Treatment of Data

Methods of determining analytical error

-Counting statistics
-Reproducibility of reference materials
-Homogeneity of sample

Detection Limits

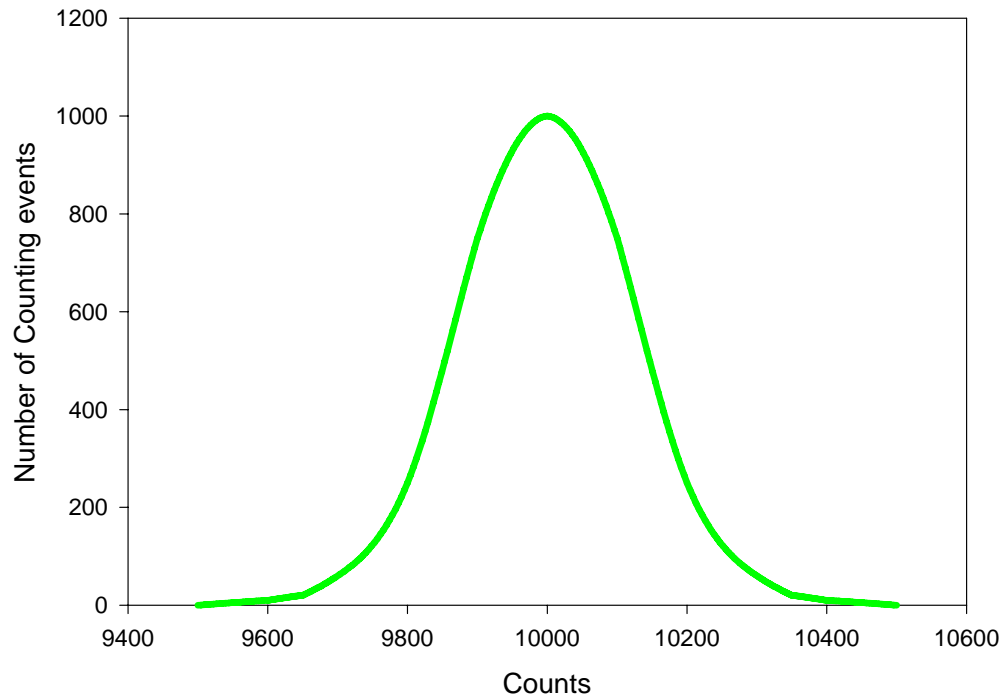## Assessment of analytical quality

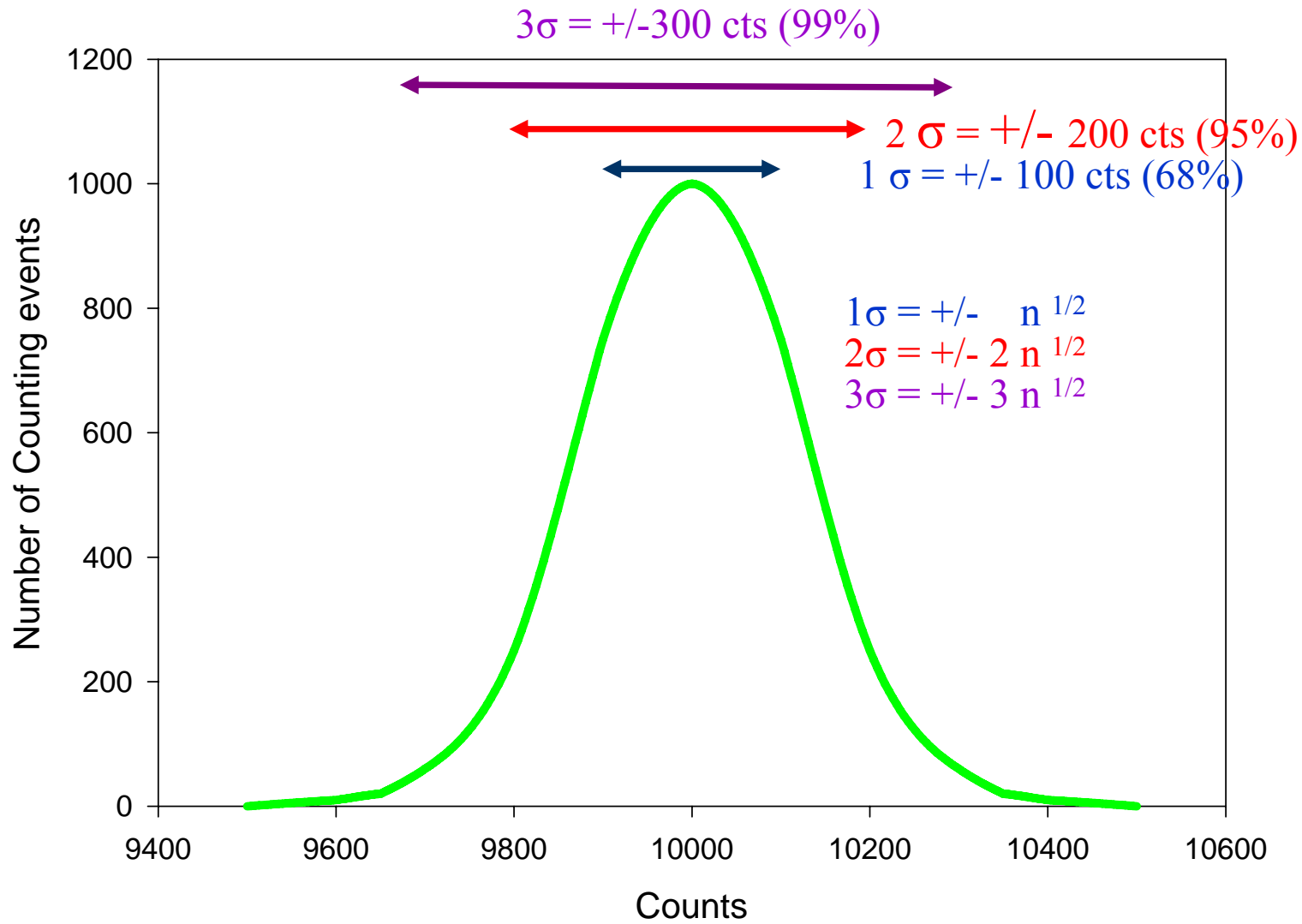-Analytical Totals
-Na loss
-Mineral Stoichiometry

Presentation of Results

Counting Statistics

X-ray intensities are measured by counting pulses generated in the detector by X-ray photons emitted from the sample.

For a mean number of counts = n, a large data set of individual measurements will form a Gaussian distribution with a standard deviation of 1 sigma of $n^{1/2}$.

$3\sigma = +/-300$ cts (99%)

$2\sigma = +/- 200$ cts (95%)

$1\sigma = +/- 100$ cts (68%)

$1\sigma = +/- \quad n^{1/2}$
$2\sigma = +/- 2\ n^{1/2}$
$3\sigma = +/- 3\ n^{1/2}$

Number of Counting events

Counts

The probability that a given counting event will lie within:

+/-1 sigma of the mean = 68%
+/- 2 sigma of the mean = 95%
+/- 3 sigma of the mean = 99%

Standard error is expressed as a percent:

standard error (in percent) =

{sigma (standard deviation)/n (number of counts)} * 100
=   x $(n^{1/2}/n)$ * 100

This is equal to

1 sigma = $((1*n^{1/2})/n)*100$
2 sigma = $((2*n^{1/2})/n)*100$
3 sigma = $((2*n^{1/2})/n)*100$

For 100,000 counts

1 sigma error in counts:
$100,000^{1/2} = 316$ count

1 sigma error in percent:
$[(100,000^{1/2})/100,000]*100$
$= (316/100,000)*100$
$= 0.003*100$
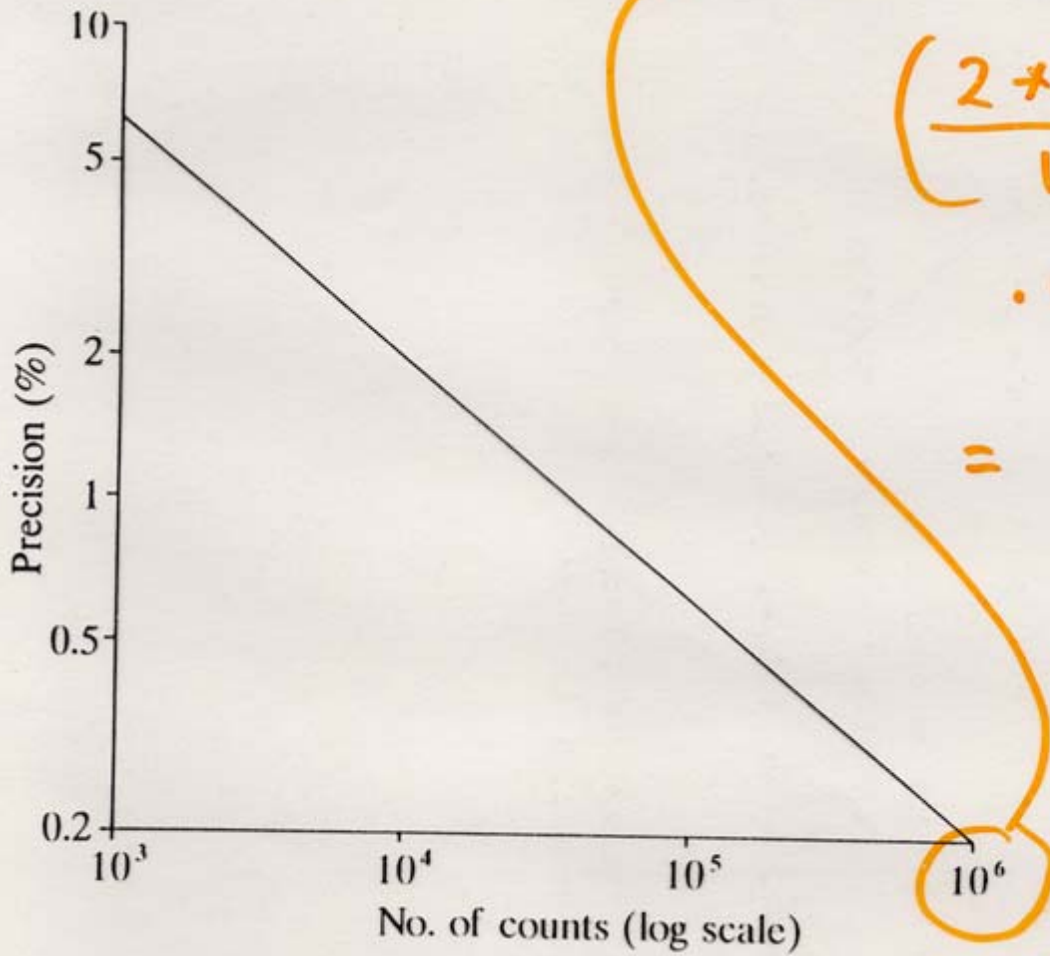$= 0.3 \%$

What does this mean for actual analyses?

Say 100,000 counts gives a value of 50 wt.% for a specific element.

What is the 1 sigma counting error for that element?

$\{100,000^{1/2}/100,000\}*100 = +/-0.3 \%$

0.3% of 50 wt.% is 0.15 wt.%

So, the 1 sigma error is 50 +/- 0.15 wt.%.

Detection limits

$$\left(\frac{2\sqrt{10^6}}{10^6} \right) * 100$$

159

$$\left(\frac{2 * 1000}{10^6} \right) \times 100$$

$.002 \quad * 100$

$= \quad 0.2$

Precision (%)

10

5

2

1

0.5

0.2

10^3 10^4 10^5 10^6

No. of counts (log scale)

Analysis of Reference Materials

Although counting statistics can provide a reliable indication of the statistical error of an individual analysis, this is may not be an accurate estimate of the TRUE error for an individual analysis.

Other factors may contribute:

-Poor optical focus
-Poor beam focus (leads to variable beam density between   standard and sample)
-Fluctuations in the electron beam
-Variations in vacuum on the sample chamber and the spectrometers
-Non-flat sample
-Poor carbon coat, or thickness different than standard
-Bad polish

Most of these should not be a problem, are things that can contribute to error above that of counting statistics.

Analysis of Reference Materials

In order to have a more accurate estimate of true analytical error, a sensible approach is analysis of reference materials.

Approach:

1. The reference material chosen should be similar in composition to your unknown.

2. The reference material should be the first thing that you analyze after completing calibration. This material should also be analyzed periodically during your analytical session.

3. If you are analyzing rare or unusual phases, you should think about finding reference materials and mounting these into a personal block. These can be loaded along with your unknowns.

4. Analyze the reference material 6-10x per analytical session.

5. Analyze the same reference materials in each similar analytical session, in order to be able to compare results from different sessions.

Sample Homogeneity

When a material is analyzed on smaller and smaller scales, the homogeneity (or lack thereof) of the sample becomes apparent. Be aware that your sample may be chemically less homogeneous than you may have expected based on optical analysis.

Homogeneity can be assessed by determining whether multiple analyzed points on a sample surface exceed the error that would be expected based on counting statistics.

- If the quantitative analyses of your unknown appear to be more variable than the reference materials, the sample may be inhomogeneous

-Examine the sample in BSE to try to detect any systematic compositional variation

-Make some qualitative line scans across the sample, selecting the elements that appear the most variable.

Detection Limits

The detection limit for an element is the minimum concentration that can be detected, ie. that the peak can be positively distinguished from the surrounding background.

Trace elements in silicates have detection limits of around 100-200 ppm, and this must be obtained through high beam currents and long counting times. For some elements, detection limits can be as low as 10 ppm.

A working definition is that the peak must have a height that is 3 standard deviations above the surrounding background.
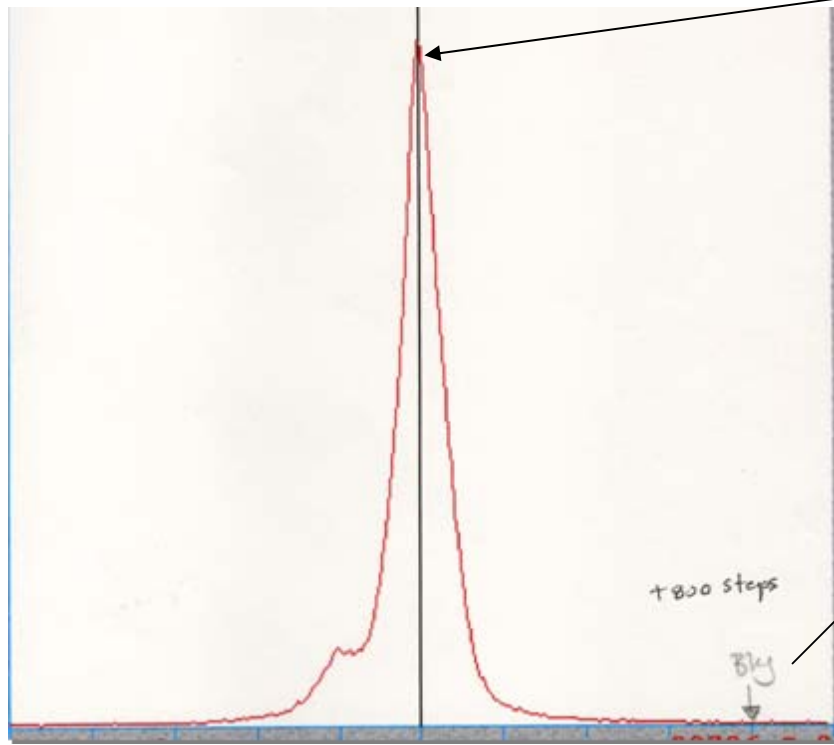
Peak for pure element 10,000 cps = 100 wt.% or $1*10^6$ ppm

so: 1 cps = 100 ppm

Background = 10 cps

+800 steps

Bkg

Determine the detection limit for a 100 second count time:

1. How many background count will be detected in 100 seconds?
     10 c/s * 100 seconds = 1000 counts

2. What is the 1 sigma deviation, in counts, for this number of background counts?
     $(1000)^{1/2}$ = 31.6 counts
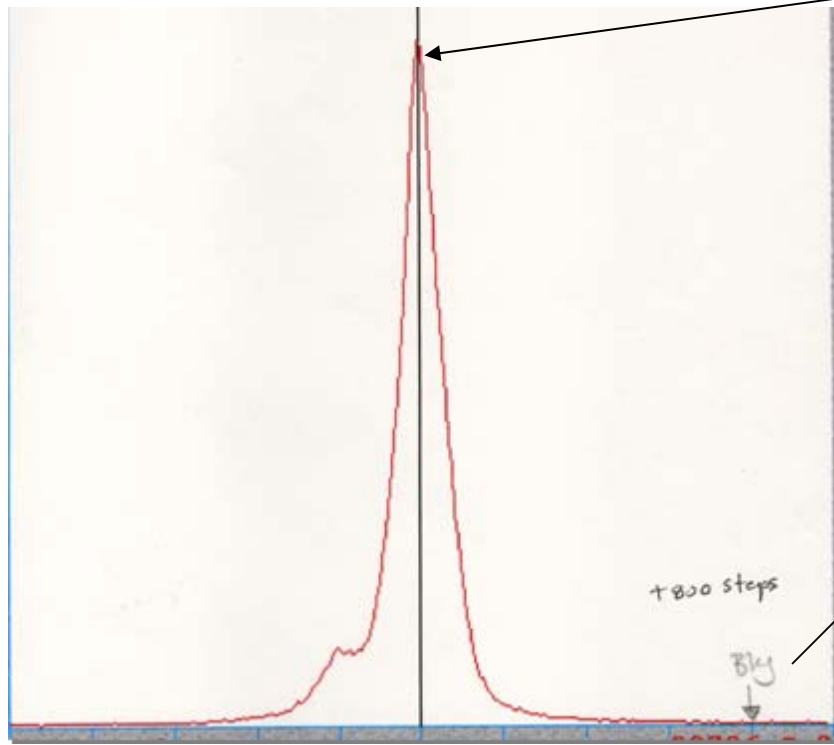
Peak for pure element 10,000 cps $= 100$ wt.% or $1*10^6$ ppm

so: 1 cps $= 100$ ppm

Background $= 10$ cps

(handwritten on figure: +800 steps, Bkg)

3. The detection limit is defined at counts 3 sigma above bkg. So, for 100 sec count time
      3*(31.6 counts) = 94.8 counts

4. How does this translate into counts per second, given that 1 cps represent 100 ppm?
      0.948 is to X
      as 1 cps is to 100 ppm

      X=94.8 ppm

Analytical Totals

For normal geological analyses, the elemental data is recalculated as oxide weight percent values, and reported as such.
The totals of mineral analyses should be close to 100 wt.%, and this is one method that can be used to estimate quality of analysis.

However, a number of factors can affect analytical totals:
1. **Trace elements** in the sample that were not measured. Can be in the range of 1 wt.%, particularly for glasses. Some feldspars can have up to 5 wt.% BaO.
2. **Samples with unanalyzed components.** A number of elements are cannot be included in quantitative analysis. These include Li, B, C, and H. So, a sample containing large amounts of any of these elements will have a low total.

> - **Clay minerals.** These can have a high H_2O content, and analytical totals can be correspondingly low.

> - **Carbonate phases.** C cannot be analyzed, so totals are typically in the range of 56%

> - **Hydrous glasses**. Glasses containing H_2O will have low totals because H is not analyzed. The difference of the total from 100% can be used to VERY ROUGHLY approximate the H_2O content of the sample.

-**Oxidation state of elements**. Magnetite contains both Fe^{+3} and Fe^{+2}. Oxide recalculations that only take into account the presence of Fe^{+2} will yield low oxide totals because Fe^{+2} bonds with less oxygen than Fe^{+3} (FeO versus Fe_2O_3). A magnetite will typically have totals of around 93%.

-Na loss.

Ions can migrate under the electrostatic field produced by the electron beam. Sodium is one of the elements that is the most affected by this phenomenon, particularly when the Na is in a glass. Feldspars, micas, nepheline, leucite, and other minerals can also be subject to this problem, to varying degrees.

Preventative measures:
-Reduce beam current
-Defocus the beam, or analyze using a small raster.

-A procedure for extrapolating from observed Na to true Na has been proposed by Nielsen and Sigurdsson (1981)

-Related problems:

-F migration in apatite, dependent on crystal orientation.

-Migration of components in sulphides realgar (AsS) and orpiment (HgS).
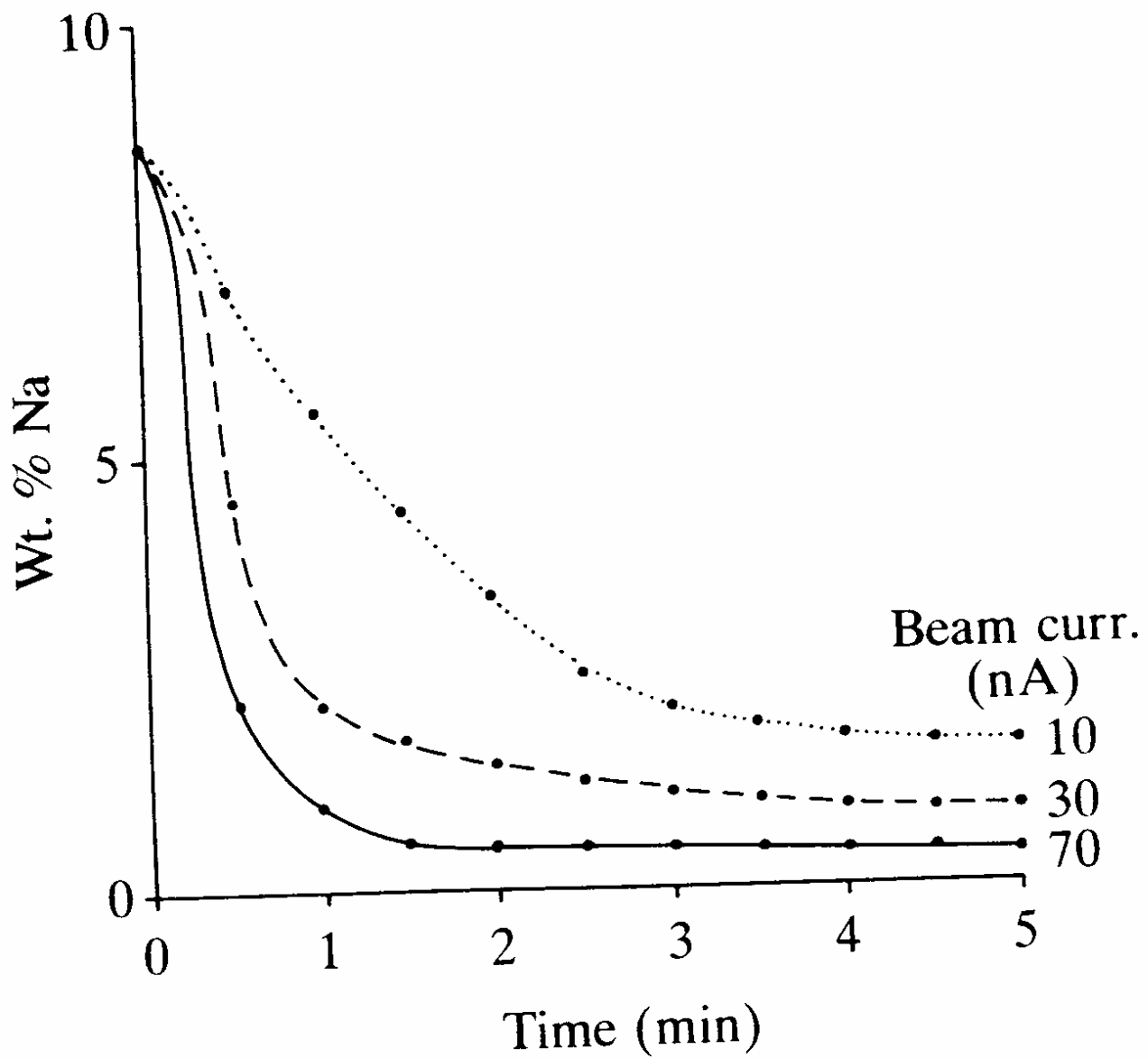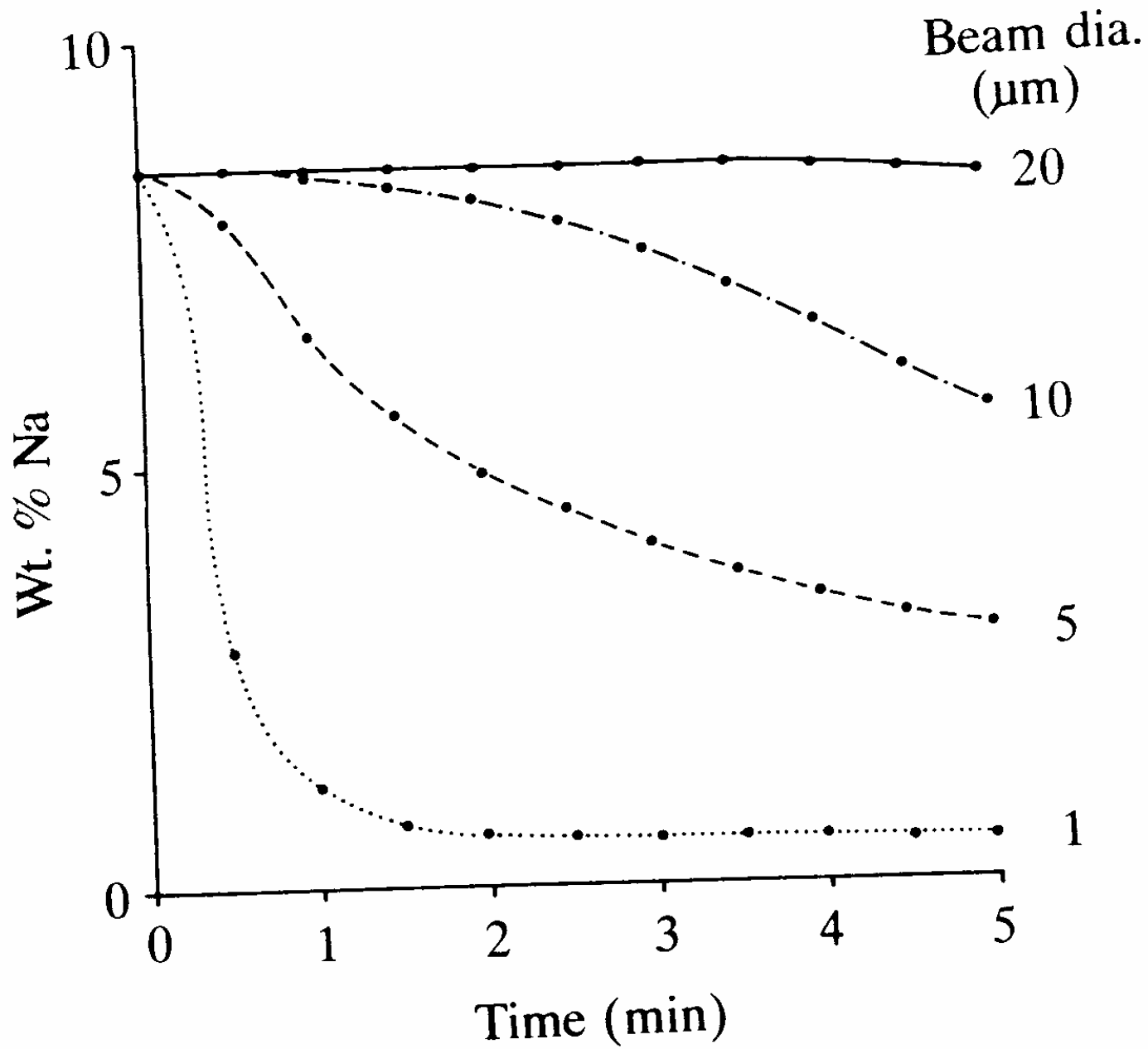
Estimation of Analytical Quality based on Mineral Stoichometry

Microprobe data can be recalculated in molecular, rather than weight percent format, and can then be fit into the stoichometric formula of the mineral.

This allows an estimate to be made of the quality of the analysis.

Table 9.4. *Numbers of oxygen atoms and total cations in formulae of common minerals*

Mineral	No. O atoms	No. cations
amphibole	23	15
chlorite	28	20
cordierite	18	11
epidote	25	16
feldspar	8	5
garnet	24	16
ilmenite	3	2
kaolinite	18	8
kyanite	5	3
mica	22	16
mullite	13	8
nepheline	16	12
olivine	4	3
pyroxene	6	4
spinel	4	3

Table 10.15 Formula unit calculation for a microprobe analysis of an olivine

Oxide	A	MW	B = A/MW	x	(B.x)	C = (B.x).4/T	C/x
	Analysed microprobe composition	Molecular weight of oxide	"moles"	Oxide ratio	Atomic proportion of oxygen from each oxide	Number of cations normalized to (O) = 4	Number of cations in formula unit
SiO_2	40.9%	60.09	0.6806	2	1.3613	2.0017	Si = 1.0008
FeO	9.6	71.85	0.1336	1	0.1336	0.1964	Fe^{II} = 0.1964
MgO	49.4	40.31	1.2255	1	1.2255	1.8020	Mg = 1.8020
Total	99.9				$T = 2.7203$		$\Sigma = 2.999$

x = ratio of oxygen to element atoms in stoichiometric oxide.
$T = \Sigma B.x$.
General formula of olivine = $(Mg, Fe^{II})_2SiO_4$.
Calculated formula from microprobe analysis = $(Mg_{1.8020}, Fe_{0.1964})Si_{1.0008})_4$.

Normalize to 40

Feldspar group: a group of silicate minerals having the general formula XZ_4O_8
where X = Ba, Ca, K, Na, NH_4, Sr
  Z = Al, B, Si
including albite*, andesine*, anorthite*, anorthoclase, bytownite*, labradorite*, microcline, oligocla
minerals constitute the plagioclase subgroup, comprising a solid solution series of general formula (Na,

Olivine group: a group of silicate minerals having the general formula A_2SiO_4
where A = Fe^{II}, Mg, Mn^{II}, Ni
including fayalite, forsterite

Pyroxene group: a group of silicate minerals having the general formula ABZ_2O_6
where A = Ca, Fe^{II}, Li, Mg, Na
  B = Al, Cr^{III}, Fe^{II}, Fe^{III}, Mg, Mn^{II}
  Z = Al, Si
including acmite, augite, diopside, enstatite, hedenbergite, jadeite, omphacite, pigeonite, spodumene.

Spinel group: a group of silicate minerals having the general formula AB_2O_4
where $A = $ Co, Cu, Fe^{II}, Ge, Mg, Mn^{II}, Ni, Ti, Zn
$\quad B = $ Al, Cr^{III}, Fe^{II}, Fe^{III}, Mg, Mn^{III}, V^{III}
including chromite, magnetite, spinel, ulvospinel.

Garnet group: a group of silicate minerals having the general formula $A_3B_2(SiO_4)_3$
where $A = $ Ca, Fe^{II}, Mg, Mn^{II}
$\quad B = $ Al, Cr^{III}, Fe^{III}, Mn^{III}, Ti, V^{III}, Zr
$\quad$ Si can be partially replaced by Ti and Al
including almandine and pyrope.

Amphibole group: a group of silicate minerals having the general formula
$A_{0-1}B_2Y_5Z_8O_{22}(OH,F,Cl)_2$

where $A = $ Ca, Na
$\quad B = $ Ca, Fe^{II}, Li, Mg, Mn^{II}, Na
$\quad Y = $ Al, Cr, Fe^{II}, Fe^{III}, Mg, Mn^{II}, Ti
$\quad Z = $ Al, Si, Ti
including actinolite, glaucophane, grunerite, kaersutite, pargasite, riebeckite and tremolite.

Mica group: a group of minerals having the general formula $XY_{2-3}Z_4O_{10}(OH, F)_2$
where $X = $ Ba, Ca, H_3O, K, Na
$\quad Y = $ Al, Cr, Fe^{II}, Fe^{III}, Li, Mg, Mn^{II}, V^{III}, Zn
$\quad Z = $ Al, Be, Fe^{III}, Si
including biotite, glauconite, lepidolite, muscovite.

Presentation of Results

Convention is to report microprobe analyses to 2 places after the decimal, although these should not be considered significant figures. The significance of figures should be determined by the reported error for the analysis.

Analyses can be reported in tabular form, with elements analyzed in order of the ratio of cations:O.

Analyses can be either normalized to 100%, or reported with actual totals. In cases where the amount of unanalyzed component in the sample is variable, the former approach may be more useful.

Table 1. Average major element composition of tephra shards in Siple and Taylor ice cores, and representative compositions of explosive eruption, determined by electron microprobe

Sample	N	P_2O_5	SiO_2	SO_2	TiO_2	Al_2O_3	MgO	CaO	MnO	FeO	Na_2O	K_2O	Cl
SipleA 33.4-33.6 mean	4	**0.63**	**44.33**	**0.11**	**3.92**	**15.15**	**5.83**	**12.83**	**0.22**	**11.80**	**3.51**	**1.37**	**0.12**
standard deviation		0.04	0.48	0.02	0.17	0.26	0.45	0.31	0.02	0.53	0.38	0.11	0.05
SipleA 33-6-33.8 mean	8	**0.07**	**63.40**	**0.05**	**0.40**	**16.77**	**0.14**	**1.21**	**0.27**	**6.30**	**5.99**	**4.91**	**0.32**
standard deviation		0.02	0.51	0.02	0.08	0.27	0.04	0.05	0.03	0.55	1.25	0.64	0.10
SipleA 34.4-34.7mean	9	**0.78**	**42.74**	**0.13**	**4.64**	**14.81**	**6.02**	**11.70**	**0.20**	**13.13**	**4.03**	**1.57**	**0.08**
standard deviation		0.08	1.18	0.02	0.52	0.87	1.09	0.67	0.03	0.93	0.64	0.23	0.01
SipleA 36.7-37.2 mean	2	**0.21**	**64.94**	**0.06**	**0.80**	**16.32**	**0.51**	**2.52**	**0.18**	**6.84**	**2.84**	**4.42**	**0.28**
standard deviation		0.03	1.37	0.00	0.02	0.34	0.01	0.12	0.02	0.09	1.25	0.69	0.08
SipleB 35.4-35.7 mean	4	**0.83**	**43.76**	**0.13**	**4.43**	**15.34**	**5.05**	**11.46**	**0.23**	**12.54**	**4.26**	**1.70**	**0.15**
standard deviation		0.09	1.25	0.02	0.47	0.37	0.39	0.55	0.03	0.87	0.51	0.27	0.05
SipleB 63.4-63.65 mean	7	**0.78**	**43.22**	**0.12**	**4.31**	**15.47**	**5.43**	**11.96**	**0.22**	**12.56**	**4.14**	**1.56**	**0.09**
standard deviation		0.11	0.75	0.03	0.54	0.24	0.67	0.54	0.03	0.60	0.32	0.21	0.05
SipleB 97.2-97.45 mean	6	**0.08**	**61.38**	**0.03**	**0.45**	**16.68**	**0.15**	**1.20**	**0.27**	**6.56**	**7.41**	**5.38**	**0.23**
standard deviation		0.03	0.75	0.02	0.03	0.29	0.02	0.07	0.04	0.42	0.43	0.12	0.04
SipleB-97.45-97.7 mean	8	**0.10**	**61.91**	**0.05**	**0.43**	**16.59**	**0.14**	**1.14**	**0.27**	**6.25**	**8.18**	**4.57**	**0.28**
standard deviation		0.01	0.70	0.02	0.05	0.62	0.03	0.28	0.05	0.27	0.00	0.70	0.08
Taylor 79.155 mean	6	**0.05**	**61.82**	**0.06**	**0.42**	**16.44**	**0.15**	**1.18**	**0.24**	**6.38**	**7.01**	**5.37**	**0.29**
standard deviation		0.03	0.75	0.02	0.03	0.32	0.02	0.08	0.05	0.18	0.46	0.19	0.05
Taylor 311.345 mean	8	**0.68**	**43.43**	**0.13**	**4.11**	**14.99**	**5.75**	**12.51**	**0.20**	**11.94**	**3.82**	**1.38**	**0.18**
standard deviation		0.09	1.05	0.04	0.50	0.41	0.36	0.71	0.03	0.97	0.10	0.12	0.12
Taylor488 mean	6	**0.03**	**61.71**	**0.03**	**0.31**	**16.19**	**0.08**	**1.05**	**0.26**	**6.45**	**7.80**	**5.16**	**0.39**
standard deviation		0.04	0.75	0.02	0.04	0.18	0.01	0.08	0.02	0.48	0.40	0.12	0.13
Representative composition of potential volcanic sources													
Mt. Takahe <8.5 ka	12	0.08	60.02	0.11	0.57	14.12	0.07	1.15	0.34	9.17	9.08	4.86	0.22
Mt. Berlin (BIT-313)	16	0.05	61.53	0.06	0.42	15.88	0.04	1.43	0.26	7.63	7.30	5.16	0.11
Mt. Melbourne	6	0.08	64.89	0.02	0.48	15.66	0.19	1.82	0.16	5.46	5.68	5.24	0.17
The Pleiades	8	0.01	64.30		0.14	17.54	0.05	0.85	0.15	3.74	7.52	5.08	0.29
Balleny (1)		0.60	44.34		2.52	15.20	10.74	10.27	0.18	10.12	3.41	1.28	0.10
Royal Society Range (2)		0.64	43.15		3.41	14.57	7.82	11.72	0.19	11.90	3.41	1.24	0.10

Notes: Geochemical quantities are in weight %.   Analyses are normalized to 100 wt.%.   N equals number of analyses. Analytical precision, based on replicate

analyses of standard reference materials of similar composition to the unknows, are as follows (all in wt.%): $P2O5\pm0.02$, $SiO_2\pm0.47$, $SO2\pm0.01$, $TiO_2\pm0.03$, $Al2O3\pm0.12$,

$MgO\pm0.07$, $CaO\pm0.02$, $MnO\pm0.06$, $FeO\pm0.06$, $Na_2O\pm0.55$, $K_2O\pm0.27$, $Cl\pm0.07$.

1. Johnson et al., 1982

2. Keyes et al., 1977

Sample	P$_2$O$_5$	SiO$_2$	SO$_2$	TiO$_2$	Al$_2$O$_3$	MgO	CaO	MnO	FeO	Na$_2$O	K$_2$O	Cl	beam size
Table 2. Major element composition of individual tephra shards from sample analyzed by electron microprobe													
SipleA 34.4-34.7 pt1	0.79	42.42	0.14	4.95	14.95	5.23	12.32	0.20	12.63	4.29	1.69	0.09	20
SipleA 34.4-34.7 pt2	0.70	42.46	0.12	4.29	13.65	7.85	10.79	0.25	14.25	3.88	1.51	0.07	15
SipleA 34.4-34.7 pt3	0.81	42.76	0.09	4.84	14.11	6.61	11.52	0.20	13.38	3.94	1.54	0.08	15
SipleA 34.4-34.7 pt4	0.87	43.00	0.12	5.04	15.05	4.82	12.25	0.19	13.18	3.84	1.40	0.10	15
Siple A 34.4-34.7 pt 5	0.79	42.88	0.13	4.34	14.87	4.72	11.03	0.23	13.74	5.25	1.67	0.08	15
Siple A 34.4-34.7 pt 6	0.63	45.12	0.10	3.81	15.64	5.47	12.68	0.21	12.15	2.95	1.18	0.07	10
Siple A 34.4-34.7 pt 7	0.71	43.62	0.13	3.79	15.27	5.77	11.94	0.23	12.62	3.92	1.93	0.09	20
Siple A 34.4-34.7 pt 8	0.83	43.30	0.16	4.49	16.55	4.41	12.15	0.17	12.27	4.01	1.54	0.09	15
Siple A 34.4-34.7 pt 9	0.65	45.74	0.10	3.66	15.76	4.95	11.06	0.17	11.14	4.76	1.89	0.12	15
mean	**0.78**	**42.74**	**0.13**	**4.64**	**14.81**	**6.02**	**11.70**	**0.20**	**13.13**	**4.03**	**1.57**	**0.08**	
standard deviation	0.08	1.18	0.02	0.52	0.87	1.09	0.67	0.03	0.93	0.64	0.23	0.01	

Notes: Geochemical quantities are in weight %.   Analyses are normalized to 100 wt.%.   N equals number of analyses. Analytical precision, based on replicate analyses of standard reference materials of similar composition to the unknows, are as follows (all in wt.%): P$_2$O$_5$±0.02, SiO$_2$±0.47, SO$_2$±0.01, TiO$_2$±0.03, Al$_2$O$_3$±0.12, MgO±0.07, CaO±0.02, MnO±0.06, FeO±0.06, Na$_2$O±0.55, K$_2$O±0.27, Cl±0.07.

Table 9.2. *Analysis of ferroan pigeonite*

Element	Wt % element	Wt % oxide	Atom %	No. of atoms	(per 6 O)
Si	24.64	52.70	19.57	1.962	
Ti	0.20	0.34	0.09	0.009	
Al	0.97	1.84	0.81	0.081	
Fe	5.82	7.33*	2.32	0.233	
Mn	0.12	0.16	0.05	0.005	4.027
Mg	9.14	15.15	8.39	0.841	
Ca	15.43	21.58	8.59	0.861	
Na	0.36	0.49	0.35	0.035	
O	43.32†	—	59.83	6.000	
	100.00	99.59	100.00		

* Calculated as FeO
† Calculated by difference