Statistical Modeling and Analysis of Trace Element Concentrations in Forensic Glass Evidence

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Outline

1. Motivation: ASTM Glass Standards
2. Available data
3. Estimating error rates: pairwise differences?
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   not dependent on specific data set
5. Using data to estimate model parameters
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Motivation: ASTM Glass Standards

Three ASTM Glass Standards proposed for OSAC Registry

1. XRF: ASTM E2926-13, *Standard Test Method for Forensic Comparison of Glass Using Micro X-ray Fluorescence (μ-XRF) Spectrometry* (approved)

2. ICP-MS: ASTM E2330-12, *Standard Test Method for Determination of Concentrations of Elements in Glass Samples Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Forensic Comparisons*

3. LA-ICP-MS: ASTM E2927-16, *Standard Test Method for Determination of Trace Elements in Soda-Lime Glass Samples Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Forensic Comparisons*

All three standards provide:

- Method for determining trace element concentrations
- List of elements (12-17)
- "**Calculation and Interpretation of Results**"

From E2330-12, Section 1.2:

"*This test method covers a procedure for quantitative determination of the concentrations of magnesium (Mg), aluminum (Al), iron (Fe), titanium (Ti), manganese (Mn), rubidium (Rb), strontium (Sr), zirconium (Zr), barium (Ba), lanthanum (La), cerium (Ce), neodymium (Nd), samarium (Sm), and lead (Pb) in glass samples.*"

Sec 10: "**Calculation and Interpretation of Results**":

1. For the Known source fragments, using a minimum of 3 measurements, calculate the mean for each element.
2. Calculate the standard deviation for each element. This is the Measured SD.
3. Calculate a value equal to 3% of the mean for each element. This is the Minimum SD.
4. Calculate a match interval for each element with a lower limit equal to the mean minus 4 times the SD (Measured or Minimum, whichever is greater) and an upper limit equal to the mean plus 4 times the SD (Measured or Minimum, whichever is greater).

5. For each Recovered fragment, using a minimum of 3 measurements, calculate the mean concentration for each element.

6. For each element, compare the mean concentration in the Recovered fragment to the match interval for the corresponding element from the Known fragments.

7. If the mean concentration of one (or more) element(s) in the Recovered fragment falls outside the match interval for the corresponding element in the Known fragments, the element(s) does not "match" and the glass samples are considered distinguishable."

`Mg, Al, Fe, Ti, Mn, Rb, Sr, Zr, Ba, La, Ce, Nd, Sm, Pb`:

1. ≥ 3 measurements of 14 elemental concentrations on **Known** source fragments (X_{i1}, X_{i2}, X_{i3}), $i = 1, ..., 14$
2. Calculate 14 means and 14 SDs (each element): $\bar{X}_i$, s_i
3. Calculate $\bar{X}_i \pm 4 \cdot \min\{0.03 \cdot \bar{X}_i, s_i\}$ = "*match interval*"
4. ≥ 3 measurements of 14 elemental concentrations on **Recovered** fragment $\Rightarrow$ means $\bar{Y}_i$, $i = 1, ..., 14$.
5. **If $\bar{Y}_i \notin$ "match interval" for all 14 elements, the glass samples are considered distinguishable.**

How well does this procedure perform in practice?

(E2927-16 LA-ICP-MS: adds Li, K, Ca, Hf; deletes Sm)

Error rates:

- **Sensitivity**: If "K" (known) and "R" (recovered) fragments came from the same source, what is the probability that the procedure claims "Same Source"?
- **False negative**: If "K" (known) and "R" (recovered) fragments came from the same source, what is the probability that the procedure claims "Different Sources"?
- **Specificity**: If "K" (known) and "R" (recovered) fragments came from different sources, what is the probability that the procedure claims "Different Sources"?
- **False positive**: If "K" (known) and "R" (recovered) fragments came from different sources, what is the probability that the procedure claims "Same Source"?

Most studies estimate error rates in this way:

- Collect a wide variety of samples, to cover the "space" of possible glass samples being produced (cars, containers, countries, manufacturers, ...)
- (sometimes) Collect several fragments from the *same* sample (or pane of glass), and measure each fragment
- (sometimes) Collect several fragments from the *same* sample (or pane of glass); measure each fragment on separate days
- Apply the "match" procedure *to all possible pairs of samples*
- Count # of times 2 different samples "matched"
- Count # of times 2 same samples failed to "match"

In most studies, error rates of $< 1\%$ are reported.

- Glass samples were collected to be representative of a diverse body of glass in existence
- Representativeness is useful for some purposes (e.g., assessing variability in the population)
- But the collection is intended to be *diverse*
- It is amazing that we find *any* false matches at all — the samples are not just different: they are *very* different
- The real question: If we *knew* that the relative difference in concentrations between Sample A and Sample B is δ, what is the probability that the procedure claims "match"? (Should be high if $\delta \approx 0$ and should approach zero as δ increases)
- What value of n in the n-*SD* procedure would render a False Positive Probability (FPP) of, say, no more than 10% when the relative difference in concentrations is, say, δ ?

Some background

- Relative SDs make sense
- Easier: Just take logs: $SD(\log(X)) \approx RSD(X)$ if $RSD(X) < 5\%$
- Ex: Li7 via LA-ICP-MS: 4.56, 4.68, 4.79, 4.25, 4.33, 4.49:
  mean = 4.517, SD = 0.205, RSD = 0.205/4.517 = 4.5%
- Log(Li7): 1.517, 1.543, 1.567, 1.447, 1.466, 1.502
  mean = 1.507 (close to log(4.517) = 1.508); sd = 0.045 = 4.5%
- Ex: Zr90: 54.16, 55.25, 51.93, 50.13, 49.97, 49.44
  mean = 51.813, SD = 2.416, RSD = 2.416/51.813 = 4.7%
- Log(Zr90): 3.992, 4.012, 3.950, 3.915, 3.911, 3.901
  mean = 3.947 (same as log(51.813)), SD = 0.046 = 4.6%

Henceforth we take logs.

- Convenient ‘t-test’-like approach to comparing concentrations: $|\bar{X}_k - \bar{Y}_k|/s_k < 4$, $k = 1, ..., p =$ #elements [actual t-statistic is $|\bar{X}_k - \bar{Y}_k|/(s_k\sqrt{1/n_x + 1/n_y})$, $n_x, n_y = 3$]
- Multivariate: Hotelling's $T^2 = (\bar{X} - \bar{Y})'[\Sigma^{-1}(1/n_x + 1/n_y)](\bar{X} - \bar{Y})$, Compare to an F-distribution (need multiplier)
- Problem: only 3 measurements $\Rightarrow$ 2 df per SD?
- Cannot estimate Covariance Matrix Σ
- Weis et al. 2011: “*If only six replicate measurements are carried out for each of the two samples to be compared, the number of elements used for the comparisons has to be reduced to 10, which leads to a loss of evidential value. Hence, Hotellings T^2-test calculations will not be addressed in this paper.*”
- Just because we don't have the data to estimate Σ does not allow us to ignore possible correlation among elements

2. Available Data

- ICP-MS: FIU, via TSWG (`jeff.huber.ctr@cttso.gov`): 590 samples: 160 container, 189 Float-Arch, 46 Float-Auto (CFS), 97 Float-Auto (non-CFS), 45 Headlamp, 10 Lab, 43 'Rare'
- LA-ICP-MS: Peter Weis, reported in Weis et al. (2011):
  - "Same source": 33 (6 reps) + 1 (6 reps, 11 days)
  - "Different source": 62 samples from 18 manufacturers: Germany (21), USA (19), Japan (13), Other (9)
- LA-ICP-MS: David Ruddell, reported in Dorn et al. (2015):
  - "Same source": 25 fragments: 24 with 9 reps + 25^{th} fragment measured 24 times (9 replicates each)
  - "Different source": 521 samples from many makes, models, years of cars (sometimes 2-3 pieces per car, such as inside and outside of windshield)
- XRF? No data.

Sources of variability in glass measurements:

1. σ_e = measurement variation: variability among measurements taken on the same single fragment at nearly the same time (i.e., only at most a few minutes apart)

2. σ_t = time variation: variability among measurements taken on a single fragment at different times (e.g., on different days, perhaps as much as weeks apart)

3. σ_f = fragment variability: variability in measurements taken on *different* fragments from the *same* pane of glass

4. σ_B = source variability: variability in measurements taken on fragments from different panes of glass

Statistical Modeling Approach

Estimating error rates by "all pairwise comparisons":

- Depends on data set: Samples that are "more alike" (e.g., all Ford cars) may have seemingly higher error rates than a highly diverse collection
- Diversity is good for representativeness, but not for estimating error rates (the samples are *very* different)
- If A (Audi) fails to match B, and B and C both were samples on Ford cars, good guess that A and C will not match
- So hard to assess variability in claimed "error rate" – which is likely to be optimistic anyway

Statistical Model

First: Estimate $p \times p$ Covariance Matrix Σ (below), estimate is V (here, $p = 17$ elements). Repeat many (6000) times:

1. Simulate a new covariance matrix, $\hat{V}$, assuming V is "true Σ" (accounts for variability in estimating Σ)

2. Simulate 3 vectors from $N_p(0, \hat{V})$ ("Known"): mean $\bar{X} = (\bar{x}_1, ...\bar{x}_p)$; SD $S_x = (s_1, ..., s_p)$; $S_x^* = (s_1^*, ..., s_p^*)$ where each $s_i^* = max(0.03, s_i)$.

3. Calculate "match interval" for i^{th} element as $(\bar{x}_i - 4s_i^*, \bar{x} + 4s_i^*)$.

4. Generate 2nd sample of 3 vectors from $N_p(\delta, \hat{V})$, representing 3 measurements of concentrations on p elements for "Recovered" fragment: $\bar{Y} = (\bar{y}_1, ...\bar{y}_p)$

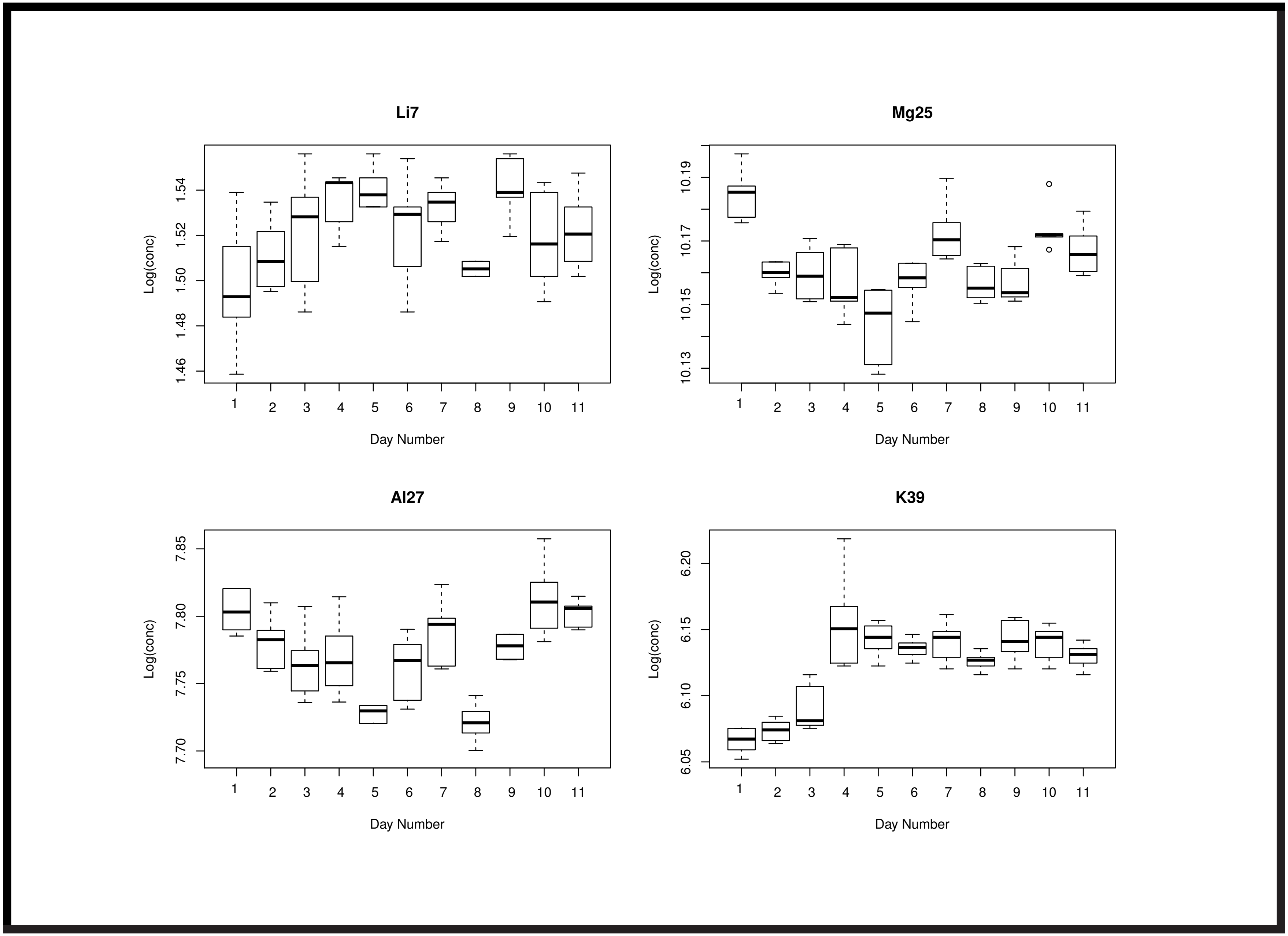
5. If $\bar{y}_i \geq \bar{x}_i - 4s_i^*$ and $\bar{y}_i \leq \bar{x}_i + 4s_i^*$ for each element $i = 1, ..., p$, then declare "match", else "no match".

Notes:

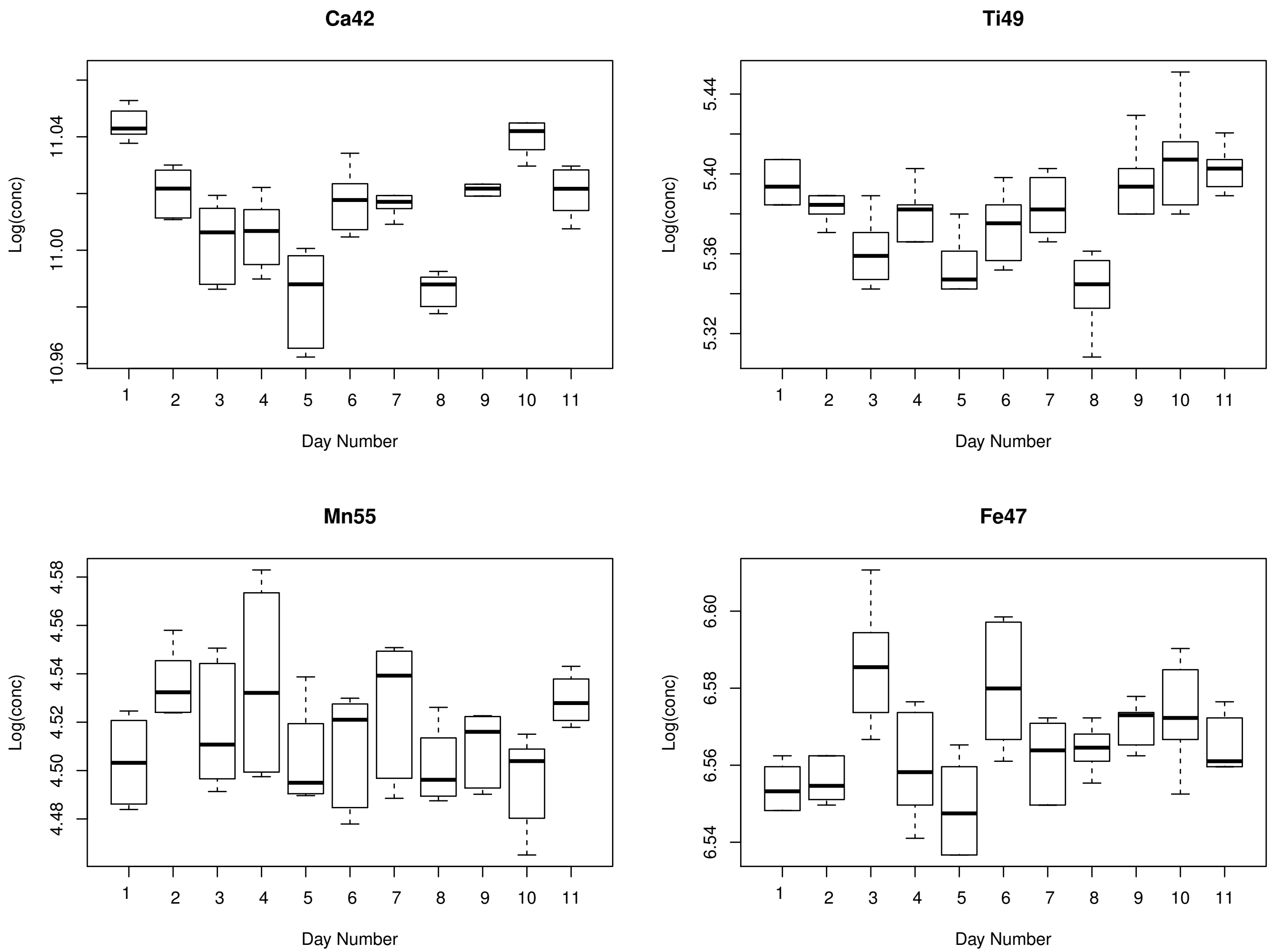
1. $\delta = 0.2, 1.1, 1.4 \Rightarrow$ relative change in raw means of 20%, 200%, 300%
2. Expect FPP $\downarrow 0$ as $\delta \uparrow$.
3. "Real data have long tails [& outliers]!" (J.W. Tukey). Even on log scale, data are more symmetric but probably not normal.
4. We also simulate measurements from Multivariate-t

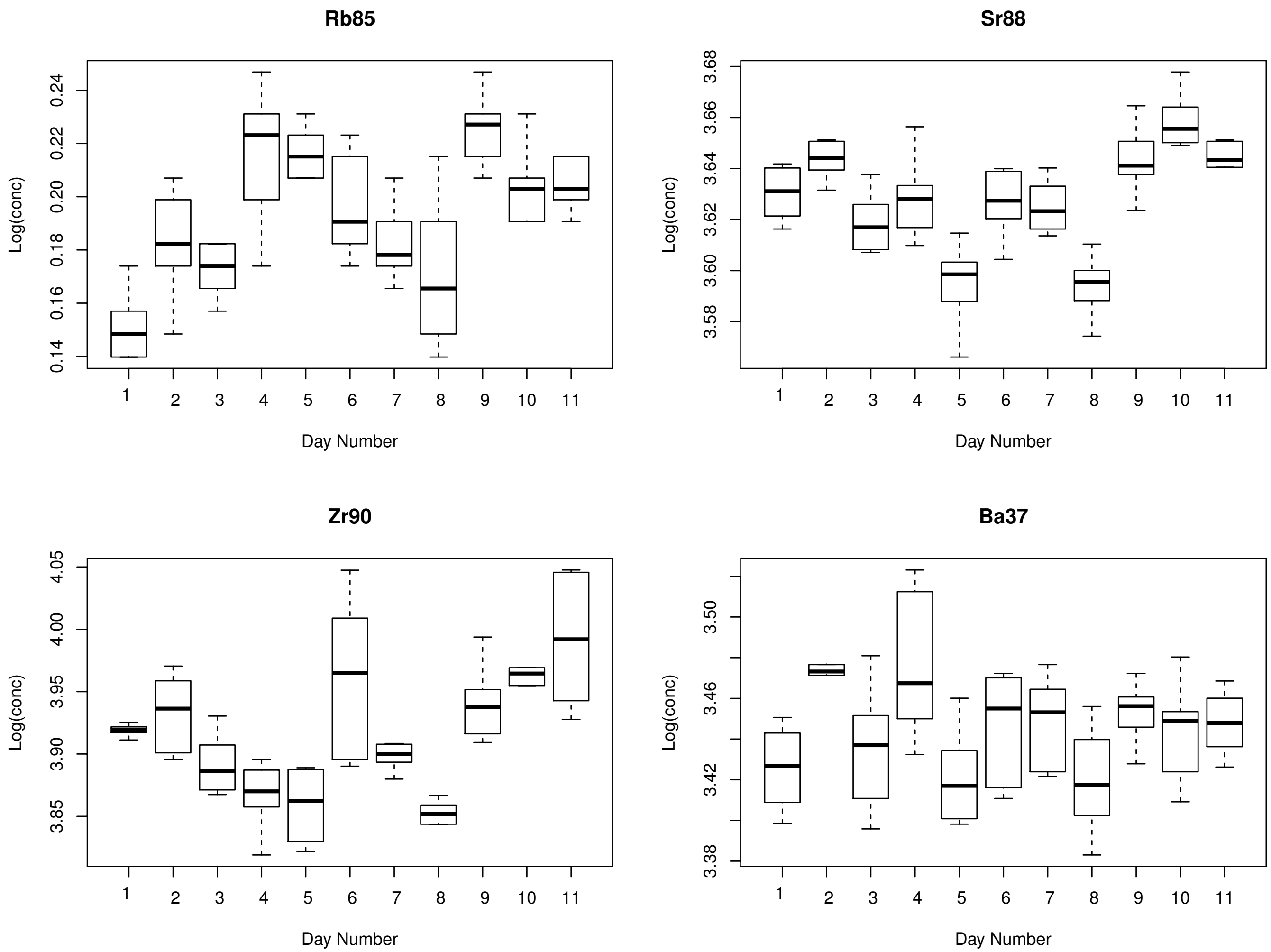
Estimate Statistical Model Parameter Σ

- As noted, need more replicates than elements (17)
- FIU: $r = 3$; Weis: $r = 6$; Ruddell: $r = 9$
- Weis: Sample 104G was measured 6 times on 11 separate days; if *day* effect is absent, we'd have 66 replicates
- Ruddell: Sample 24 was measured 9 times on 24 different occasions: if *occasion* effect is absent, we'd have 216 replicates (note: on Occasion#3, only 3, not 9, replicates, so drop #3)
- Alas, *day* and *occasion* factor usually significant in One-way A/V (6×11 or 9×23) for each element

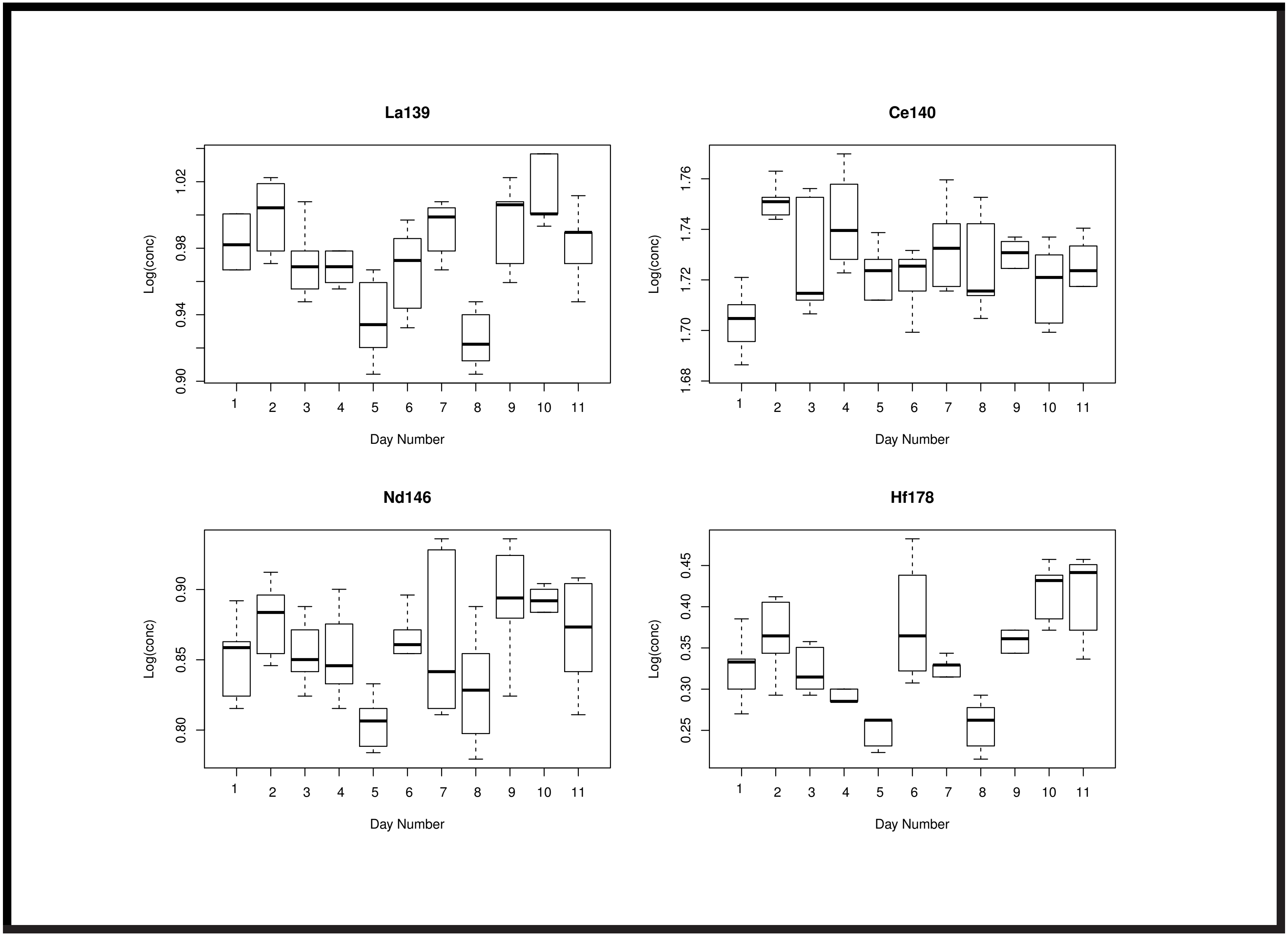


Li7
Mg25
Al27
K39
Log(conc)
Day Number
1.46
1.48
1.50
1.52
1.54
10.13
10.15
10.17
10.19
7.70
7.75
7.80
7.85
6.05
6.10
6.15
6.20
1
2
3
4
5
6
7
8
9
10
11

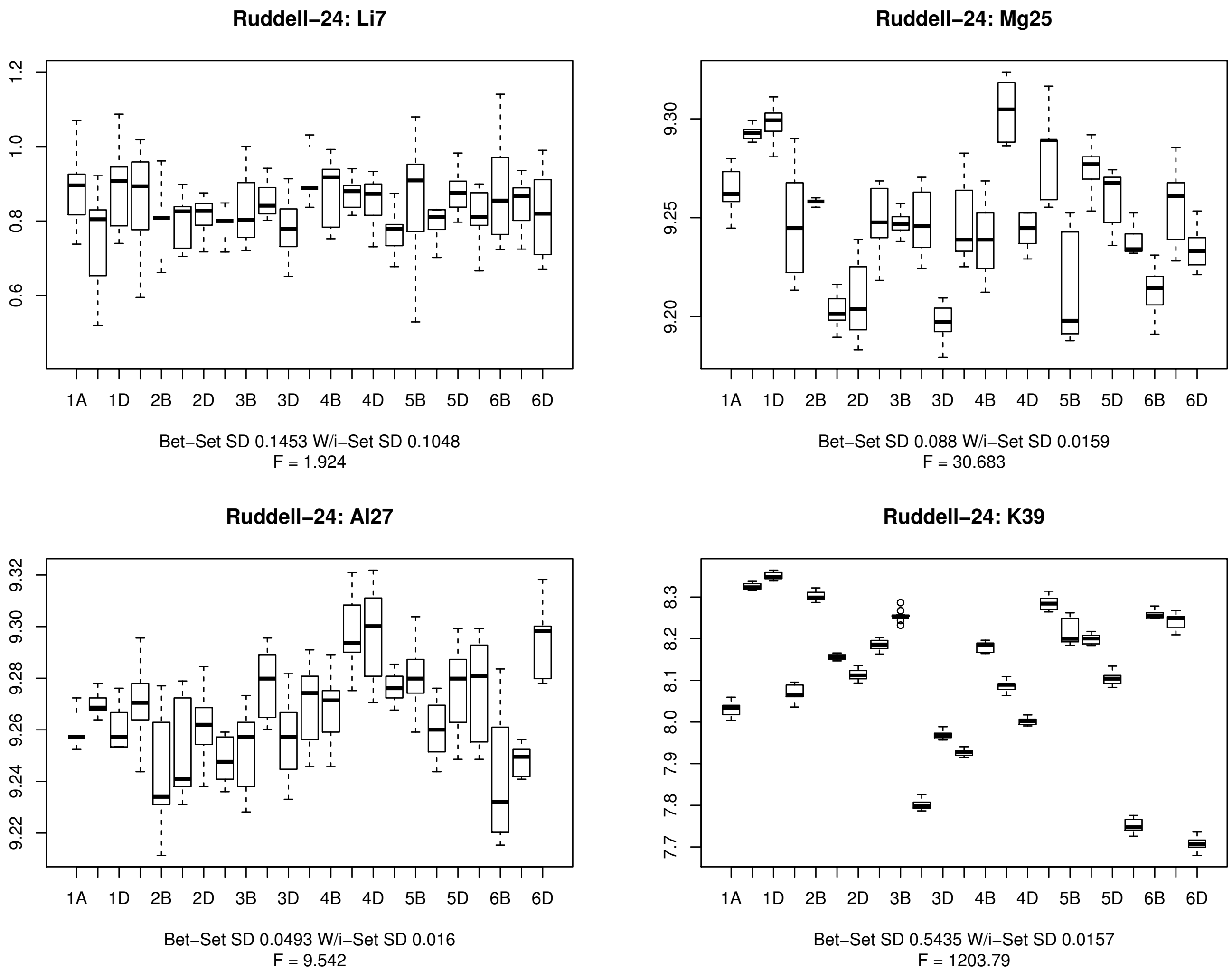

Ca42
Ti49
Mn55
Fe47
Log(conc)
Day Number
10.96
11.00
11.04
5.32
5.36
5.40
5.44
4.48
4.50
4.52
4.54
4.56
4.58
6.54
6.56
6.58
6.60
1 2 3 4 5 6 7 8 9 10 11

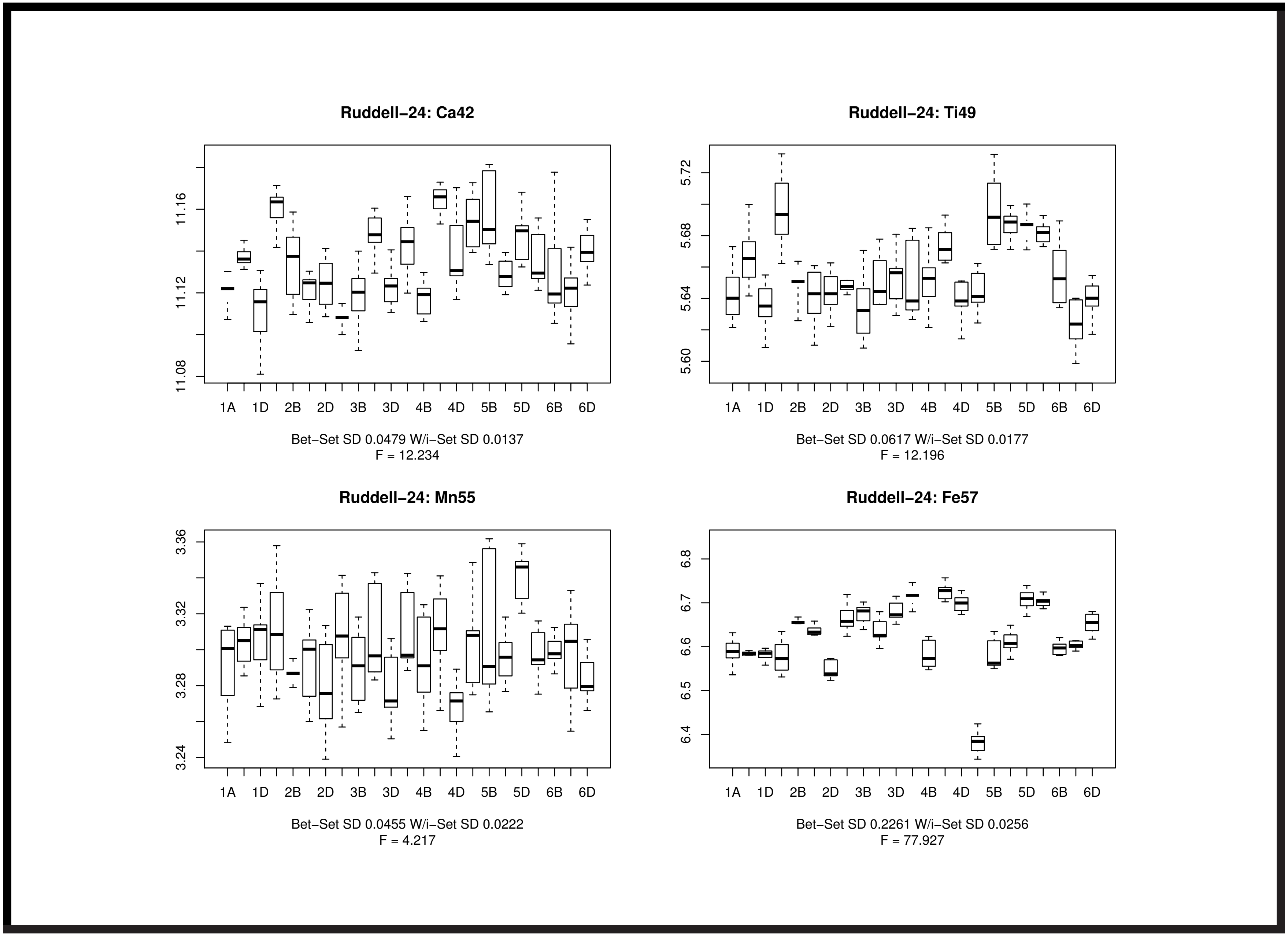


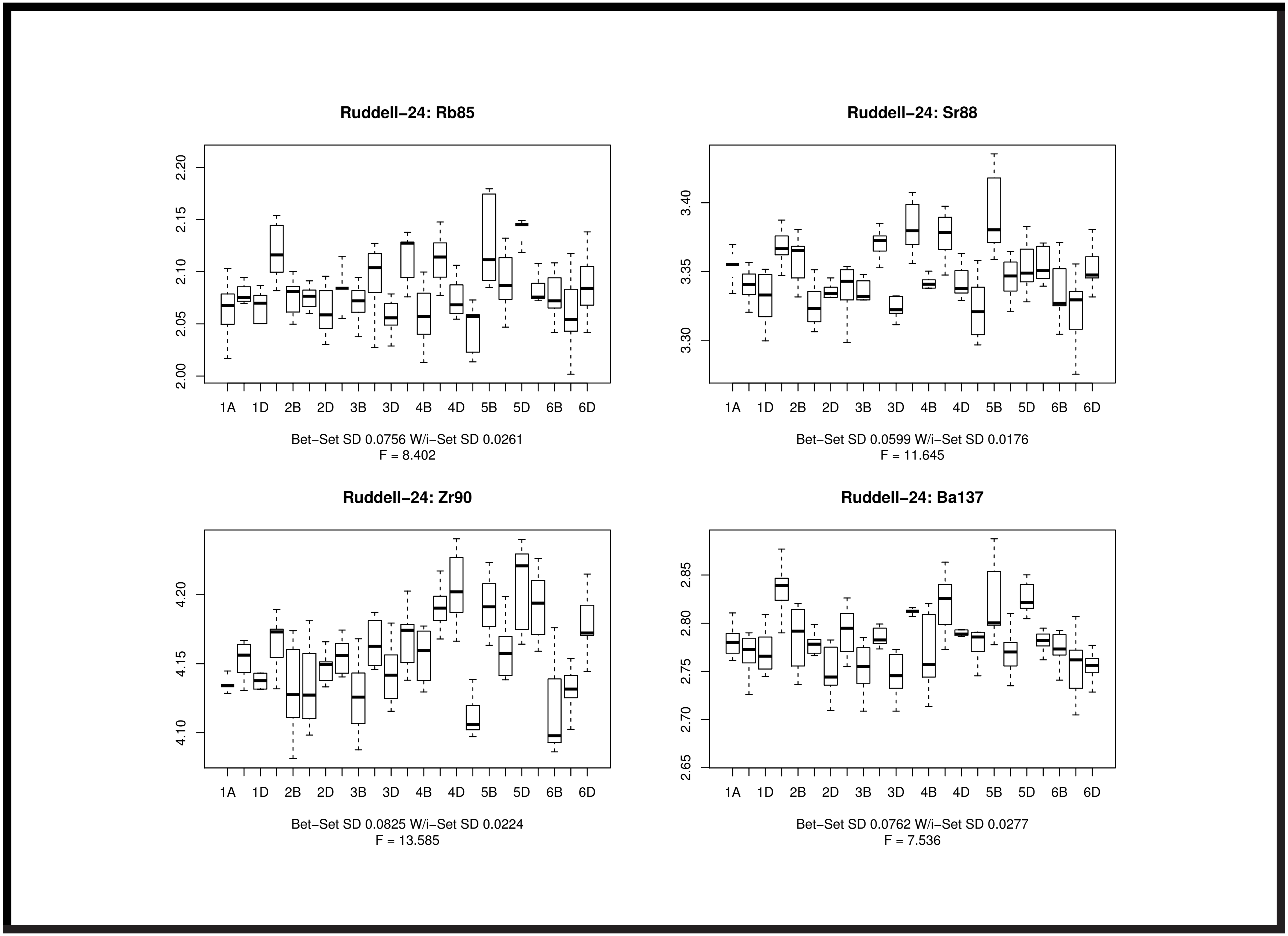
Rb85
Sr88
Zr90
Ba37
Log(conc)
Day Number
1
2
3
4
5
6
7
8
9
10
11
0.14
0.16
0.18
0.20
0.22
0.24
3.58
3.60
3.62
3.64
3.66
3.68
3.85
3.90
3.95
4.00
4.05
3.38
3.42
3.46
3.50

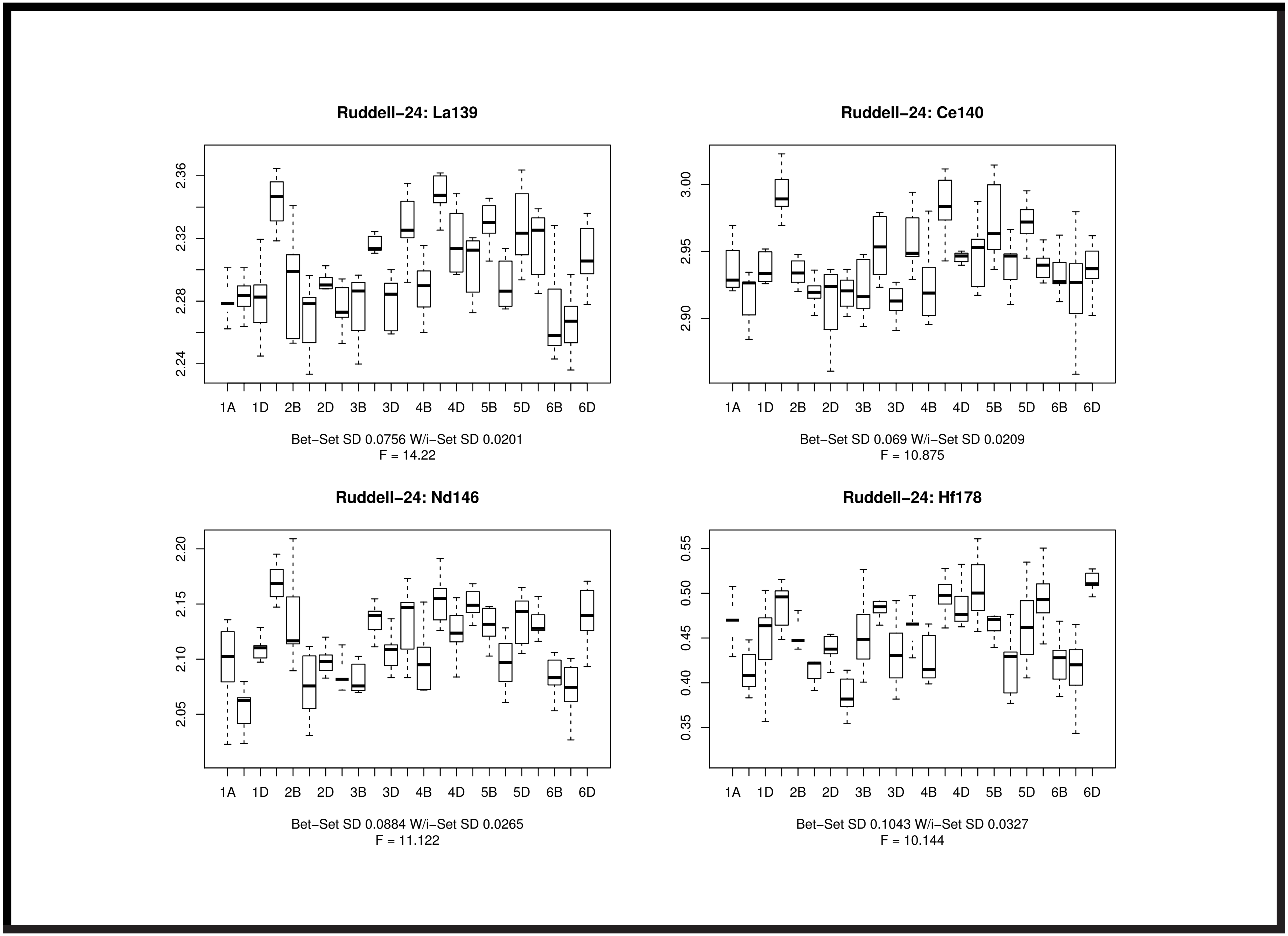


La139
Ce140
Nd146
Hf178
Log(conc)
Day Number


Ruddell−24: Li7
1.2
1.0
0.8
0.6
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.1453 W/i−Set SD 0.1048
F = 1.924
Ruddell−24: Mg25
9.30
9.25
9.20
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.088 W/i−Set SD 0.0159
F = 30.683
Ruddell−24: Al27
9.32
9.30
9.28
9.26
9.24
9.22
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.0493 W/i−Set SD 0.016
F = 9.542
Ruddell−24: K39
8.3
8.2
8.1
8.0
7.9
7.8
7.7
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.5435 W/i−Set SD 0.0157
F = 1203.79

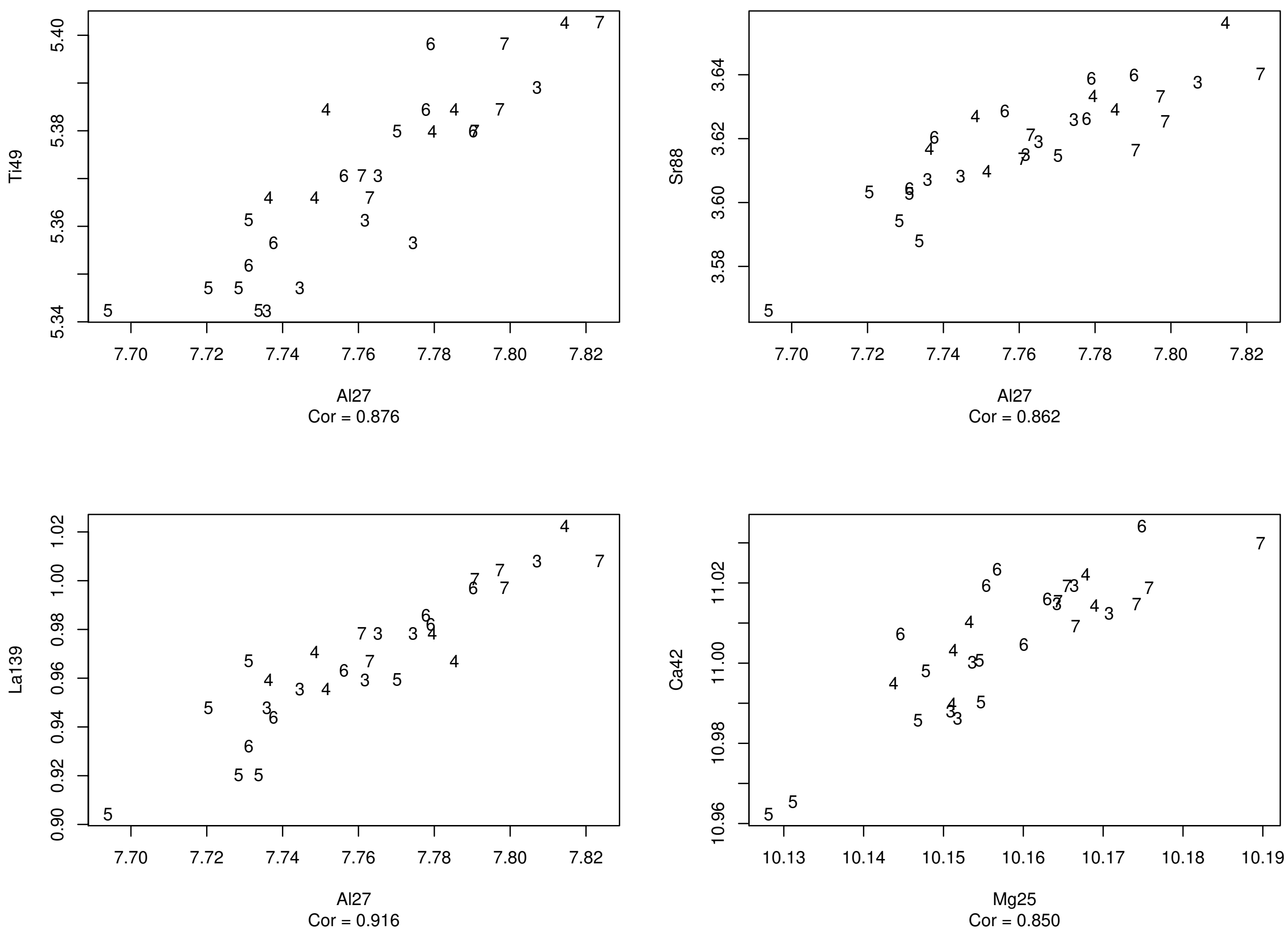

Ruddell−24: Ca42
11.08
11.12
11.16
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.0479 W/i−Set SD 0.0137
F = 12.234
Ruddell−24: Ti49
5.60
5.64
5.68
5.72
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.0617 W/i−Set SD 0.0177
F = 12.196
Ruddell−24: Mn55
3.24
3.28
3.32
3.36
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.0455 W/i−Set SD 0.0222
F = 4.217
Ruddell−24: Fe57
6.4
6.5
6.6
6.7
6.8
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.2261 W/i−Set SD 0.0256
F = 77.927

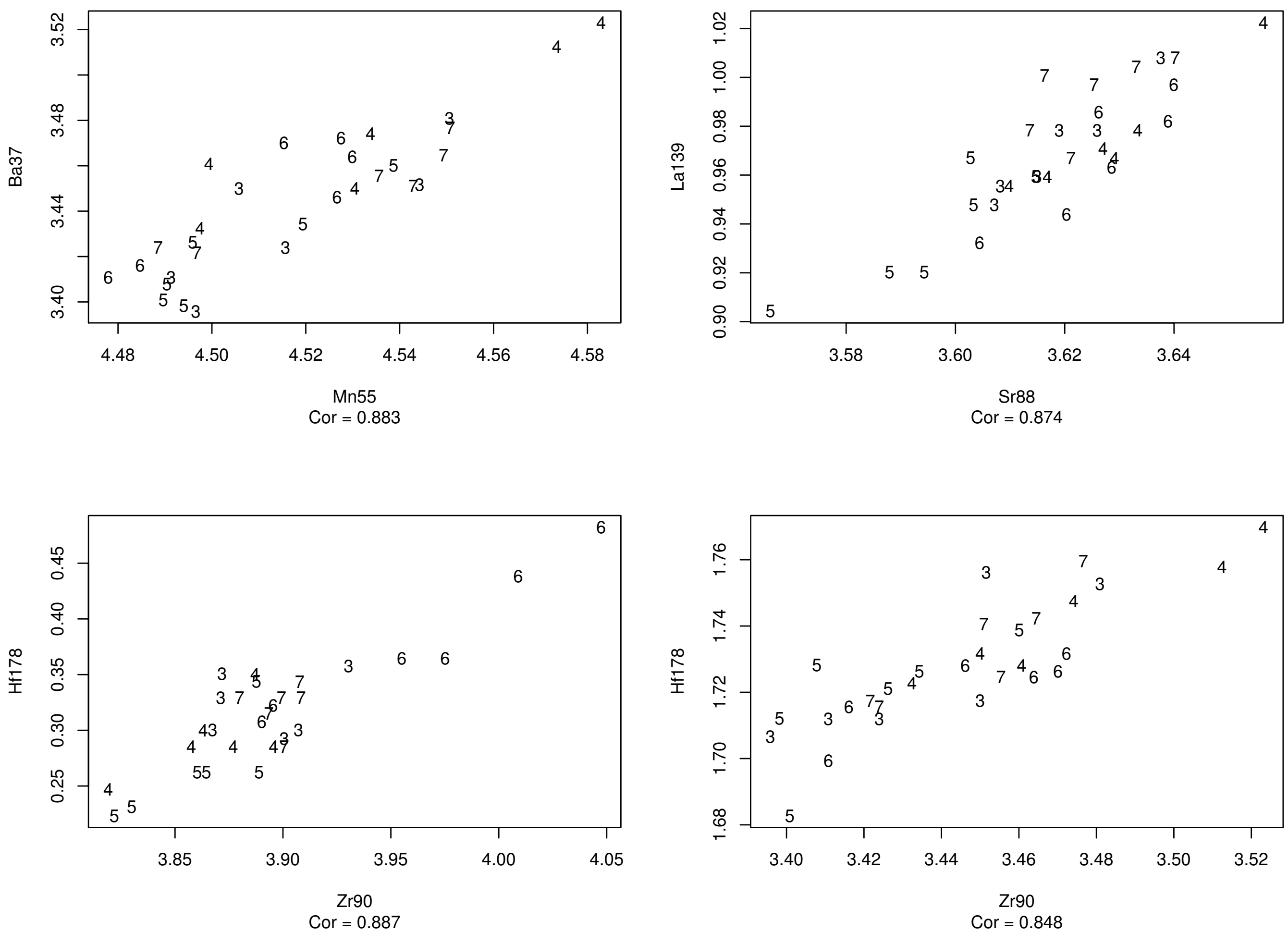

Ruddell−24: Rb85
Bet−Set SD 0.0756 W/i−Set SD 0.0261
F = 8.402
Ruddell−24: Sr88
Bet−Set SD 0.0599 W/i−Set SD 0.0176
F = 11.645
Ruddell−24: Zr90
Bet−Set SD 0.0825 W/i−Set SD 0.0224
F = 13.585
Ruddell−24: Ba137
Bet−Set SD 0.0762 W/i−Set SD 0.0277
F = 7.536

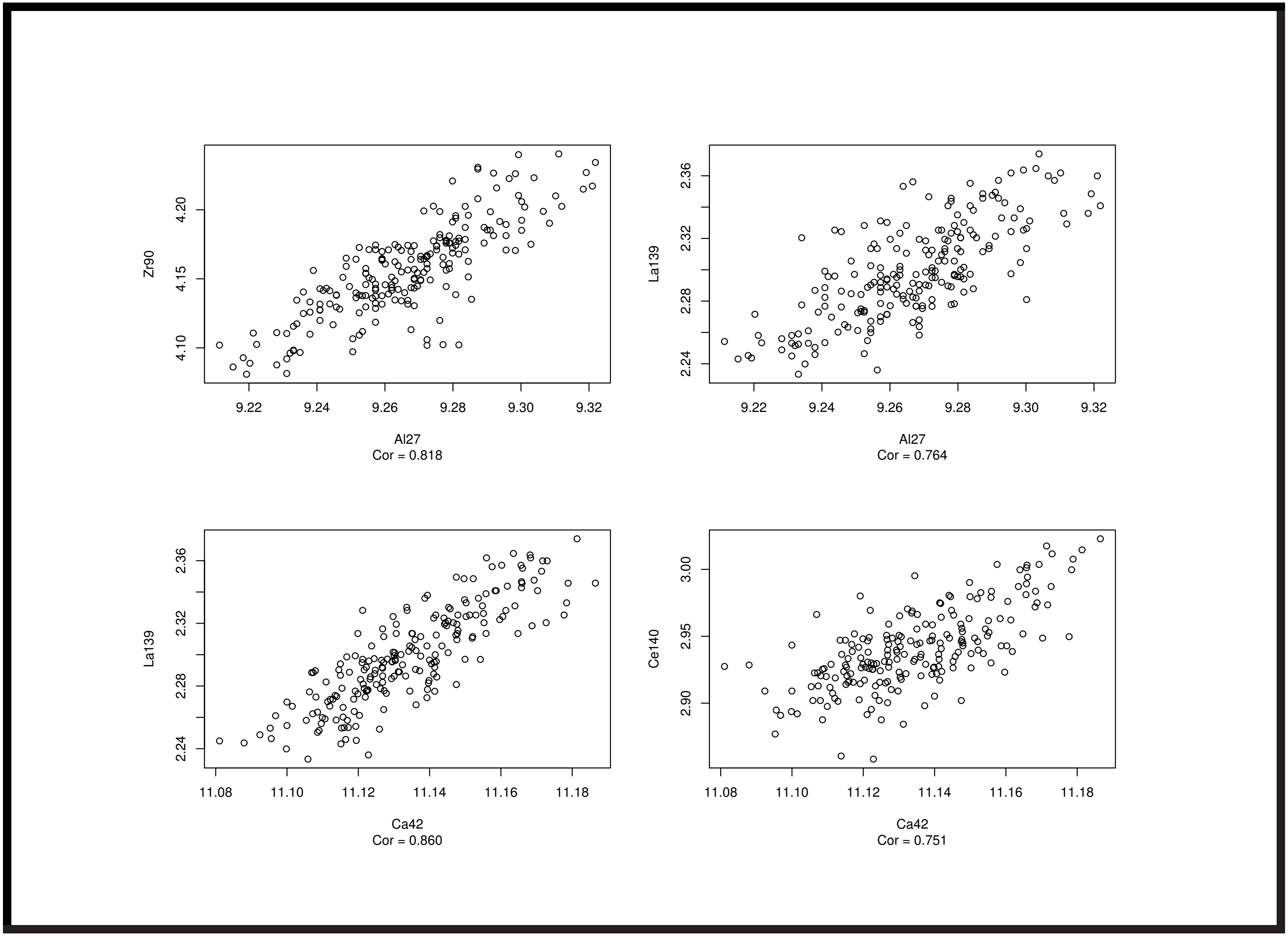

Ruddell−24: La139
2.24
2.28
2.32
2.36
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.0756 W/i−Set SD 0.0201
F = 14.22
Ruddell−24: Ce140
2.90
2.95
3.00
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.069 W/i−Set SD 0.0209
F = 10.875
Ruddell−24: Nd146
2.05
2.10
2.15
2.20
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.0884 W/i−Set SD 0.0265
F = 11.122
Ruddell−24: Hf178
0.35
0.40
0.45
0.50
0.55
1A 1D 2B 2D 3B 3D 4B 4D 5B 5D 6B 6D
Bet−Set SD 0.1043 W/i−Set SD 0.0327
F = 10.144

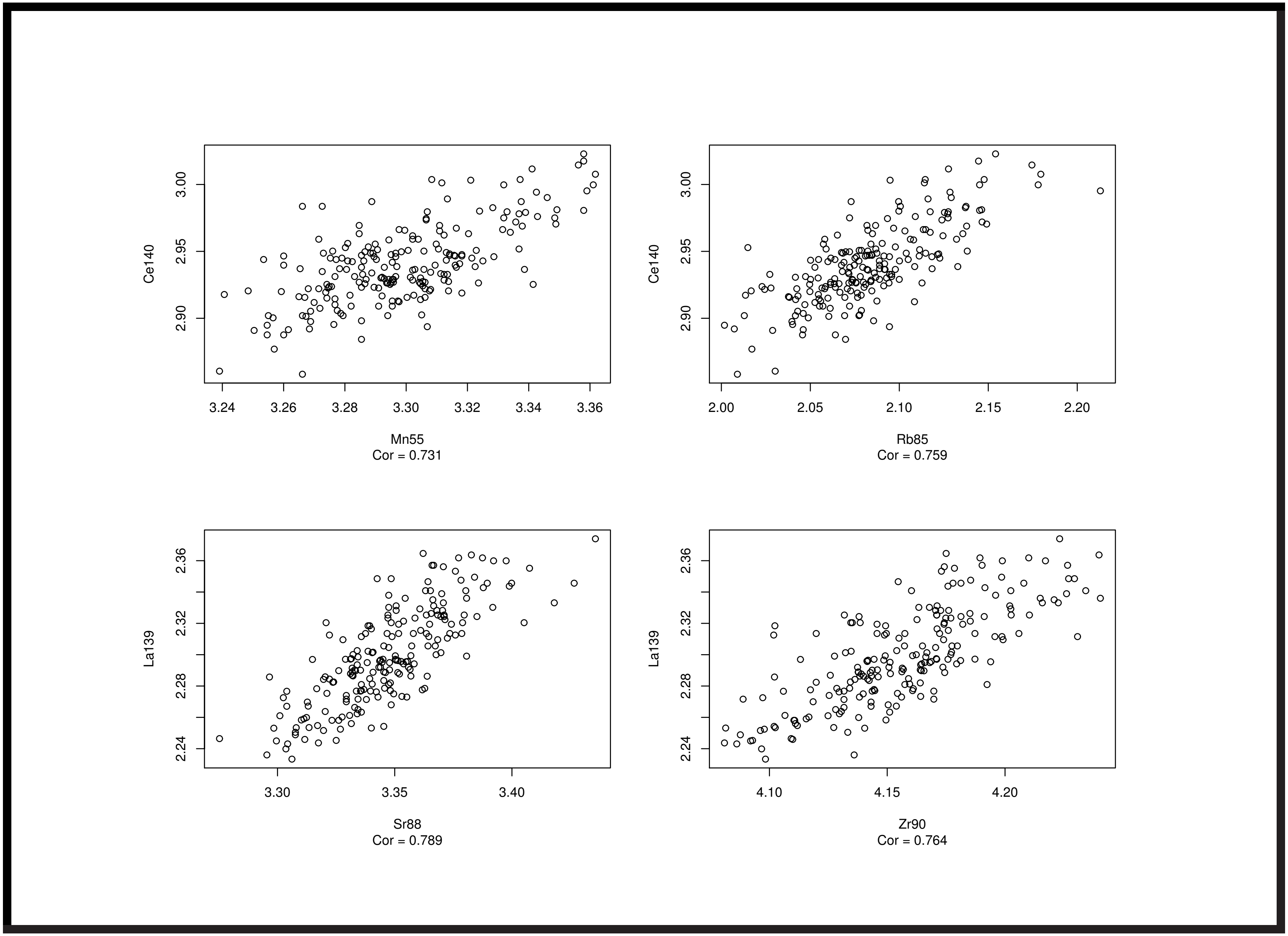
Three estimates of correlation (covariance) matrix among elements

- Weis Sample 104G: treat 6 reps on 11 days as 66 reps (days 3-7 somewhat more consistent)
- Ruddell, Sample #24: measured 24 times, each 9 times: Ignored 1 that had only 3 reps $\Rightarrow$ 207 “reps”
- FIU data: estimated from means of different samples (least appropriate)
- Sample covariance matrices are different
- But SVD of each one suggests effective dimension ≈ 7, not 17 (cumulative sum of first 7 singular values $> 95\%$)
- We used all three methods
- For FIU matrix, each run generated from simulated $\hat{V}$

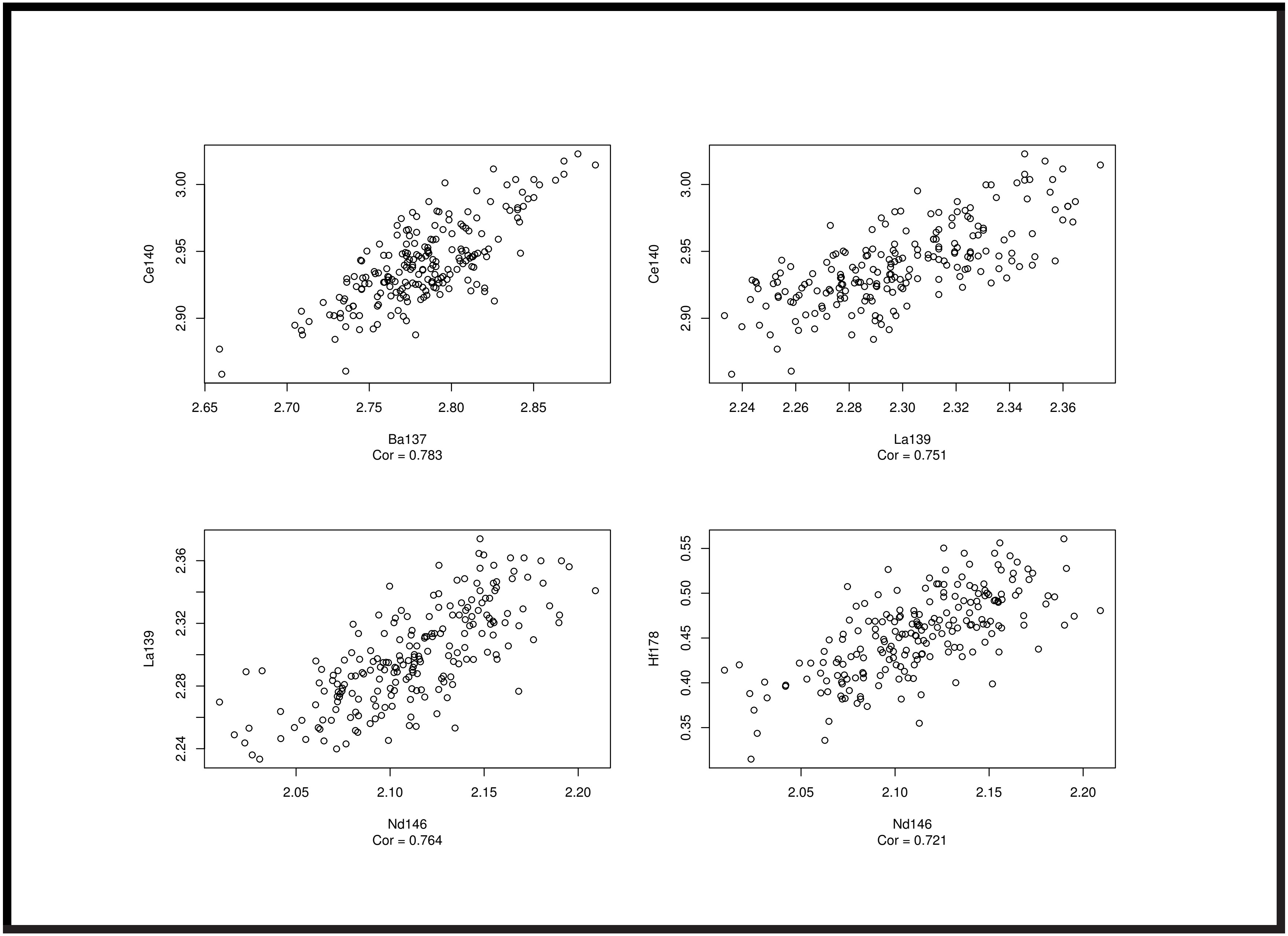

Ti49
Al27
Cor = 0.876
Sr88
Al27
Cor = 0.862
La139
Al27
Cor = 0.916
Ca42
Mg25
Cor = 0.850


Ba37
Mn55
Cor = 0.883
La139
Sr88
Cor = 0.874
Hf178
Zr90
Cor = 0.887
Hf178
Zr90
Cor = 0.848


Zr90
4.10
4.15
4.20
9.22
9.24
9.26
9.28
9.30
9.32
Al27
Cor = 0.818
La139
2.24
2.28
2.32
2.36
9.22
9.24
9.26
9.28
9.30
9.32
Al27
Cor = 0.764
La139
2.24
2.28
2.32
2.36
11.08
11.10
11.12
11.14
11.16
11.18
Ca42
Cor = 0.860
Ce140
2.90
2.95
3.00
11.08
11.10
11.12
11.14
11.16
11.18
Ca42
Cor = 0.751



Ce140
Mn55
Cor = 0.731
Ce140
Rb85
Cor = 0.759
La139
Sr88
Cor = 0.789
La139
Zr90
Cor = 0.764


Ce140
Ba137
Cor = 0.783
Ce140
La139
Cor = 0.751
La139
Nd146
Cor = 0.764
Hf178
Nd146
Cor = 0.721

100×Correlation Matrix for Weis Sample 104: 11 Days

	Li7	Mg25	Al27	K39	Ca42	Ti49	Mn55	Fe47	Rb85
Li7	--	-30	-8	49	-23	-7	15	1	38
Mg25	-30	--	72	-26	82	59	6	21	-35
Al27	-8	72	--	-5	81	93	47	24	12
K39	49	-26	-5	--	-24	4	15	6	60
Ca42	-23	82	81	-24	--	78	0	22	-16
Ti49	-7	59	93	4	78	--	41	17	19
Mn55	15	6	47	15	0	41	--	2	33
Fe47	1	21	24	6	22	17	2	--	11
Rb85	38	-35	12	60	-16	19	33	11	--
Sr88	0	56	87	-1	83	88	36	30	19
Zr90	-3	41	63	-8	61	66	9	35	11
Ba37	13	16	58	18	27	60	83	14	41
La139	-7	61	88	-5	78	84	43	31	19
Ce140	30	-7	28	19	-5	28	79	7	40

Nd146	-2	46	66	6	55	64	39	31	29
Hf178	5	39	63	0	59	65	12	35	17
Pb208	40	-45	-7	48	-38	1	33	25	59

100×Correlation Matrix for Weis Sample 104: 11 Days

	Sr88	Zr90	Ba37	La139	Ce140	Nd146	Hf178	Pb208
Li7	0	-3	13	-7	30	-2	5	40
Mg25	56	41	16	61	-7	46	39	-45
Al27	87	63	58	88	28	66	63	-7
K39	-1	-8	18	-5	19	6	0	48
Ca42	83	61	27	78	-5	55	59	-38
Ti49	88	66	60	84	28	64	65	1
Mn55	36	9	83	43	79	39	12	33
Fe47	30	35	14	31	7	31	35	25
Rb85	19	11	41	19	40	29	17	59
Sr88	--	67	63	89	34	74	70	10
Zr90	67	--	25	60	5	49	91	1
Ba37	63	25	--	63	80	59	29	35
La139	89	60	63	--	36	71	61	3
Ce140	34	5	80	36	--	43	11	50

Nd146	74	49	59	71	43	--	54	22
Hf178	70	91	29	61	11	54	--	12
Pb208	10	1	35	3	50	22	12	--

100×Corrln matrix for Ruddell Sample 25: 24 Occasions

	Li7	Mg25	Al27	K39	Ca42	Ti49	Mn55	Fe57	Rb85
Li7	--	17	8	-7	17	10	32	21	27
Mg25	17	--	24	25	38	27	58	9	33
Al27	8	24	--	-36	71	42	7	13	26
K39	-7	25	-36	--	-15	-5	9	-41	-11
Ca42	17	38	71	-15	--	65	48	11	57
Ti49	10	27	42	-5	65	--	51	17	60
Mn55	32	58	7	9	48	51	--	26	72
Fe57	21	9	13	-41	11	17	26	--	47
Rb85	27	33	26	-11	57	60	72	47	--
Sr88	25	28	54	-24	73	59	45	35	67
Zr90	14	9	82	-39	60	53	12	42	43
Ba137	23	40	39	-2	67	56	62	26	68
La139	21	29	76	-30	86	63	37	26	57
Ce140	31	53	41	-11	75	60	73	27	76

Nd146	18	27	62	-30	74	45	32	13	39
Hf178	18	26	63	-37	67	30	23	9	26
Pb208	11	34	12	-10	31	16	52	14	35

100×Corrln matrix for Ruddell Sample 25: 24 Occasions

	Sr88	Zr90	Ba137	La139	Ce140	Nd146	Hf178	Pb208
Li7	25	14	23	21	31	18	18	11
Mg25	28	9	40	29	53	27	26	34
Al27	54	82	39	76	41	62	63	12
K39	-24	-39	-2	-30	-11	-30	-37	-10
Ca42	73	60	67	86	75	74	67	31
Ti49	59	53	56	63	60	45	30	16
Mn55	45	12	62	37	73	32	23	52
Fe57	35	42	26	26	27	13	9	14
Rb85	67	43	68	57	76	39	26	35
Sr88	--	63	69	79	71	60	49	25
Zr90	63	--	46	76	41	52	47	-1
Ba137	69	46	--	68	78	56	49	21
La139	79	76	68	--	75	76	67	19
Ce140	71	41	78	75	--	68	57	38

Nd146	60	52	56	76	68	--	72	28
Hf178	49	47	49	67	57	72	--	30
Pb208	25	-1	21	19	38	28	30	--

Next Page: High Correlations between these two data sets:

Ruddell-25	Weis-104G
Sr & La 0.789	Ca & Mg 0.822
Sr & Ce 0.712	Al & Ca 0.811
Zr & La 0.764	Ti & Al 0.929
Ba & Ce 0.783	Sr & Al 0.872
La & Ce 0.751	La & Al 0.877
La & Nd 0.764	Ca & Sr 0.826
Nd & Hf 0.721	Ti & Sr 0.883
Al & La 0.764	Ti & La 0.843
Ca & Sr 0.733	Mn & Ce 0.742
Ca & La 0.860	Ca & La 0.776
Mn & Ce 0.730	Ba & Mn 0.829
Rb & Mn 0.722	Ce & Mn 0.792
Rb & Ce 0.759	La & Sr 0.893
Al & Ca 0.714	Zr & Hf 0.911
La & Zr 0.818	Ba & Ca 0.799

1 Robust Correlation Tables

Robust correlations calculated using the minimum covariance determinant method.

The table with only elements in the standard:

	Ce-La	Ce-Sm	La-Sm	Mn-Sm	Ba-Mn	Ba-Sm	Mn-Ti	La-Mn	Sm-Ti
Container	**0.97**	**0.94**	**0.96**	**0.81**	0.11	0.24	0.42	0.78	0.53
Float Arch *	**0.96**	**0.92**	**0.95**	**0.81**	0.78	**0.82**	**0.91**	0.72	0.63
Float Auto (CFS) *		0.24		**0.9**	**-0.83**	-0.73	-0.77		-0.72
Float Auto (non CFS) *	0.47	0.49	0.72	0.61	0.53	0.22	0.51	**0.81**	0.29
Headlamp	**0.98**	**0.97**	**0.94**	-0.22	-0.08	0.15	-0.34	-0.22	0.6
Lab	**0.99**	**1**	**0.99**	**0.85**	0.79	**0.97**	0.78	**0.9**	**0.97**
Rare	**0.98**	**0.93**	**0.95**	0.07	**0.95**	0.26	0.14	0.11	0.77

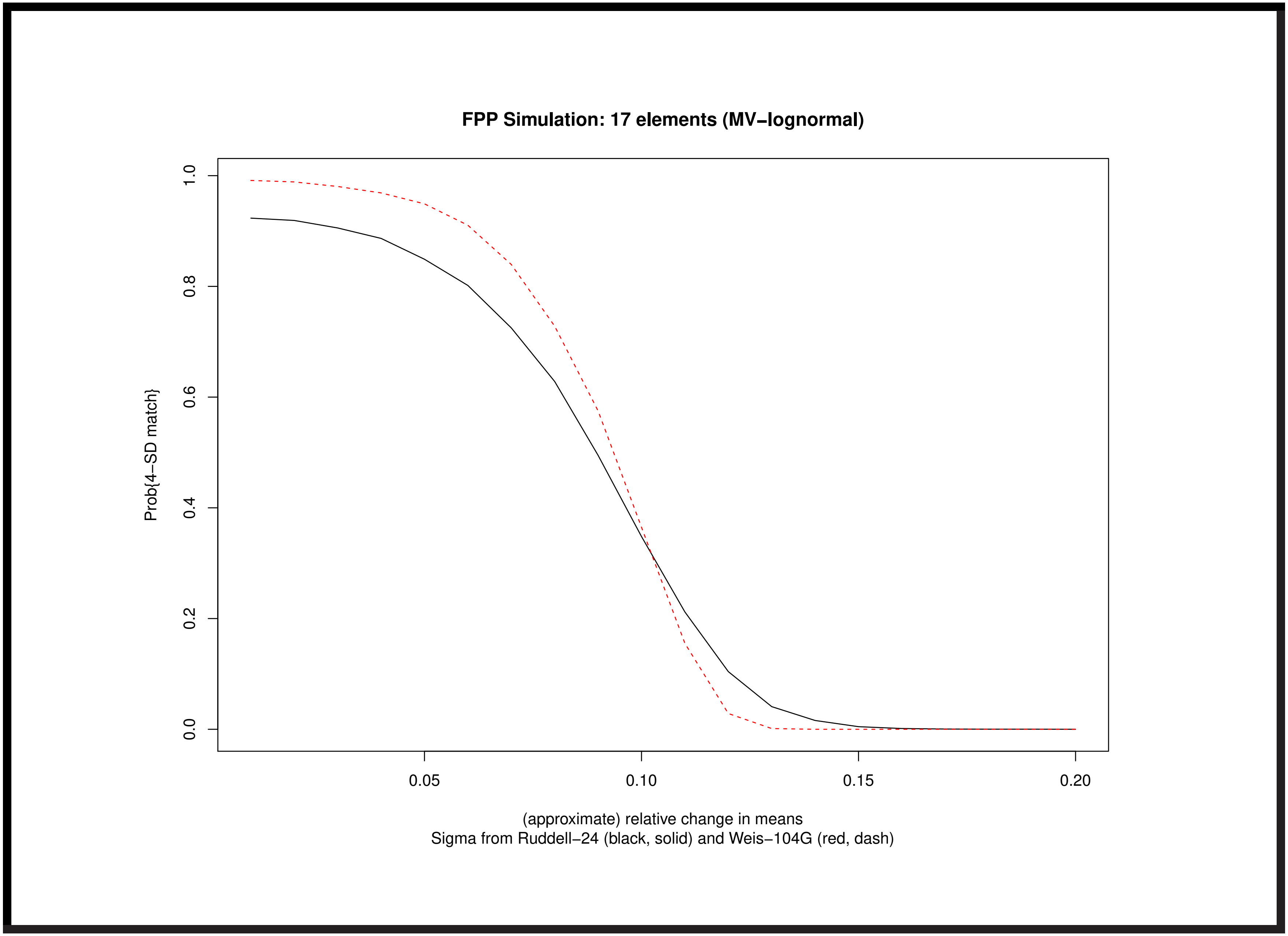
Table 1: Large Correlations with 13 elements in E2230-12 (Teal: $0.6 \leq x < 0.7$, Blue: $0.7 \leq x < 0.8$, Red: $0.8 \leq x \leq 1$)
Note: Float arch does not contain Sb, float auto (CFS) does not contain Sb or La, float auto (non CFS) does not contain Sb

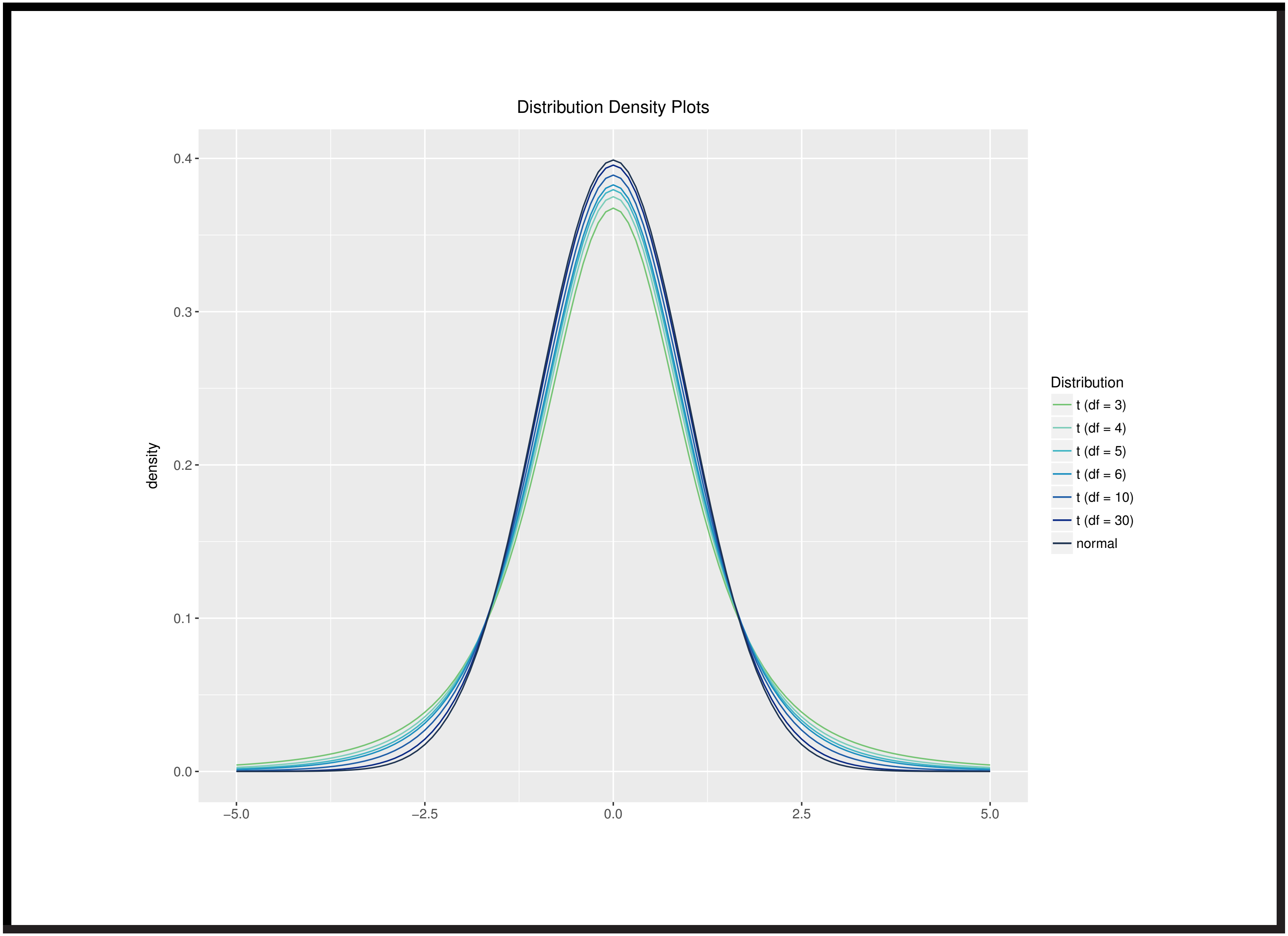
Results: FPP from Statistical Modeling

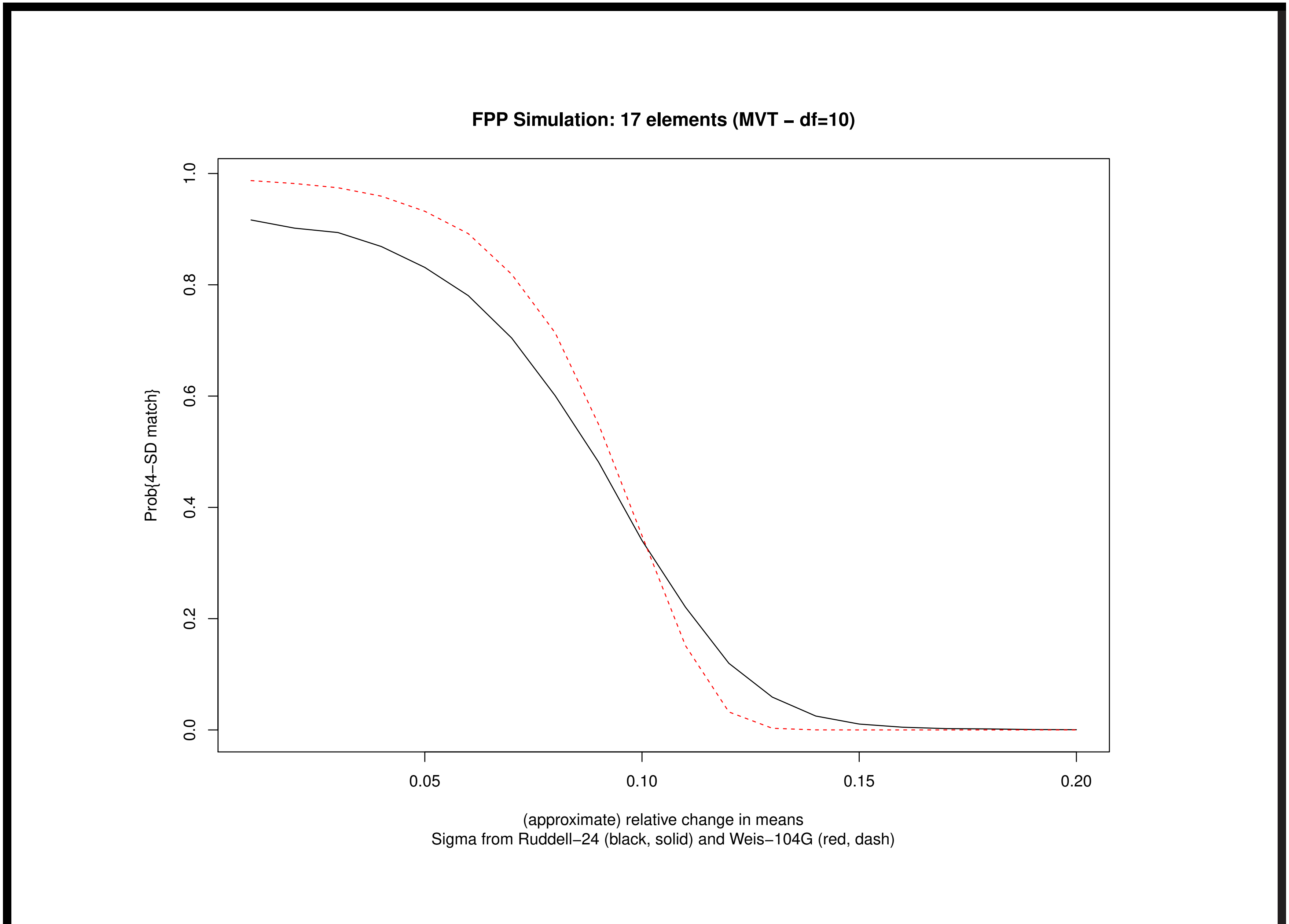
Three estimates of correlation (covariance) matrix among elements

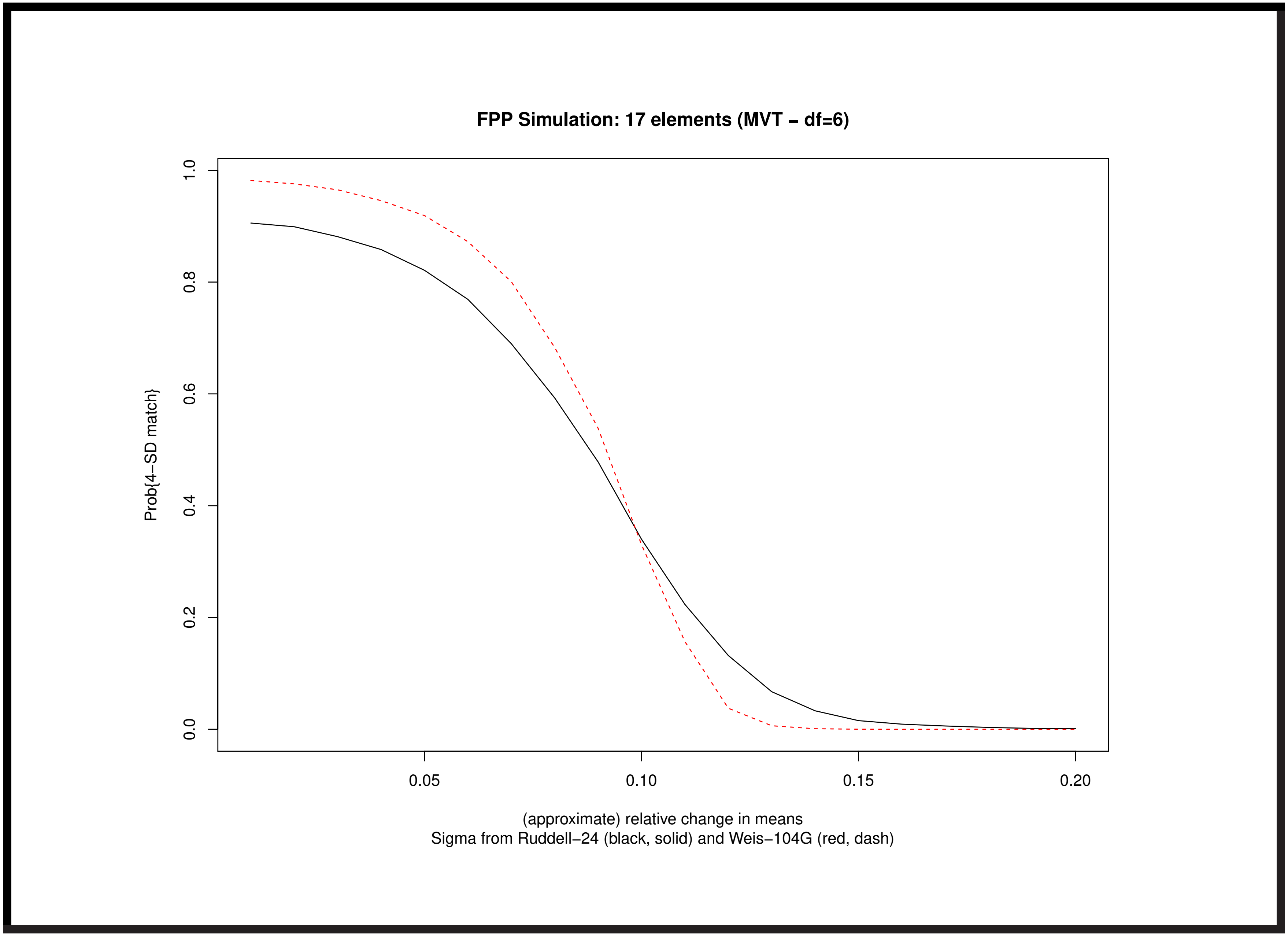
1. Weis Sample 104G: treat 6 reps on 11 days as 66 reps (days 3-7 somewhat more consistent)
2. Ruddell, Sample #24: measured 24 times, each 9 times: Ignored 1 that had only 3 reps $\Rightarrow$ 207 "reps"
3. FIU data: estimated from means of different samples (least appropriate; used `robmcd`)

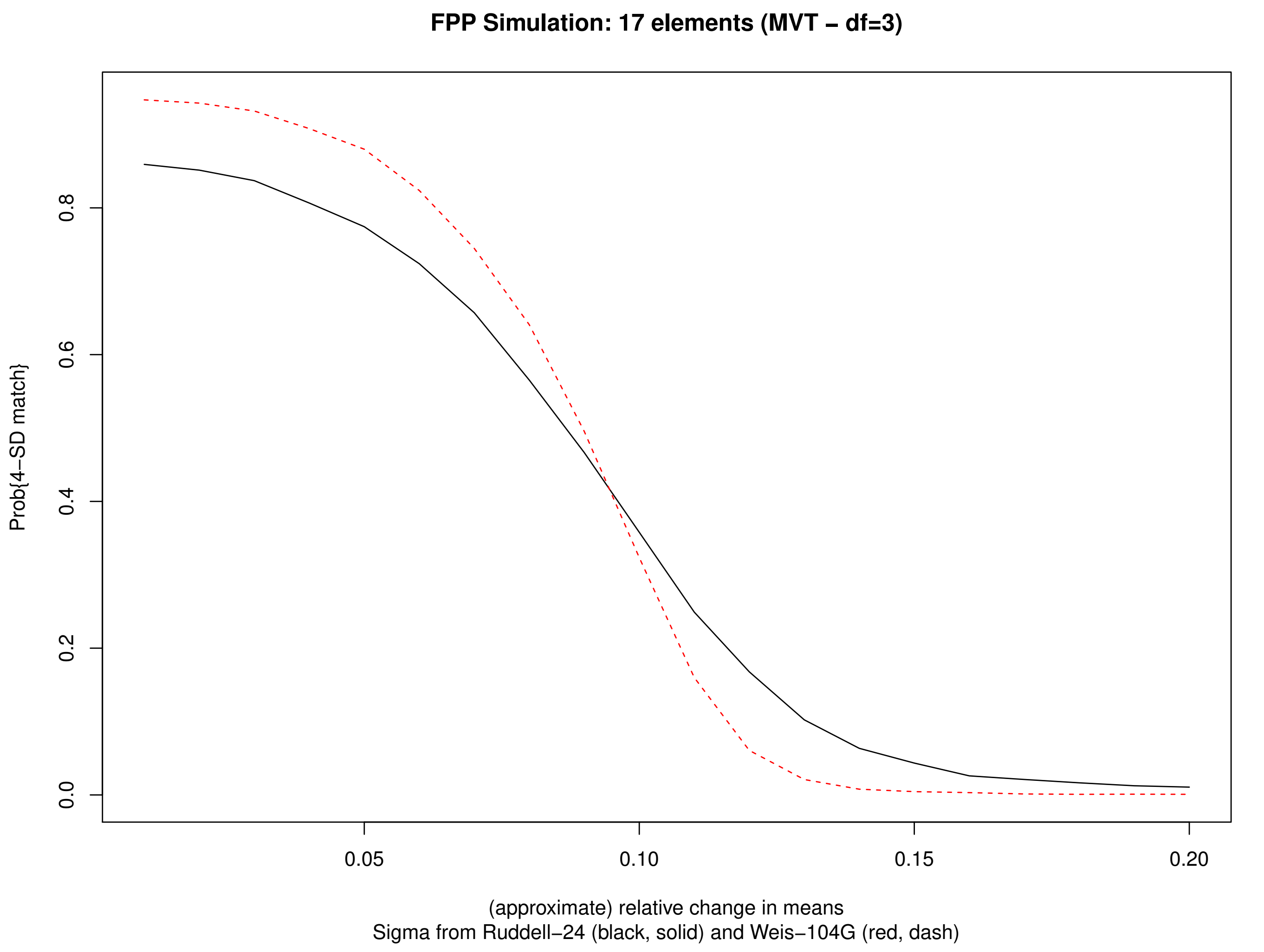
- Simulate samples: means 0, δ (for **each** element)
- Calculate probability of match in 6000 samples, many δs
- $\delta = 0.20, 1.1, 1.4 \Rightarrow$ *relative* mean change 0.2, 2, 3

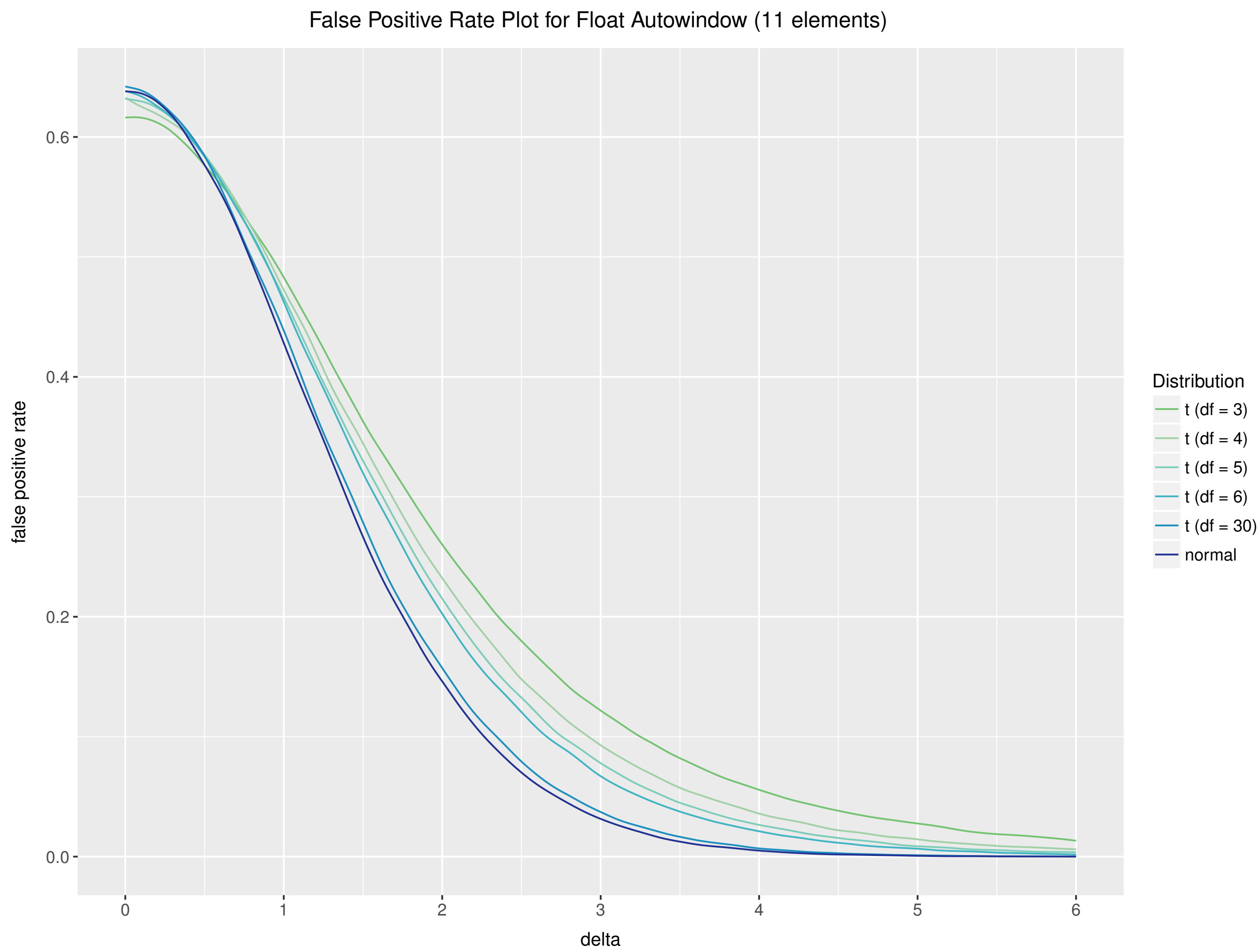

FPP Simulation: 17 elements (MV−lognormal)
Prob{4−SD match}
0.0
0.2
0.4
0.6
0.8
1.0
0.05
0.10
0.15
0.20
(approximate) relative change in means
Sigma from Ruddell−24 (black, solid) and Weis−104G (red, dash)


Distribution Density Plots
density
0.4
0.3
0.2
0.1
0.0
−5.0
−2.5
0.0
2.5
5.0
Distribution
t (df = 3)
t (df = 4)
t (df = 5)
t (df = 6)
t (df = 10)
t (df = 30)
normal

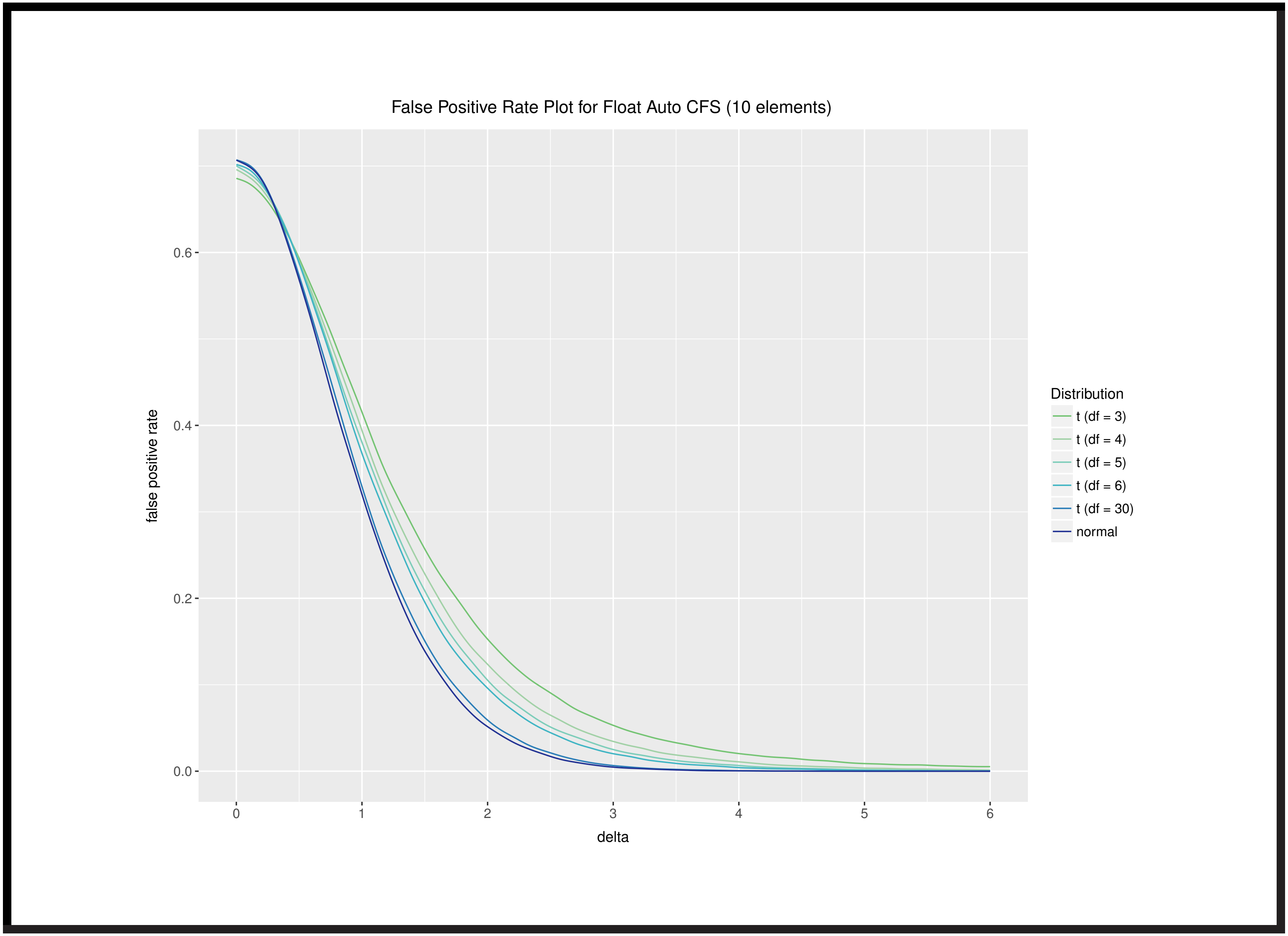

FPP Simulation: 17 elements (MVT – df=10)
Prob{4–SD match}
1.0
0.8
0.6
0.4
0.2
0.0
0.05
0.10
0.15
0.20
(approximate) relative change in means
Sigma from Ruddell–24 (black, solid) and Weis–104G (red, dash)


FPP Simulation: 17 elements (MVT – df=6)
Prob{4–SD match}
0.0
0.2
0.4
0.6
0.8
1.0
0.05
0.10
0.15
0.20
(approximate) relative change in means
Sigma from Ruddell–24 (black, solid) and Weis–104G (red, dash)

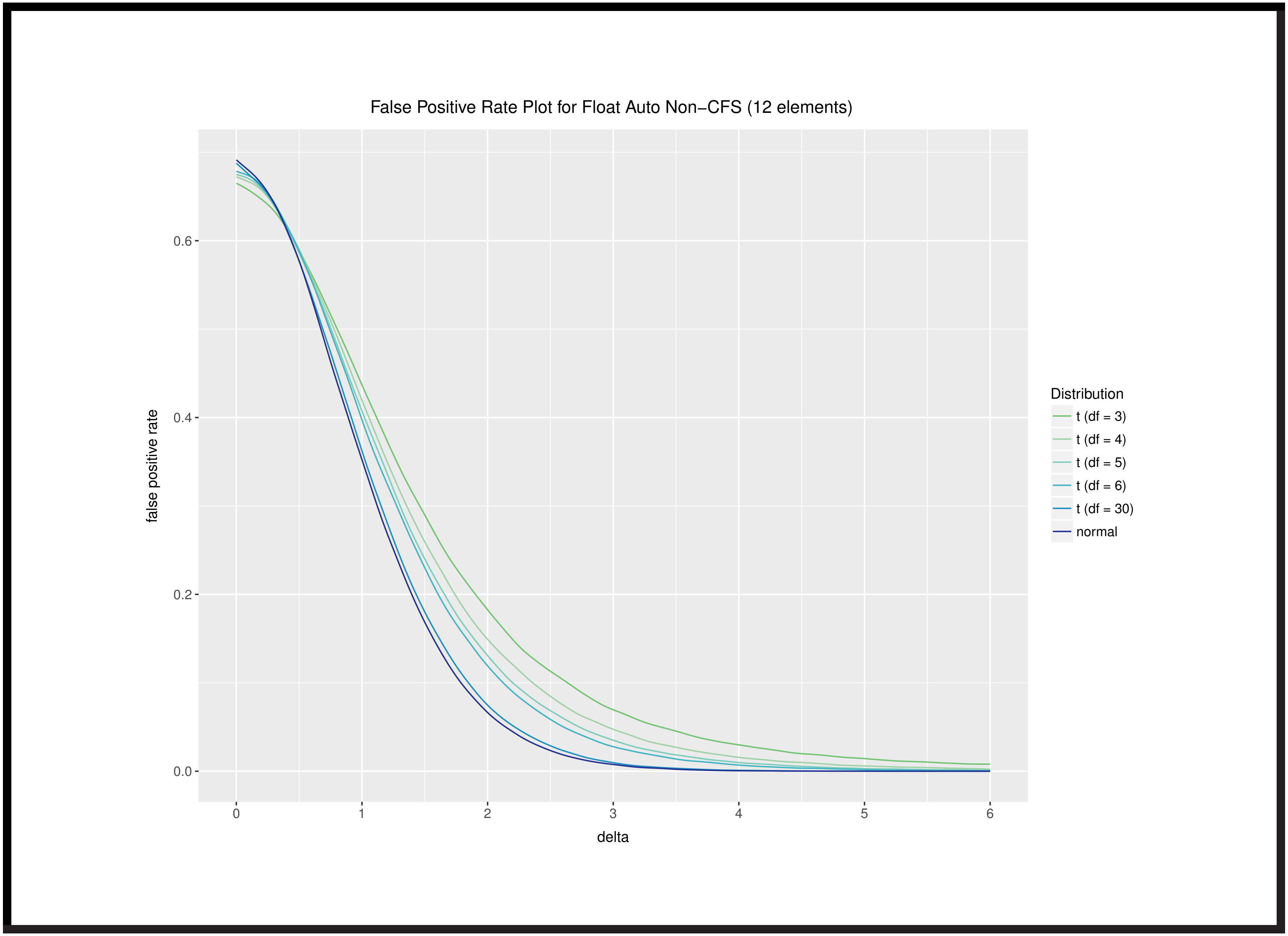

FPP Simulation: 17 elements (MVT − df=3)
Prob{4−SD match}
0.0
0.2
0.4
0.6
0.8
0.05
0.10
0.15
0.20
(approximate) relative change in means
Sigma from Ruddell−24 (black, solid) and Weis−104G (red, dash)

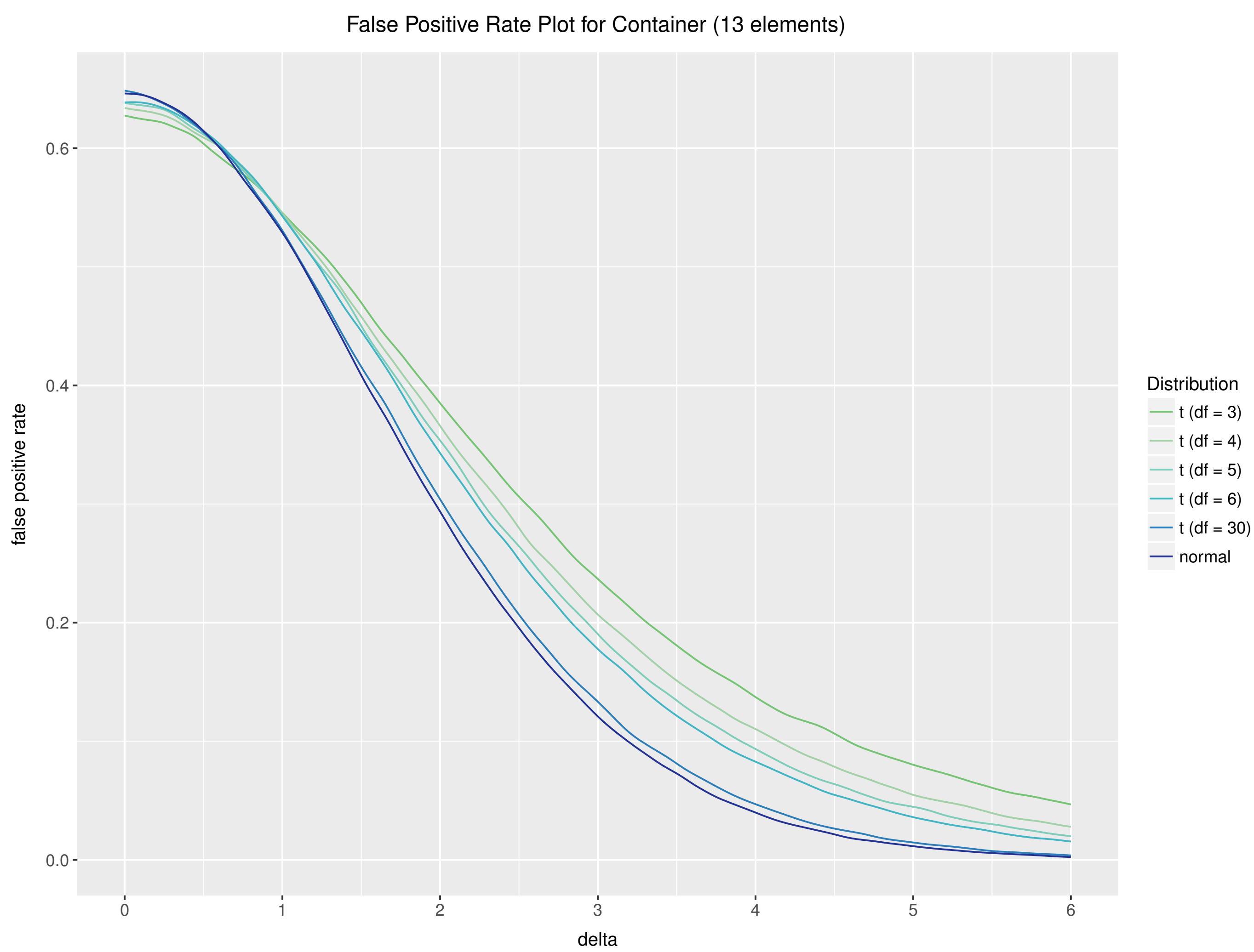


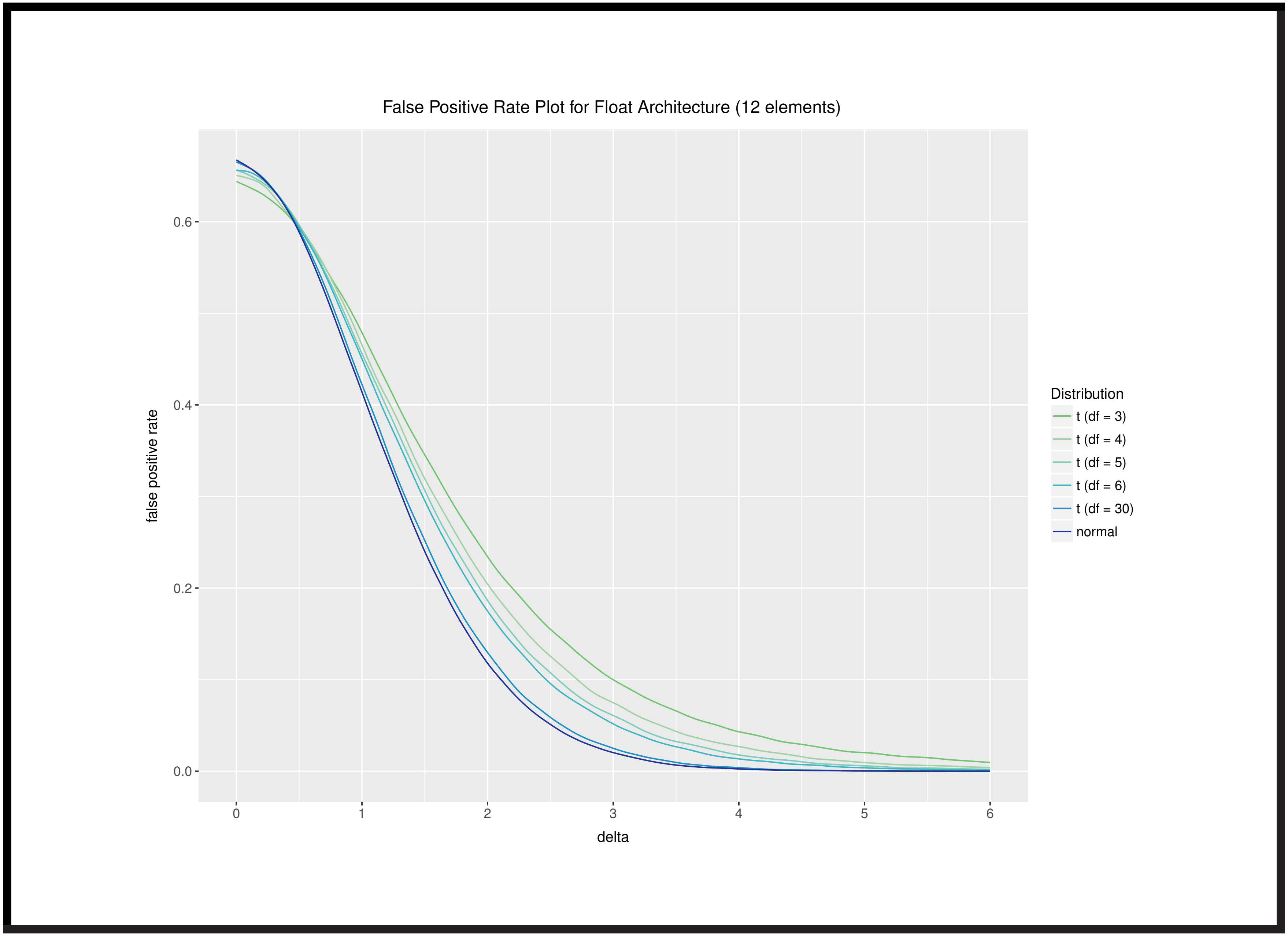
False Positive Rate Plot for Float Autowindow (11 elements)
false positive rate
0.0
0.2
0.4
0.6
0
1
2
3
4
5
6
delta
Distribution
t (df = 3)
t (df = 4)
t (df = 5)
t (df = 6)
t (df = 30)
normal



False Positive Rate Plot for Float Auto CFS (10 elements)
false positive rate
0.0
0.2
0.4
0.6
0
1
2
3
4
5
6
delta
Distribution
t (df = 3)
t (df = 4)
t (df = 5)
t (df = 6)
t (df = 30)
normal


False Positive Rate Plot for Float Auto Non−CFS (12 elements)
false positive rate
0.0
0.2
0.4
0.6
0
1
2
3
4
5
6
delta
Distribution
t (df = 3)
t (df = 4)
t (df = 5)
t (df = 6)
t (df = 30)
normal


False Positive Rate Plot for Container (13 elements)
false positive rate
0.0
0.2
0.4
0.6
delta
0
1
2
3
4
5
6
Distribution
t (df = 3)
t (df = 4)
t (df = 5)
t (df = 6)
t (df = 30)
normal

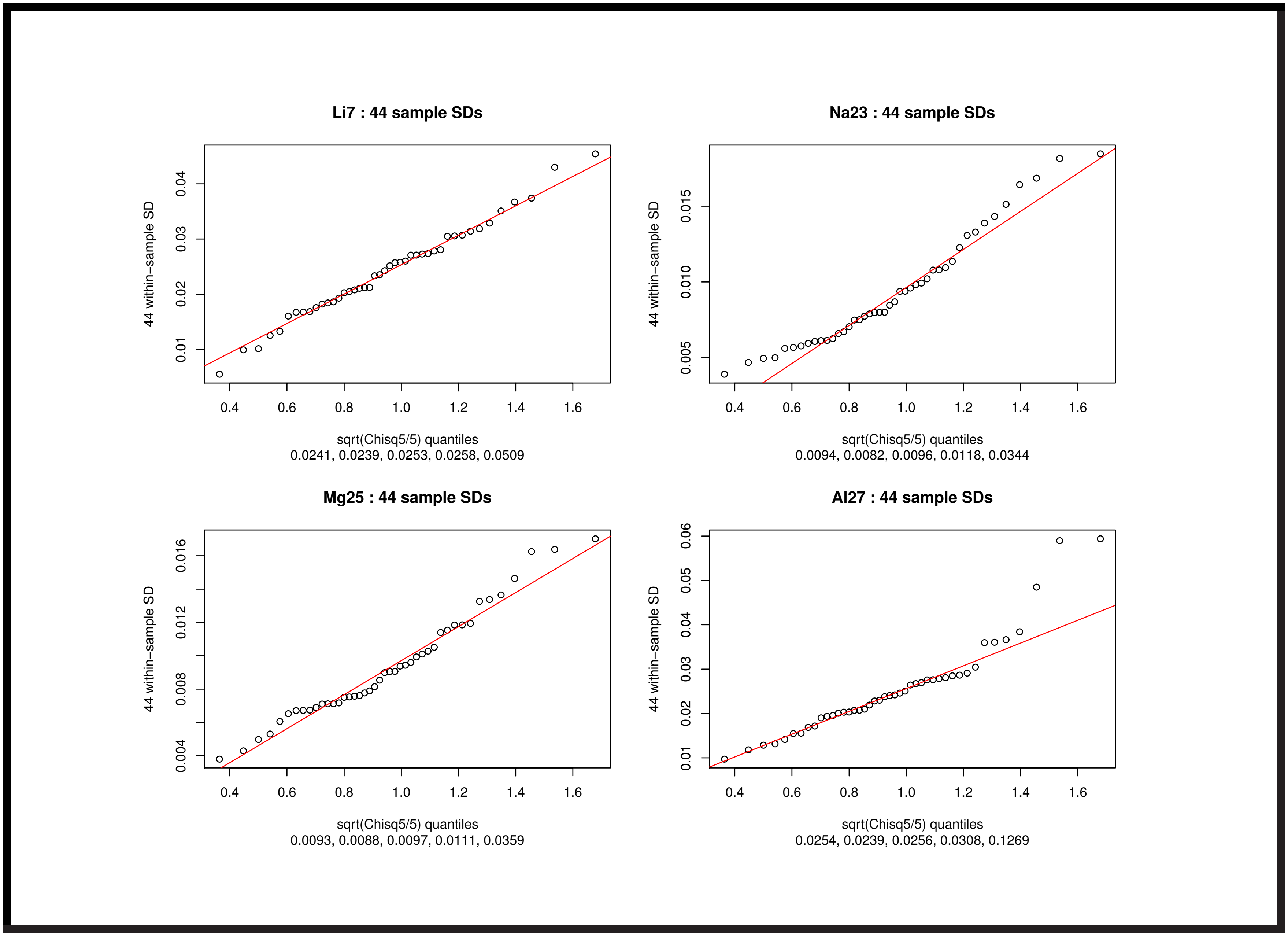


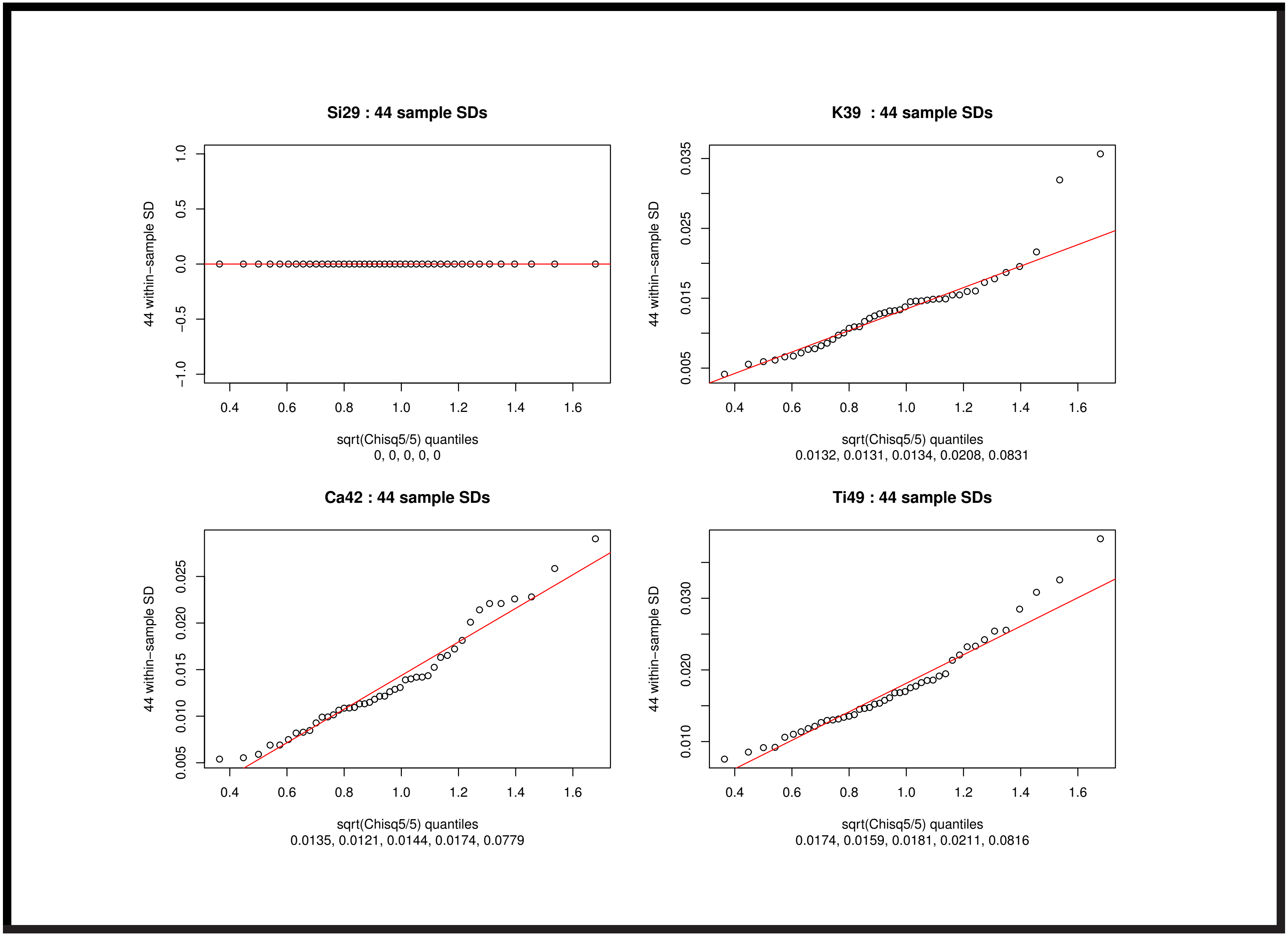
False Positive Rate Plot for Float Architecture (12 elements)
false positive rate
0.0
0.2
0.4
0.6
0
1
2
3
4
5
6
delta
Distribution
t (df = 3)
t (df = 4)
t (df = 5)
t (df = 6)
t (df = 30)
normal

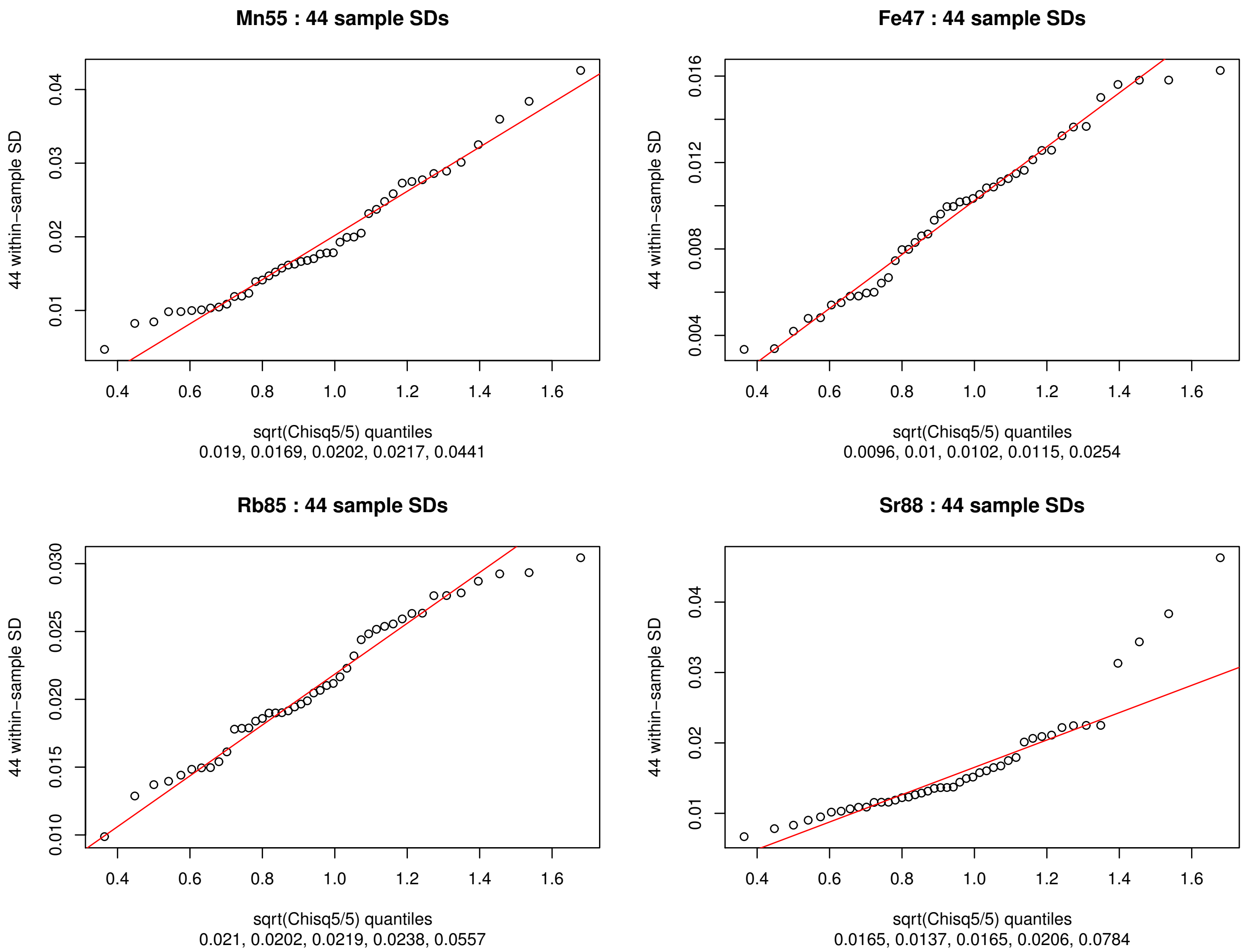
Explorations of Weis data

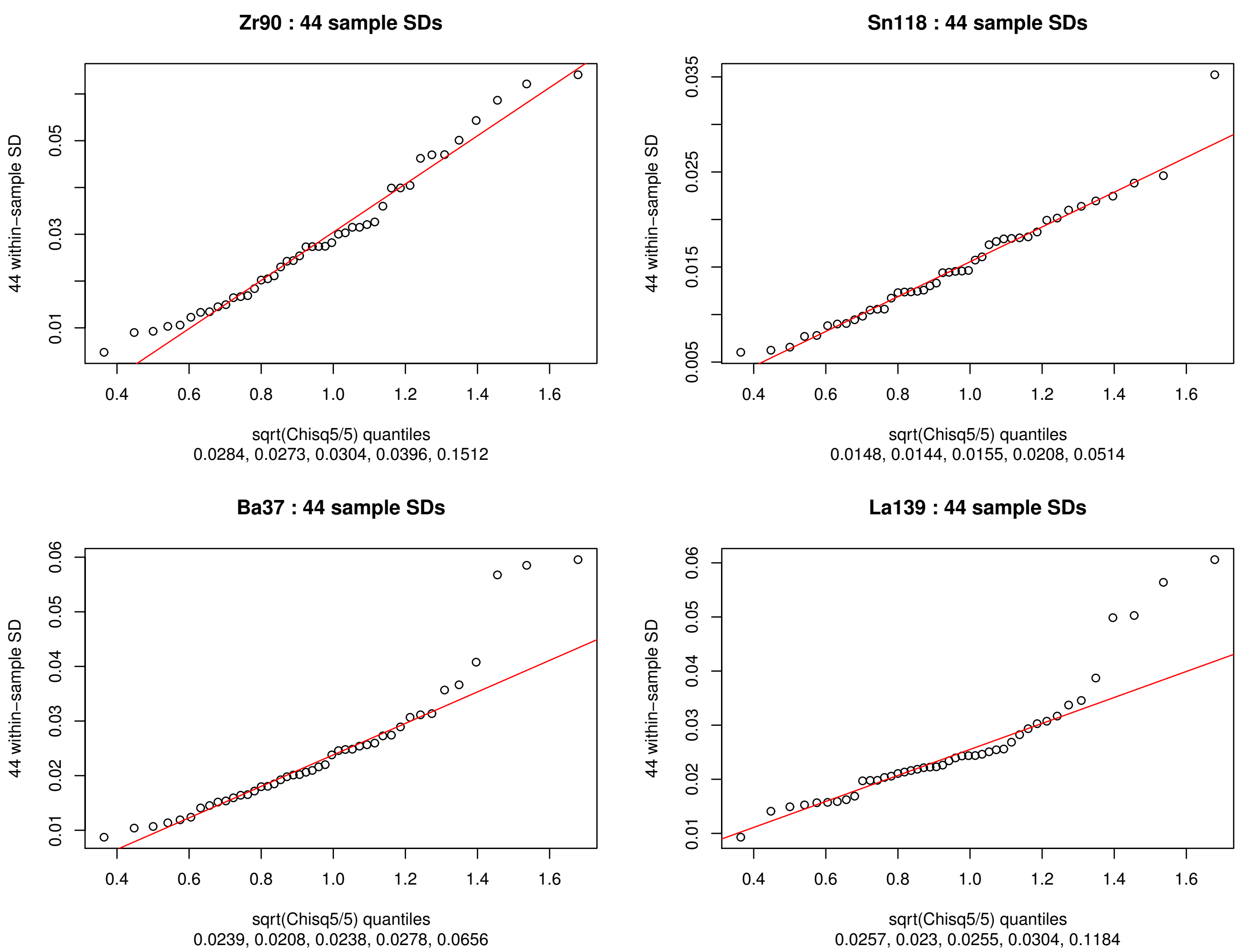
1. Are the measurement SDs of log(concentrations) $\sigma_e \sim \sqrt{\chi^2_5}$?
2. Sample #34: Between-Day σ^2_d / Within-Day σ^2_e?
3. Variance(33 fragments from same source) $= \sigma^2_s$
4. Variance(fragments from different sources) $= \sigma^2_f$
   $>> \sigma^2_s =$ Variance(fragments from same source)?
5. More consistency for samples w/i `GER, USA, JAP, OTH`?

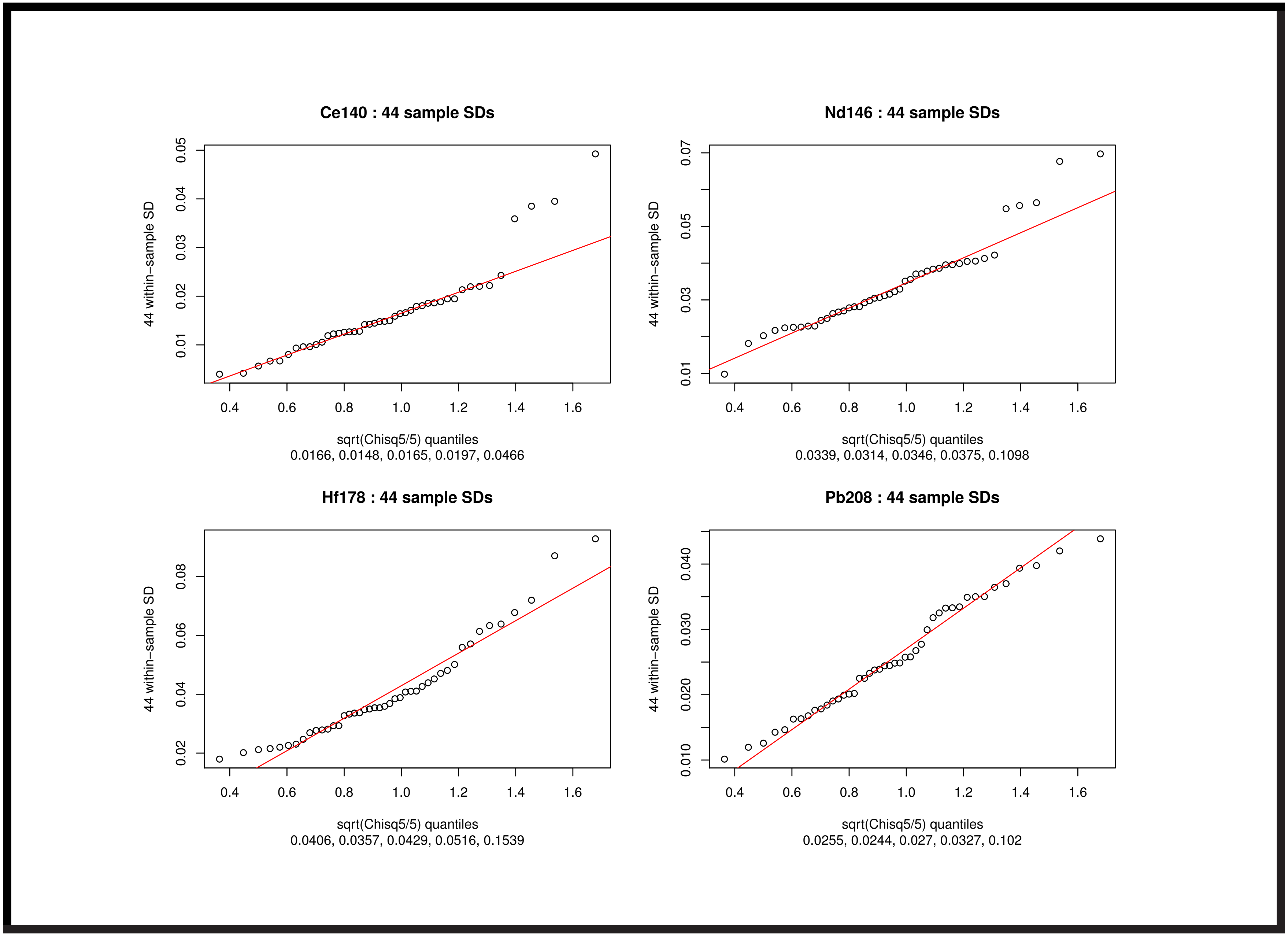
1. QQ plots: 44 SDs of "same" samples (for each element)
2. QQ plots: 62 SDs of "different" samples (each element)
3. Boxplots & one-way A/V estimates of σ_d and σ_e;
   $F =$ MS-betweenDays/MS-withinDays
4. QQ plots and estimates of σ_f for each element from 62 different samples
5. Using means (of 6), 62 samples in 4 countries:
   Boxplots & one-way A/V estimates of σ_c and σ_{ce}


Li7 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.0241, 0.0239, 0.0253, 0.0258, 0.0509
Na23 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.0094, 0.0082, 0.0096, 0.0118, 0.0344
Mg25 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.0093, 0.0088, 0.0097, 0.0111, 0.0359
Al27 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.0254, 0.0239, 0.0256, 0.0308, 0.1269


Si29 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0, 0, 0, 0, 0
K39 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.0132, 0.0131, 0.0134, 0.0208, 0.0831
Ca42 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.0135, 0.0121, 0.0144, 0.0174, 0.0779
Ti49 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.0174, 0.0159, 0.0181, 0.0211, 0.0816


Mn55 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.019, 0.0169, 0.0202, 0.0217, 0.0441
Fe47 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.0096, 0.01, 0.0102, 0.0115, 0.0254
Rb85 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.021, 0.0202, 0.0219, 0.0238, 0.0557
Sr88 : 44 sample SDs
44 within−sample SD
sqrt(Chisq5/5) quantiles
0.0165, 0.0137, 0.0165, 0.0206, 0.0784

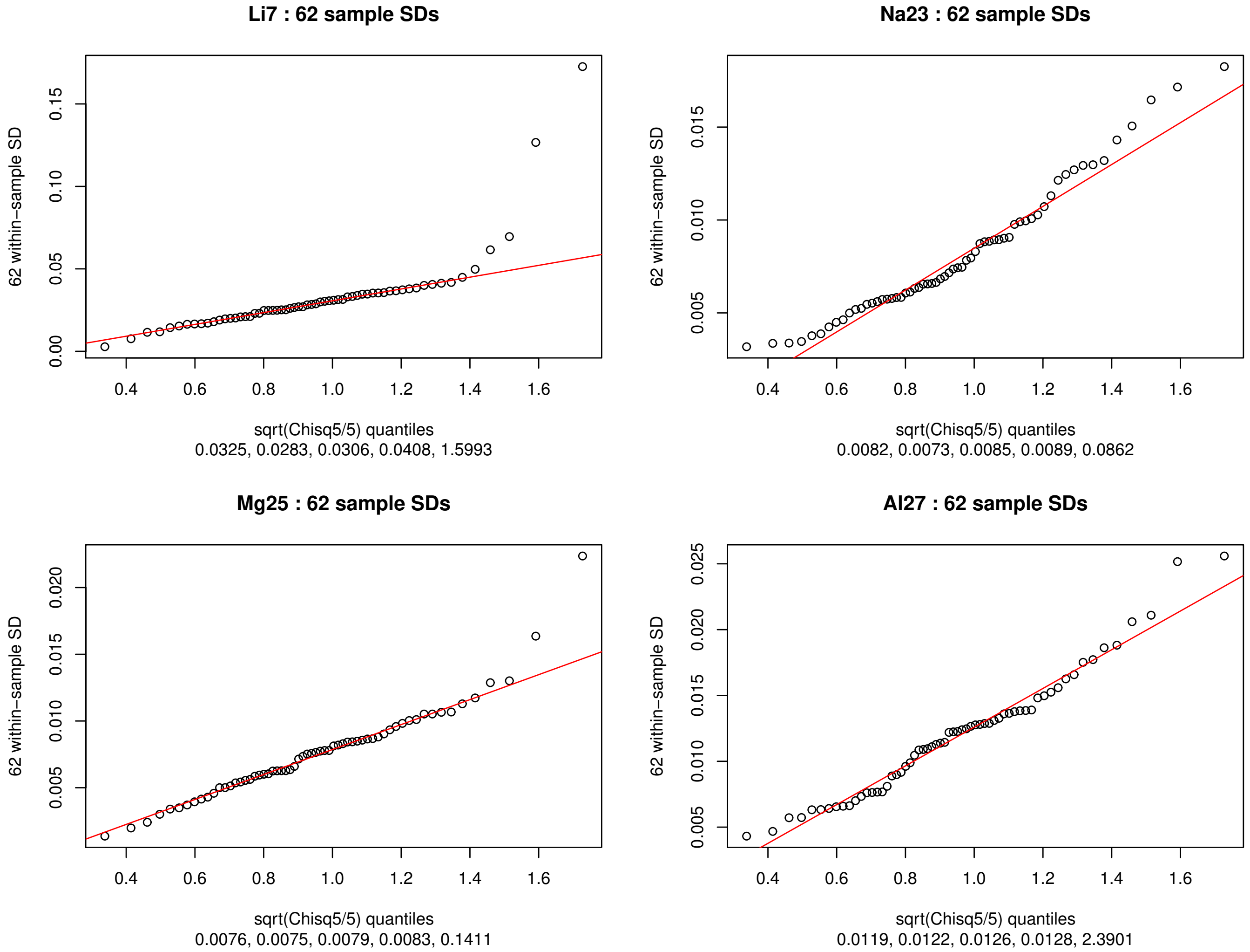

Zr90 : 44 sample SDs
44 within-sample SD
sqrt(Chisq5/5) quantiles
0.0284, 0.0273, 0.0304, 0.0396, 0.1512
Sn118 : 44 sample SDs
44 within-sample SD
sqrt(Chisq5/5) quantiles
0.0148, 0.0144, 0.0155, 0.0208, 0.0514
Ba37 : 44 sample SDs
44 within-sample SD
sqrt(Chisq5/5) quantiles
0.0239, 0.0208, 0.0238, 0.0278, 0.0656
La139 : 44 sample SDs
44 within-sample SD
sqrt(Chisq5/5) quantiles
0.0257, 0.023, 0.0255, 0.0304, 0.1184

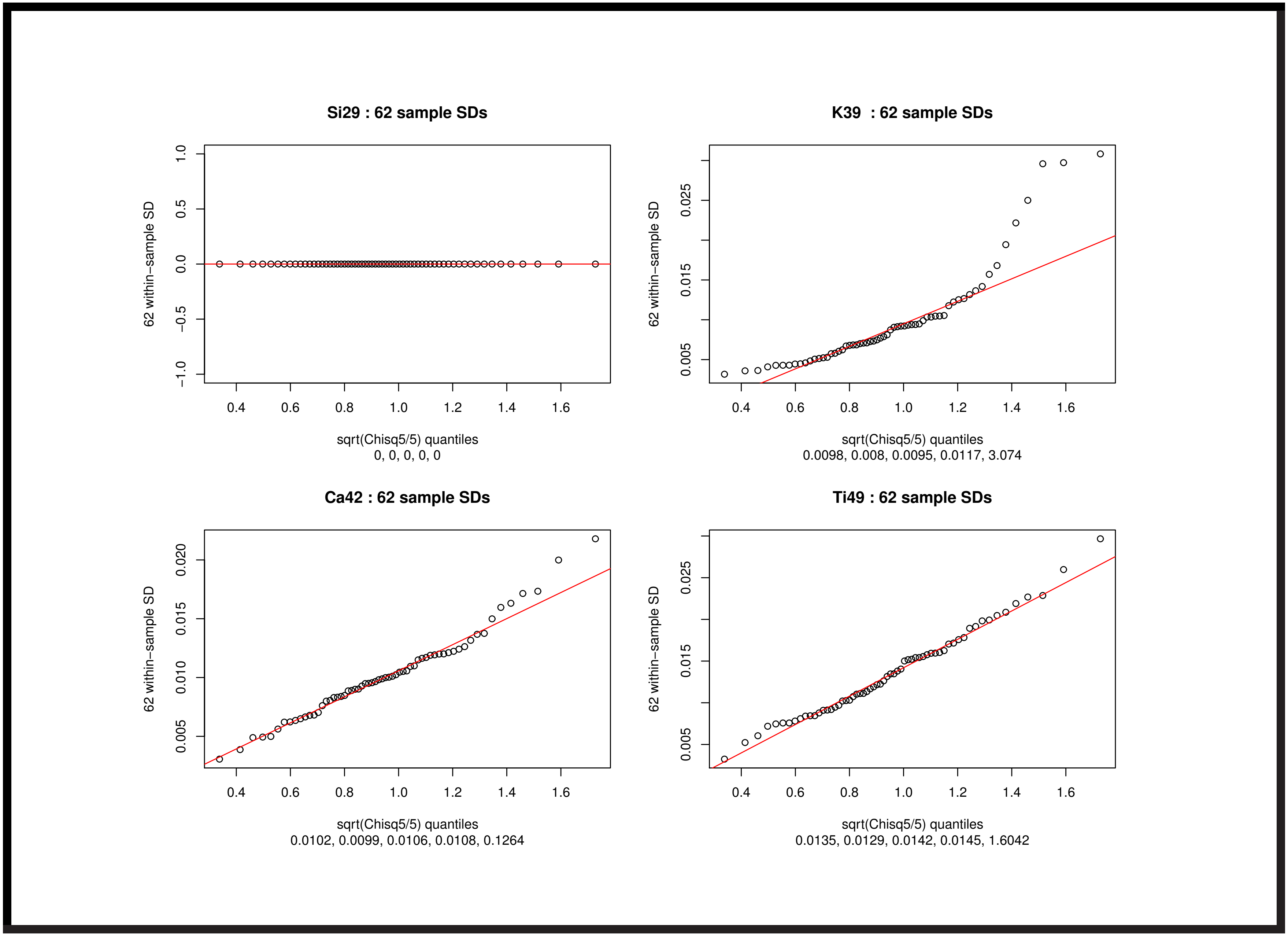

Ce140 : 44 sample SDs
44 within-sample SD
sqrt(Chisq5/5) quantiles
0.0166, 0.0148, 0.0165, 0.0197, 0.0466
Nd146 : 44 sample SDs
44 within-sample SD
sqrt(Chisq5/5) quantiles
0.0339, 0.0314, 0.0346, 0.0375, 0.1098
Hf178 : 44 sample SDs
44 within-sample SD
sqrt(Chisq5/5) quantiles
0.0406, 0.0357, 0.0429, 0.0516, 0.1539
Pb208 : 44 sample SDs
44 within-sample SD
sqrt(Chisq5/5) quantiles
0.0255, 0.0244, 0.027, 0.0327, 0.102

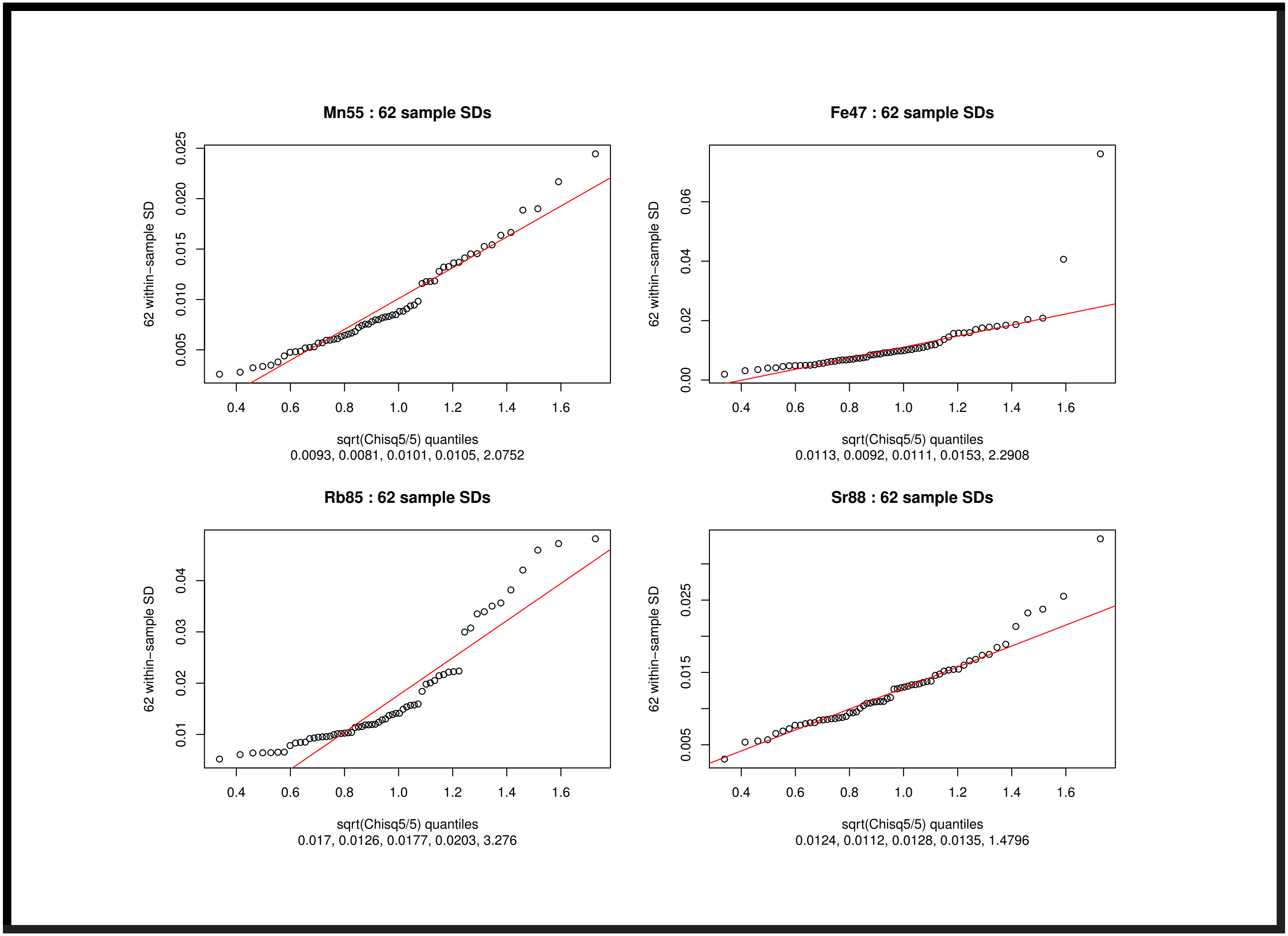
Ratio of Between-fragment SD to Within-fragment SD (1 or 2)
Row 1: Generous SD (AOV); Row 2: Average of 4 within-SDs

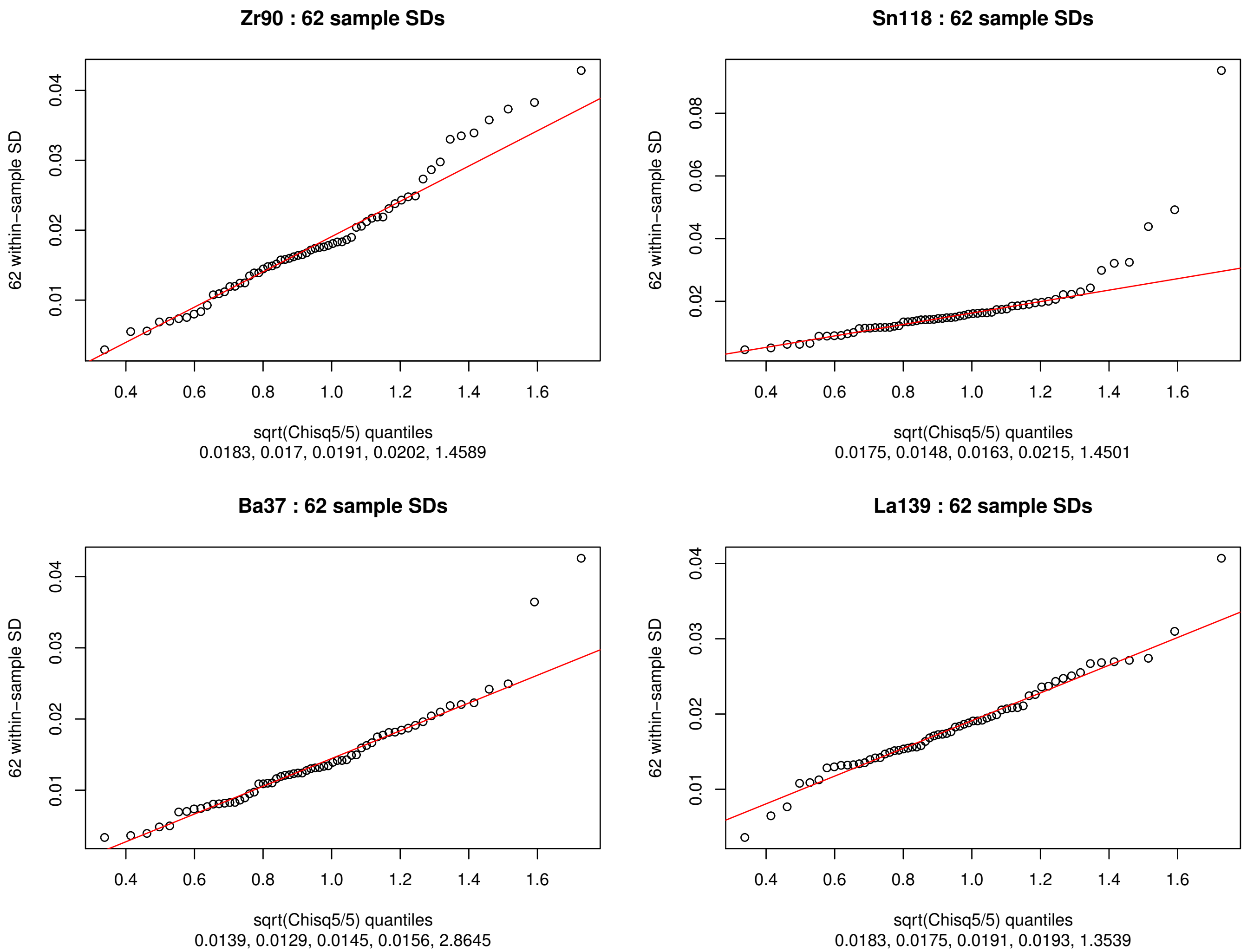
	Li7	Na23	Mg25	Al27	Si29	K39	Ca42	Ti49	Mn55	Fe47
1	1.97	2.92	3.22	4.12	---	4.00	4.47	3.86	2.03	2.21
2	2.05	3.52	3.69	4.80	---	5.50	5.42	4.50	2.27	2.46

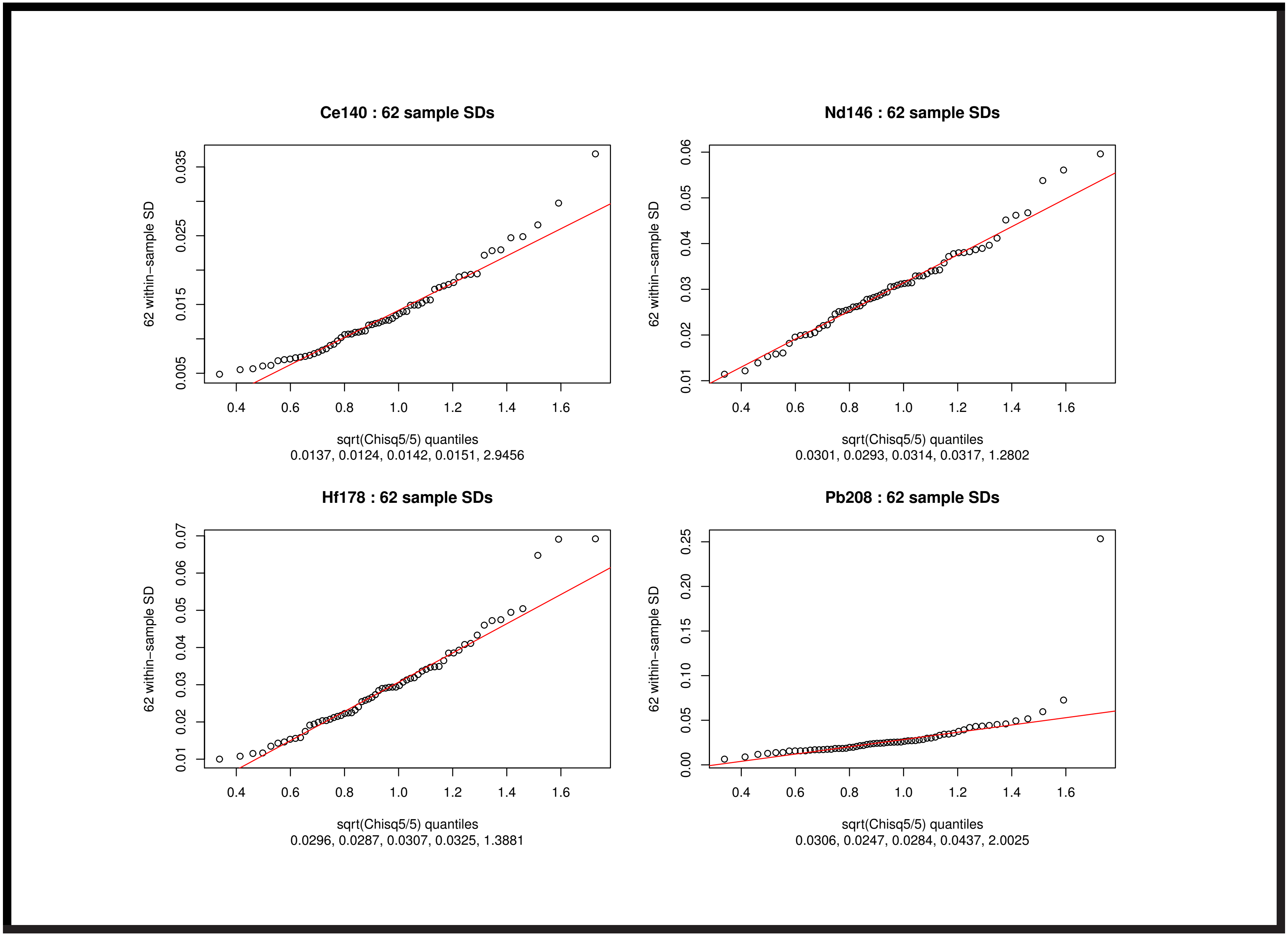
	Rb85	Sr88	Zr90	Sn118	Ba37	La139	Ce140	Nd146	Hf178	Pb208
1	2.34	3.80	3.82	2.47	2.36	3.90	2.37	2.93	2.98	3.12
2	2.57	4.66	4.81	3.13	2.73	4.53	2.76	3.20	3.60	3.72


Li7 : 62 sample SDs
62 within−sample SD
sqrt(Chisq5/5) quantiles
0.0325, 0.0283, 0.0306, 0.0408, 1.5993
Na23 : 62 sample SDs
62 within−sample SD
sqrt(Chisq5/5) quantiles
0.0082, 0.0073, 0.0085, 0.0089, 0.0862
Mg25 : 62 sample SDs
62 within−sample SD
sqrt(Chisq5/5) quantiles
0.0076, 0.0075, 0.0079, 0.0083, 0.1411
Al27 : 62 sample SDs
62 within−sample SD
sqrt(Chisq5/5) quantiles
0.0119, 0.0122, 0.0126, 0.0128, 2.3901

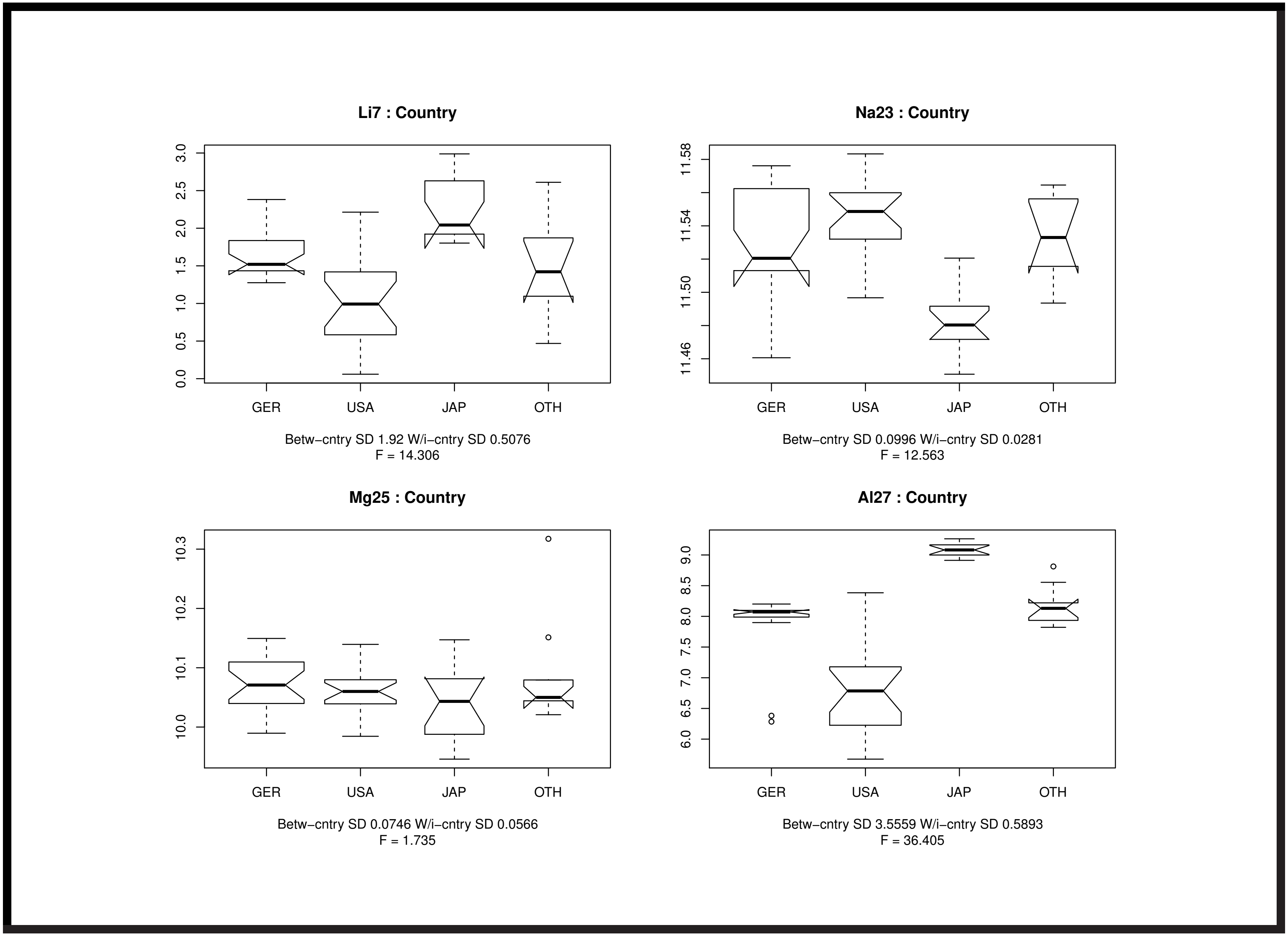

Si29 : 62 sample SDs
62 within−sample SD
sqrt(Chisq5/5) quantiles
0, 0, 0, 0, 0
K39 : 62 sample SDs
62 within−sample SD
sqrt(Chisq5/5) quantiles
0.0098, 0.008, 0.0095, 0.0117, 3.074
Ca42 : 62 sample SDs
62 within−sample SD
sqrt(Chisq5/5) quantiles
0.0102, 0.0099, 0.0106, 0.0108, 0.1264
Ti49 : 62 sample SDs
62 within−sample SD
sqrt(Chisq5/5) quantiles
0.0135, 0.0129, 0.0142, 0.0145, 1.6042

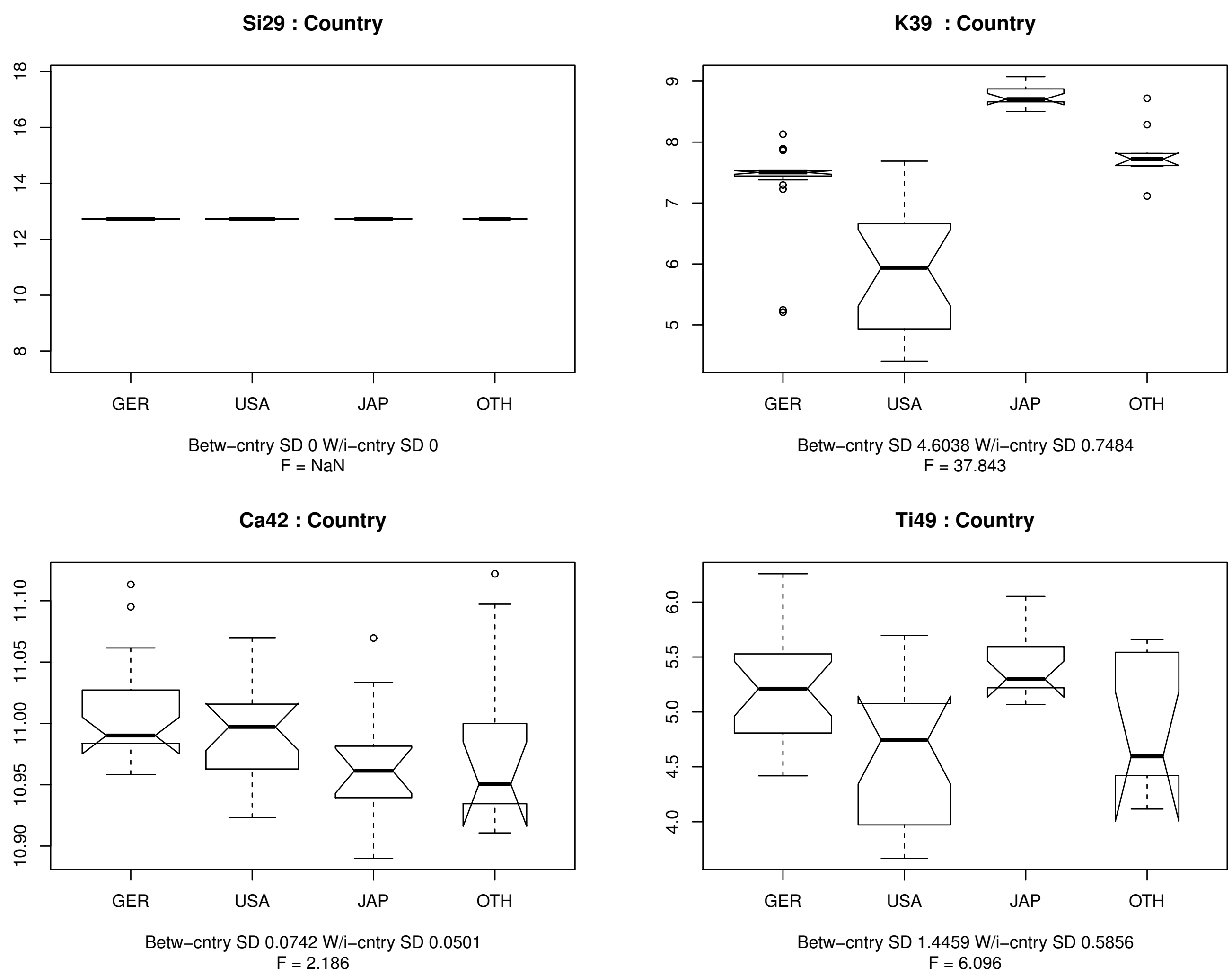

Mn55 : 62 sample SDs
62 within−sample SD
0.005
0.010
0.015
0.020
0.025
0.4
0.6
0.8
1.0
1.2
1.4
1.6
sqrt(Chisq5/5) quantiles
0.0093, 0.0081, 0.0101, 0.0105, 2.0752
Fe47 : 62 sample SDs
62 within−sample SD
0.00
0.02
0.04
0.06
sqrt(Chisq5/5) quantiles
0.0113, 0.0092, 0.0111, 0.0153, 2.2908
Rb85 : 62 sample SDs
62 within−sample SD
0.01
0.02
0.03
0.04
sqrt(Chisq5/5) quantiles
0.017, 0.0126, 0.0177, 0.0203, 3.276
Sr88 : 62 sample SDs
62 within−sample SD
0.005
0.015
0.025
sqrt(Chisq5/5) quantiles
0.0124, 0.0112, 0.0128, 0.0135, 1.4796

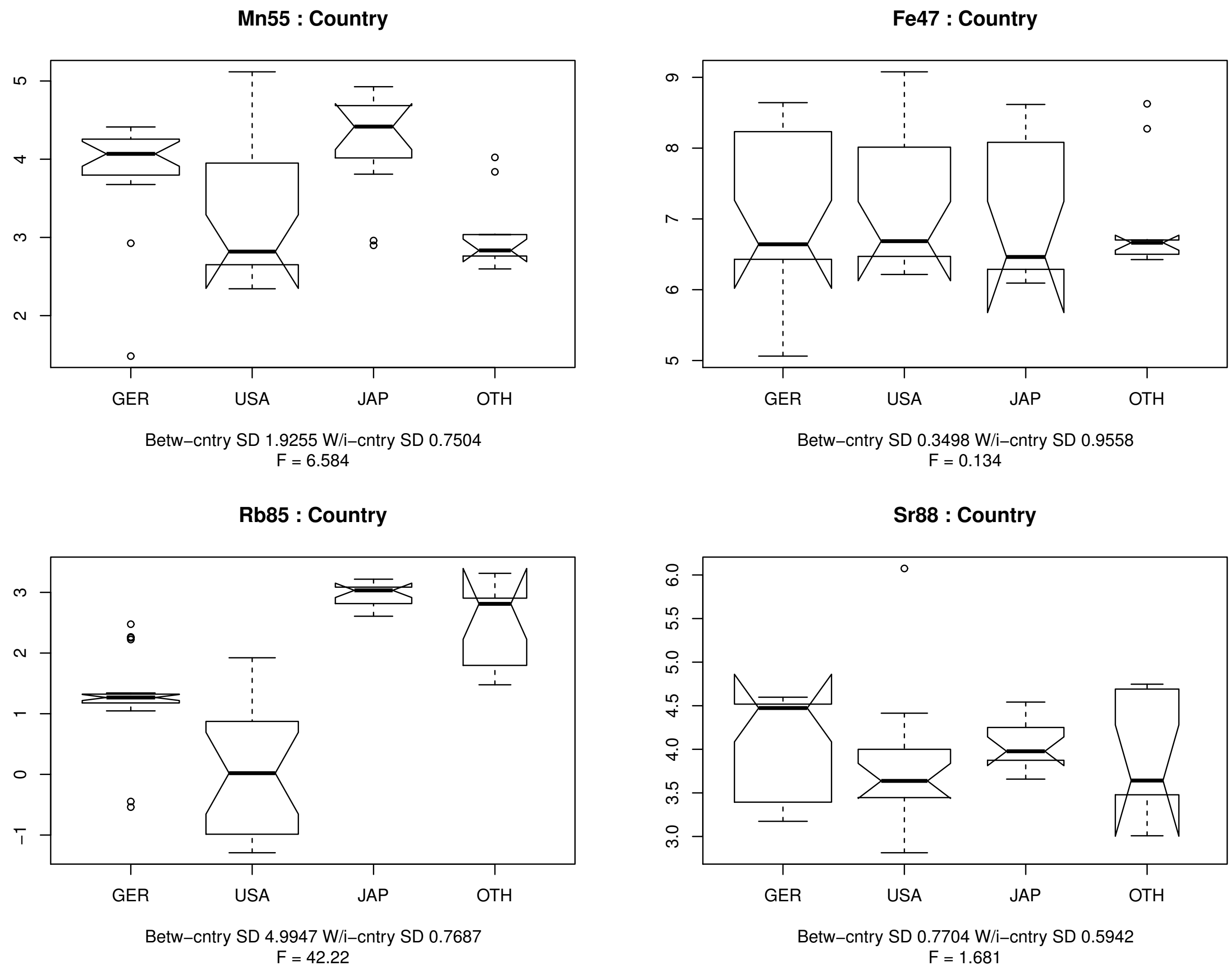

Zr90 : 62 sample SDs
62 within−sample SD
0.01 0.02 0.03 0.04
0.4 0.6 0.8 1.0 1.2 1.4 1.6
sqrt(Chisq5/5) quantiles
0.0183, 0.017, 0.0191, 0.0202, 1.4589
Sn118 : 62 sample SDs
62 within−sample SD
0.02 0.04 0.06 0.08
0.4 0.6 0.8 1.0 1.2 1.4 1.6
sqrt(Chisq5/5) quantiles
0.0175, 0.0148, 0.0163, 0.0215, 1.4501
Ba37 : 62 sample SDs
62 within−sample SD
0.01 0.02 0.03 0.04
0.4 0.6 0.8 1.0 1.2 1.4 1.6
sqrt(Chisq5/5) quantiles
0.0139, 0.0129, 0.0145, 0.0156, 2.8645
La139 : 62 sample SDs
62 within−sample SD
0.01 0.02 0.03 0.04
0.4 0.6 0.8 1.0 1.2 1.4 1.6
sqrt(Chisq5/5) quantiles
0.0183, 0.0175, 0.0191, 0.0193, 1.3539

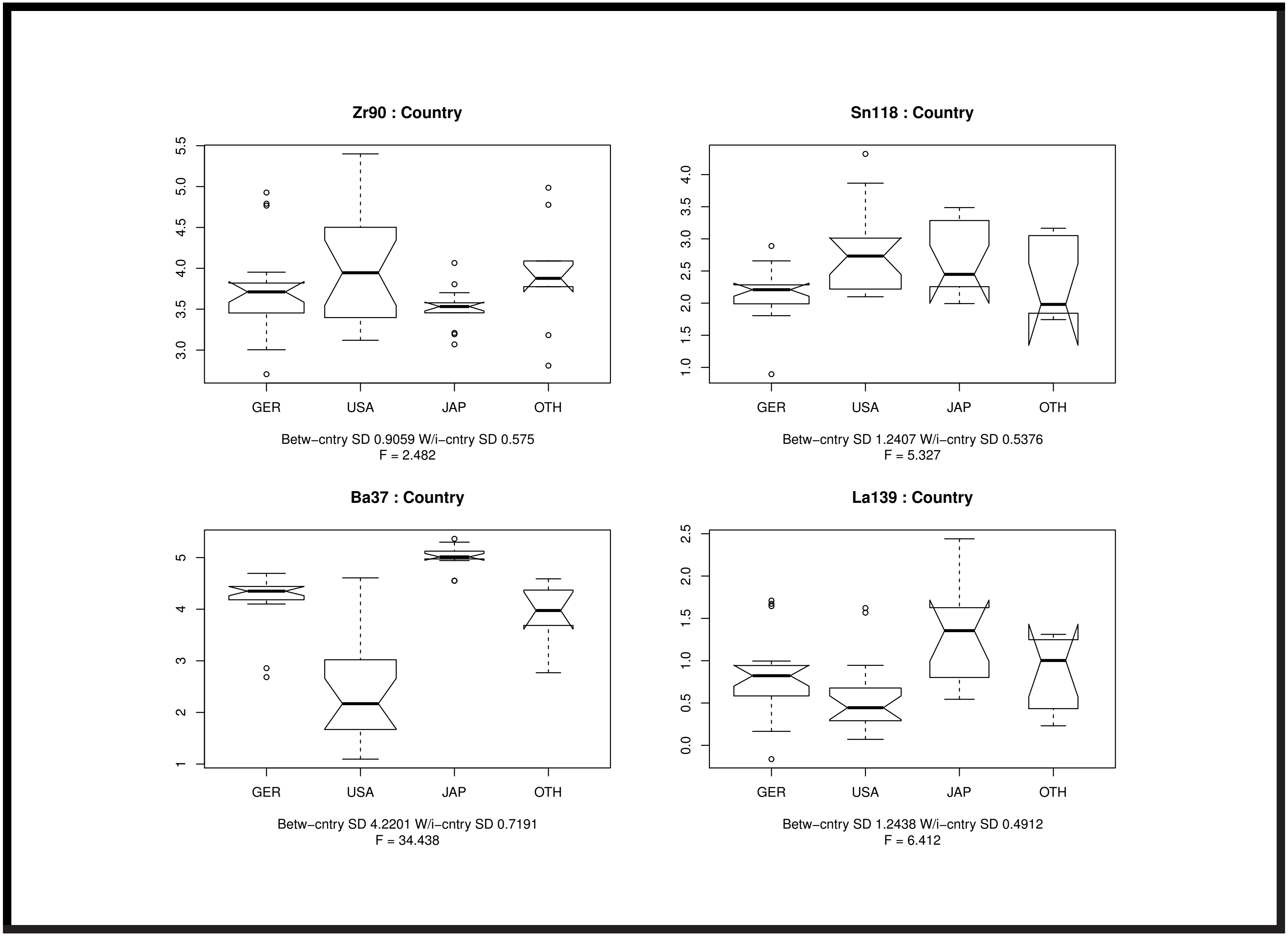

Ce140 : 62 sample SDs
62 within-sample SD
sqrt(Chisq5/5) quantiles
0.0137, 0.0124, 0.0142, 0.0151, 2.9456
Nd146 : 62 sample SDs
62 within-sample SD
sqrt(Chisq5/5) quantiles
0.0301, 0.0293, 0.0314, 0.0317, 1.2802
Hf178 : 62 sample SDs
62 within-sample SD
sqrt(Chisq5/5) quantiles
0.0296, 0.0287, 0.0307, 0.0325, 1.3881
Pb208 : 62 sample SDs
62 within-sample SD
sqrt(Chisq5/5) quantiles
0.0306, 0.0247, 0.0284, 0.0437, 2.0025

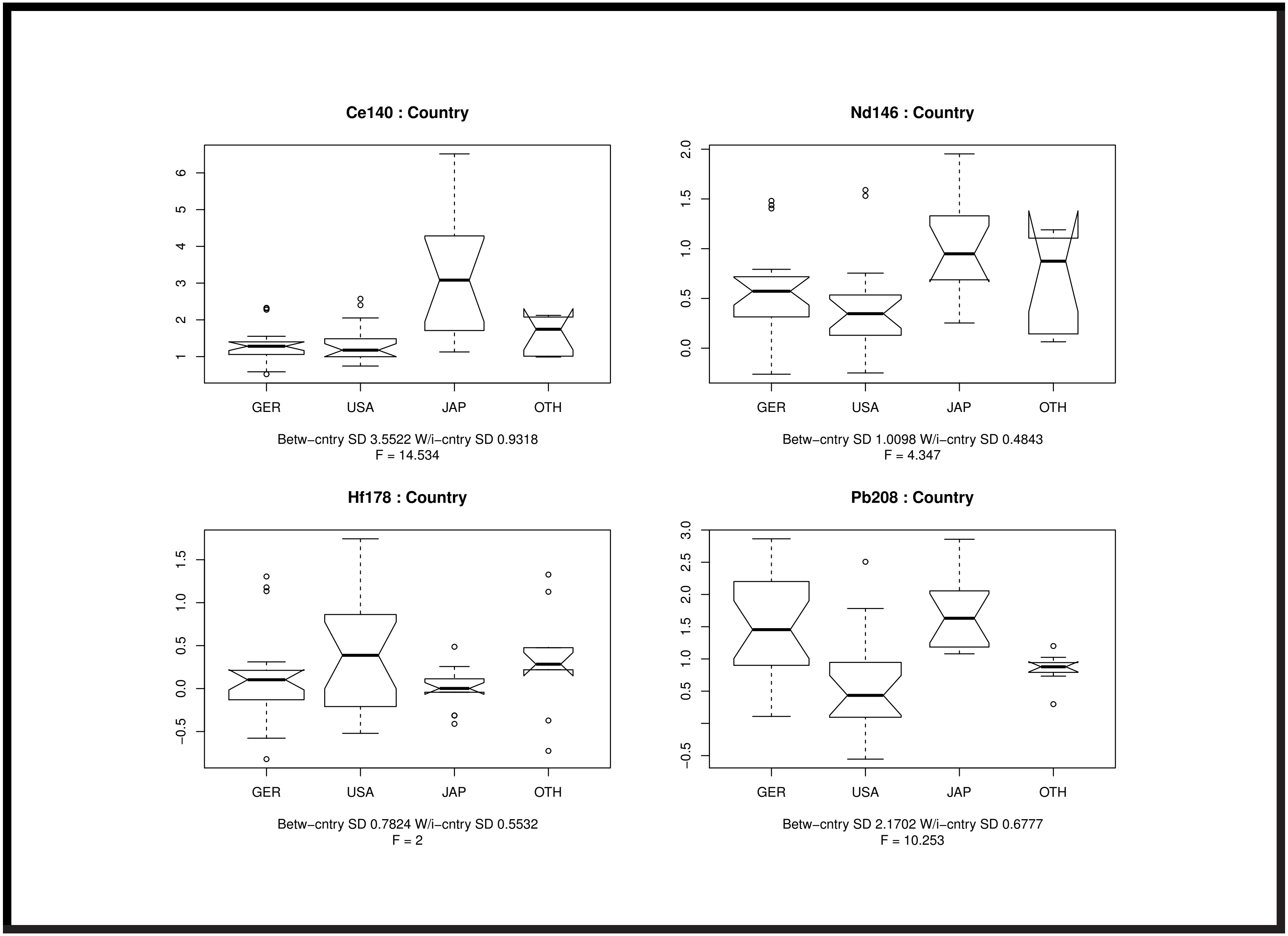
	Betw-DaySD	W/i-DaySD	F
Li7	3.18	2.05	2.41
Mg25	2.71	0.86	10.06
Al27	7.18	2.20	10.62
K39	7.30	1.64	19.79
Ca42	4.76	1.08	19.48
Ti49	5.15	1.64	9.83
Mn55	3.52	2.14	2.70
Fe47	2.78	1.10	6.41
Rb85	5.26	2.13	6.11
Sr88	4.88	1.23	15.71
Zr90	11.53	3.21	12.90
Ba37	4.69	2.40	3.81
La139	6.41	2.14	8.98
Ce140	3.11	1.55	4.06
Hf178	13.60	3.98	11.65
Pb208	9.30	2.19	17.94


Li7 : Country
0.0
0.5
1.0
1.5
2.0
2.5
3.0
GER
USA
JAP
OTH
Betw−cntry SD 1.92 W/i−cntry SD 0.5076
F = 14.306
Na23 : Country
11.46
11.50
11.54
11.58
GER
USA
JAP
OTH
Betw−cntry SD 0.0996 W/i−cntry SD 0.0281
F = 12.563
Mg25 : Country
10.0
10.1
10.2
10.3
GER
USA
JAP
OTH
Betw−cntry SD 0.0746 W/i−cntry SD 0.0566
F = 1.735
Al27 : Country
6.0
6.5
7.0
7.5
8.0
8.5
9.0
GER
USA
JAP
OTH
Betw−cntry SD 3.5559 W/i−cntry SD 0.5893
F = 36.405


Si29 : Country
GER
USA
JAP
OTH
Betw−cntry SD 0 W/i−cntry SD 0
F = NaN
K39 : Country
GER
USA
JAP
OTH
Betw−cntry SD 4.6038 W/i−cntry SD 0.7484
F = 37.843
Ca42 : Country
GER
USA
JAP
OTH
Betw−cntry SD 0.0742 W/i−cntry SD 0.0501
F = 2.186
Ti49 : Country
GER
USA
JAP
OTH
Betw−cntry SD 1.4459 W/i−cntry SD 0.5856
F = 6.096


Mn55 : Country
5
4
3
2
GER
USA
JAP
OTH
Betw−cntry SD 1.9255 W/i−cntry SD 0.7504
F = 6.584
Fe47 : Country
9
8
7
6
5
GER
USA
JAP
OTH
Betw−cntry SD 0.3498 W/i−cntry SD 0.9558
F = 0.134
Rb85 : Country
3
2
1
0
−1
GER
USA
JAP
OTH
Betw−cntry SD 4.9947 W/i−cntry SD 0.7687
F = 42.22
Sr88 : Country
6.0
5.5
5.0
4.5
4.0
3.5
3.0
GER
USA
JAP
OTH
Betw−cntry SD 0.7704 W/i−cntry SD 0.5942
F = 1.681


Zr90 : Country
GER
USA
JAP
OTH
Betw−cntry SD 0.9059 W/i−cntry SD 0.575
F = 2.482
Sn118 : Country
GER
USA
JAP
OTH
Betw−cntry SD 1.2407 W/i−cntry SD 0.5376
F = 5.327
Ba37 : Country
GER
USA
JAP
OTH
Betw−cntry SD 4.2201 W/i−cntry SD 0.7191
F = 34.438
La139 : Country
GER
USA
JAP
OTH
Betw−cntry SD 1.2438 W/i−cntry SD 0.4912
F = 6.412


Ce140 : Country
1
2
3
4
5
6
GER
USA
JAP
OTH
Betw−cntry SD 3.5522 W/i−cntry SD 0.9318
F = 14.534
Nd146 : Country
0.0
0.5
1.0
1.5
2.0
GER
USA
JAP
OTH
Betw−cntry SD 1.0098 W/i−cntry SD 0.4843
F = 4.347
Hf178 : Country
−0.5
0.0
0.5
1.0
1.5
GER
USA
JAP
OTH
Betw−cntry SD 0.7824 W/i−cntry SD 0.5532
F = 2
Pb208 : Country
−0.5
0.5
1.0
1.5
2.0
2.5
3.0
GER
USA
JAP
OTH
Betw−cntry SD 2.1702 W/i−cntry SD 0.6777
F = 10.253

	Betw-cntrySD	W/i-cntrySD	F
Li7	192.00	50.76	14.31
Mg25	7.46	5.66	1.74
Al27	355.58	58.93	36.40
K39	460.38	74.84	37.84
Ca42	7.42	5.02	2.19
Ti49	144.59	58.56	6.10
Mn55	192.55	75.04	6.58
Fe47	34.98	95.58	0.13
Rb85	499.47	76.87	42.22
Sr88	77.04	59.42	1.68
Zr90	90.59	57.50	2.48
Ba37	422.01	71.91	34.43
La139	124.38	49.12	6.41
Ce140	355.22	93.18	14.53
Hf178	78.24	55.32	2.00
Pb208	217.02	67.77	10.25

FLACH:	Betw-fragSD	W/i-fragSD	F (12 samples)
Li7	4.79	3.02	2.51
Mg25	3.38	1.10	9.42
Al27	12.55	3.37	13.89
K39	8.99	1.25	51.74
Ca42	6.13	1.56	15.37
Ti49	7.20	2.00	12.94
Mn55	4.51	2.28	3.92
Fe47	2.73	1.06	6.67
Rb85	6.03	2.09	8.33
Sr88	6.58	2.21	8.85
Zr90	10.44	3.52	8.82
Ba37	5.80	2.99	3.76
La139	9.26	3.20	8.37
Ce140	3.78	2.13	3.16
Nd146	8.70	4.17	4.36
Hf178	13.27	4.45	8.89

Conclusions & Further work

- False positive rates likely much higher than "less than 0.1%"
- variation across fragments (same pane)
- day-to-day variation
- between-country variation >> within-country variation
- other variables to be considered: manufacturer, time, ... ?
- Modeling log(concentrations) as Gaussian or t may suggest other "match" intervals
- Concern over use of term "distinguishable":
  "not distinguishable" could imply "same source"

References

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