished report.

#### **GeoPT9**

Potts P.J., Thompson M., Webb, P.C. and Watson J.S. (2001)

GEOPT9 - an international proficiency test for analytical geochemistry laboratories - report on round 9 / July 2001 (OU-6 Penrhyn slate). International Association of Geoanalysts: Unpublished report.

#### **GeoPT10**

Potts P.J., Thompson M., Webb, P.C., Watson J.S. and Wang Yimin (2001)

GEOPT10 - an international proficiency test for analytical geochemistry laboratories - report on round 10 / December 2001 (CH-1 Marine sediment). International Association of Geoanalysts: Unpublished report.

#### **GeoPT11**

Potts P.J., Thompson M., S.R. Chenery, Webb, P.C. and Watson J.S. (2002)

GEOPT11 - an international proficiency test for analytical geochemistry laboratories - report on round 11 / July 2002 (OU-5 Leaton dolerite). International Association of Geoanalysts: Unpublished report.

#### **GeoPT12**

Potts P.J., Thompson M., S.R. Chenery, Webb, P.C. and B. Batjargal (2003)

GEOPT12 - an international proficiency test for analytical geochemistry laboratories - report on round 12 / January 2003 (GAS Serpentinite). International Association of Geoanalysts: Unpublished report.

## **Appendix 2 - 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 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 showing the results of homogeneity testing on the WD-XRF major element data and LOI.**

Analyte	Data test	Analytical precision	Harmonised Protocol test	Fearn-Thompson test
SiO <sub>2</sub>	OK	OK	OK	OK
TiO <sub>2</sub>	OK	*	SIG	OK
Al <sub>2</sub> O <sub>3</sub>	OK	*	OK	OK
Fe <sub>2</sub> O <sub>3</sub>	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 showing the results of homogeneity testing on the WD-XRF trace element data.**

Analyte	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
TiO <sub>2</sub>	OK	*	OK	OK
Fe <sub>2</sub> O <sub>3</sub>	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 1: GeoPT13

Results submitted (May 2003) by laboratories to the GeoPT13 round for UoK LOESS

	Table 1: GeoPT13 Results submitted (May 2003) by laboratories to the GeoPT13 round for UoK LOESS.																						
Round identifier	N1	N2	N3	N4	N5	N5	N6	N6	N7	N8	N9	N10	N11	N12	N13	N14	N15	N16	N17	N18	N19		
Sample	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS			
Technique codes	IR,X	IR,T,X	IR,X	X	M	M	X	X	X	A,M,X	AA,A, W,X	M,X	O,X	M,X	A,AA	A,M	M	M,T,X	X	M			
Test portion (g)	0.7-1	0.1-0.8	0.2-5	0.7-5	0.1	0.1	1-4.5	5	0.5	1	0.3-0.5	0.1-5	0.05-0.5	0.01-0.7	0.27	0.2-0.3	0.1	0.1	0.05-4.5	0.75-11	0.1		
Data quality	2	2	2	2	1	2	1	2	1	2	2	1	1	1	2	2	1	2	2	2			
La	mg kg <sup>-1</sup>			21.9			26			28			26	26.6	46	25.93	27.3	26.5	25.8	25.9	26.8		
Li	mg kg <sup>-1</sup>													22.13			24		26.1	23.9	25.8		
Lu	mg kg <sup>-1</sup>					0.36								0.39		0.4	0.36	0.4	0.353	0.4	0.33		
Mo	mg kg <sup>-1</sup>					2								1.25	9	1.4	1.2	1.2	1.29		1.2		
N	mg kg <sup>-1</sup>																						
Nb	mg kg <sup>-1</sup>			10.8	7.5		7.5		8.5					9.55	10	8.9	10	8	8.41	8.7	9	7	
Nd	mg kg <sup>-1</sup>			20.1	23		23						25	24.8	29	24.39	24.7	24.1	23.4	25.9		25.5	
Ni	mg kg <sup>-1</sup>			35.1	56	55.2	54.712	41.2					38.5	39.3	90	32	44	42	42.8	45.5	45		
Os	mg kg <sup>-1</sup>																						
Pb	mg kg <sup>-1</sup>			12.1	12	10.2	8.0		13.1					11.5	13	13.5	12	10	11.4	11.1	12		
Pd	mg kg <sup>-1</sup>																						
Pr	mg kg <sup>-1</sup>					4		6.1					6.3	6.49	8	6.42	6.54	6.47	6.28	6.5		6.58	
Pt	mg kg <sup>-1</sup>																						
Rb	mg kg <sup>-1</sup>			48.4	53		48		50.6					55	52.1	55	52.6	54.4	48.2	50.6	50.2	44	54.1
Re	mg kg <sup>-1</sup>																						
Rh	mg kg <sup>-1</sup>																						
Ru	mg kg <sup>-1</sup>																						
S	mg kg <sup>-1</sup>		230		1020										111	130	60				748		
Sb	mg kg <sup>-1</sup>					0.60								0.39	8	0.6	0.48	0.41	0.585			0.54	
Sc	mg kg <sup>-1</sup>						4.9							6.58	27	6	5	5.6	6.31	5.8		6.4	
Se	mg kg <sup>-1</sup>			0.5																			
Sm	mg kg <sup>-1</sup>			3		4.7							5.2	4.99	6	4.91	5	4.91	5.07	5.3		5.29	
Sn	mg kg <sup>-1</sup>					2.6								1.67	1	2.4	1.6	1.55					
Sr	mg kg <sup>-1</sup>			289	314	275	276		270.8				267	270	275	308	284	290	280	291	268	236	282
Ta	mg kg <sup>-1</sup>					0.41								0.88	0	0.8	0.9	0.76	0.771	0.8			
Tb	mg kg <sup>-1</sup>					0.68							0.6	0.71	2	0.74	0.72	0.76	0.705	0.8		0.66	
Te	mg kg <sup>-1</sup>																						
Th	mg kg <sup>-1</sup>		14.1		7.7	7.7			8.2			8.1		8.64	7	8.2	8.5	8.3	8.21	8	8	8.1	
Tl	mg kg <sup>-1</sup>													0.33				0.37				0.39	
Tm	mg kg <sup>-1</sup>					0.35								0.37			0.41	0.4	0.336	0.4		0.42	
U	mg kg <sup>-1</sup>					2.7			1.2			2.8		2.38	3	2.8	2.9	2.7	2.56	2.8	9	2.1	
V	mg kg <sup>-1</sup>		34	46		35		41.1			31	41.32	39.5	51	50	35	38	26.1	32.3	30	38.1		
W	mg kg <sup>-1</sup>													1.17	2		1.1	1.3	1.63			1.2	
Y	mg kg <sup>-1</sup>			26.5	27		23		25.5			25		21.5	24	27	24.5	26.2	23.9	20	10	20.9	
Yb	mg kg <sup>-1</sup>					2.4							2.8	2.44	4	2.5	2.6	2.26	2.48	2.7		1.98	
Zn	mg kg <sup>-1</sup>			35.3	36	38.1	46			35.6			25		35.4	42	35	31	36	35.8	314	32	
Zr	mg kg <sup>-1</sup>			343	345		332		313.9					342	309	317	355	338	360	292	289	467	

**Table 1: GeoPT13**

## Results submitted (May 2003) by laboratories to the GeoPT13 round for UoK LOESS.



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## Results submitted (May 2003) by laboratories to the GeoPT13 round for UoK LOESS.

	Table 1: GeoPT13 Results submitted (May 2003) by laboratories to the GeoPT13 round for UoK LOESS.																				
Round identifier	N35	N35	N36	N37	N38	N39	N40	N41	N42	N43	N43	N44	N45	N46	N47	N48	N49*	N50	N51	N52	N52
Sample	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	
Technique codes	X	X	AA,O	A	M,X	M	I	X	A,M	X	X	A,M	AA,C,IS	A,AA	A,IR	A,M,X	X	AO,,X	X,M	M	
Test portion (g)	0.6-6	0.6-6	0.1	0.2	0.1-5	0.25	0.15	1.0-5.0	0.25	1.2	9	0.25	0.5-10	0.2-3	0.2-7	0.2	0.17	0.25-5	0.1-0.6	0.1	
Data quality	1	2	1	2	1	1	1	2	1	2	2	2	2	1	2	2	1	2	1	2	
La	mg kg <sup>-1</sup>			360		26	25.7	25.67	26.1		26.05			24.2		23.4	24.7	27.0		27	25.818
Li	mg kg <sup>-1</sup>					26		21.72								23		21.2		22	
Lu	mg kg <sup>-1</sup>					0.38	0.217			0.37					0.38	0.35	0.27		0.38	0.309	
Mo	mg kg <sup>-1</sup>						1.279	1.48		1.53			1.863	1.4		2.02	1.1				
N	mg kg <sup>-1</sup>																				
Nb	mg kg <sup>-1</sup>			19			5	7.458		14	7.08		8.4		7.8		7.5		9.3		7.867
Nd	mg kg <sup>-1</sup>			26			24.5	24.57		17	24.54				20.22	22.7	25.0		22	25.83	
Ni	mg kg <sup>-1</sup>	43			42		44.06	44	49	44.8		31.6	59.93	40.9	36	51.7	46.4		39		
Os	mg kg <sup>-1</sup>																				
Pb	mg kg <sup>-1</sup>				13		10.72		12	17.07		10.3	10.76	12.2		12.7	10.5		12	10.88	
Pd	mg kg <sup>-1</sup>																				
Pr	mg kg <sup>-1</sup>			56			6.3	6.459		6.32					5.2	5.83	6.7		6.3	6.561	
Pt	mg kg <sup>-1</sup>																				
Rb	mg kg <sup>-1</sup>	56				42	51.18	51.4	57	51.87		48		46.2	56	52.1	50.6		53	50.66	
Re	mg kg <sup>-1</sup>																				
Rh	mg kg <sup>-1</sup>																				
Ru	mg kg <sup>-1</sup>																				
S	mg kg <sup>-1</sup>															179					
Sb	mg kg <sup>-1</sup>						0.471	0.7							0.26	0.58	0.5				
Sc	mg kg <sup>-1</sup>				5		6.557	5.9	12	5.6						5.61	5.3		6.49		
Se	mg kg <sup>-1</sup>													1.1							
Sm	mg kg <sup>-1</sup>					4.9	4.988	5.16		5.02					4.96	4.54	5.01		4.6	5.047	
Sn	mg kg <sup>-1</sup>						1.55			1.04			1.444			1.62	0.7				
Sr	mg kg <sup>-1</sup>	280		271	206	275.3	288	308	337.9		265		274	246	287	275		290	295.2		
Ta	mg kg <sup>-1</sup>					0.611	0.81		0.7							0.6				0.601	
Tb	mg kg <sup>-1</sup>					0.7	0.61	0.65		0.71					0.69	0.60		0.7	0.683		
Te	mg kg <sup>-1</sup>																				
Th	mg kg <sup>-1</sup>					6	8.117	8.57	14	8.7		8	8.852	5.7	10	7.92	8.0			7.861	
Tl	mg kg <sup>-1</sup>						0.345			0.34						0.31					
Tm	mg kg <sup>-1</sup>					0.38	0.228								0.35	0.32	0.27		0.4	0.301	
U	mg kg <sup>-1</sup>				3	2.112	2.92	6	2.76		1.9	1.033	0.4		3.49	2.6				2.488	
V	mg kg <sup>-1</sup>	44		39		33.78			33.81		49		45.1	16	41.2	11.8		34			
W	mg kg <sup>-1</sup>					1.419	1.5					1.759									
Y	mg kg <sup>-1</sup>	21		18	23	18.067		27	27.1		22		20.1	21.8	24.5	18.3		25	20.189		
Yb	mg kg <sup>-1</sup>				1.5	2.4	1.526	2.65		2.44				2.38	1.79	1.87		2.5	2.032		
Zn	mg kg <sup>-1</sup>			24	14	32.16	33	38	33		30		33.3	36	35.5	31.4		35			
Zr	mg kg <sup>-1</sup>	330			279	62.77	374	361	315.9		294		302	317	366			337		181.1	

Table 1: GeoPT13

Results submitted (May 2003) by laboratories to the GeoPT13 round for UoK LOESS.

		<b>Table 1: GeoPT13</b>																					
		<b>Results submitted (May 2003) by laboratories to the GeoPT13 round for UoK LOESS.</b>																					
Round identifier		N53	N54	N55	N56	N57	N58	N59	N59	N60	N61	N62	N63	N64	N65	N65	N66	N67	N68	N69	N70	N71	
Sample		LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	LOESS	
Technique codes		X	A,AA	A,X	X	AA,X	AA,IR	X	X	AA,E	A,T,X	A,IR,M	M,X	I	I	X	X	A	X	X	X	X	
							T,X			O,T,X		O,X											
Test portion (g)		0.6-5.4	0.5	1-1.5	1.0-6	0.5-1	0.1-4	1.0-20	20	1	0.02-5	0.1-4	0.25-2	0.1-10	1.0	1.0-10	0.7	0.28	0.25	0.18	0.3	0.4	
Data quality		2	1	2	2	2	1	1	2	1	2	2	2	1	1	2	1	2	1	2	2	2	
La	mg kg <sup>-1</sup>	22.1			18				36				30	27.84	25.11			15					
Li	mg kg <sup>-1</sup>		18								20		21	21.4									
Lu	mg kg <sup>-1</sup>												0.2	0.42	0.35								
Mo	mg kg <sup>-1</sup>				4.5						5.5	1.98		1.38									
N	mg kg <sup>-1</sup>																						
Nb	mg kg <sup>-1</sup>	8.4			10	10	7	10			9	10.42	5.7	8.84			12		10				
Nd	mg kg <sup>-1</sup>	11											27	26.47	23.7								
Ni	mg kg <sup>-1</sup>	35.3	22	30	41	39.91	37	39			42	33.6	40	43.6			43	48	109	38			
Os	mg kg <sup>-1</sup>																						
Pb	mg kg <sup>-1</sup>				2	11	12	12	9		9.3	9.632		11.2							16		
Pd	mg kg <sup>-1</sup>														6.5								
Pr	mg kg <sup>-1</sup>																						
Pt	mg kg <sup>-1</sup>																						
Rb	mg kg <sup>-1</sup>	49.5			52		48	52			60	50.52	54	51.1		58.18	52	35		50	130		
Re	mg kg <sup>-1</sup>																						
Rh	mg kg <sup>-1</sup>																						
Ru	mg kg <sup>-1</sup>																						
S	mg kg <sup>-1</sup>				132			82		112		140											
Sb	mg kg <sup>-1</sup>												0.58		0.57								
Sc	mg kg <sup>-1</sup>	18.2					12	1			11		5	6.08		5.75	14		20				
Se	mg kg <sup>-1</sup>												5.6	5.44	4.82								
Sm	mg kg <sup>-1</sup>												2.48										
Sn	mg kg <sup>-1</sup>																						
Sr	mg kg <sup>-1</sup>	271.1	294	200	265	351	277	270			310	270	282	289			287	375	294	273			
Ta	mg kg <sup>-1</sup>				4								0.4	0.55									
Tb	mg kg <sup>-1</sup>												0.7	0.79	0.76								
Te	mg kg <sup>-1</sup>																						
Th	mg kg <sup>-1</sup>	13.9			6		7	8			6.5	7.032	9.4	9.11		8.39							
Tl	mg kg <sup>-1</sup>													0.37									
Tm	mg kg <sup>-1</sup>												0.3	0.44									
U	mg kg <sup>-1</sup>				3.3								2.55	2.4	2.94		2.43						
V	mg kg <sup>-1</sup>	34.7	26		34	36.92	30		50		52	56	35	40.7			41	120	37				
W	mg kg <sup>-1</sup>					0.27								1.46									
Y	mg kg <sup>-1</sup>	24.3			26		25	24			23.5	22.72	17	23			26	25	29	18			
Yb	mg kg <sup>-1</sup>												1.4	2.69	2.44								
Zn	mg kg <sup>-1</sup>	30.4	22	28	41	53.93	33	34			36		38	36.8			34	45	32	70			
Zr	mg kg <sup>-1</sup>	302.3	25	330	308		395	302			291	325	374	345			348	145	346				
		N49* Results withdrawn by participating laboratory after assessment of assigned value.																					
		N88**, N89**, N90**: Results submitted too late to contribute to the assessment of the assigned value.																					
		Technique codes: A=ICP-AES; AA=AAS; C=colorimetry; E=(atomic) emission spectrometry; G=gravimetric;																					
		I=INAA; IR= infra red detection; ISE=ion selective electrodes; M=ICP-MS; O=other;																					
		T=titrimetry; W=wet chemistry; X=X-ray fluorescence.																					





**Table 2 GeoPT 13 (UoK LOESS)****Assigned values and robust statistical analysis of contributed data**

Element	X <sub>a</sub> % m/m	H <sub>a</sub> % m/m	sdm % m/m	s/H <sub>a</sub>	Status	Element	X <sub>a</sub> mg kg <sup>-1</sup>	H <sub>a</sub> mg kg <sup>-1</sup>	sdm mg kg <sup>-1</sup>	s/H <sub>a</sub>	Status
SiO <sub>2</sub>	53.24	0.59	0.08	0.13	assigned	Hf	9.100	0.522	0.293	0.56	provisional
TiO <sub>2</sub>	0.423	0.010	0.003	0.31	assigned	Ho	0.80	0.07	0.03	0.45	assigned
Al <sub>2</sub> O <sub>3</sub>	6.2	0.0942	0	0.20	assigned	La	25.54	1.25	0.28	0.22	assigned
Fe <sub>2</sub> O <sub>3</sub>	2.1	0.038	0	0.20	assigned	Li	21.90	1.10	0.57	0.51	assigned
MnO	0.0644	0.0019	0.0006	0.32	assigned	Lu	0.370	0.034	0.008	0.22	assigned
MgO	2.9	0.049	0	0.30	assigned	Mo	1.400	0.106	0.061	0.57	provisional
CaO	16.31	0.21	0.04	0.17	assigned	Nb	8.61	0.50	0.18	0.37	assigned
Na <sub>2</sub> O	1.058	0.021	0.008	0.37	assigned	Nd	24.32	1.20	0.30	0.25	assigned
K <sub>2</sub> O	1.3	0.025	0	0.30	assigned	Ni	42.71	1.94	0.82	0.42	assigned
P <sub>2</sub> O <sub>5</sub>	0.13	0.004	0.002	0.43	assigned	Pb	11.34	0.63	0.22	0.34	assigned
CO <sub>2</sub>	14.94	0.20	0.07	0.36	assigned	Pr	6.24	0.38	0.06	0.17	assigned
LOI	16.03	0.21	0.02	0.11	assigned	Rb	51.2	2.3	0.4	0.19	assigned
	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>			Sb	0.5800	0.0500	0.0090	0.19	assigned
As	6.7	0.4	0.3	0.76	assigned	Sc	5.93	0.36	0.15	0.42	provisional
Ba	200.97	7.24	1.98	0.27	assigned	Sm	5.01	0.31	0.06	0.19	assigned
Be	1.102	0.087	0.053	0.61	assigned	Sr	278.5	9.5	1.7	0.18	assigned
Bi	0.1	0.014	0.0	0.53	assigned	Ta	0.73	0.06	0.03	0.50	provisional
Ce	53	2.32	0	0.20	assigned	Tb	0.687	0.058	0.013	0.22	assigned
Co	5.95	0.36	0.12	0.33	assigned	Th	8.111	0.473	0.123	0.26	assigned
Cr	105.7	4.2	2.7	0.64	assigned	Tl	0.338	0.032	0.012	0.38	assigned
Cs	2.72	0.19	0.04	0.19	assigned	Tm	0.339	0.032	0.014	0.43	assigned
Cu	11.31	0.63	0.40	0.63	assigned	U	2.697	0.186	0.081	0.44	assigned
Dy	4.02	0.26	0.10	0.38	assigned	V	37.56	1.74	1.05	0.60	provisional
Er	2.382	0.167	0.060	0.36	assigned	W	1.45	0.11	0.09	0.84	provisional
Eu	0.888	0.072	0.012	0.16	assigned	Y	23.18	1.16	0.43	0.37	assigned
Ga	7.087	0.422	0.174	0.41	assigned	Yb	2.420	0.169	0.074	0.44	assigned
Gd	4.465	0.285	0.074	0.26	assigned	Zn	34.4	1.6	0.6	0.36	assigned

X<sub>a</sub>=assigned value calculated as the robust mean of submitted data.H<sub>a</sub>=target precision calculated using a modified version of the Horwitz equation  
for Data quality 1 ( $H_a=0.01X_a^{0.8495}$ ).

sdm=standard deviation of the mean calculated from submitted data using robust statistics.

Full=full a Assigned v: Sigma      Uncertainty Uncertainty/Target

	<b>Table 3</b> <b>Z-scores for GeoPT13 - LOESS</b>																		
Round identifier	N1	N2	N3	N4	N5	N5	N6	N6	N7	N8	N9	N10	N11	N12	N13	N14	N15	N16	
Sample	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess		
Technique codes	IR,X	IR,T,X	IR,X	X	M	M	X	X	X	A,M,X	AA,A,	M,X	O,X	M,X	A,AA	A,M	M		
											W,X					IR,M,O			
Test portion (g)	0.7-1	0.1-0.8	0.2-5	0.7-5	0.1	0.1	1-4.5	5	0.5	1	0.3-0.5	0.1-5	0.05-0.5	0.01-0.7	0.27	0.2-0.3	0.1	0.1	
Data quality	2	2	2	2	1	2	1	2	1	2	2	2	1	1	1	2	2	1	
SiO <sub>2</sub>	0.7	-0.2	0.1	0.0	*	*	1.5	*	0.8	8.8	-0.2	-0.2	-0.1	-0.1	-1.5	0.1	-0.7	*	
TiO <sub>2</sub>	0.2	0.4	0.7	-0.1	*	*	-1.3	*	3.9	4.2	0.4	0.4	1.3	2.8	-0.9	-1.2	0.4	*	
Al <sub>2</sub> O <sub>3</sub>	-0.3	-0.5	-0.1	-0.5	*	*	-1.2	*	-0.6	6.6	0.3	-1.0	0.0	-1.3	-1.2	-0.1	1.1	*	
Fe <sub>2</sub> O <sub>3</sub>	2.0	-0.3	0.3	-0.1	*	*	-0.1	*	0.4	6.6	0.1	2.5	-1.5	-1.7	-0.6	0.6	1.3	*	
MnO	0.3	0.4	1.4	0.2	*	*	-2.3	*	-2.3	2.2	*	1.4	-0.2	2.9	-0.7	-0.4	0.4	*	
MgO	1.2	0.2	0.1	-0.2	*	*	0.6	*	-0.4	4.2	-0.1	2.0	0.4	-6.4	-1.5	0.1	0.7	*	
CaO	1.0	0.3	1.6	-0.1	*	*	0.0	*	0.4	6.6	0.0	-0.1	-1.1	0.4	-0.8	-0.5	2.4	*	
Na <sub>2</sub> O	-3.3	1.0	2.4	0.0	*	*	0.6	*	3.0	4.1	-0.9	2.2	0.1	-0.9	-1.3	1.5	0.0	*	
K <sub>2</sub> O	0.7	-0.1	0.3	-0.1	*	*	1.0	*	1.4	4.4	2.2	-1.3	0.2	-0.6	-0.5	1.1	0.3	*	
P <sub>2</sub> O <sub>5</sub>	-0.1	0.0	2.1	-1.4	*	*	0.0	*	0.0	15.6	0.0	1.4	-1.7	-2.8	0.3	-2.8	-1.4	*	
CO <sub>2</sub>	1.6	0.0	-1.5	*	*	*	*	*	*	*	*	-3.9	*	0.6	*	0.5	*	*	
LOI	-0.3	0.0	-2.2	0.3	*	*	-0.5	*	-1.5	1.0	0.2	0.2	-0.3	0.1	*	0.2	0.1	*	
As	*	*	-6.8	6.5	*	*	*	*	*	*	*	6.1	-2.6	-1.8	-3.6	-0.9	*	*	
Ba	*	0.4	2.0	2.8	-0.8	*	0.9	*	*	*	-0.3	-1.3	2.1	2.2	1.5	-0.1	-0.2	-0.6	
Be	*	*	*	*	*	*	*	*	*	*	*	*	-0.5	*	0.0	0.6	*	3.7	
Bi	*	*	*	*	0.2	*	*	*	*	*	*	-0.6	-9.2	-2.0	0.8	*	3.0	*	
Ce	*	-0.2	-3.4	*	-0.3	*	*	0.9	*	*	-0.2	*	0.1	-0.3	-0.3	0.6	-0.1	0.4	
Co	*	*	5.6	3.6	-2.3	*	-5.6	*	*	*	*	*	1.4	19.4	*	0.5	0.8	3.4	
Cr	*	-0.8	0.8	-3.0	-0.2	*	3.5	*	*	*	*	3.4	1.5	33.3	3.4	-3.1	1.6	-3.3	
Cs	*	*	*	*	*	*	*	*	7.4	*	*	*	*	0.5	-3.8	-0.7	0.0	-1.7	-0.5
Cu	*	*	0.5	0.0	1.1	*	3.5	*	*	*	-1.4	*	-0.7	9.1	-10.0	1.3	3.7	1.4	
Dy	*	*	*	*	1.1	*	*	*	*	*	0.7	*	0.6	-11.6	0.5	1.1	0.1	-0.2	
Er	*	*	*	*	0.1	*	*	*	*	*	1.3	*	0.6	9.7	0.6	0.7	0.4	0.2	
Eu	*	*	*	*	-0.5	*	*	*	*	*	-0.6	*	1.3	1.5	0.6	0.4	0.0	-0.5	
Ga	*	-2.7	-1.5	*	-14.8	*	2.4	*	*	*	*	*	1.3	4.5	-0.4	-0.5	*	1.6	
Gd	*	*	*	*	1.5	*	*	*	*	*	1.3	*	0.4	1.9	0.0	0.1	-0.5	-0.5	
Hf	*	*	-1.1	*	0.0	*	*	0.4	*	*	*	*	-0.8	3.6	1.7	0.5	0.4	-2.1	
Ho	*	*	*	*	0.2	*	*	*	*	*	-2.3	*	0.9	3.1	1.7	0.6	0.6	0.7	
La	*	-1.5	*	*	0.4	*	*	1.0	*	*	0.2	*	0.8	16.3	0.3	0.7	0.4	0.2	
Li	*	*	*	*	*	*	*	*	*	*	*	*	0.2	*	*	1.0	*	3.8	
Lu	*	*	*	*	-0.3	*	*	*	*	*	*	*	0.6	*	0.9	-0.1	0.4	-0.5	
Mo	*	*	2.8	*	*	*	*	*	*	*	*	*	-1.4	71.4	0.0	-0.9	-0.9	-1.0	
Nb	*	2.2	-1.1	*	-2.2	*	-0.2	*	*	*	*	*	1.9	2.8	0.6	1.4	-0.6	-0.4	
Nd	*	-1.8	-0.5	*	-1.1	*	*	*	*	*	0.3	*	0.4	3.9	0.1	0.2	-0.1	-0.8	
Ni	*	-2.0	3.4	3.2	*	3.1	-0.8	*	*	*	-1.1	-1.8	24.4	-5.5	0.3	-0.2	0.0		
Pb	*	0.6	0.5	-0.9	-5.3	*	2.8	*	*	*	*	*	0.3	2.6	3.4	0.5	-1.1	0.1	
Pr	*	*	-3.0	*	-0.4	*	*	*	*	*	0.1	*	0.7	4.7	0.5	0.4	0.3	0.1	
Rb	*	-0.6	0.4	*	-1.4	*	-0.2	*	*	*	*	*	0.8	0.4	1.7	0.6	0.7	-0.2	
Sb	*	*	*	*	0.4	*	*	*	*	*	*	*	-3.8	147.4	0.4	-1.0	-1.7	0.1	
Sc	*	*	*	*	*	*	-2.8	*	*	*	*	*	1.8	58.1	0.2	-1.3	-0.4	1.1	
Sm	*	*	-3.2	*	-1.0	*	*	*	*	*	0.3	*	-0.1	3.1	-0.3	0.0	-0.2	0.2	
Sr	*	0.5	1.9	-0.2	-0.3	*	-0.8	*	*	*	-0.6	-0.4	-0.4	3.1	0.6	0.6	0.1	1.3	
Ta	*	*	*	*	-5.2	*	*	*	*	*	*	*	2.5	-11.9	1.2	1.4	0.3	0.7	
Tb	*	*	*	*	-0.1	*	*	*	*	*	-0.7	*	0.4	22.6	0.9	0.3	0.6	0.3	
Th	*	6.3	*	-0.4	-0.9	*	*	0.1	*	*	0.0	*	1.1	-2.3	0.2	0.4	0.2	0.2	
Tl	*	*	*	*	*	*	*	*	*	*	*	*	-0.2	*	*	0.5	*	*	
Tm	*	*	*	*	0.4	*	*	*	*	*	*	*	1.0	*	*	1.1	1.0	-0.1	
U	*	*	*	*	0.0	*	*	-4.0	*	*	0.3	*	-1.7	1.6	0.6	0.5	0.0	-0.7	
V	*	-1.0	2.4	*	-1.5	*	2.0	*	*	*	-1.9	1.1	1.1	7.7	7.1	-0.7	0.1	-6.6	
W	*	*	*	*	*	*	*	*	*	*	*	*	-2.6	5.0	*	-1.6	-0.7	1.6	
Y	*	1.4	1.7	*	-0.2	*	2.0	*	*	*	0.8	*	-1.5	0.7	3.3	0.6	1.3	0.6	
Yb	*	*	*	*	-0.1	*	*	*	*	*	1.1	*	0.1	9.3	0.5	0.5	-0.5	0.4	
Zn	*	0.3	0.5	1.1	7.1	*	*	0.4	*	*	-2.9	*	0.6	4.7	0.3	-1.1	0.5	0.8	

N49\* Results withdrawn by participating laboratory after assessment of assigned value.

N88\*\*, N89\*\*, N90\*\*: Results submitted too late to contribute to the assessment of the assigned value.

Technique codes: A=ICP-AES; AA=AAS; C=colorimetry; E=(atomic) emission spectrometry; G=gravimetric;

I=INAA; IR= infra red detection; ISE=ion selective electrodes; M=ICP-MS; O=other;

T=titrimetry; W=wet chemistry; X=X-ray fluorescence.

	<b>Table 3</b> <b>Z-scores for GeoPT13 - LOESS</b>																		
Round identifier	N17	N18	N19	N20	N21	N22	N23	N23	N24	N25	N25	N26	N26	N27	N27	N28	N29	N30	
Sample	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	
Technique codes	M,T,X	X	M	X	M,X	X	AA,M,	X	M	X	X	T,X	X	A,O,X	A,O	M	A,M,X	A	
Test portion (g)	0.05-4.5	0.75-11	0.1	0.7-2	0.1-4	7.7	0.1-8	8	0.1	0.7-10	Jan-00	0.2-6	6	0.1-5	0.3	0.06	0.1-3	0.05	
Data quality	2	2	2	2	2	1	2	1	1	2	1	2	1	2	1	2	1	2	
SiO <sub>2</sub>	-0.1	0.2	*	-6.1	0.7	-4.4	0.5	*	*	0.8	*	0.4	*	0.1	*	*	-0.3	0.0	
TiO <sub>2</sub>	0.4	-0.1	*	3.0	-2.2	0.2	-1.1	*	*	0.4	*	0.2	*	*	*	*	1.4	0.1	
Al <sub>2</sub> O <sub>3</sub>	-0.2	0.1	*	-4.6	1.9	2.6	-2.0	*	*	-1.2	*	-0.1	*	0.3	*	*	0.7	-0.8	
Fe <sub>2</sub> O <sub>3</sub>	-0.3	0.3	*	-0.5	-0.5	2.6	-0.1	*	*	0.4	*	-1.8	*	0.1	*	*	0.3	-0.9	
MnO	1.4	1.4	*	6.3	-3.4	0.1	-5.3	*	*	0.3	*	0.8	*	-3.3	*	*	-1.1	0.3	
MgO	0.2	-0.1	*	*	-0.7	1.3	2.8	*	*	2.2	*	0.2	*	1.4	*	*	0.4	-0.6	
CaO	0.4	-0.6	*	0.2	-0.3	7.3	-0.3	*	*	-1.1	*	0.1	*	0.0	*	*	1.4	-0.4	
Na <sub>2</sub> O	0.3	-2.1	*	*	-1.4	*	-0.4	*	*	7.8	*	1.3	*	-1.8	*	*	0.8	0.6	
K <sub>2</sub> O	0.3	-2.0	*	4.0	-0.9	0.4	-1.4	*	*	-3.7	*	0.4	*	-0.6	*	*	2.2	-38.0	
P <sub>2</sub> O <sub>5</sub>	0.0	-2.8	*	*	0.0	5.5	-2.8	*	*	-2.8	*	0.3	*	2.8	*	*	-1.4	0.0	
CO <sub>2</sub>	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	-1.2	*	
LOI	0.3	0.2	*	*	-0.1	*	1.0	*	*	0.7	*	-1.4	*	-0.4	*	*	-0.3	0.2	
As	*	*	*	*	-2.0	0.4	-6.0	*	*	*	3.2	*	*	*	*	-6.2	*	-0.7	
Ba	0.6	-2.6	2.1	0.3	0.2	-0.4	1155	*	0.0	*	-1.0	7.4	*	*	-1.2	-0.3	-0.6	*	
Be	0.0	*	1.4	*	-0.6	*	*	*	*	*	*	*	*	*	*	0.0	-1.2	*	
Bi	*	*	*	*	0.4	*	*	*	*	*	*	*	*	*	*	*	-0.6	*	
Ce	-0.4	12.5	-0.3	0.5	-0.6	0.1	-9.2	*	0.2	*	*	*	*	1.3	*	*	0.1	-0.2	*
Co	-0.6	4.2	0.8	*	-0.3	*	3.7	*	*	*	0.2	*	*	*	*	-0.5	4.0	-1.4	*
Cr	-0.4	2.2	*	-7.0	0.2	8.7	9.0	*	*	*	-0.7	22.0	*	*	-2.4	-1.3	1.5	*	
Cs	0.2	*	0.8	*	-0.1	*	*	*	-0.2	*	*	*	*	*	*	*	1.2	-0.6	*
Cu	0.2	-0.2	*	8.5	-0.2	0.7	10.3	*	*	-5.0	*	-3.7	*	*	-2.6	-0.7	-0.2	*	
Dy	0.9	*	-1.3	*	-2.0	*	-5.1	*	-1.8	*	*	*	*	*	*	-2.4	0.5	*	
Er	0.4	*	-1.0	*	-2.7	*	-4.1	*	-3.3	*	*	*	*	*	*	-3.5	0.6	*	
Eu	0.1	*	0.1	*	-0.5	*	-3.8	*	-0.8	*	*	*	*	*	*	0.0	0.2	*	
Ga	-0.5	5.8	-0.9	*	-0.2	1.8	*	*	*	*	-1.4	*	*	*	*	-1.2	-1.1	*	
Gd	0.8	*	-0.1	*	-1.2	*	-5.1	*	-1.1	*	*	*	*	*	*	-1.3	-0.1	*	
Hf	0.3	6.6	*	*	*	*	*	*	-11.8	*	*	*	*	*	*	-12.5	0.9	*	
Ho	0.8	*	0.2	*	-2.0	*	-2.8	*	-2.1	*	*	*	*	*	*	-2.2	0.4	*	
La	0.1	*	0.5	-0.6	-0.6	-7.5	-7.0	*	-0.3	*	*	*	-0.6	*	*	0.3	0.0	*	
Li	0.9	*	1.8	*	-0.4	*	-3.5	*	*	*	*	*	*	*	*	*	-1.3	*	
Lu	0.4	*	-0.6	*	-2.6	*	-1.5	*	-3.0	*	*	*	*	*	*	-3.8	0.1	*	
Mo	*	*	-0.9	*	0.0	*	-0.9	*	*	*	*	*	*	*	*	*	-2.3	*	
Nb	0.1	0.4	-1.6	-3.6	-2.5	1.1	*	*	-0.6	-0.6	*	-1.4	*	*	*	-0.8	-0.6	*	
Nd	0.7	*	0.5	1.1	-0.5	*	-7.7	*	0.0	*	*	*	*	*	*	*	0.2	0.0	*
Ni	0.7	0.6	*	-0.4	0.1	2.1	2.3	*	*	0.1	*	0.8	*	*	-1.5	3.8	-1.0	*	
Pb	-0.2	0.5	*	2.9	-0.4	3.5	-3.2	*	-3.6	-0.9	*	7.3	*	*	-2.7	-0.4	-0.1	*	
Pr	0.3	*	0.5	-3.0	-0.3	*	-6.2	*	-0.4	*	*	*	*	*	*	0.4	0.1	*	
Rb	-0.2	-1.6	0.7	-0.5	-0.3	1.0	*	-2.0	-0.6	-0.1	*	0.8	*	*	*	0.4	0.6	-2.3	
Sb	*	*	-0.4	*	-1.2	*	0.4	*	*	*	*	*	*	*	48.9	*	0.2	*	
Sc	-0.2	*	0.7	*	-1.1	*	*	*	*	7.6	*	*	*	*	4.6	-1.1	*		
Sm	0.5	*	0.4	*	-0.7	*	-6.1	*	-1.0	*	*	*	*	*	-0.3	0.1	*		
Sr	-0.6	-2.2	0.2	-0.4	-0.4	0.5	*	-2.5	0.0	-0.9	*	-0.4	*	*	*	0.5	0.1	0.6	
Ta	0.6	*	*	*	*	*	*	*	0.3	*	*	*	*	*	*	-0.4	-0.2	*	
Tb	1.0	*	-0.2	*	-0.7	*	-3.0	*	-1.6	*	*	*	*	*	*	-1.2	0.5	*	
Th	-0.1	-0.1	0.0	-3.3	0.0	*	-4.0	*	0.4	*	0.8	*	*	*	*	0.2	0.1	*	
Tl	*	*	0.8	*	-0.1	*	-9.4	*	*	*	*	*	*	*	*	1.6	-0.6	*	
Tm	1.0	*	1.3	*	-2.0	*	-0.9	*	-2.4	*	*	*	*	*	*	-2.1	0.5	*	
U	0.3	17.0	-1.6	*	-2.3	*	-3.8	*	-2.3	*	5.7	*	*	*	*	-2.6	1.0	*	
V	-1.5	-2.2	0.2	*	1.6	*	-3.8	*	*	*	0.4	9.0	*	*	-2.6	-0.3	-0.2	*	
W	*	*	-1.1	*	-0.7	*	*	*	*	*	*	*	*	*	*	*	*	*	
Y	-1.4	-5.7	-1.0	-0.1	2.1	0.7	-5.4	*	*	1.1	*	0.3	*	*	*	-2.9	0.4	*	
Yb	0.8	*	-1.3	*	-3.1	*	-5.4	*	-4.3	*	*	*	*	*	*	-4.8	0.8	*	
Zn	86.4	-0.8	*	-0.4	2.0	1.6	-1.3	*	*	-3.1	*	1.0	*	*	-1.6	*	-0.1	*	

N49\* Results withdrawn by participating laboratory after assessment of assigned value.

N88\*\*, N89\*\*, N90\*\*: Results submitted too late to contribute to the assessment of the assigned value.

Technique codes: A=ICP-AES; AA=AAS; C=colorimetry; E=(atomic) emission spectrometry; G=gravimetric;

I=INAA; IR= infra red detection; ISE=ion selective electrodes; M=ICP-MS; O=other;

T=titrimetry; W=wet chemistry; X=X-ray fluorescence.

	<b>Table 3</b> <b>Z-scores for GeoPT13 - LOESS</b>																	
Round identifier	N30	N31	N32	N32	N33	N34	N35	N35	N36	N37	N38	N39	N40	N41	N42	N43	N43	N44
Sample	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess
Technique codes	A	AA,M	M	M	X	X	X	X	AA,O	A	M,X	M	I	X	A,M	X	X	A,M
	O,X																	
Test portion (g)	0.05	0.1-0.75	0.1	0.1	0.3-6	1	0.6-6	0.6-6	0.1	0.2	0.1-5	0.25	0.15	1.0-5.0	0.25	1.2	9	0.25
Data quality	2	1	1	2	1	2	1	2	1	2	2	1	1	1	2	1	2	2
SiO <sub>2</sub>	*	0.1	*	*	-0.1	-0.9	-1.2	*	0.2	*	-0.3	*	*	3.0	0.9	0.3	*	*
TiO <sub>2</sub>	*	-1.0	*	*	0.8	1.9	0.8	*	4.9	46.1	-0.7	*	*	1.8	0.1	-1.8	*	-11.5
Al <sub>2</sub> O <sub>3</sub>	*	0.4	*	*	-1.4	1.2	-0.4	*	1.7	-1.2	-0.1	*	*	0.7	0.3	-0.1	*	*
Fe <sub>2</sub> O <sub>3</sub>	*	1.3	*	*	-3.9	-0.9	-0.9	*	-0.1	-0.9	0.3	*	-0.9	1.2	1.0	-0.9	*	-2.3
MnO	*	-2.3	*	*	-2.3	*	-2.3	*	4.4	-0.9	-1.1	*	*	-2.3	0.7	-1.7	*	-1.9
MgO	*	-0.2	*	*	-1.2	-4.0	-4.0	*	2.8	-1.3	0.2	*	*	-0.6	0.9	-7.2	*	0.8
CaO	*	-1.3	*	*	2.0	-0.3	-0.7	*	-5.4	-2.0	0.0	*	*	3.8	0.0	-1.7	*	1.1
Na <sub>2</sub> O	*	-0.4	*	*	-12.3	4.3	-4.2	*	6.3	-2.1	-1.1	*	6.3	-3.2	-0.3	-1.8	*	-1.5
K <sub>2</sub> O	*	-1.0	*	*	-0.6	-1.5	-2.9	*	-2.1	-0.7	1.1	*	*	4.1	-0.8	0.6	*	-0.2
P <sub>2</sub> O <sub>5</sub>	*	-0.3	*	*	5.7	*	0.0	*	0.0	-4.2	0.0	*	*	0.0	-0.7	5.9	*	*
CO <sub>2</sub>	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
LOI	*	-1.4	*	*	-0.5	0.4	-2.8	*	1.2	*	0.6	*	*	*	*	0.1	*	*
As	*	*	*	*	-1.8	*	*	*	*	*	*	*	-0.2	0.6	*	*	-0.8	2.8
Ba	-1.1	-1.0	-1.7	*	-0.8	*	8.2	*	*	-0.6	0.3	-0.1	0.6	*	0.7	*	0.6	-2.1
Be	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	-1.7
Bi	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Ce	*	-0.7	-0.3	*	-5.1	*	1.8	*	*	-1.2	0.1	0.1	1.5	*	0.2	*	*	*
Co	2.8	4.4	*	*	0.1	*	*	*	*	-4.1	*	-1.0	-0.4	*	-0.5	*	1.6	-2.1
Cr	0.3	-0.9	*	*	0.8	*	4.6	*	*	-2.5	*	-3.8	2.5	*	-1.3	*	2.2	-3.5
Cs	*	-0.7	-0.4	*	*	*	*	*	19.5	*	*	-0.4	-0.5	*	0.2	*	*	2.7
Cu	6.9	-3.0	*	*	-0.5	*	*	0.5	*	3.7	*	-1.2	*	2.7	-1.6	*	-3.0	-2.9
Dy	*	-1.9	0.1	*	*	*	*	*	*	-1.6	0.3	-3.1	*	*	0.4	*	*	*
Er	*	-3.7	-0.1	*	*	*	*	*	*	*	*	0.4	-4.7	*	*	0.3	*	*
Eu	*	-1.1	-0.4	*	*	*	*	*	*	*	*	0.0	-0.6	0.7	*	0.3	*	*
Ga	*	-0.3	*	*	-0.2	*	*	*	*	*	*	0.6	*	*	0.0	*	0.0	*
Gd	*	4.1	-0.2	*	*	*	*	*	*	*	*	0.1	-1.3	*	*	-0.3	*	*
Hf	*	-12.8	*	-3.5	-11.7	*	-1.7	*	*	*	*	-14.0	2.3	*	-0.1	*	*	*
Ho	*	-1.8	-0.3	*	*	*	*	*	*	*	*	0.4	-3.0	*	*	0.8	*	*
La	*	-0.3	0.0	*	-4.4	*	*	133.3	*	0.2	0.1	0.1	0.4	*	0.2	*	*	-0.5
Li	*	*	*	*	*	*	*	*	*	1.9	*	-0.2	*	*	*	*	*	*
Lu	*	-4.1	-1.5	*	*	*	*	*	*	*	*	0.1	-4.5	*	*	0.0	*	*
Mo	*	*	*	*	5.6	*	*	*	*	*	*	-1.1	0.8	*	0.6	*	*	2.2
Nb	*	-0.3	*	-0.1	2.8	*	*	10.4	*	*	-3.6	-2.3	*	10.8	-1.5	*	-0.2	*
Nd	*	-1.0	-0.3	*	*	*	*	0.7	*	*	0.1	0.2	*	-6.1	0.1	*	*	*
Ni	*	-0.5	*	*	-3.5	*	0.1	*	*	-0.2	*	0.7	0.7	3.2	0.5	*	-2.9	4.4
Pb	*	-0.4	0.1	*	1.1	*	*	*	*	1.3	*	-1.0	*	1.1	4.6	*	-0.8	-0.5
Pr	*	-0.1	-0.3	*	*	*	*	65.7	*	*	0.1	0.6	*	*	0.1	*	*	*
Rb	*	-2.0	0.0	*	0.4	*	2.1	*	*	*	-2.0	0.0	0.1	2.6	0.2	*	-0.7	*
Sb	*	*	*	*	*	*	*	*	*	*	*	-2.2	2.4	*	*	*	*	*
Sc	*	-0.5	*	*	36.1	*	*	*	*	-1.3	*	1.7	-0.1	16.8	-0.4	*	*	*
Sm	*	-1.1	-0.3	*	*	*	*	*	*	*	-0.2	-0.1	0.5	*	0.0	*	*	*
Sr	*	0.3	0.7	*	-1.1	*	0.2	*	*	-0.4	-3.8	-0.3	1.0	3.1	3.1	*	-0.7	*
Ta	*	-1.2	*	-0.2	*	*	*	*	*	*	*	-1.9	1.4	*	-0.2	*	*	*
Tb	*	-0.5	-0.4	*	*	*	*	*	*	*	0.1	-1.3	-0.6	*	0.2	*	*	*
Th	*	-0.7	0.4	*	-2.3	*	*	*	*	*	-2.2	0.0	1.0	12.4	0.6	*	-0.1	0.8
Tl	*	*	*	*	*	*	*	*	*	*	0.2	*	*	0.0	*	*	*	*
Tm	*	-2.8	-0.3	*	*	*	*	*	*	*	0.7	-3.5	*	*	*	*	*	*
U	*	-2.2	-0.9	*	7.0	*	*	*	*	*	0.8	-3.1	1.2	17.8	0.2	*	-2.1	-4.5
V	-2.7	-1.4	*	*	2.6	*	3.7	*	*	0.4	*	-2.2	*	*	-1.1	*	3.3	*
W	*	*	*	*	*	*	*	*	*	*	*	-0.3	0.4	*	*	*	*	1.4
Y	*	-3.1	-0.4	*	1.6	*	*	-0.9	*	-2.2	-0.1	-4.4	*	3.3	1.7	*	-0.5	*
Yb	*	-4.8	-1.4	*	*	*	*	*	*	-2.7	-0.1	-5.3	1.4	*	0.1	*	*	*
Zn	*	-1.9	*	*	1.6	*	*	-3.2	*	-6.3	*	-1.4	-0.9	2.2	-0.4	*	-1.4	*

N49\* Results withdrawn by participating laboratory after assessment of assigned value.

N88\*\*, N89\*\*, N90\*\*: Results submitted too late to contribute to the assessment of the assigned value.

Technique codes: A=ICP-AES; AA=AAS; C=colorimetry; E=(atomic) emission spectrometry; G=gravimetric;

I=INAA; IR= infra red detection; ISE=ion selective electrodes; M=ICP-MS; O=other;

T=titrimetry; W=wet chemistry; X=X-ray fluorescence.

	<b>Table 3</b> <b>Z-scores for GeoPT13 - LOESS</b>																	
Round identifier	N45	N46	N47	N48	N49	N50	N51	N52	N52	N53	N54	N55	N56	N57	N58	N59	N59	N60
Sample	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess
Technique codes	AAC,IS	A,AA	A,IR	A,M,X		X	AO,,X	X,M	M	X	A,AA	A,X	X	AA,X	AA,IR	X	X	X
	TX	O,X	M,X													TX		
Test portion (g)	0.5-10	0.2-3	0.2-7	0.2		0.17	0.25-5	0.1-0.6	0.1	0.6-5.4	0.5	1-1.5	1.0-6	0.5-1	0.1-4	1.0-20	20	1
Data quality	2	1	2	2		1	2	1	2	1	2	2	2	2	1	1	2	1
SiO <sub>2</sub>	-0.1	0.6	1.1	-0.6		0.7	0.1	-0.7	*	0.4	*	0.0	-0.7	0.4	0.3	-0.9	*	-10.9
TiO <sub>2</sub>	-3.8	4.9	0.9	0.4		3.5	-0.1	0.8	*	-0.2	-11.7	0.4	0.1	-1.7	-0.3	-1.3	*	5.9
Al <sub>2</sub> O <sub>3</sub>	-0.6	-0.7	-0.2	-0.6		0.7	-0.6	-1.2	*	-0.5	0.9	0.0	0.4	1.4	-0.5	0.2	*	18.0
Fe <sub>2</sub> O <sub>3</sub>	-1.4	-6.0	0.2	-0.1		0.9	1.1	-0.9	*	0.2	3.8	0.1	0.1	-2.6	-0.7	-1.2	*	8.6
MnO	-0.6	-1.7	0.4	-0.1		14.7	0.7	-2.3	*	0.1	5.5	1.4	-0.1	-3.7	-2.3	-2.3	*	8.0
MgO	-2.6	-2.4	0.3	-0.1		0.0	-0.1	1.4	*	-0.1	3.8	-0.2	-0.8	2.9	0.6	-4.4	*	8.0
CaO	1.3	-1.0	0.8	0.3		1.8	0.0	-0.3	*	0.5	-4.9	0.0	-0.1	-0.7	0.9	2.4	*	14.8
Na <sub>2</sub> O	1.5	-0.4	0.8	0.5		-7.5	0.3	1.1	*	-0.9	2.0	0.5	*	-3.8	2.5	-2.8	*	-25.6
K <sub>2</sub> O	2.4	-2.5	0.3	-0.3		-1.8	0.5	-0.2	*	-0.4	-4.9	0.5	-0.3	-1.8	1.7	-1.0	*	-0.6
P <sub>2</sub> O <sub>5</sub>	1.0	-3.1	-0.1	-3.8		-9.9	-1.0	0.0	*	-1.2	232.0	-1.4	0.4	-4.2	0.0	0.0	*	-11.3
CO <sub>2</sub>	-5.2	-0.3	1.4	*		*	0.7	*	*	*	*	*	*	*	*	0.4	*	*
LOI	0.1	0.2	-0.2	0.1		-2.1	0.0	*	*	0.0	*	-0.3	0.2	-0.4	-0.4	-0.6	*	4.6
As	-1.3	-3.4	-1.0	3.2		*	0.3	*	*	0.7	*	-2.7	2.8	*	*	*	*	*
Ba	3.5	-5.4	-0.2	-0.3		*	0.4	*	-0.4	0.2	1.7	-4.6	0.5	*	-2.1	*	0.5	*
Be	*	*	*	*		*	-1.2	*	*	*	*	*	*	*	*	*	*	*
Bi	*	0.2	*	0.4		*	*	*	*	*	*	*	*	*	*	*	*	*
Ce	*	-1.8	-0.5	0.5		*	-0.4	0.8	*	-4.1	*	*	-1.0	*	*	*	0.9	*
Co	-0.1	*	1.4	-1.4		*	-1.3	*	*	-0.5	-12.5	2.8	-4.1	*	0.1	*	-5.4	*
Cr	2.7	-5.2	-1.7	-1.3		-25.2	1.0	*	*	1.6	22.5	-4.1	-2.5	-0.9	-0.9	*	*	*
Cs	*	*	-0.1	-0.3		*	*	-0.2	*	*	*	*	*	*	*	*	*	*
Cu	2.1	1.1	3.6	-1.2		*	1.3	*	*	0.7	-1.3	*	-2.6	0.5	-3.7	-2.1	*	*
Dy	*	-1.4	-0.2	-0.8		*	0.3	-1.3	*	*	*	*	*	*	*	*	*	*
Er	*	-0.4	-0.7	-1.0		*	-0.2	-2.1	*	*	*	*	*	*	*	*	*	*
Eu	*	-1.1	-0.4	-0.5		*	0.1	0.0	*	*	*	*	*	*	*	*	*	*
Ga	*	*	0.1	-3.5		*	-0.7	*	*	*	*	*	-1.3	*	2.2	2.2	*	*
Gd	*	-0.4	0.3	-0.2		*	-0.5	-0.9	*	*	*	*	*	*	*	*	*	*
Hf	*	*	-1.5	*		*	*	*	-4.2	2.0	*	*	-3.9	*	-0.2	*	*	*
Ho	*	1.4	-0.3	-1.0		*	-1.5	-1.2	*	*	*	*	*	*	*	*	*	*
La	*	-1.7	-0.3	0.6		*	0.6	0.2	*	-1.4	*	*	-3.0	*	*	*	4.2	*
Li	*	1.0	*	-0.3		*	0.0	*	*	*	-3.5	*	*	*	*	*	*	*
Lu	*	0.3	-0.3	-1.5		*	0.1	-1.8	*	*	*	*	*	*	*	*	*	*
Mo	0.0	*	2.9	-1.4		*	*	*	*	*	*	*	*	14.6	*	*	*	*
Nb	-0.8	*	-1.1	*		*	0.7	*	-0.8	-0.2	*	*	1.4	1.4	-3.2	2.8	*	*
Nd	*	-3.4	-0.7	0.3		*	-1.0	1.3	*	-5.5	*	*	*	*	*	*	*	*
Ni	-0.5	-3.5	2.3	1.0		*	-1.0	*	*	-1.9	-10.7	-3.3	-0.4	-0.7	-2.9	-1.9	*	*
Pb	0.7	*	1.1	-0.7		*	0.5	-0.7	*	*	*	-7.4	-0.3	0.5	1.1	-3.7	*	*
Pr	*	-2.7	-0.5	0.6		*	0.1	0.9	*	*	*	*	*	*	*	*	*	*
Rb	-1.1	2.1	0.2	-0.1		*	0.4	-0.2	*	-0.4	*	*	0.2	*	-1.4	0.4	*	*
Sb	*	-6.4	0.0	-0.8		*	*	*	*	*	*	*	*	*	*	*	*	*
Sc	*	*	-0.4	-0.9		*	*	1.6	*	16.9	*	*	*	*	16.8	-13.6	*	*
Sm	*	-0.2	-0.7	0.0		*	-0.7	0.1	*	*	*	*	*	*	*	*	*	*
Sr	-0.2	-3.4	0.4	-0.2		*	0.6	1.7	*	-0.4	1.6	-4.1	-0.7	3.8	-0.2	-0.9	*	*
Ta	*	*	-1.0	*		*	*	*	-1.0	*	*	*	*	26.9	*	*	*	*
Tb	*	*	0.0	-0.7		*	0.1	-0.1	*	*	*	*	*	*	*	*	*	*
Th	-2.5	4.0	-0.2	-0.1		*	*	-0.5	*	6.1	*	*	-2.2	*	-2.3	-0.2	*	*
Tl	*	*	-0.4	*		*	*	*	*	*	*	*	*	*	*	*	*	*
Tm	*	0.4	-0.3	-1.1		*	1.0	-1.2	*	*	*	*	*	*	*	*	*	*
U	-6.2	*	2.1	-0.3		*	*	-1.1	*	*	*	*	*	1.6	*	*	*	*
V	2.2	-12.4	1.0	-7.4		*	-1.0	*	*	-0.8	-6.6	*	-1.0	-0.2	-4.3	*	3.6	*
W	*	*	*	*		*	*	*	*	*	*	*	*	*	-5.4	*	*	*
Y	-1.3	-1.2	0.6	-2.1		*	0.8	-2.6	*	0.5	*	*	1.2	*	1.6	0.7	*	*
Yb	*	-0.2	-1.9	-1.6		*	0.2	-2.3	*	*	*	*	*	*	*	*	*	*
Zn	-0.4	1.0	0.3	-0.9		*	0.2	*	*	-1.3	-7.7	-2.0	2.0	6.0	-0.9	-0.3	*	*

N49\* Results withdrawn by participating laboratory after assessment of assigned value.

N88\*\*, N89\*\*, N90\*\*: Results submitted too late to contribute to the assessment of the assigned value.

Technique codes: A=ICP-AES; AA=AAS; C=colorimetry; E=(atomic) emission spectrometry; G=gravimetric;

I=INAA; IR= infra red detection; ISE=ion selective electrodes; M=ICP-MS; O=other;

T=titrimetry; W=wet chemistry; X=X-ray fluorescence.

	<b>Table 3</b> <b>Z-scores for GeoPT13 - LOESS</b>																		
Round identifier	N61	N62	N63	N64	N65	N65	N66	N67	N68	N69	N70	N71	N72	N73	N73	N74	N75	N76	
Sample	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	
Technique codes	AA,E	A,T,X	A,IR,M	M,X	I	I	X	X	A	X	X	X	M,V,X	I	I	A,IR,M	X	A,M	
	O,T,X		O,X														T,X		
Test portion (g)	0.02-5	0.1-4	0.25-2	0.1-10	1	1.0-10	0.7	0.28	0.25	0.18	0.3	0.4	0.2-7	0.23	0.23	0.2-4	10	0.2-0.25	
Data quality	2	2	2	1	1	2	1	2	1	2	2	2	2	1	2	2	2	2	
SiO <sub>2</sub>	-0.4	0.7	0.1	0.3	*	*	0.1	*	-0.3	*	*	0.7	0.6	*	0.4	-0.5	*	0.2	
TiO <sub>2</sub>	-0.7	1.5	-0.7	-0.9	*	*	-0.1	-1.2	26.7	-5.4	*	-0.7	-1.4	-0.3	*	-2.7	0.7	-0.7	
Al <sub>2</sub> O <sub>3</sub>	0.3	-0.5	-0.3	0.1	*	*	-0.5	*	3.6	*	*	0.2	0.0	4.1	*	-1.5	*	-0.2	
Fe <sub>2</sub> O <sub>3</sub>	0.9	1.6	-0.5	-0.9	*		1.5	0.9	3.9	-0.7	-4.6	-2.7	-0.6	-0.7	-0.4	*	1.5	-0.1	-0.6
MnO	0.4	1.2	-1.1	-0.7	*	*	0.3	7.4	0.8	-0.6	*	-1.1	0.9	0.3	*	-1.1	-0.4	*	
MgO	-0.4	-1.4	-1.4	-1.2	*	*	-0.2	*	-0.8	*	*	0.9	-1.2	1.8	*	0.8	*	-0.3	
CaO	1.1	-1.0	-0.5	-0.5	*	-0.1	0.4	3.5	-2.5	-7.3	-5.4	-0.4	0.8	2.9	*	0.1	4.3	-1.1	
Na <sub>2</sub> O	-0.8	-1.6	-1.4	2.0	*	0.6	2.0	*	1.8	*	*	0.8	-1.1	1.1	*	1.0	*	*	
K <sub>2</sub> O	-0.4	-0.1	0.3	0.0	*	-1.1	-0.2	*	-1.8	-11.2	*	0.1	-0.7	2.9	*	0.9	-2.8	0.3	
P <sub>2</sub> O <sub>5</sub>	2.1	-2.8	-1.4	7.9	*	*	0.3	*	-0.6	*	*	0.0	-1.3	*	*	-1.4	*	*	
CO <sub>2</sub>	0.1	-9.1	0.4	*	*	*	*	*	*	*	*	*	*	*	*	*	-2.4	*	
LOI	0.2	-0.3	-0.1	-0.3	*	*	*	*	-36.8	-0.1	*	*	*	-0.1	*	*	0.8	*	
As	*	*	*	3.8	*	-0.1	*	*	*	*	*	*	*	*	1.3	*	*	*	
Ba	-3.5	5.1	-0.6	0.7	*	1.0	0.4	-1.5	0.7	*	*	*	-1.5	0.3	*	*	*	*	
Be	*	*	*	0.1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
Bi	*	*	*	0.2	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
Ce	*	*	1.1	1.4	-1.0	*	*	0.3	*	*	*	*	*	-0.6	0.8	*	-0.7	*	
Co	0.6	0.5	2.8	1.8	*	-0.1	2.9	*	5.6	*	*	*	0.1	-1.5	*	*	*	-0.3	
Cr	4.1	-2.2	-0.7	5.3	*	0.8	1.3	-3.3	-3.5	-3.2	*	*	3.0	1.5	*	*	*	-0.7	
Cs	*	*	0.8	1.1	*	-0.6	*	*	*	*	*	*	*	-0.8	*	0.4	*	-0.3	
Cu	2.9	*	-2.6	0.1	*	*	-10.0	*	-0.5	2.1	*	*	0.5	*	*	-1.8	7.7	-1.0	
Dy	*	*	-1.0	3.1	*	*	*	*	*	*	*	*	-2.2	2.8	*	0.3	*	*	
Er	*	*	-1.7	2.6	*	*	*	*	*	*	*	*	-2.9	*	*	0.3	*	*	
Eu	*	*	0.8	1.3	-0.1	*	*	*	*	*	*	*	-0.8	0.1	*	0.0	*	*	
Ga	*	*	0.7	0.3	*	*	2.2	*	*	1.7	*	*	*	*	*	*	7.0	*	
Gd	*	*	0.9	1.9	*	*	*	*	*	*	*	*	-1.3	*	*	-0.3	*	*	
Hf	*	*	-7.7	1.1	*	0.3	*	*	*	*	*	*	*	3.1	*	-3.2	*	*	
Ho	*	*	-0.7	2.9	3.5	*	*	*	*	*	*	*	-2.0	*	*	0.4	*	*	
La	*	*	1.8	1.8	-0.3	*	*	-4.2	*	*	*	*	-0.4	-1.1	*	-0.5	*	0.0	
Li	-0.9	*	-0.4	-0.5	*	*	*	*	*	*	*	*	*	*	*	0.5	*	*	
Lu	*	*	-2.5	1.5	-0.6	*	*	*	*	*	*	*	-3.1	1.3	*	0.1	*	*	
Mo	19.3	2.7	*	-0.2	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
Nb	0.4	1.8	-2.9	0.5	*	*	6.8	*	2.8	*	*	*	-0.6	*	*	0.4	*	*	
Nd	*	*	1.1	1.8	-0.5	*	*	*	*	*	*	*	-0.8	0.7	*	-0.6	*	*	
Ni	-0.2	-2.3	-0.7	0.5	*	*	0.1	1.4	34.1	-1.2	*	*	3.9	*	*	*	*	0.3	
Pb	-1.6	-1.4	*	-0.2	*	*	*	*	*	*	*	*	0.5	*	*	*	*	0.7	
Pr	*	*	0.3	*	*	*	*	*	*	*	*	*	-0.8	*	*	-0.2	*	*	
Rb	2.0	-0.1	0.6	0.0	*	1.6	0.4	-3.6	*	-0.3	17.4	*	0.0	-0.3	*	*	0.2	*	
Sb	*	*	*	0.0	*	-0.1	*	*	*	*	*	*	*	0.2	*	*	*	*	
Sc	7.0	*	-1.3	0.4	*	-0.2	22.3	*	38.8	*	*	*	*	-0.5	*	*	*	*	
Sm	*	*	0.9	1.4	-0.6	*	*	*	*	*	*	*	-0.8	-0.1	*	-0.6	*	*	
Sr	1.6	-0.4	0.2	1.1	*	*	0.9	5.1	1.6	-0.3	*	*	-2.0	1.0	*	0.7	-0.6	0.5	
Ta	*	*	-2.7	-2.9	*	*	*	*	*	*	*	*	*	-2.4	*	-0.1	*	*	
Tb	*	*	0.1	1.8	1.3	*	*	*	*	*	*	*	-1.4	-0.5	*	0.0	*	*	
Th	-1.7	-1.1	1.4	2.1	*	0.3	*	*	*	*	*	*	-0.1	0.0	*	-0.9	*	*	
Tl	*	*	*	1.0	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
Tm	*	*	-0.6	3.2	*	*	*	*	*	*	*	*	-3.0	*	*	0.4	*	*	
U	*	-0.4	-0.8	1.3	*	-0.7	*	*	*	*	*	*	*	*	0.2	*	-0.2	*	
V	4.1	5.3	-0.7	1.8	*	*	2.0	23.7	-0.3	*	*	*	2.1	0.5	*	*	*	-0.4	
W	*	*	*	0.1	*	*	*	*	*	*	*	*	*	1.8	*	*	*	*	
Y	0.1	-0.2	-2.7	-0.2	*	*	2.4	0.8	5.0	-2.2	*	*	-0.1	*	*	1.3	-0.5	*	
Yb	*	*	-3.0	1.6	0.1	*	*	*	*	*	*	*	-3.4	2.1	*	-0.1	*	*	
Zn	0.5	*	1.1	1.5	*	*	-0.3	3.3	-1.5	11.0	*	*	0.8	0.3	*	0.8	3.3	-0.4	

N49\* Results withdrawn by participating laboratory after assessment of assigned value.

N88\*\*, N89\*\*, N90\*\*: Results submitted too late to contribute to the assessment of the assigned value.

Technique codes: A=ICP-AES; AA=AAS; C=colorimetry; E=(atomic) emission spectrometry; G=gravimetric;

I=INAA; IR= infra red detection; ISE=ion selective electrodes; M=ICP-MS; O=other;

T=titrimetry; W=wet chemistry; X=X-ray fluorescence.

	<b>Table 3</b> <b>Z-scores for GeoPT13 - LOESS</b>															
Round identifier	N77	N78	N79	N80	N81	N82	N82	N83	N84	N85	N86	N87	N88	N89	N90	
Sample	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess	Loess
Technique codes	X M,X	A,AA,I	X	X T,X	I	A,IR	A,X ISE,M,X	AA,E, ISE,M,X	AA,E, ISE,M,X	A,G,T	X I	I,X	X,M	M		
Test portion (g)	1.0-10	0.1-0.8	1.5	0.125-3.5	2.3	0.1-7.5	0.5-7.5	0.1-1.2	0.1-1.2	0.1-1	5	0.035	0.04-15	0.1-12		0.25
Data quality	1	1	2	1	1	2	1	2	2	2	2	2	2	2	2	1
SiO <sub>2</sub>	*	-0.1	0.1	0.7	*	-1.1	*	0.0	*	0.3	-2.7	*	*	0.3	-0.4	*
TiO <sub>2</sub>	0.2	-0.5	-0.2	-0.6	*	-3.3	*	-0.2	*	-6.0	*	*	-10.1	-0.2	-1.2	*
Al <sub>2</sub> O <sub>3</sub>	*	-1.0	0.1	1.2	3.4	0.4	*	0.4	*	0.2	*	*	*	-0.7	1.0	*
Fe <sub>2</sub> O <sub>3</sub>	*	-1.5	-2.5	-1.7	-1.5	1.7	*	-0.5	*	-1.3	*	0.3	*	-0.3	-0.1	*
MnO	0.8	-0.2	-0.6	0.0	1.7	0.8	*	*	-1.9	-0.4	*	*	-2.7	0.4	0.7	*
MgO	*	0.4	2.0	-0.6	-1.6	1.4	*	*	0.3	-0.1	*	*	*	-0.9	0.0	*
CaO	*	-0.4	0.0	0.5	*	1.0	*	0.8	*	0.3	11.9	*	8.7	0.1	-0.2	*
Na <sub>2</sub> O	*	-4.7	-0.2	-0.3	0.6	2.5	*	2.5	*	-0.9	*	1.7	1.7	-2.0	1.2	*
K <sub>2</sub> O	*	-0.4	0.3	1.1	5.2	2.1	*	0.2	*	*	*	*	38.0	0.9	5.4	*
P <sub>2</sub> O <sub>5</sub>	1.4	0.6	-0.7	-0.6	*	-3.1	*	*	-0.1	-3.3	2.8	*	*	-0.8	0.0	*
CO <sub>2</sub>	*	0.0	*	*	*	-1.1	*	*	*	*	*	*	*	*	*	*
LOI	0.4	0.7	0.1	-2.3	*	1.4	*	*	-0.2	0.0	*	*	*	0.0	-0.4	*
As	*	0.4	*	*	0.9	*	*	*	2.4	*	*	-0.1	-0.1	-1.9	*	*
Ba	6.9	0.4	*	1.2	-0.1	-1.0	*	*	-1.8	-0.3	-1.2	*	*	-0.8	*	-0.5
Be	*	-1.4	*	*	*	*	*	*	2.2	*	*	*	*	-0.6	*	*
Bi	*	*	*	*	*	*	*	*	*	*	*	*	*	34.9	*	*
Ce	1.5	0.2	*	-0.1	7.8	-0.4	*	*	2.4	-3.4	*	0.4	0.4	-3.2	*	0.0
Co	-0.7	-1.0	*	*	-2.6	*	0.1	*	-0.8	*	*	-0.2	-0.2	0.5	*	*
Cr	10.3	-1.3	*	-3.8	0.3	4.4	*	*	-2.1	-2.4	*	-0.3	-0.3	-1.2	*	*
Cs	*	0.1	*	0.5	1.0	*	*	-3.8	*	*	*	-0.1	-0.1	-0.1	*	-1.2
Cu	*	-3.0	*	-8.6	*	-0.5	*	2.7	*	*	*	*	*	-4.1	0.1	*
Dy	*	-0.1	*	3.1	0.7	*	*	*	*	*	*	*	*	*	*	0.7
Er	*	-0.8	*	1.7	*	*	0.5	*	*	*	*	*	*	*	*	-1.5
Eu	*	-0.1	*	1.3	2.9	1.1	*	*	*	*	*	-0.3	-0.3	*	*	0.4
Ga	-0.7	-1.5	*	-0.7	*	-0.2	*	*	*	*	*	*	*	-1.6	*	-0.2
Gd	*	-0.3	*	1.5	*	*	0.4	*	*	*	*	*	*	*	*	-0.1
Hf	*	1.0	*	1.0	1.1	*	-2.0	*	*	*	*	1.4	1.4	-1.8	*	-0.5
Ho	*	4.3	*	2.6	*	2.8	*	*	*	*	*	*	*	*	*	1.2
La	*	0.9	*	1.4	0.4	0.4	*	*	-1.0	*	*	0.8	0.8	-3.0	*	-1.0
Li	*	-1.8	*	*	*	*	*	0.1	*	-0.4	*	*	*	-0.1	*	*
Lu	*	0.9	*	0.8	0.9	0.9	*	*	*	*	*	0.6	0.6	*	*	-2.5
Mo	*	*	*	*	*	*	*	*	-3.1	*	*	*	*	-0.6	0.7	*
Nb	-1.8	0.6	*	0.6	*	*	-0.6	*	0.4	*	*	*	*	-0.4	*	-2.5
Nd	*	0.8	*	-0.6	1.4	0.7	*	*	*	*	*	2.2	2.2	-2.2	*	-0.3
Ni	2.6	-0.5	*	-3.7	*	-0.9	*	*	1.1	-0.2	*	*	*	-0.6	*	*
Pb	1.8	0.6	*	1.2	*	-5.3	*	*	-0.7	*	*	*	*	-0.4	*	*
Pr	*	-0.8	*	-0.5	*	*	-0.1	*	*	*	*	*	*	*	*	0.0
Rb	-0.8	0.1	*	1.6	1.7	-0.1	*	-2.7	*	*	-1.4	-0.2	-0.2	-0.6	*	-1.7
Sb	*	-0.2	*	*	0.4	*	*	*	*	*	*	*	*	-0.8	*	*
Sc	25.6	0.1	*	2.7	-0.3	-0.3	*	*	*	*	*	-0.3	-0.3	5.1	*	*
Sm	*	1.5	*	1.0	0.6	1.0	*	*	*	*	*	1.1	1.1	-2.4	*	-0.1
Sr	-1.2	-0.2	*	1.2	*	-0.3	*	*	-0.1	-0.4	-1.4	*	-2.9	-0.2	*	0.5
Ta	*	1.2	*	1.1	1.2	*	*	*	*	*	*	2.5	2.5	*	*	-0.2
Tb	*	1.0	*	2.0	1.9	*	0.2	*	*	*	*	-0.7	-0.7	*	*	0.7
Th	-1.5	1.5	*	2.5	1.9	*	2.0	*	*	*	*	-0.1	-0.1	0.2	*	-0.5
Tl	*	-1.1	*	*	*	*	*	*	*	*	*	*	*	-0.1	*	*
Tm	*	1.7	*	1.7	*	*	1.0	*	*	*	*	*	*	*	*	0.1
U	3.2	1.4	*	1.0	1.6	*	0.8	*	*	*	*	0.8	0.8	-1.3	*	-0.8
V	-2.2	-3.0	*	-4.5	0.6	0.8	*	*	*	-2.9	*	*	*	-2.4	*	*
W	*	2.5	*	*	*	*	*	*	*	*	*	*	*	11.2	-1.1	*
Y	-2.5	-0.3	*	3.8	*	1.1	*	*	1.2	-3.6	*	*	*	0.1	*	-0.8
Yb	*	1.5	*	0.4	3.4	0.9	*	*	-1.2	*	*	2.5	2.5	*	*	-0.9
Zn	-0.2	-0.2	*	-1.4	-0.9	-0.3	*	-1.5	*	-4.4	*	*	-4.8	-0.4	*	*

N49\* Results withdrawn by participating laboratory after assessment of assigned value.  
N88\*\*, N89\*\*, N90\*\*: Results submitted too late to contribute to the assessment of the assigned value.  
Technique codes: A=ICP-AES; AA=AAS; C=colorimetry; E=(atomic) emission spectrometry; G=gravimetric;  
I=INAA; IR= infra red detection; ISE=ion selective electrodes; M=ICP-MS; O=other;  
T=titrimetry; W=wet chemistry; X=X-ray fluorescence.

**Table 4**

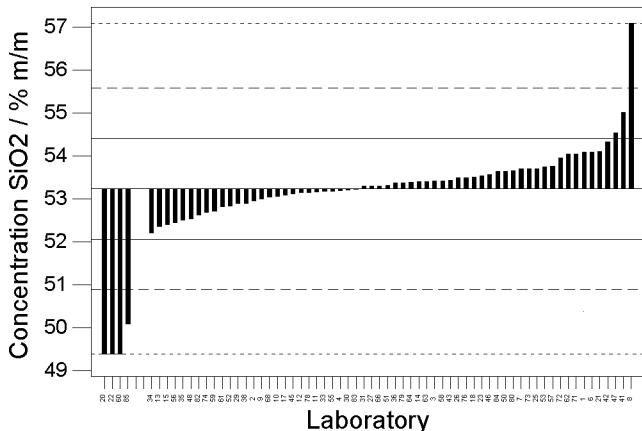
**Laboratories and names of principal contacts that participated in the GeoPT13 proficiency testing round.**

Nikolla Civici, Institute of Nuclear Physics, Tirana, Albania.
J. Pyke, Australian Geological Survey Organisation, Canberra City, ACT, Australia.
D. M. Hill, ANSTO, Menai, NSW, Australia.
H. Waldron, Becquerel Laboratories Pty Ltd., Menai, NSW, Australia.
Michael Lawrence, University of Queensland, St Lucia, Queensland, Australia.
Phil Robinson, University of Tasmania, Australia.
T.K. Chan, Genalysis Laboratory Services Pty Ltd., Maddington, WA, Australia.
Heinz Froeschl, ARC Seibersdorf research GmbH, Seibersdorf, Austria.
Andrzej Markowicz Head, IAEA Laboratories, Seibersdorf, Austria.
J. Enzweiler and Maria Aparecida V. Penereiro UNICAMP, Campinas, SP, Brazil.
Ana Maria Graciano Figueiredo, IPEN, Cidade Universitaria, Sao Paulo, Brazil.
Horst Peter H. G. J. Ulbrich, Universidade de São Paulo, Cidade Universitaria, São Paulo - SP, Brazil.
B. Caughlin, A.L.S. Chemex, North Vancouver, BC, Canada.
Hugh de Souza, XRAL Laboratories, Don Mills, Ontario, Canada.
Diane Wingett, Lakefield Research Ltd., Lakefield, Ontario, Canada.
J. Schweyer, Geoscience Laboratories, Sudbury, Ontario, Canada.
L. Paul Bedard, Université du Quebec à Chicoutimi, Quebec, Canada.
Yin Ming, National Research Centre for Geoanalysis, Beijing, P.R.China.
Qi Liang , Institute of Geochemistry, Guiyang, Guizhou Province, P.R.China.
Zheng Cunjiang, Xian Comprehensive Mineral and Rock, Xian, Shaanxi Province, P.R.China.
Xiaoming Liu, The Key Laboratory of Continental Dynamics, Northwest University, Xian, P.R. China.
Tong Chunyan / Ge Liangquan, Chengdu University of Technology, Chengdu, Sichuan, P.R.China.
Ludmila Dempirova, Czech Geological Survey, Prague 5-Barrandov, Czech Republic.
S. Grundvig, Aarhus University, Aarhus, Denmark.
Jorgen Kystol, Geological Survey of Denmark and Greenland, Copenhagen, Denmark.
Kirsten Theisen, F.L.Smidt, Valby, Denmark.
Tarmo Kiipli, Geological Survey of Estonia, Tallinn, Estonia.
Juha Virtasalo, Geological Survey of Finland, Rovaniemi, Finland.
J. C. Germanique, CEREGE, CNRS, Université Aix-Marseille III, Aix en Provence, France.
J-L. Joron, Laboratoire Pierre Sue, CE / Saclay, Gif sur Yvette, France.
Jean-Louis Bodinier, Université de Montpellier II, Montpellier, France.
C. Leduc, BRGM, Orleans, France.
Jean Samuel, Centre de Géochimie de la Surface, Strasbourg, France.
Mireille Polvé, Université Toulouse 3, Toulouse, France.
Paul Capiez, Universite Claude Bernard Lyon 1, Villeurbanne, France.
G. Matheis, Technical University of Berlin, Berlin, Germany.
Thomas Fockenberg, Ruhr-Universität Bochum, Bochum, Germany.
H. Mueller-Sigmund, Universität Friburg, Friburg, Germany.
Gerald Hartmann, Geowissenschaftliches Zentrum, Universtat Göttingen, Germany.
Stefan Pierdzig, CRB Analyse Service GmbH, Hardegsen, Germany.
Haino Uwe Kasper/Thorbjörn Schönbeck, Universitaet zu Koeln, Koeln, Germany.
U. Rast and A. Andres, Bayerisches Geologisches Landesamt, München, Germany.
Peter Dulski, Geoforschungs Zentrum Potsdam, Potsdam, Germany.
William Kwarteng, Huk Umweltlabor GmbH, Wenden, Germany.
G.K.D. Mazumdar, Science Instrumentation Centre, Gauhati University, Guwahati, India.
Zoltan Szokefalvi-Nagy, MTA KFKI RMKI, Hungary.
C.R.M.Rao, Geochemistry Division, CSI Complex, Hyderabad, India.
M. D’Orazio, Centro di Studio per la Geologia Strutturale e Dinamica dell’Appennino, Pisa, Italy.
Man Sik Choi, Korea Basic Science Institute, Daejeon, Korea.
Byoung-Ouk Kim, HANKUK Glass Industries, Inc., Gunsan, Jeonbuk, Korea.
Rufino Lozano Instituto de Geologia, UNAM, Ciudad Universitaria, D.F., Mexico.
B. Batjargal, Central Geological Laboratory, Ulaanbaatar, Mongolia.
Børre Davidsen, Geological Survey of Norway, Trondheim, Norway.
Jerzy Ostachowicz, AGH-University of Science and Technology, Krakow, Poland.
E. Popolek, Polish Geological Institute, Warsaw, Poland.
Fernando Castro, Campus de Azurem da Universidade do Minho, Azurem, Guimaraes, Portugal.

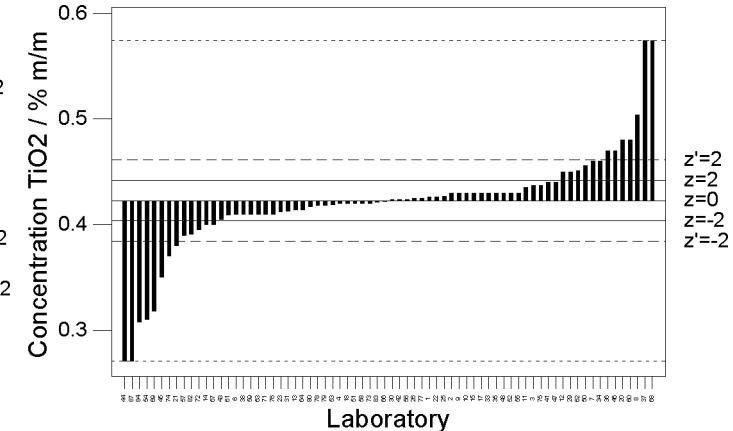
Maria Eugénia Moreira, Laboratorio do Instituto Geologico e Mineiro, S. Mamede de Infesta, Portugal.  
Maria Carlos Figueiredo, Centro Technológico da Cerâmica e do Vidro, Coimbra, Portugal.  
Bogdan Constantinescu, National Institute for Physics and Nuclear Engineering, Bucharest, Romania.  
Anatoly Revenko, Institute of the Earth's Crust, Irkutsk, Russia.  
L. Petrov, Institute of Geochemistry, Irkutsk, Russia.  
E. M. Sedykh / Irma A. Rostchina / Irina Koshcheeva, Vernadsky Institute of Geochemistry, Russian Academy of Sciences, Moscow, Russia.  
I. Borine, VSEGEI - All Russia Geological Research Institute, St Petersburg, Russia.  
Pavol Lucivansky, Geological Survey of Slovak Republic, Spisská Nová Ves, Slovakia.  
Peter Kump, J. Stefan Institute, Lubljana, Slovenia.  
Maria Fernanda Gazulla Barreda, Campus Universitario Riu Sec, Castellón, Spain.  
J.A. Martin Rubí, Instituto Geológico i Minero de España, Tres Cantos (Madrid), Spain.  
S. Turner / S. Hall, Wits University, Wits, Johannesburg, South Africa.  
M. Loubser, University of Pretoria, Pretoria, South Africa.  
J. O. Bomani, Southern and Eastern Africa Mineral Centre, Dar es Salaam, Tanzania.  
Thea G. van Meerten, Interfacultair Reactor Instituut, Delft, The Netherlands.  
J.N. Walsh, Royal Holloway, University of London, Egham, Surrey, UK.  
David S. Wray, The University of Greenwich, Chatham Maritime, Kent, UK.  
P.C. Webb / J.S. Watson, The Open University, Milton Keynes, UK.  
Charles J.B. Gowing, British Geological Survey, Keyworth, Nottingham, UK.  
D. Weights, University of Portsmouth, Portsmouth, UK.  
Michael J. Dobby, Sheffield Assay Office, Sheffield, UK.  
Karen Johnson, Ceram Research, Stoke-on-Trent, Staffs, UK.  
R. Sanzolone, U.S. Geological Survey, Denver, Colorado, USA.  
Henry E. Francis, Kentucky Geological Survey, University of Kentucky, Lexington, KY, USA.  
J. Thole, Macalester College, St Paul, Minnesota, USA.  
P R Kyle, New Mexico Tech, Socorro, NM, USA.  
R. Michael Kroc, Minerals Technologies, Inc, Easton, PA, USA.  
Arthur R. Jurgensen, Savannah River Site, Aiken, SC, USA.  
J. A. Wolff, Washington State University, Pullman, WA, USA.

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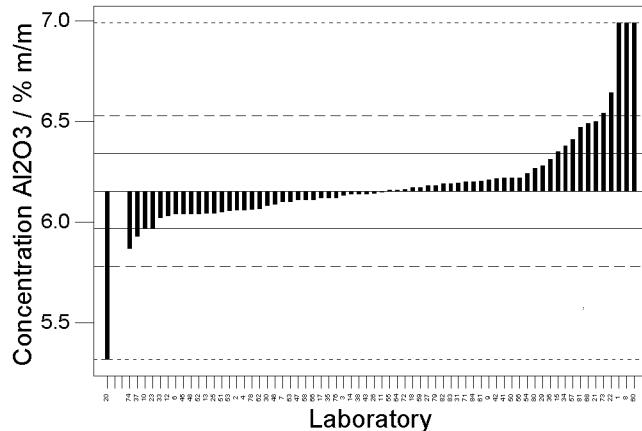
GeoPT13 Loess - Barchart for SiO<sub>2</sub>



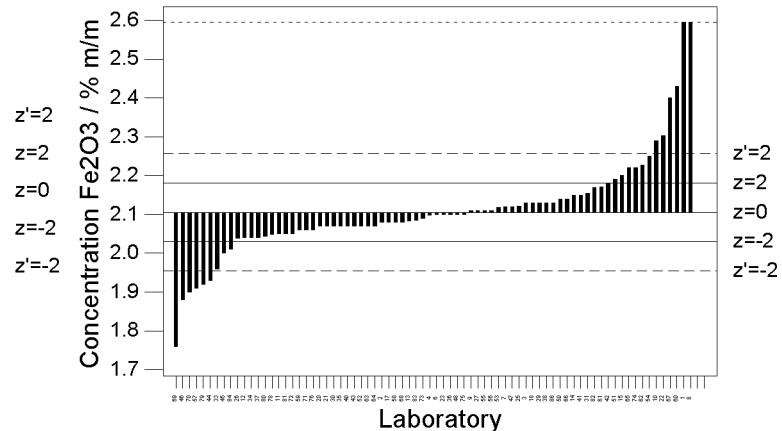
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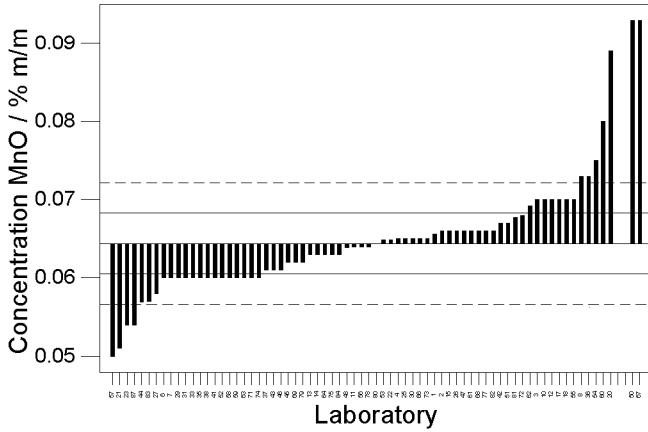
GeoPT13 Loess - Barchart for Al<sub>2</sub>O<sub>3</sub>



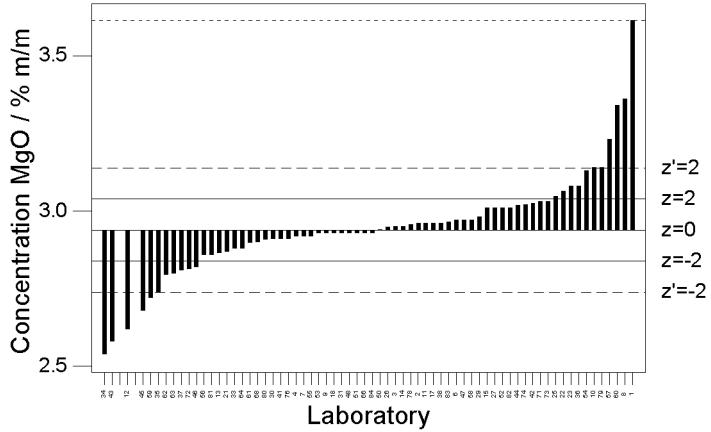
GeoPT13 Loess - Barchart for Fe<sub>2</sub>O<sub>3</sub>



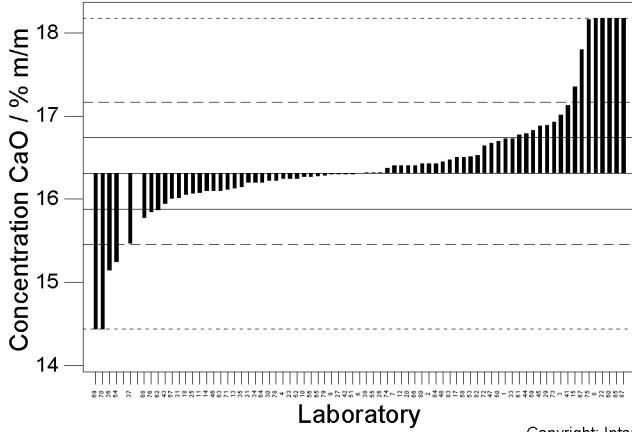
GeoPT13 Loess - Barchart for MnO



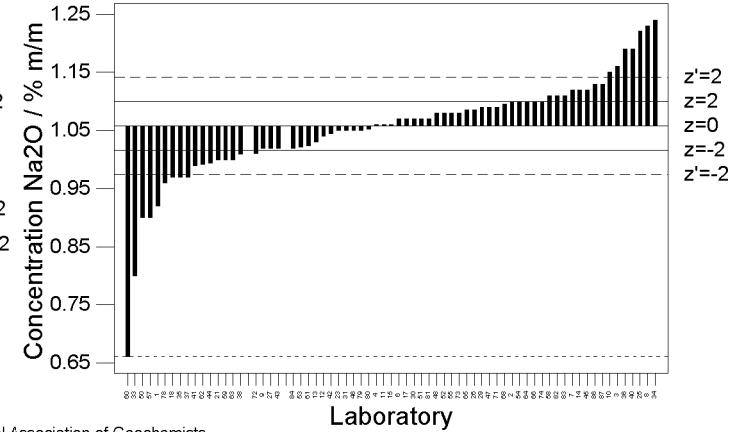
GeoPT13 Loess - Barchart for MgO



GeoPT13 Loess - Barchart for CaO



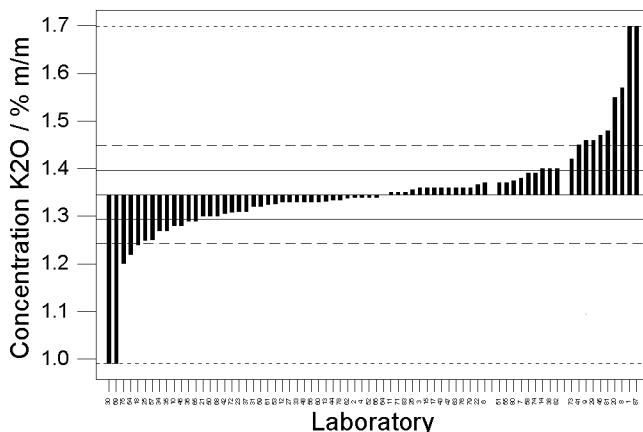
GeoPT13 Loess - Barchart for Na<sub>2</sub>O



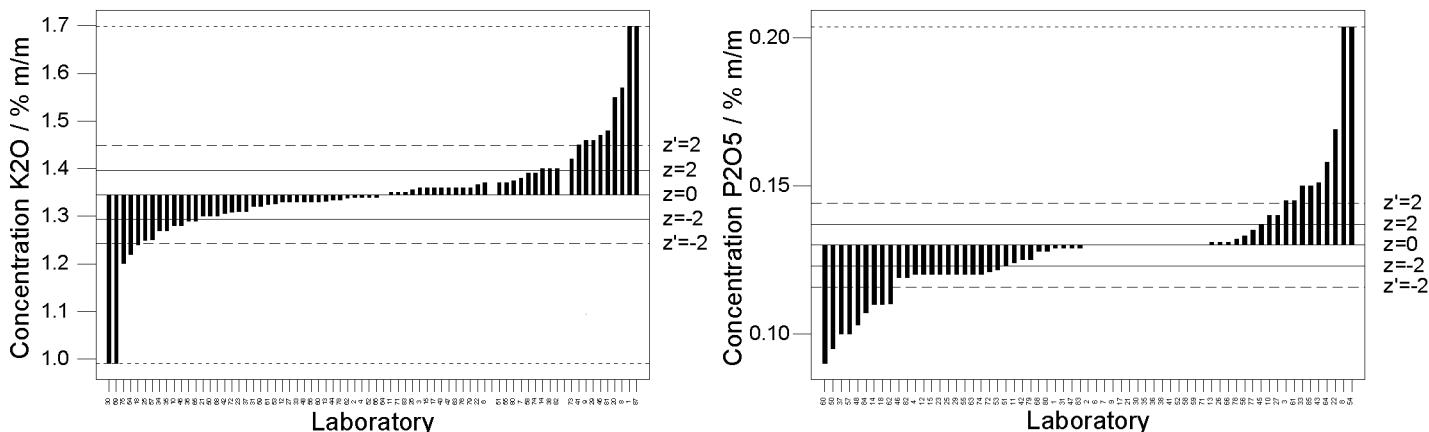
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**Figure 1 GeoPT13 –Loess:** Data distribution charts for elements for which values were assigned. Horizontal lines show the limits for  $-2 < z < 2$  for pure geochemistry labs (solid lines) and  $-2 < z' < 2$  for applied geochemistry labs (pecked lines).

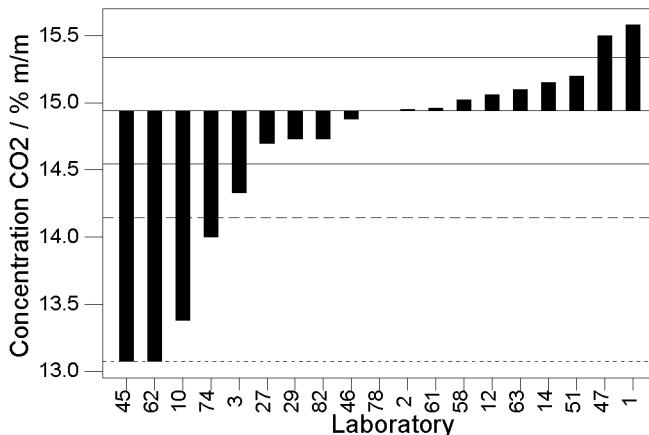
GeoPT13 Loess - Barchart for K2O



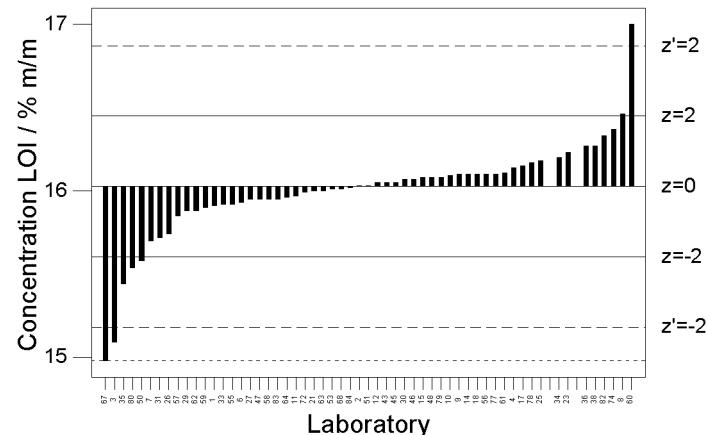
GeoPT13 Loess - Barchart for P2O5



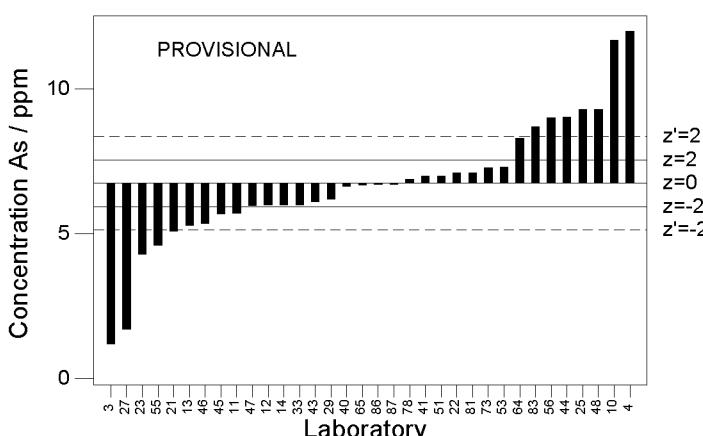
GeoPT13 Loess - Barchart for CO2



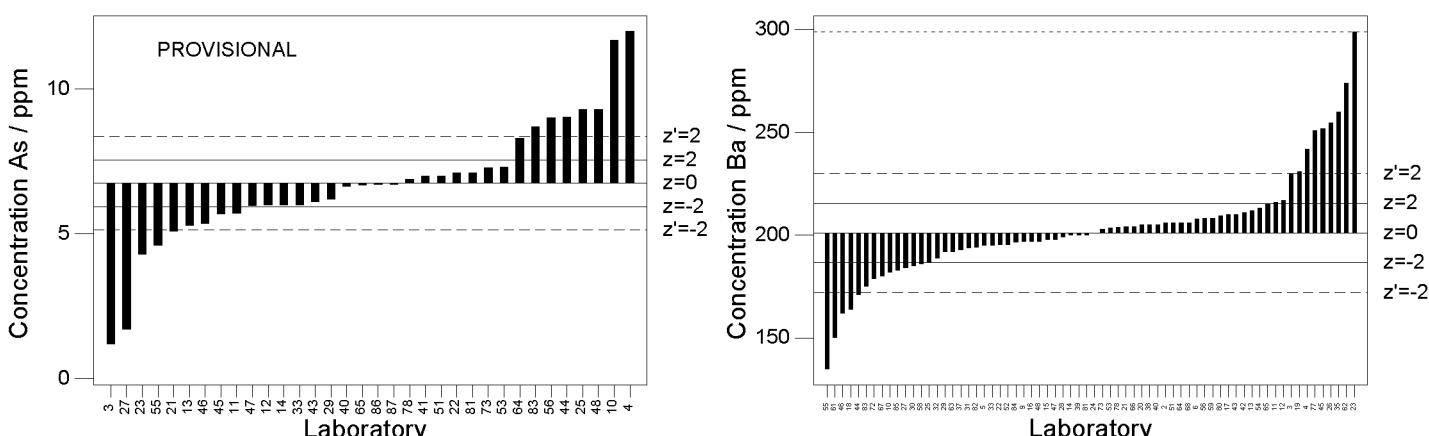
GeoPT13 Loess - Barchart for LOI



GeoPT13 Loess - Barchart for As

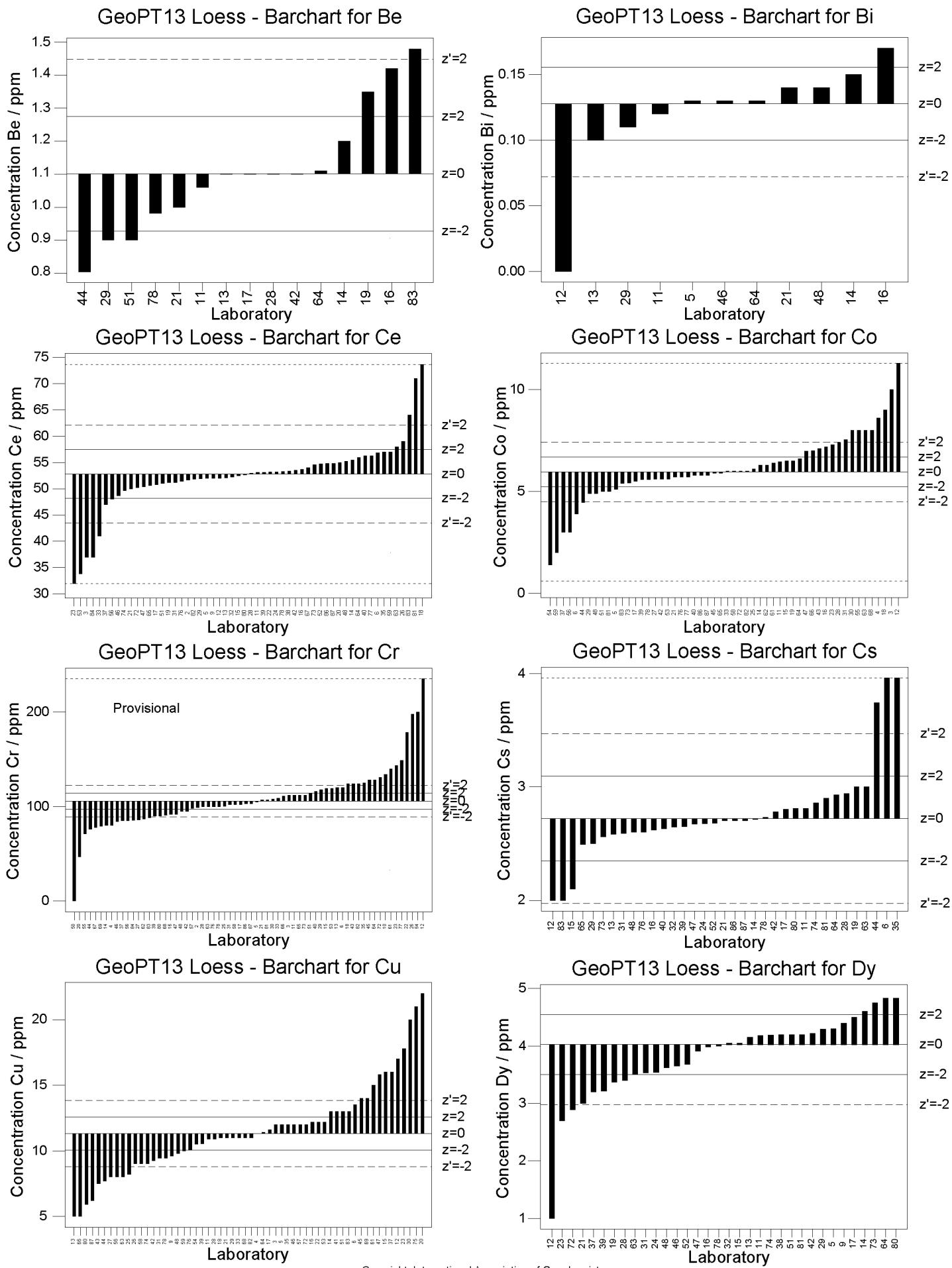


GeoPT13 Loess - Barchart for Ba



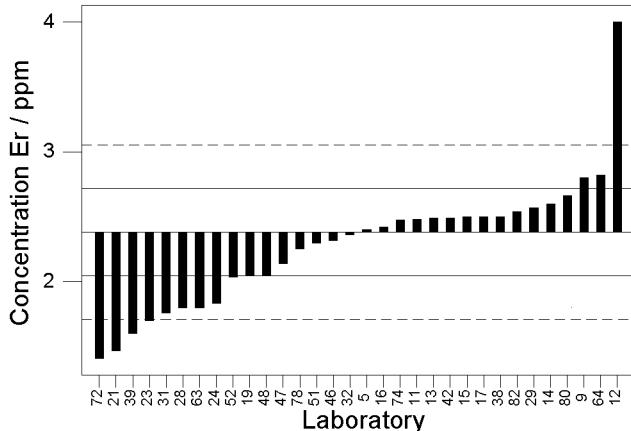
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**Figure 1 GeoPT13 –Loess:** Data distribution charts for elements for which values were assigned. Horizontal lines show the limits for  $-2 < z < 2$  for pure geochemistry labs (solid lines) and  $-2 < z' < 2$  for applied geochemistry labs (pecked lines).

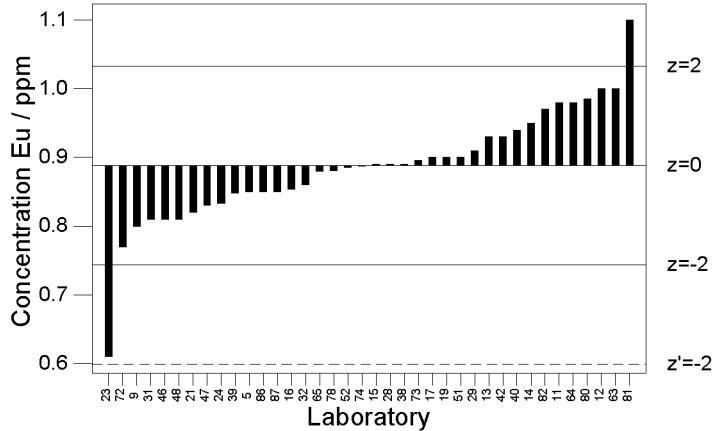


**Figure 1 GeoPT13 –Loess:** Data distribution charts for elements for which values were assigned. Horizontal lines show the limits for  $-2 < z < 2$  for pure geochemistry labs (solid lines) and  $-2 < z' < 2$  for applied geochemistry labs (pecked lines).

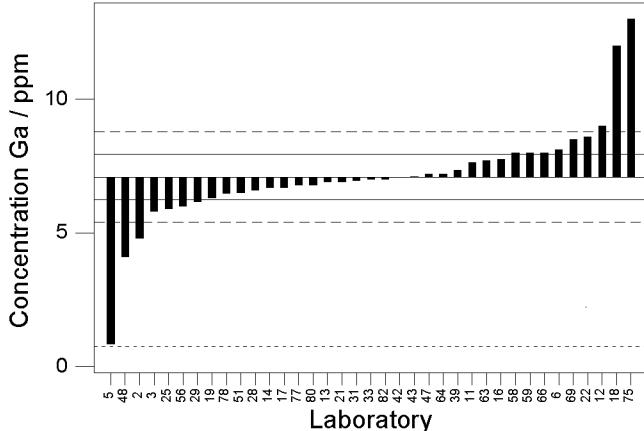
GeoPT13 Loess - Barchart for Er



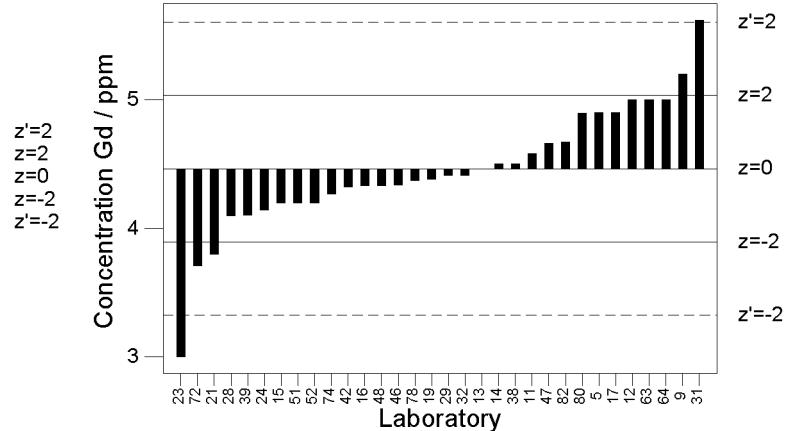
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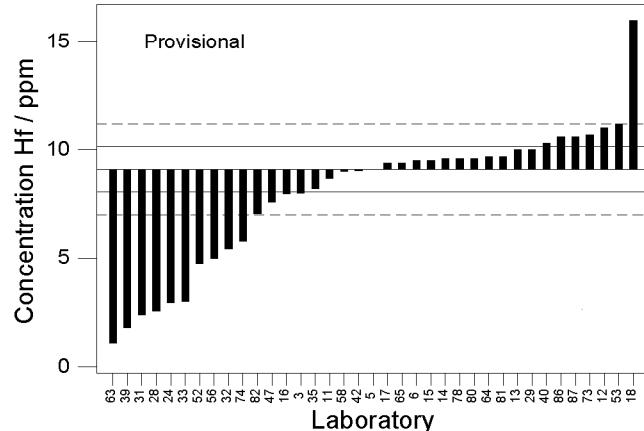
GeoPT13 Loess - Barchart for Ga



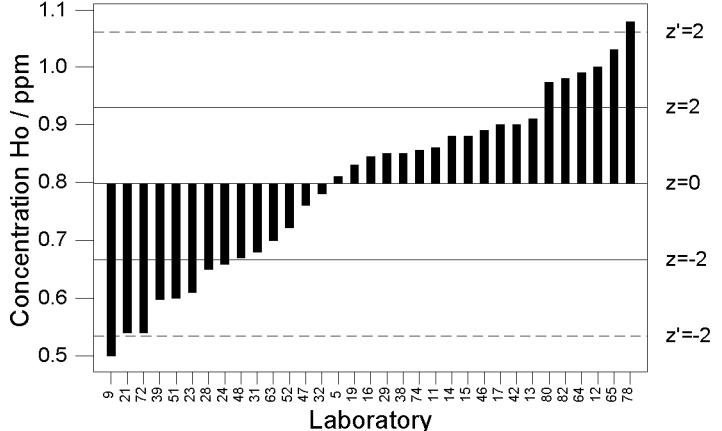
GeoPT13 Loess - Barchart for Gd



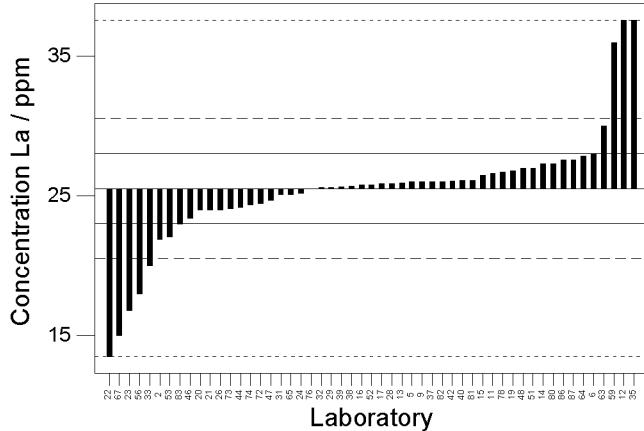
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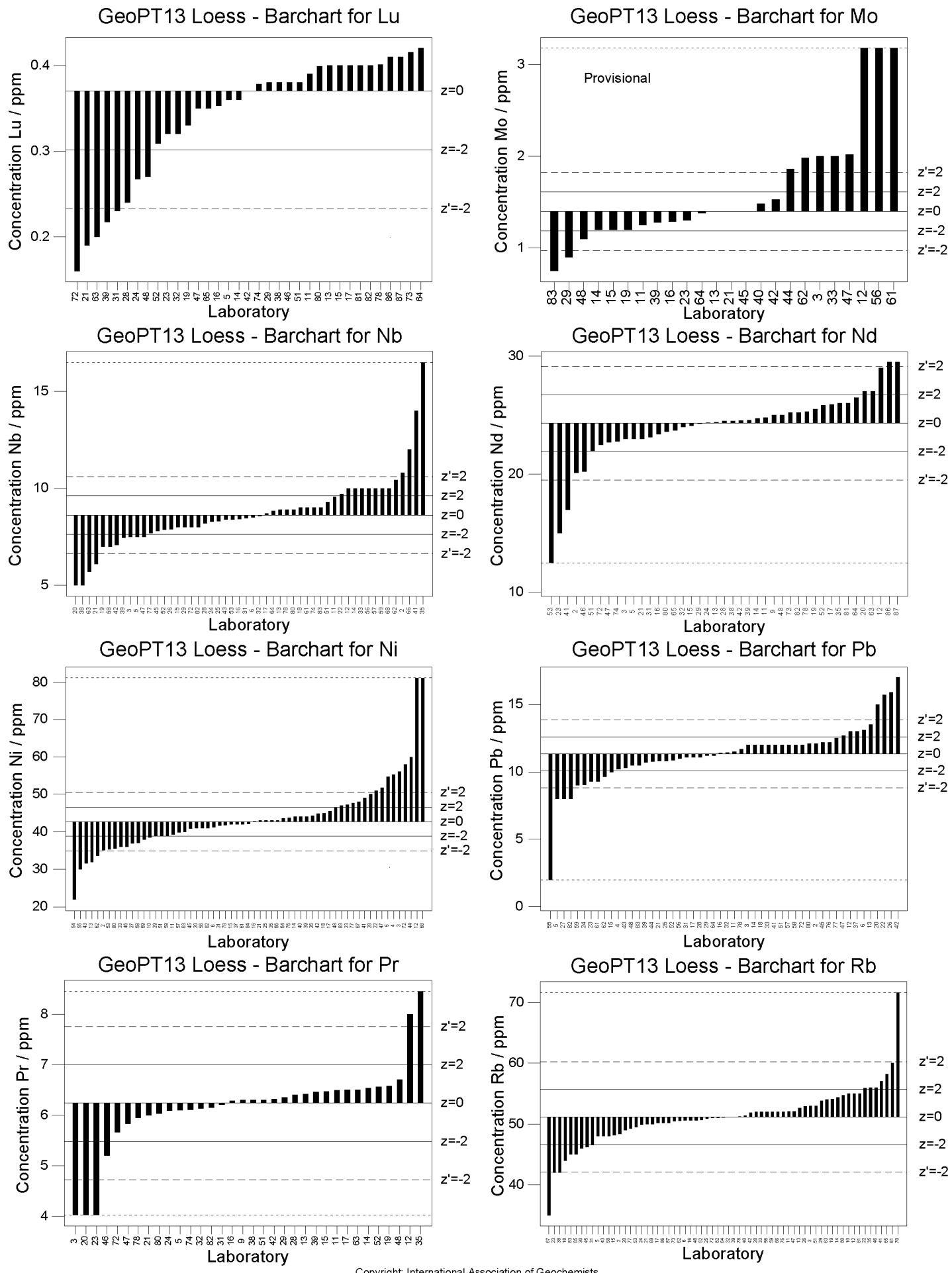


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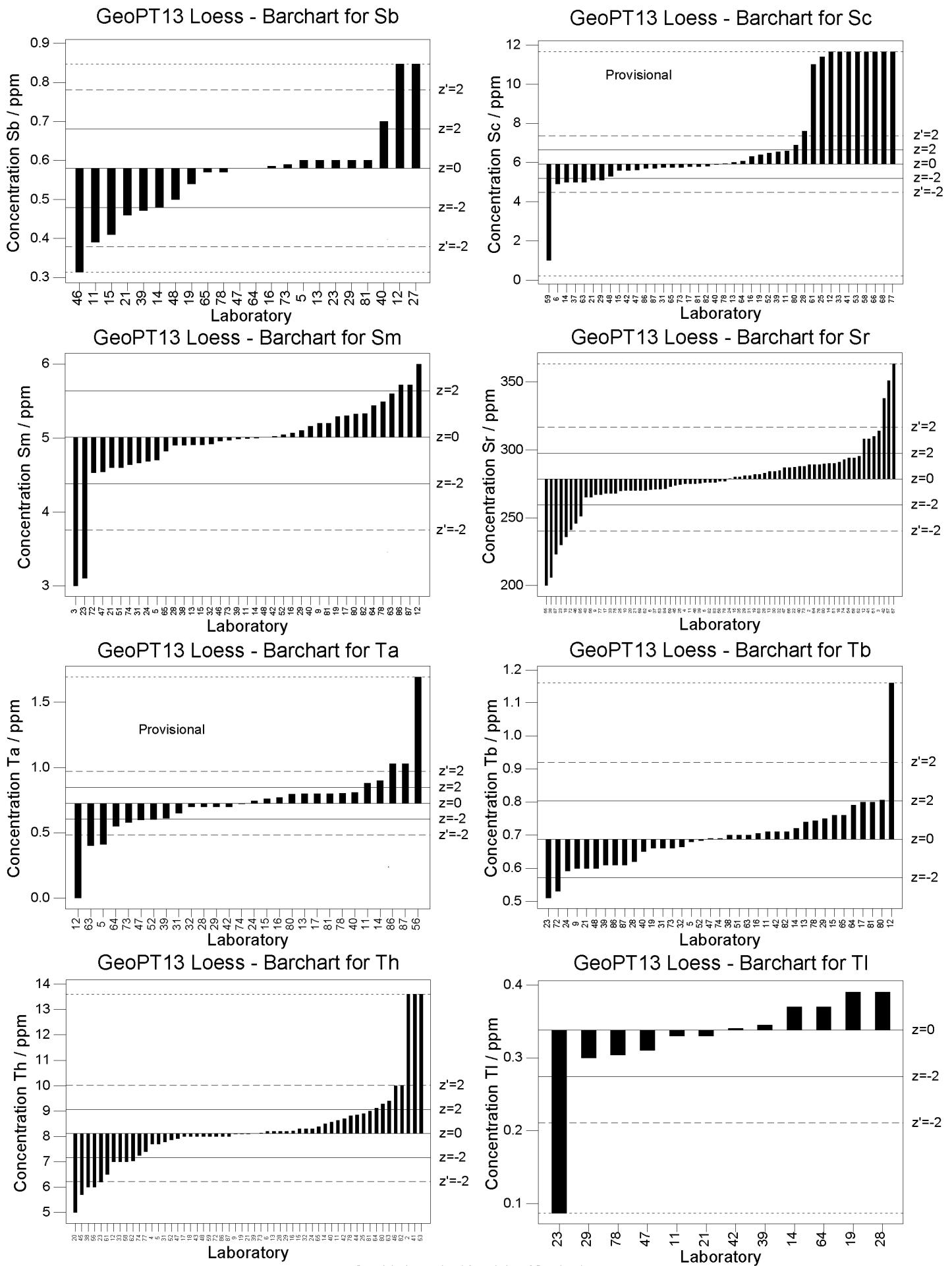


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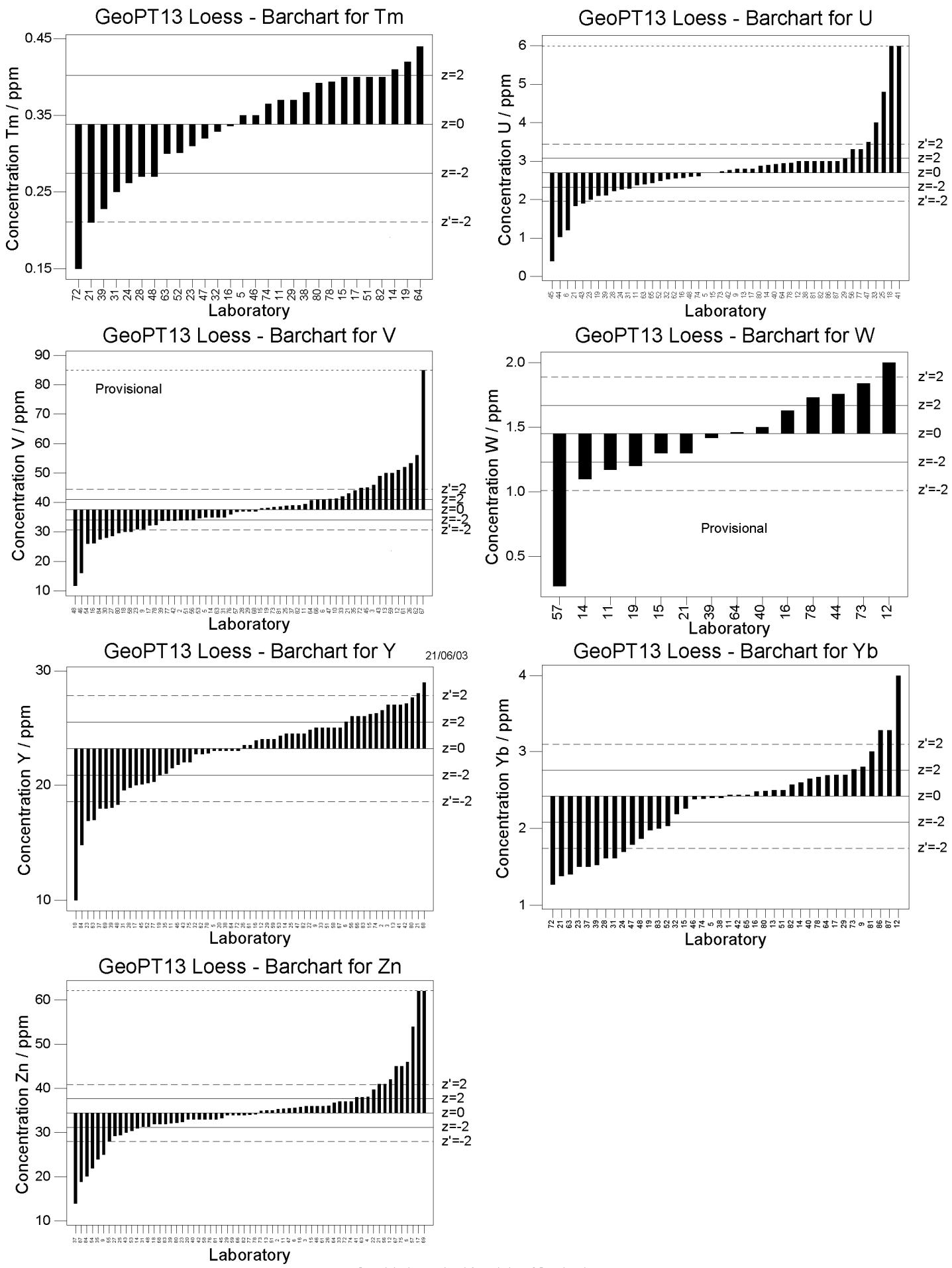




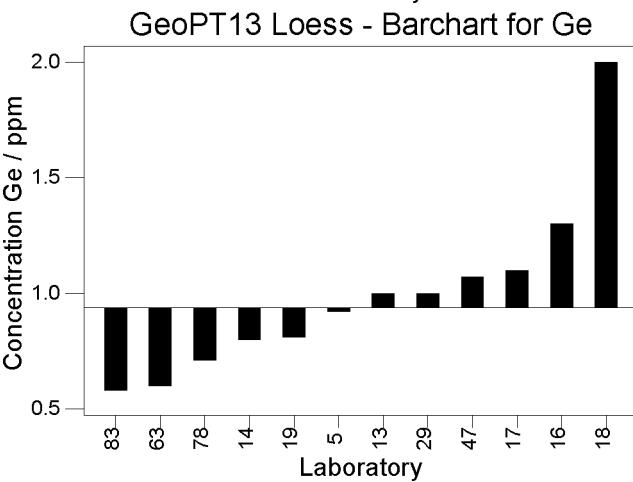
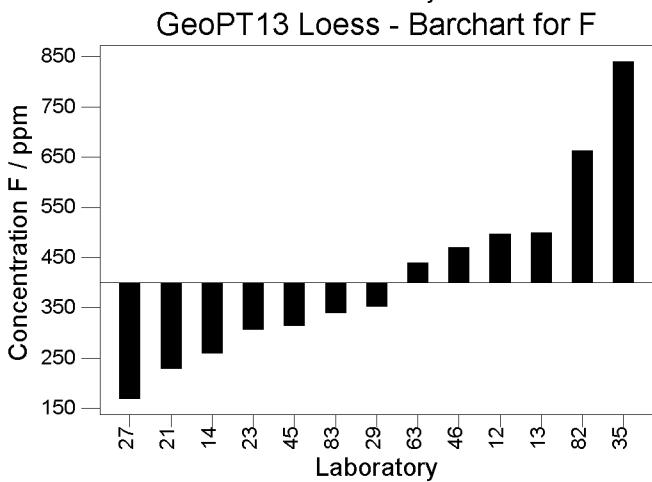
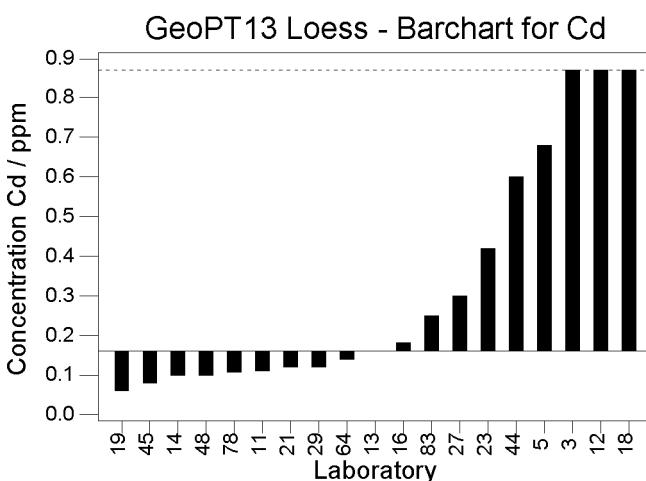
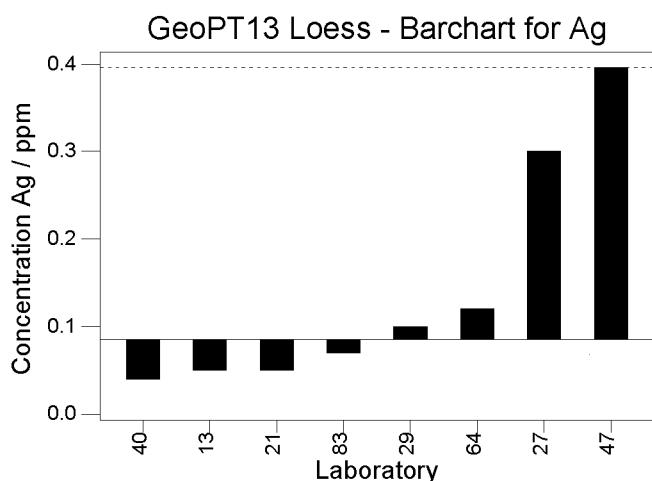
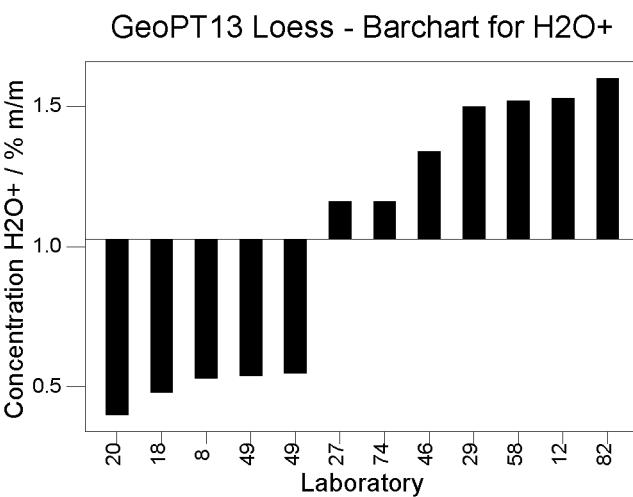
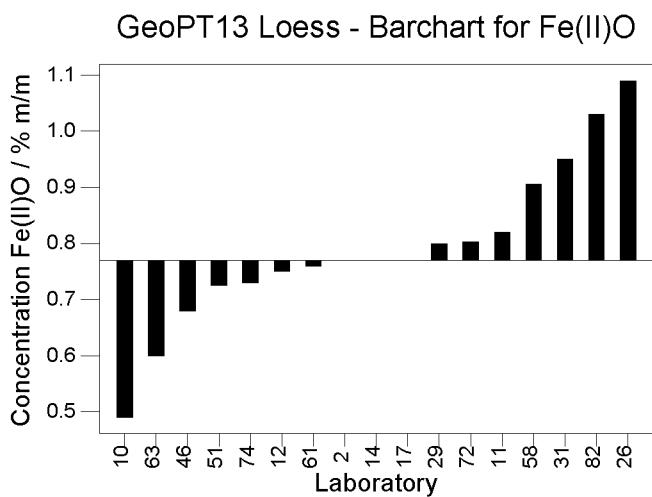
**Figure 1 GeoPT13 –Loess:** Data distribution charts for elements for which values were assigned. Horizontal lines show the limits for  $-2 < z < 2$  for pure geochemistry labs (solid lines) and  $-2 < z' < 2$  for applied geochemistry labs (pecked lines).



**Figure 1 GeoPT13 –Loess:** Data distribution charts for elements for which values were assigned. Horizontal lines show the limits for  $-2 < z' < 2$  for pure geochemistry labs (solid lines) and  $-2 < z' < 2$  for applied geochemistry labs (pecked lines).

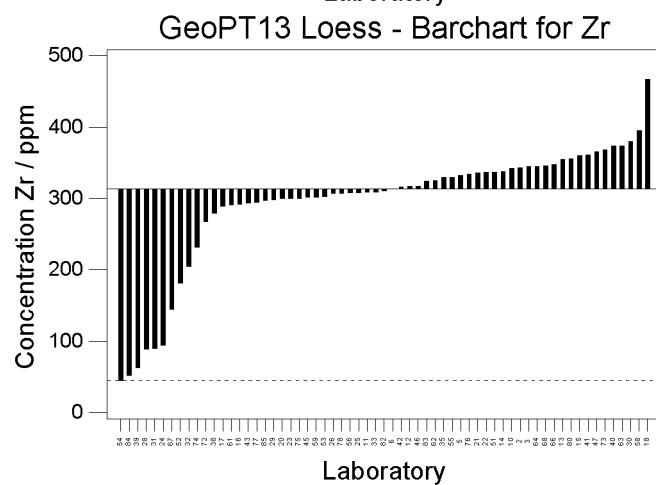
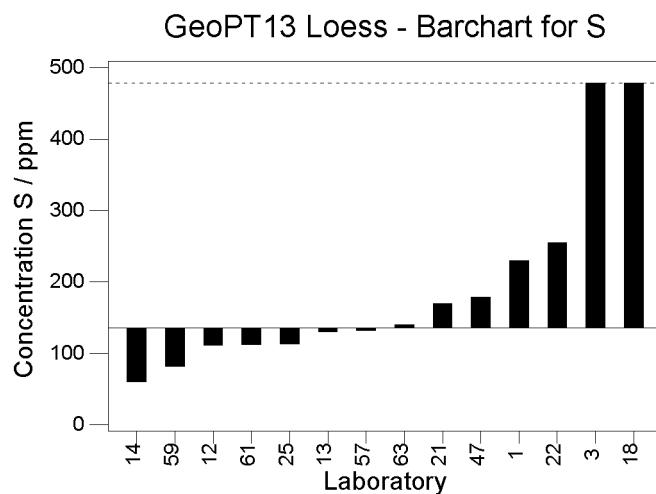
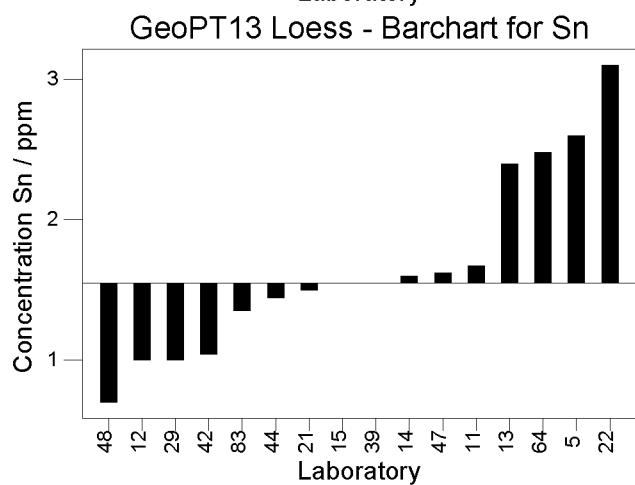
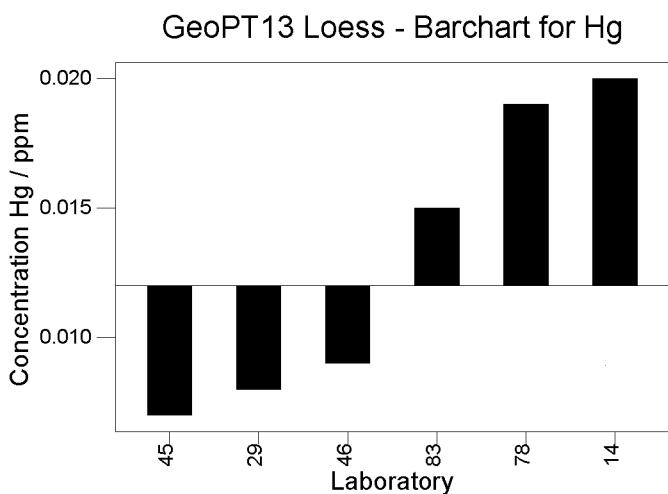


**Figure 1 GeoPT13 –Loess:** Data distribution charts for elements for which values were assigned. Horizontal lines show the limits for  $-2 < z < 2$  for pure geochemistry labs (solid lines) and  $-2 < z' < 2$  for applied geochemistry labs (pecked lines).



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**Figure 2 GeoPT13 –Loess:** Data distribution charts for elements for which values were not assigned.

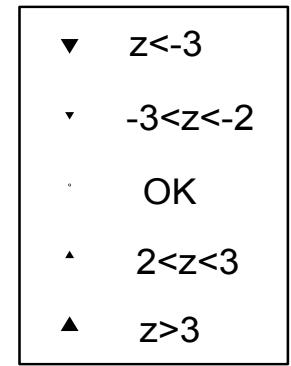
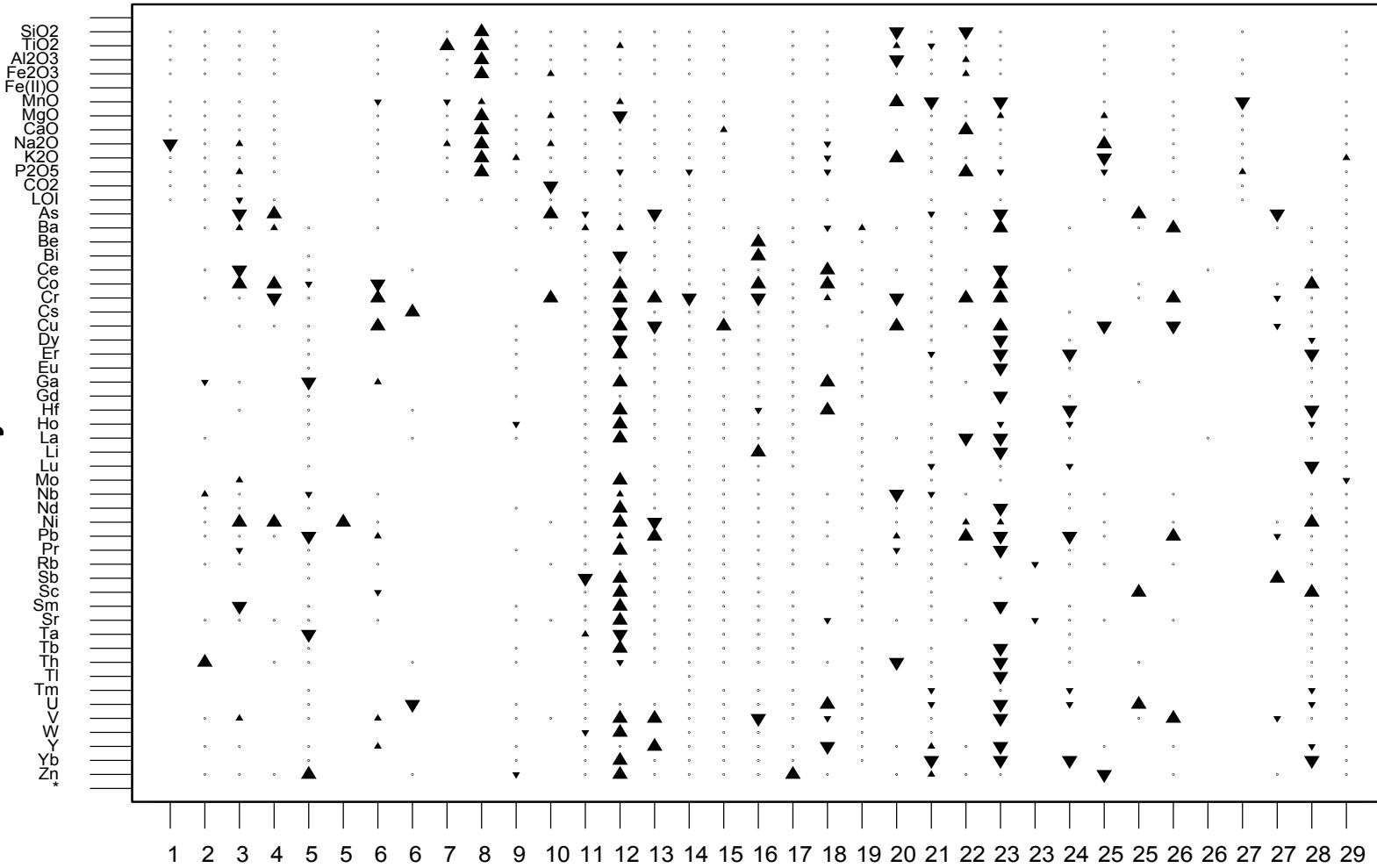


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**Figure 2 GeoPT13 –Loess:** Data distribution charts for elements for which values were not assigned.

# GeoPT13 - Multiple z-score Chart

Analyte Name



GeoPT13 Loess  
21/06/03

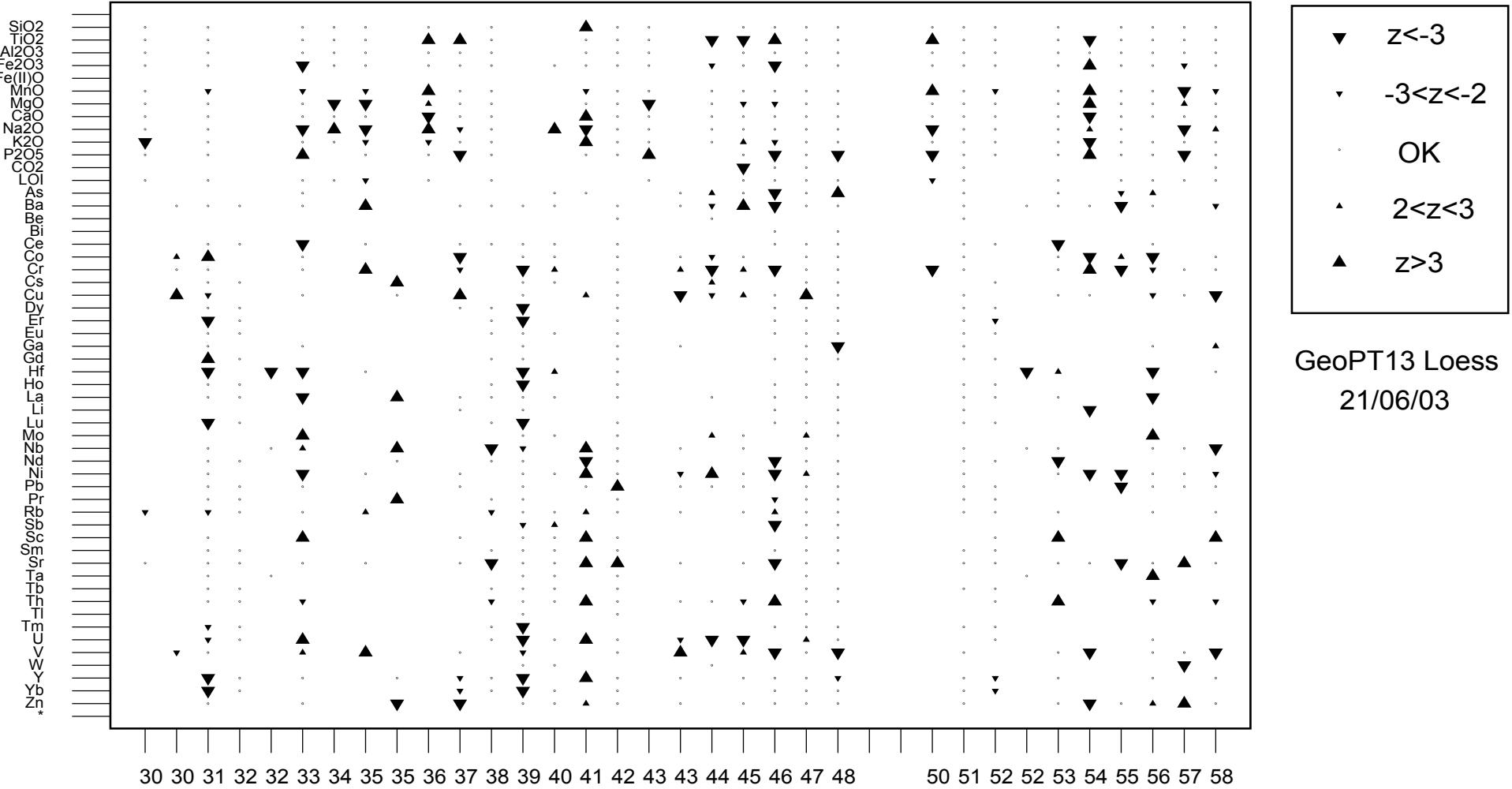
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**Figure 3 GeoPT13 –Loess:** Multiple z-score charts for laboratories participating in the GeoPT12 round. Symbols indicate whether or not an elemental result complies with the  $-2 < z < +2$  criteria. Satisfactory data are plotted as '.'.

Data for other categories are plotted as follows:  $z < -3$  (t),  $-3 < z < -2$  (t),  $+2 < z < +3$  (s),  $z > +3$  (s).

# GeoPT13 - Multiple z-score Chart

Analyte Name



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**Figure 3 GeoPT13 –Loess:** Multiple z-score charts for laboratories participating in the GeoPT12 round. Symbols indicate whether or not an elemental result complies with the  $-2 < z < +2$  criteria. Satisfactory data are plotted as '.'.

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GeoPT13 Loess  
21/06/03

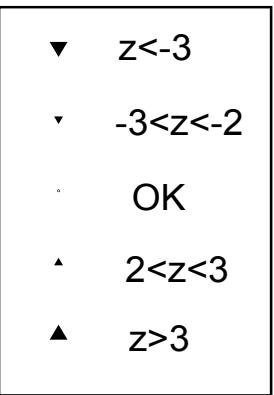
# GeoPT13 - Multiple z-score Chart

Analyte Name

SiO<sub>2</sub>  
TiO<sub>2</sub>  
Al<sub>2</sub>O<sub>3</sub>  
Fe<sub>2</sub>O<sub>3</sub>  
Fe(II)O  
MnO  
MgO  
CaO  
Na<sub>2</sub>O  
K<sub>2</sub>O  
P<sub>2</sub>O<sub>5</sub>  
CO<sub>2</sub>  
LOI  
As  
Ba  
Be  
Bi  
Ce  
Co  
Cr  
Cs  
Cu  
Dy  
Er  
Eu  
Ga  
Ge  
Hf  
Ho  
La  
Li  
Lu  
Mo  
Nb  
Nd  
Ni  
Pb  
Pr  
Rb  
Sb  
Sc  
Sm  
Sr  
Ta  
Tb  
Th  
Tl  
U  
V  
W  
Y  
Yb  
Zn\*

59 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87

Laboratory Identity Code



GeoPT13 Loess  
21/06/03

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**Figure 3 GeoPT13 –Loess:** Multiple z-score charts for laboratories participating in the GeoPT12 round. Symbols indicate whether or not an elemental result complies with the  $-2 < z < +2$  criteria. Satisfactory data are plotted as '!'). Data for other categories are plotted as follows:  $z < -3$  (t),  $-3 < z < -2$  (t),  $+2 < z < +3$  (s),  $Z > +3$  (s).