Electronic Supplementary information (ESI)

1 Table A1

Table A 1: Certificate values, concentrations from the GeoReM Database (MPI für Chemie, Mainz, 2011 and references therein) as well as concentrations obtained in this study for the reference materials NIST SRM 2702, USGS SGR-1 (same composition as reference material USGS SGR-1b used in this study) and the in-house standard GeoB_0-160 by ICP-MS and ICP-OES analysis after full acid digestion.

	Certificate / ppm NIST SRM 2702	This study min / ppm	max / ppm	weighted average ppm (n = 48)	SD	GeoRem Database min / ppm	max / ppm
Al	84100 ± 2200	42750	86084	72243	± 31		
S	15000 ± 820	12789	18351	15570	± 11		
K	20540 ± 720	14052	22924	19906	± 14		
Ca	3430 ± 240	2381	3160	2789	± 4		
Ti	8840 ± 820	7127	9169	8745	± 2		
Mn	1757 ± 58	240	2090	1649	± 1		
Fe	79100 ± 2400	23694	80336	74629	± 25		
Zn	485 ± 4	76.3	524	454	± 0.4		
Rb	128 ± 9	42.3	123	67.6	± 0.1		
Sr	120 ± 3	86.6	154	107	± 0.1		
Ba	397 ± 3	302	413	391	± 0.1		
Pb	133 ± 1	113	145	130	± 0.2	107	134

	Certificate / ppm SGR-1b	This study (SGR-1b) min / ppm	max / ppm	weighted average ppm (n = 24)	SD	GeoRem Database (SGR-1) min / ppm	max / ppm
Al	34510 ± 1110	34810	38086	36624	± 9		
S	15300 ± 1100	15207	18392	16528	± 13		
K	13780 ± 830	14479	16771	15380	± 18	12400	14113
Ca	59890 ± 1210	47980	58376	52070	± 37	58200	
Ti	1517 ± 150	1376	1529	1442	± 1		
Mn	267 ± 34	189	214	201	± 1	252	
Fe	21190 ± 980	19745	21923	20626	± 13	20280	
Zn	74 ± 9	58.3	85.4	72.0	± 0.3	54.9	236
Rb		68.9	81.3	82.0	± 0.1		
Sr	420 ± 30	386	429	413	± 0.3	381	403
Ba	290 ± 40	276	309	289	± 0.1	265	311
Pb	38 ± 4	38.4	86.7	42.3	± 0.1	36.2	42.0

	GeoB_0-160 min / ppm	max / ppm	weighted average ppm (n = 12)	SD
Al	66210	70413	68617	± 207
S	3114	3390	3275	± 10
K	19082	21011	20225	± 118
Ca	46614	50073	48148	± 289
Ti	3829	4092	3927	± 17
Mn	422	454	440	± 2.3
Fe	39409	41283	40452	± 171
Zn	86.6	93.5	90.9	± 0.7
Rb	105	113	106	± 0.2
Sr	161	168	165	± 0.6
Ba	225	241	229	± 0.7
Pb	14.6	15.8	15.0	± 0.1

2 Formulas to calculate the weighted mean and the weighted SD:

weighted mean: $x_{weighted} = \left(\sum_{k=1}^{n} x_k / SD_k^2\right) \Big/ \left(\sum_{k=1}^{n} 1/SD_k^2\right)$

weighted SD: $SD_{weighted} = 1 \Big/ \sqrt{\sum_{k=1}^{n} 1/SD_k^2}$

3 Element patterns and element ratios obtained by XRF core scanning and ICP-MS/OES for Core GeoB12309-5

Figure A1: Element pattern for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Br, Rb, Sr, Zr, Pb and Ba for the whole sediment core in 1 cm (XRF core scanner, black lines) and 5 cm (ICP-MS and ICP-OES, red lines) resolution with additional scatter plots showing the coherence between both methods. The x-axis of scatter plots represent XRF core scanner and y-axis the ICP data, both having the same tick labels as the corresponding elemental pattern plots. SD are not shown here. RSD for each element are given in Table 5.

Figure A2: Element ratio pattern for K/Ca, Fe/Ti and Ti/Al for the whole sediment core in 1 cm (XRF core scanner, black lines) and 5 cm (ICP-MS, red lines) resolution.

Figure A3: Element pattern for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Rb, Sr, Zr and Pb for chosen depths intervals in 0.8 mm (XRF core scanner, black lines) and 1 mm (ICP-MS and ICP-OES, red lines) with additional scatter plots showing the coherence between both methods. The x-axis of scatter plots represent XRF core scanner and the y-axis the ICP data, both having the same tick labels as the corresponding elemental pattern plots. Purple symbols indicate the correlation between 2 cm-16 cm, green symbols between 31 cm-54 cm and orange symbols between 152 cm-172 cm core depth. SD are not shown here. RSD for each element are given in Table 5.

Figure A4: Element ratio pattern for K/Ca, Fe/Ti and Ti/Al for chosen depth intervals in 0.8 mm (XRF core scanner, black lines) and 1 mm (ICP-MS, red lines) resolution.

4 Details for one tailed Student's t-test and fit of regression line

We calculate the correlation coefficient r of the $i = 1 \ldots n$ pairs of measurments $cnts_{XRF}(i)$ $c_{ICP}(i)$ and test the significance of the correlation on a given significance level α by calculating Student's $t_r = r\sqrt{(n-2)/(1-r^2)}$. The null hypothesis assumes that there is no positive correlation, or mathematically: $r \leq 0$. We will accept the null hypothesis if t_r falls into a range between $-\infty$ and a certain positive critical value $t_{(n-2\,,\,\alpha)}$ that is only with a probability of $\alpha = 1 - \mathrm{cdf}(t_{(n-2\,,\,\alpha)}\,,\, n-2)$ exceeded by statistical fluctuations – where cdf denotes the cumulative distribution function. We reject the null hypothesis if $t_r > t_{(n-2\,,\,\alpha)}$, which is equal to $\mathrm{cdf}(t_r, n\text{–}2) > \mathrm{cdf}(t_{(n-2\,,\,\alpha)}\,,\, n-2) = 1 - \alpha$. In the paper itself we decided to argue on the 1% significance level and thus list the corresponding critical values $t_{(n-2\,,\,1\%)}$. In this ESI we list the corresponding significance level $\alpha(t_r\,,\, n\text{–}2) = 1 - \mathrm{cdf}(t_r, n\text{–}2)$, which has the advantage that the reader can choose the significance level him- or herself. Formally we perform a one tailed Student's t test for positive and significant correlation.

For the elements Ti, Mn, Zn, Pb, Ba, Ti/Al in low resolution and Al, K, Ti, Mn, Zn an Pb in high resolution we will not reject the null hypothesis on the 1% significance level. While the correlation for the other elements is supported by the rejection of the null hypothesis, for the just mentioned elements we have not disapproved the existence of a positive correlation. To do so, we test the null hypothesis: there is positive correlation $r \geq 0$, which we will accept if t_r falls into a range between a certain negative critical value $t'_{(n-2\,,\,\alpha)}$ and ∞ that is only undercut due to statistical fluctuations with a probability of $\alpha = \mathrm{cdf}(t'_{(n-2\,,\,\alpha)}\,,\, n-2)$. We will reject the null hypothesis if $t_r < t'_{(n-2\,,\,\alpha)}$, which is equal to $\mathrm{cdf}(t_r, n\text{–}2) < \mathrm{cdf}(t'_{(n-2\,,\,\alpha)}\,,\, n-2) = \alpha$. As Student's t distribution is symmetrical around zero, $t'_{(n-2\,,\,\alpha)} = -\,t_{(n-2\,,\,\alpha)}$. On the 1% significance level we can reject this null hypothesis for Ti in the high resolution, which supports that there is no positive correlation.

The regression line we fit using the method of least squares by minimizing

$\chi^2_{\text{reg}} = \sum_{i=1}^{n} \left(\text{cnts}_{\text{XRF}}(i) - m\ \text{c}_{\text{ICP}}(i) - b\right)^2$ with analytical expressions as *e.g.* given in Barlow's[33] section 6.2.1, that simultaneously solve $\partial\chi^2_{\text{reg}} / \partial m(m_r, b_r) = 0$ and $\partial\chi^2_{\text{reg}} / \partial b(m_r, b_r) = 0$.

5 Details for χ^2-tests and fits

As the regression line is often used for inter-calibration between methods in general, we test the consistency of a linear regression $\text{cnts}_{\text{XRF}} = m_r\ \text{c}_{\text{ICP}} + b_r$ in relation to the quoted errors for both XRF and ICP respectively. We first assume the null hypothesis that the errors are underestimated or the linear relation is not appropriate and thus $\chi^2(m,b) = \sum_{i=1}^{n} \left(\text{cnts}_{\text{XRF}}(i) - m\ \text{c}_{\text{ICP}}(i) - b\right)^2 \Big/ \left((\text{SD}_{\text{XRF}}(i))^2 + m^2\ (\text{SD}_{\text{ICP}}(i))^2\right) \geq \chi^2_{(\alpha,n-2)}$, which is only undercut by statistical fluctuations with a probability $\alpha = \text{cdf}(\chi^2_{(\alpha,n-2)}, n-2)$. In the paper we again list $\chi^2_{(1\%,n-2)}$ for the chosen significance level of 1%, while in this ESI we list $\alpha(\chi^2, n-2)$ for reasons of generality as discussed above. On the 1% significance level the null hypothesis will be rejected only for the Fe/Ti element ratio in high resolution, which supports that the Fe/Ti ratio is described consistently. Except for the above mentioned Fe/Ti in high resolution ($\alpha(\chi^2, n-2) \cong 0$) as well as Mn and Zn in low resolution ($\alpha(\chi^2, n-2) > 50\%$), all other elements have calculated values of $\alpha(\chi^2, n-2) > 99\%$. Thus, apart form the just above mentioned three exceptions this leads to a rejection of the null hypothesis of at the utmost overestimated errors and a consistent linear description ($\chi^2 \leq \chi^2_{(\alpha,n-2)}'$) for all other elements. Remark and warning: When arguing with critical values the null hypothesis is $\chi^2 \leq \chi^2_{(\alpha,n-2)}'$, which is only exceeded by statistical fluctuations with a probability $\alpha = 1 - \text{cdf}(\chi^2_{(\alpha,n-2)}', n-2)$. Differently from the above discussed Student's t the χ^2-distribution is not symmetrical and thus $\chi^2_{(\alpha,n-2)}' \neq \chi^2_{(\alpha,n-2)}$, *e.g.* $\chi^2_{(1\%,88-2)}' = 134.6$ but $\chi^2_{(1\%,88-2)} = 69.2$.

At least for the elements where we have observed a significant linear correlation the rejection of the null hypothesis supports the hypothesis of underestimated errors. As we conservatively

at the utmost overestimated the ICP errors SD(c_{ICP}), we estimate by which factor we expect an underestimation of the SD($cnts_{XRF}$) errors. Guided by a remark in Barlow's[33] section 6.4., that the χ^2-distribution's expectation value is close to the number of samples reduced by the number of fitted parameters and it can thus be used to estimate errors, we introduce a factor c of the underestimation of SD_{XRF} in the weight of χ^2:

$$\chi^2_{fac}(m,b,c) = \sum_{i=1}^{n} \left(cnts_{XRF}(i) - m\, c_{ICP}(i) - b\right)^2 \Big/ \left((c\, SD_{XRF}(i))^2 + m^2\, (SD_{ICP}(i))^2\right)$$

We first assume the null hypothesis that the errors even with c-stretched $SD_{XRF}(i)$ errors are underestimated and thus $\chi^2_{fac} \geq \chi^2_{(\alpha,n-2)}$, which is only undercut by statistical fluctuations with a probability α = cdf($\chi^2_{(\alpha,n-3)}$, n–3). The rejection of the null hypothesis supports the assumption of a proper representation of the data with the stretched errors. To present the issue in optimized generality we decided to numerically fit the c_α to a critical $\chi^2_{fac\,(\alpha,n-3)}$ corresponding to a certain significance level α, that would have just lead to the rejection of the null hypothesis. We selected the α = 50%, 1% and 0.1% in this presentation to give an idea of minimal c_α one could have chosen successfully on the certain significance level as well as the critical $\chi^2_{(\alpha,n-3)}$, where we reduced the degrees of freedom further by one, as c_α is also fitted. The variation between $c_{50\%}$ and $c_{0.1\%}$ is generally moderate in the range less than a factor of 1.6 at most.

5.1 Calculation of errors for the fitted properties

If the null hypothesis is rejected, resulting in the support of the hypothesis that the χ^2_{reg}-fitted regression line, the χ^2-fitted linear relation or the χ^2_{fac}-fitted linear relation to stretched errors describes the data with consistent errors respectively, one can propagate the errors of the measurement SD($c_{ICP}(i)$) and SD($cnts_{XRF}(i)$) towards the errors

- Minimization criterion χ^2_{reg}: SD(m_r), SD(b_r) and the covariance cov(m_r , b_r) of the

slope and the ordinate for the fitted regression line by minimizing χ^2_{reg}, thus simultaneously solving $\partial\chi^2_{\mathrm{reg}}/\partial m\ (m_r,b_r)=0$ and $\partial\chi^2_{\mathrm{reg}}/\partial b\ (m_r,b_r)=0$.

- Minimization criterion χ^2: SD(m_f), SD(b_f) and the covariance cov(m_f , b_f) of the slope and the ordinate for the fitted linear relation by minimizing χ^2, thus simultaneously solving $\partial\chi^2/\partial m\,(m_f,b_f)=0$ and $\partial\chi^2/\partial b\,(m_f,b_f)=0$

- Minimization criterion χ^2_{fac}: SD(m_α), SD(b_α), SD(c_α) and the covariance cov(m_α , b_α) of the slope and the ordinate for the fitted linear relation by minimizing χ^2, thus simultaneously solving $\partial\chi^2_{\mathrm{fac}}/\partial m\,(m_\alpha,b_\alpha,c_\alpha)=0$, $\partial\chi^2_{\mathrm{fac}}/\partial b\,(m_\alpha,b_\alpha,c_\alpha)=0$ and $\chi^2_{\mathrm{fac}}(m_\alpha,b_\alpha,c_\alpha)=\chi^2_{(\alpha,n-3)}$, where the critical value is defined by $\mathrm{cdf}(\chi^2_{(\alpha,n-3)},n-3)=\alpha$.

To actually calculate the errors we generated the 2*n* x 2*n* diagonal covariance matrix $V(\mathrm{c_{ICP}},\mathrm{cnts_{XRF}})$ (as the ICP and XRF measurements are independent, off-the-diagonal covariance vanishes) with the given errors $(\mathrm{SD}(\mathrm{c_{ICP}}(i)))^2$ in the top *n* rows/columns and the $(\mathrm{SD}(\mathrm{cnts_{XRF}}(i)))^2$ in the bottom n rows/columns. We propagate the errors of the measurement by multiplication with the respective Jacobi matrix $\mathfrak{I}_{(x_1,\mathsf{K},x_n)}(f_1(x_1,\mathsf{K},x_n),\mathsf{K},f_l(x_1,\mathsf{K},x_n)) = \left(\partial f_j/\partial x_i\right)_{l\times n}$ from the left and the transposed of the Jacobi matrix from the right, thus using the respective minimization criteria $\aleph\in\{\chi^2_{\mathrm{reg}},\chi^2,\chi^2_{\mathrm{fac}}\}$, as *e.g.* described in Barlow's[33] section 4.3.4., towards the covariance matrix of the fitted parameters $V(m,b[,c]) = \mathfrak{I}^{\aleph}_{(\mathrm{c_{ICP}},\mathrm{cnts_{XRF}})}(m,b[,c])\ \mathrm{o}\ V(\mathrm{c_{ICP}},\mathrm{cnts_{XRF}})\ \mathrm{o}\ {}^{\mathrm{T}}\mathfrak{I}^{\aleph}_{(\mathrm{c_{ICP}},\mathrm{cnts_{XRF}})}(m,b[,c])$. The Jacobi matrix we calculate with the chain rule and the rule on the inverse of the Jacobi matrix $\mathfrak{I}_{(\partial\aleph/\partial m,\partial\aleph/\partial b[,\aleph])}(m,b[,c]) = \mathfrak{I}^{-1}_{(m,b[,c])}(\partial\aleph/\partial m,\partial\aleph/\partial b[,\aleph]):\ \mathfrak{I}^{\aleph}_{(\mathrm{c_{ICP}},\mathrm{cnts_{XRF}})}(m,b[,c]) = \mathfrak{I}_{(\partial\aleph/\partial m,\partial\aleph/\partial b[,\aleph])}(m,b[,c])\ \mathrm{o}\ \mathfrak{I}_{(\mathrm{c_{ICP}},\mathrm{cnts_{XRF}})}(\partial\aleph/\partial m,\partial\aleph/\partial b[,\aleph]) = \mathfrak{I}^{-1}_{(m,b[,c])}(\partial\aleph/\partial m,\partial\aleph/\partial b[,\aleph])\ \mathrm{o}\ \mathfrak{I}_{(\mathrm{c_{ICP}},\mathrm{cnts_{XRF}})}(\partial\aleph/\partial m,\partial\aleph/\partial b[,\aleph])$. The respective matrices we calculate from partial derivatives of the explicit functions both of the fitting parameters m, b [and c] and the measured

concentrations c_{ICP} and counts $cnts_{XRF}$ depending whether we minimized χ^2_{reg}, χ^2 or χ^2_{fac}.

For the fitted lines $m\ c_{ICP} + b$ one calculates the error interval to $SD(cnts_{XRF}) = \sqrt{SD(b)^2 + SD(m)^2 c_{ICP}^2 + 2\,cov(m,b) c_{ICP}}$ by propagation of the covariance matrix of m and b with the Jacobi matrix $\mathfrak{J}_{(m,b)}(m \cdot c_{ICP} + b) = (c_{ICP}, 1)$ of $cnts_{XRF} = m\ c_{ICP} + b$.

Figure A5 shows the original data with their respective error-bars and the different curves we fitted to the data. **Table A2** provides all the properties as mentioned above.

Figure A5: Scatter plots of XRF Core Scanner counts (y-axis) versus ICP-MS/OES concentratrions (x-axis) for the low- and high-resolution mode with their respective error-bars, the regression line, and the fitted lines for error strech factors on different significants levels.

5.2 Chi-square test: Table A2

Table A 2: Statistic values for the correlation of XRF core scanner and ICP-OES/MS results with: n = number of sample points; r = correlation coefficient; t_r = calculated Student's t-value (significant values in bold), $\alpha(t_r, n\text{-}2) = 1\text{-cdf}(t_r,n\text{-}2)$; m_r = slope of regression line, b_r = axis intercept of regression line; $\chi^2(m_r,b_r)$ = calculated Chi-square value of regression line; $\alpha(\chi^2(m_r,b_r),n\text{-}2) = \text{cdf}(\chi^2(m_r,b_r),n\text{-}2)$; $SD(m_r)$ = SD of slope of the regression line; $SD(b_r)$ = SD of axis intercept of the regression line; $cov(m_r,b_r)$ = covariance of slope and axis intercept of the regression line; m_f = slope of χ^2-fitted line, b_f = axis intercept of χ^2-fitted line; $\chi^2(m_f,b_f)$ = calculated Chi-square value of χ^2-fitted line; $\alpha(\chi^2(m_f,b_f),n\text{-}2) = \text{cdf}(\chi^2(m_f,b_f),n\text{-}2)$; $SD(m_f)$ = SD of slope of the χ^2-fitted line; $SD(b_f)$ = SD of axis intercept of the χ^2-fitted line; $cov(m_f,b_f)$ = covariance of slope and axis intercept of the χ^2-fitted line; $m_{50\%}$= slope of χ^2-fitted line, $b_{50\%}$ = axis intercept of χ^2-fitted line; $c_{50\%}$ = stretch factor for the XRF core scanner error; $\chi^2_{(50\%,\ n\text{-}3)}$ = critical Chi-square value for 50% significance level; $SD(m_{50\%})$ = SD of slope of the χ^2-fitted line with XRF streched errors to match critical $\chi^2_{(50\%,\ n\text{-}3)}$ value; $SD(b_{50\%})$ = SD of axis intercept of the χ^2-fitted line with XRF streched errors to match critical $\chi^2_{(50\%,\ n\text{-}3)}$ value; $cov(m_{50\%},b_{50\%})$ = covariance of slope and axis intercept of the χ^2-fitted line with XRF streched errors to match critical $\chi^2_{(50\%,\ n\text{-}3)}$ value; The same properties for 1% and 0.1%.

Chi-square test: Table A2 continued

element	res	n	r	t_r	$\alpha(t_r, n-2)$	m_r	b_r	$\chi^2(m_r, b_r)$	$\alpha(\chi^2(m_r, b_r), n-2)$	SD(m_r)	SD(b_r)	cov(m_r, b_r)
Al	low	101	0.287	2.977	0.2%	0.086	-625.596	355	100.0%	0.000	29.2	0.000
S	low	101	0.340	3.600	0.0%	0.228	1008	2412	100.0%	0.002	12.6	0.000
K	low	101	0.482	5.478	0.0%	1.27	11220	220	100.0%	0.001	215	-0.023
Ca	low	101	0.581	7.100	0.0%	1.05	60683	291	100.0%	0.001	633	-0.081
Ti	low	101	0.171	1.723	4.4%	1.03	8803	698	100.0%	0.004	69	-0.013
Mn	low	86	0.245	2.320	1.1%	1.45	1123	91.2	72.3%	0.026	8.11	-0.002
Fe	low	88	0.514	5.550	0.0%	2.24	40017	143	100.0%	0.001	744	-0.156
Zn	low	103	0.145	1.469	7.3%	0.7	329	102	55.5%	0.024	1.43	0.000
Rb	low	103	0.633	8.226	0.0%	13.6	990	234	100.0%	0.054	9.38	-0.008
Sr	low	103	0.528	6.253	0.0%	15.6	1783	410	100.0%	0.043	15.5	-0.013
Pb	low	103	0.184	1.877	3.2%	4.7	84.2	137	99.0%	0.104	0.632	0.000
Ba	low	101	0.209	2.123	1.8%	2.73	1031	167	100.0%	0.046	6.06	-0.002
K/Ca	low	101	0.822	14.360	0.0%	0.526	0.111	173	100.0%	0.001	0.002	0.000
Fe/Ti	low	88	0.355	3.518	0.0%	0.232	7.86	173	100.0%	0.001	0.057	0.000
Ti/Al	low	101	-0.075	-0.751	77.3%	-17.153	3.25	1089	100.0%	0.095	0.012	0.000
Al	high	534	-0.003	-0.059	52.3%	-0.001	4355	136372	100.0%	0.000	10.1	0.000
S	high	534	0.213	5.032	0.0%	0.095	3634	4193	100.0%	0.002	10.5	-0.001
K	high	534	-0.032	-0.729	76.7%	-0.066	31113	163607	100.0%	0.001	76.7	-0.001
Ca	high	534	0.262	6.262	0.0%	0.663	63059	13550	100.0%	0.000	232	-0.002
Ti	high	534	-0.199	-4.684	100.0%	-1.334	16521	4878	100.0%	0.002	26.4	0.000
Mn	high	534	-0.026	-0.599	72.5%	-0.226	1817	688	100.0%	0.019	3.32	-0.001
Fe	high	534	0.132	3.069	0.1%	0.765	91432	29776	100.0%	0.001	283	-0.004
Zn	high	518	-0.013	-0.305	62.0%	-0.017	244	800	100.0%	0.008	0.294	0.000
Rb	high	532	0.242	5.744	0.0%	1.87	558	2606	100.0%	0.015	1.26	0.000
Sr	high	533	0.450	11.598	0.0%	3.09	867	2827	100.0%	0.011	2.17	0.000
Pb	high	532	0.036	0.823	20.6%	0.22	82.1	612	99.2%	0.032	0.16	0.000
K/Ca	high	534	0.483	12.712	0.0%	0.323	0.176	6993	100.0%	0.000	0.001	0.000
Fe/Ti	high	534	0.444	11.419	0.0%	0.481	6.09	304	0.0%	0.001	0.042	0.000
Ti/Al	high	534	0.151	3.513	0.0%	55	-0.48	3544	100.0%	0.058	0.006	0.000

Chi-square test: Table A2 continued

element	res	m_f	b_f	$\chi^2(m_f, b_f)$	$\alpha(\chi^2(m_f, b_f), n-2)$	SD(m_f)	SD(b_f)	cov(m_f, b_f)
Al	low	0.981	-63278	35.3	0.000	0.548	38364	-21023
S	low	1.24	-3083	863	1.000	0.114	451	-51.4
K	low	4.89	-60630	59.5	0.001	1.09	21637	-23527
Ca	low	3.22	-44069	95.2	0.409	0.47	22776	-10693
Ti	low	26.9	-86687	34.3	0.000	21.5	79492	-1712813
Mn	low	6.44	-1473	73.5	0.214	3.51	1812	-6359
Fe	low	7.9	-188204	40.5	0.000	1.97	79287	-155797
Zn	low	1.56	248	99.4	0.474	1.21	111	-134
Rb	low	25.8	-284	164	1.000	2.6	270	-702
Sr	low	46.3	-3614	187	1.000	5.5	966	-5306
Pb	low	24.5	-200	109	0.729	13.3	188	-2501
Ba	low	10.4	-656	143	0.998	4.36	944	-4116
K/Ca	low	0.782	0.008	114	0.863	0.049	0.02	-0.001
Fe/Ti	low	1.69	-8.075	42.7	0.000	0.756	8.26	-6.244
Ti/Al	low	-3580.51	191	14.8	0.000	14514	764	-11094579
Al	high	-8.162	570895	590	0.958	13.4	929086	-12434987
S	high	0.135	3468	4044	1.000	0.011	31.6	-0.357
K	high	-123.2	2512729	1282	1.000	218	4383587	-953453053
Ca	high	9.62	-362322	929	1.000	1.14	54142	-61681
Ti	high	-30.085	131302	291	0.000	8.29	33096	-274356
Mn	high	-3.423	3302	625	0.997	1.83	884	-1614
Fe	high	37	-1367014	637	0.999	9.94	399801	-3975401
Zn	high	-0.054	244	778	1.000	0.055	5.25	-0.287
Rb	high	6.09	119	2171	1.000	0.395	39.5	-15.6
Sr	high	6.56	219	2326	1.000	0.277	50.2	-13.9
Pb	high	0.46	76.1	575	0.915	0.348	4.93	-1.71
K/Ca	high	1.36	-0.258	1732	1.000	0.058	0.024	-0.001
Fe/Ti	high	2.24	-11.6	71	0.000	0.503	5.06	-2.55
Ti/Al	high	2288	-128	125	0.000	1256	72	-90438

Chi-square test: Table A2 continued

element	res	$m_{50\%}$	$b_{50\%}$	$c_{50\%}$	$\chi^2_{(50\%,\, n\text{-}3)}$	SD($m_{50\%}$)	SD($b_{50\%}$)	SD($c_{50\%}$)	cov($m_{50\%}$, $b_{50\%}$)
Al	low	0.981	-63278	1	35.3	0.548	38364	0	-21023
S	low	0.286	540	5.52	97.3	0.065	268	0.574	-17.2
K	low	4.89	-60630	1	59.5	1.09	21637	0	-23527
Ca	low	3.22	-44069	1	95.2	0.47	22776	0	-10693
Ti	low	26.9	-86687	1	34.3	21.5	79492	0	-1712813
Mn	low	6.44	-1473	1	73.5	3.51	1812	0	-6359
Fe	low	7.9	-188204	1	40.5	1.97	79287	0	-155797
Zn	low	1.56	248	1	99.4	1.21	111	0	-134
Rb	low	19.2	402	1.8	99.3	3.01	313	0.283	-940
Sr	low	24.1	258	2.84	99.3	5.14	901	0.415	-4630
Pb	low	19.2	-125	1.08	99.3	12.5	177	0.161	-2210
Ba	low	5.82	338	1.28	97.3	3.09	671	0.146	-2070
K/Ca	low	0.735	0.027	3.12	97.3	0.072	0.029	1.81	-0.002
Fe/Ti	low	1.69	-8.08	1	42.7	0.756	8.26	0	-6.24
Ti/Al	low	-3581	191	1	14.8	14514	764	0	-11094579
Al	high	-0.003	3904	14.3	530	0.006	421	0.621	-2.49
S	high	0.094	3579	2.79	530	0.018	51.7	0.122	-0.889
K	high	0.502	18343	18.7	530	0.523	10629	0.838	-5563
Ca	high	2.39	-20912	27.5	530	0.309	14488	1.91	-4469
Ti	high	-30.085	131302	1	291	8.29	33096	0	-274356
Mn	high	-2.167	2694	1.09	530	1.69	815	0.05	-1374
Fe	high	6.5	-140905	25.9	530	1.86	74115	2.62	-137680
Zn	high	-0.053	244	1.23	514	0.066	6.26	0.054	-0.407
Rb	high	2.57	471	2.22	528	0.47	47.9	0.099	-22.5
Sr	high	3.71	735	2.45	529	0.354	65.1	0.112	-23.0
Pb	high	0.453	76.2	1.04	528	0.355	5.04	0.045	-1.78
K/Ca	high	0.44	0.122	10.1	530	0.04	0.017	0.502	-0.001
Fe/Ti	high	2.24	-11.6	1	71	0.503	5.06	0	-2.55
Ti/Al	high	2288	-128	1	125	1256	72	0	-90438

Chi-square test: Table A2 continued

element	res	$m_{1\%}$	$b_{1\%}$	$c_{1\%}$	$\chi^2_{(1\%,\, n\text{-}3)}$	SD($c_{1\%}$)	SD($m_{1\%}$)	SD($b_{1\%}$)	cov($m_{1\%}$, $b_{1\%}$)
Al	low	0.981	-63278	1	35.3	0	0.548	38364	-21023
S	low	0.276	577	6.61	68.4	0.813	0.074	304	-22.1
K	low	4.89	-60630	1	59.5	0	1.09	21637	-23527
Ca	low	2.05	12029	12.2	68.4	3.88	0.599	28919	-17326
Ti	low	26.9	-86687	1	34.3	0	21.5	79492	-1712813
Mn	low	3.8	-110	1.23	56	0.209	2.63	1358	-3572
Fe	low	7.9	-188204	1	40.5	0	1.97	79287	-155797
Zn	low	1.19	281	1.2	70.1	0.146	1.05	96.4	-101
Rb	low	17.1	620	2.3	70.1	0.351	2.93	305	-891
Sr	low	20.6	871	3.57	70.1	0.517	4.7	826	-3880
Pb	low	12	-23.0	1.34	70.1	0.181	7.29	103	-754
Ba	low	4.51	622	1.55	68.4	0.197	2.63	574	-1510
K/Ca	low	0.669	0.053	5.63	68.4	1.51	0.065	0.026	-0.002
Fe/Ti	low	1.69	-8.08	1	42.7	0	0.756	8.26	-6.244
Ti/Al	low	-3581	191	1	14.8	0	14514	764	-11094579
Al	high	-0.004	3943	15.4	458	0.719	0.007	499	-3.52
S	high	0.093	3581	3	458	0.141	0.019	55.1	-1.01
K	high	0.344	21554	20.1	458	0.953	0.504	10266	-5172
Ca	high	2.12	-8396	30.7	458	2.03	0.32	15041	-4806
Ti	high	-30.085	131302	1	291	0	8.29	33096	-274356
Mn	high	-1.6	2421	1.18	458	0.056	1.43	691	-990
Fe	high	4.86	-75453	29.8	458	2.26	1.16	46365	-53924
Zn	high	-0.053	244	1.33	443	0.063	0.07	6.68	-0.464
Rb	high	2.49	480	2.4	456	0.114	0.484	49.4	-23.9
Sr	high	3.63	749	2.65	457	0.128	0.37	68.2	-25.2
Pb	high	0.443	76.3	1.12	456	0.053	0.37	5.25	-1.94
K/Ca	high	0.421	0.13	11	458	0.57	0.04	0.017	-0.001
Fe/Ti	high	2.24	-11.6	1	71	0	0.503	5.06	-2.55
Ti/Al	high	2288	-128	1	125	0	1256	72	-90438

Chi-square test: Table A2 continued

element	res	$m_{0.1\%}$	$b_{0.1\%}$	$c_{0.1\%}$	$\chi^2_{(0.1\%,\, n\text{-}3)}$	SD($c_{0.1\%}$)	SD($m_{0.1\%}$)	SD($b_{0.1\%}$)	cov($m_{0.1\%}$, $b_{0.1\%}$)
Al	low	0.981	-63278	1	35.3	0	0.548	38364	-21023
S	low	0.274	586	7.04	60.4	0.92	0.077	320	-24.3
K	low	4.89	-60630	1	59.5	0	1.09	21637	-23527
Ca	low	1.85	21575	14.1	60.4	3.63	0.512	24712	-12643
Ti	low	26.9	-86687	1	34.3	0	21.5	79492	-1712813
Mn	low	3.25	177	1.34	48.8	0.224	2.26	1169	-2642
Fe	low	7.9	-188204	1	40.5	0	1.97	79287	-155797
Zn	low	1.12	288	1.28	61.9	0.165	1.02	94.4	-96.515
Rb	low	16.6	674	2.48	61.9	0.386	2.96	308	-911
Sr	low	19.8	1013	3.84	61.9	0.571	4.68	824	-3856
Pb	low	10.8	-6.27	1.44	61.9	0.2	6.83	97	-662
Ba	low	4.25	680	1.66	60.4	0.222	2.59	563	-1456
K/Ca	low	0.653	0.059	6.4	60.4	1.57	0.065	0.026	-0.002
Fe/Ti	low	1.69	-8.075	1	42.7	0	0.756	8.26	-6.24
Ti/Al	low	-3580.51	191	1	14.8	0	14514	764	-11094579
Al	high	-0.004	3958	15.8	436	0.756	0.008	530	-3.97
S	high	0.093	3581	3.08	436	0.148	0.019	56.4	-1.06
K	high	0.308	22285	20.6	436	0.998	0.48	9795	-4705
Ca	high	2.04	-4465	31.8	436	2.08	0.328	15433	-5055
Ti	high	-30.085	131302	1	291	0	8.29	33096	-274356
Mn	high	-1.47	2359	1.21	436	0.059	1.36	657	-894
Fe	high	4.49	-60791	31	436	2.23	1.1	43689	-47862
Zn	high	-0.053	244	1.36	421	0.066	0.072	6.83	-0.486
Rb	high	2.46	482	2.46	434	0.12	0.49	50	-24.4
Sr	high	3.61	753	2.72	435	0.135	0.376	69.3	-26.0
Pb	high	0.44	76.4	1.15	434	0.055	0.376	5.33	-2.00
K/Ca	high	0.416	0.132	11.3	436	0.596	0.04	0.017	-0.001
Fe/Ti	high	2.24	-11.6	1	71	0	0.503	5.06	-2.55
Ti/Al	high	2288	-128	1	125	0	1256	72	-90438

6 Grain size measurement

In order to investigate variations in the continental sediment supply the terrigenous grain size distribution was determined using a laser diffraction particle size analyzer (Beckman Coulter) LS200, resulting in 92 size classes from 0.4 to 2000 µm. 28 samples à 7 cm^3 were treated with HCl to dissolve the carbonate and with H_2O_2 to remove the organic fraction.