Complexities of Using Natural Minerals as Standard Reference Materials: Personal Experiences from a Geological Microprobe Lab

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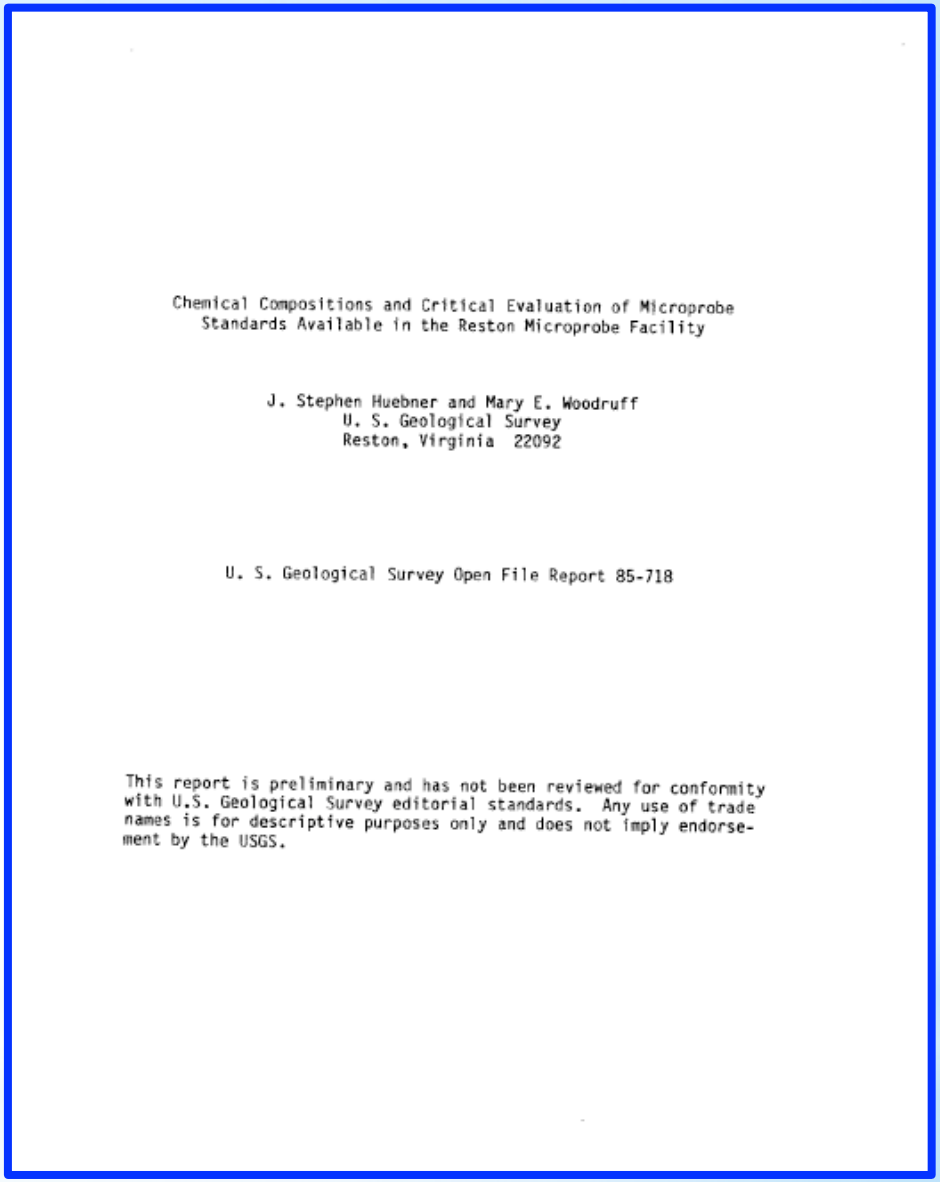
Preface 1

USGS Open File Report 85-718

One of few published attempts to critically assess a wide set of EPMA standards in use in the USGS Reston probe lab, including the NMNH ones, was done by Huebner and Woodruff, released in 1985.

They evaluated
(a) the stoichiometry of the stated compositions of standards, and
(b) whether the compositions of the grains in their mounts are the same as the published ones (using other 'good' standards).



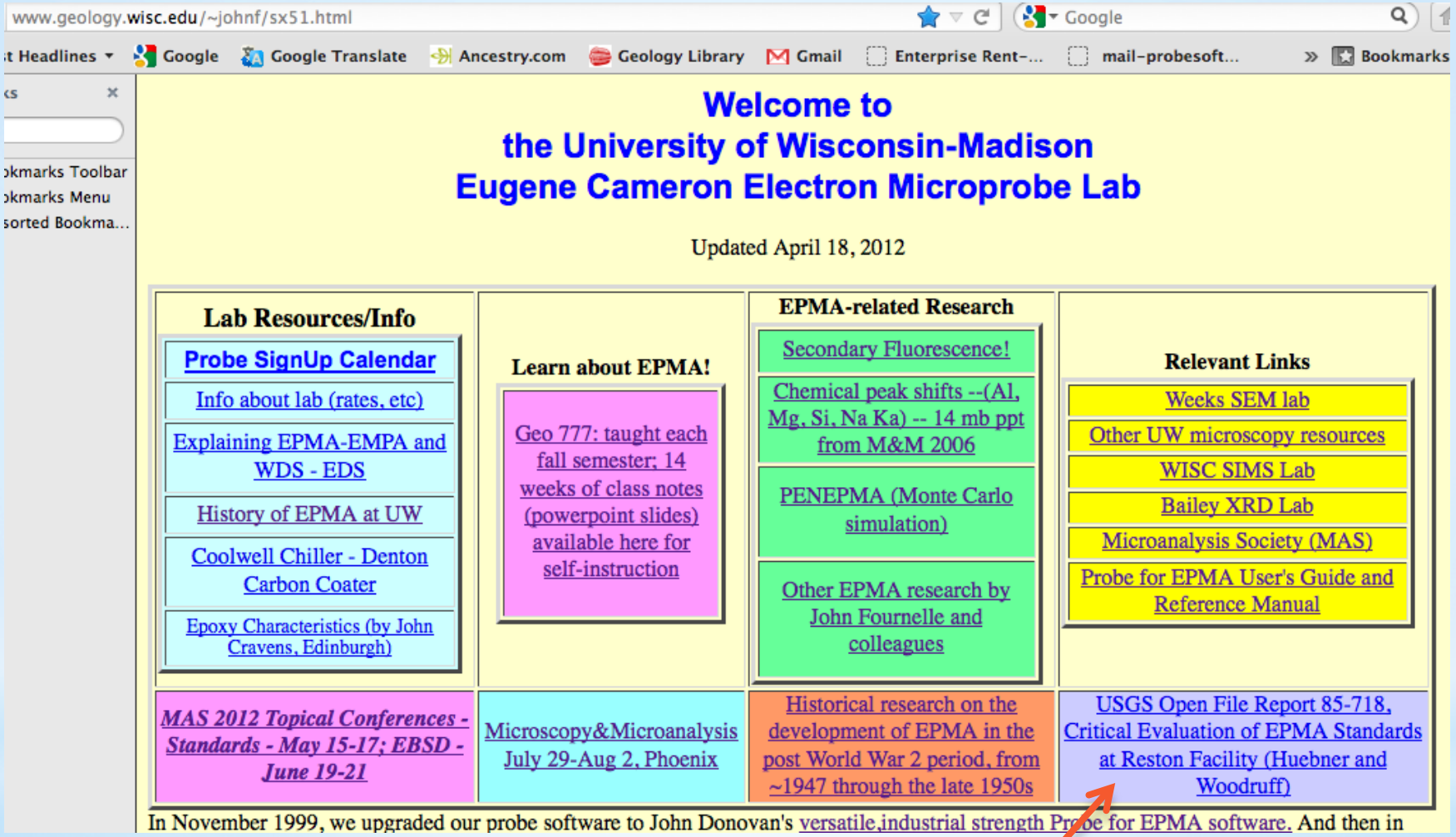
Chemical Compositions and Critical Evaluation of Microprobe Standards Available in the Reston Microprobe Facility

J. Stephen Huebner and Mary E. Woodruff
U. S. Geological Survey
Reston, Virginia 22092

U. S. Geological Survey Open File Report 85-718

This report probably has not received the attention it deserves. All probe labs should have it and read it.

www.geology.wisc.edu/~johnf/sx51.html



Pdf available

Preface 2

Smithsonian Microbeam Standards Web page

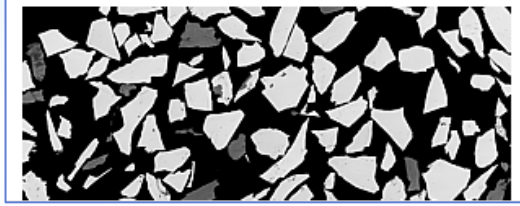
If you use these standards, you need to refer to this page for updates….

<mineralsciences.si.edu/facilities/standards.htm>

Impurities in the Smithsonian Microbeam Standards

The following table lists impurities observed in reference samples from the Smithsonian Microbeam Standards (SMS). The impurities as they were referred to by Jarosewich et al. (1980), are grains of other minerals and inclusions in individual grains of the original minerals or glasses chosen to become SMS. Additions to this will be made as they are identified. Please contact Tim Rose for further information or of additional impurities so that we may add them to the list.

SMS	impurities	abundance
augite (NMNH 1221420)	grains with lower Na, Al and more Fe,Mg, Ca	rare
diopside (NMNH 117733)	calcite/barite inclusions	common
	apatite	rare
	pyrite	rare
fayalite (NMNH 85276)	amphibole (grunerite?)	10% of grains, some intergrown
glass VG-2 (NMNH 111240)	olivine: tiny crystals	common
	plagioclase: large crystal	on one grain
glass A-99 (NMNH 113498)	plagioclase: tiny	common
	clinopyroxene: tiny	rare
Glass VG-568 (NMNH 72854)	Fe oxide: 5 micron crystals	common
hornblende (NMNH 143965)	FeTi oxide: tiny crystals in inclusions	abundant
	FeTi oxide: larger individual crystals	rare
hypersthene (NMNH 746)	chromite veins and included crystals	common
ilmenite (NMNH 96189)	NbFeTi oxide	abundant tiny
	Nb and Zn phases	rare
magnetite (NMNH 114887)	ilmenite	rare
microcline (NMNH 143966)	albite: included crystals	rare
omphacite (NMNH 110607)	different CaNaMgAl silicate enclosed in jadeite	



Backscattered electron image of grains of the SMS fayalite reference material. About ten per cent of the grains are a darker gray color. Preliminary data suggest the impurity is an amphibole, possibly grunerite, a mineral found associated with the fayalite from Rockport, Massachusetts chosen to

Preface 2

Smithsonian Microbeam Standards Web page

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If you use these standards, you need to refer to this page for updates….

SMITHSONIAN MICROBEAM STANDARDS

The Jarosewich microbeam reference materials.

Introduction

Largely because of the work of Eugene Jarosewich, reference samples for microbeam analysis have been characterized and distributed worldwide. As of 2002, 750 requests totaling about 11,000 samples have been made. Although not technically standards, these reference materials are referred to as the Smithsonian Microbeam Standards (SMS). A short history of the SMS by Gene (Jarosewich 2002) and other publications relating to these materials can be found at the links and reference below.

References:

Jarosewich (2002) *Smithsonian Microbeam Standards* [Full Text]

Jarosewich et al. publications on the SMS: [Full Text]

Jarosewich et al.(1980) *Reference Samples for Electron Microprobe Analysis*

Jarosewich and McIntyre (1983) *Carbonate Reference Samples for Electron Microprobe and Scanning Electron Microscope Analysis*

Jarosewich and White (1987) *Strontianite Reference Sample for Electron Microprobe and SEM Analyses*

Jarosewich et al. (1987) *Chromium Augite- A New Microprobe Reference Sample*

Jarosewich and Boatner (1991) *Rare-Earth Element Reference Samples for Electron Microprobe Analysis*

provided us with material for use as microprobe reference samples. B. **Mason's** careful examination and assistance in separation of minerals is also greatly appreciated.

RESUME

Les analyses chimiques sur vingt six minéraux, quatre verres naturels et un verre synthétique préparés comme échantillons de reference

Electron microprobe reference samples for mineral ... types, **Smithsonian** Contributions to the Earth Scienc... 22: 69-72.

(3) **W.F.** Hillebrand, G.E.F. **Lundell**, H.A. Bright and ... **Hoffman** (1953)
Applied Inorganic Analysis, 2nd edition, 1034 pp, **Wiley**

(4) **L.C.** Peck (1964)
Systematic analysis of **silicates**, U.S. Geological Su... Bulletin 1170, 88 pp.

(5) F.R. Boyd, **L.W.** Finger and F. Chayes (1967)
Computer reduction of electron-probe **data**, Carn... Institution Year Book, 67: 210-215.

Please Note!

These standards are offered primarily for major and minor element analysis.

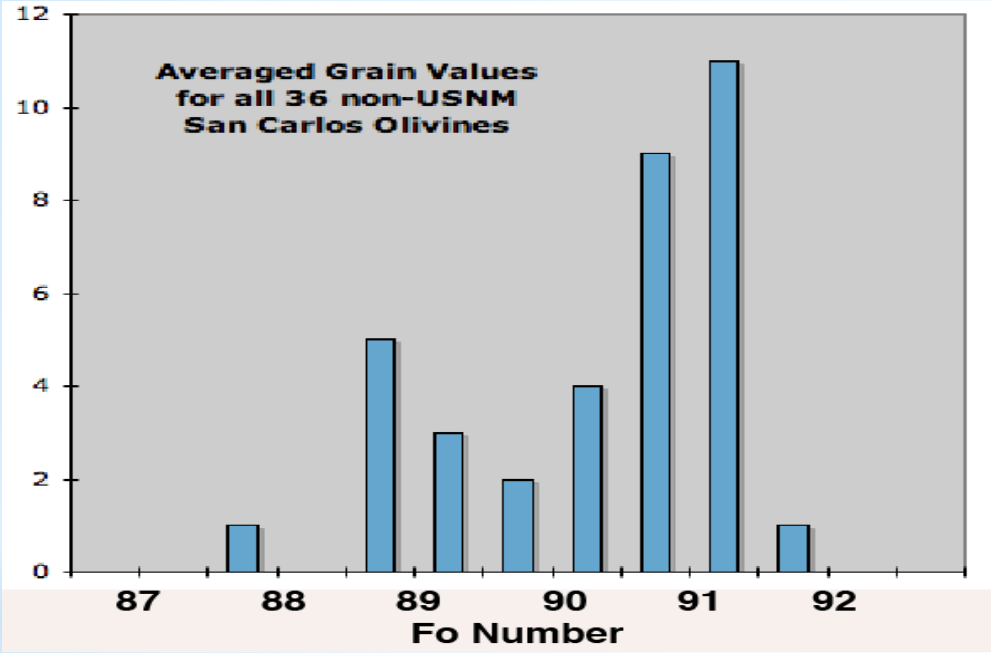
Trace elements (<0.1%) are reported as a matter of convention; they need to be thoroughly checked if they are to be used in any probe work.

Based on our experience the oxides in the standards listed below may give inferior results. Other oxides in the same standards give excellent results.

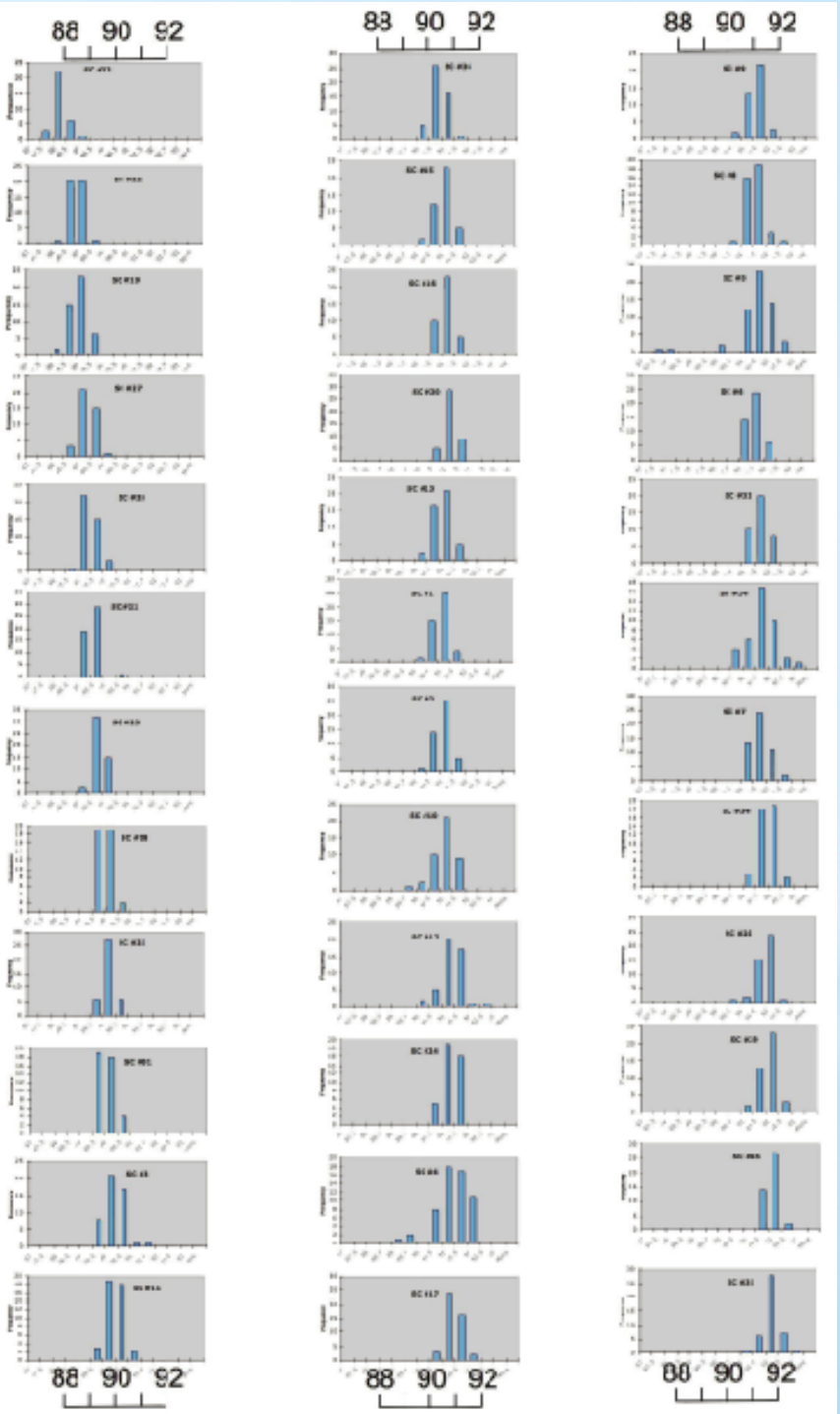
SiO2	springwater olivine
A12O3, CaO	Johnstown hyperstene
A12O3	hornblende, Arenal volcano

Background to this talk

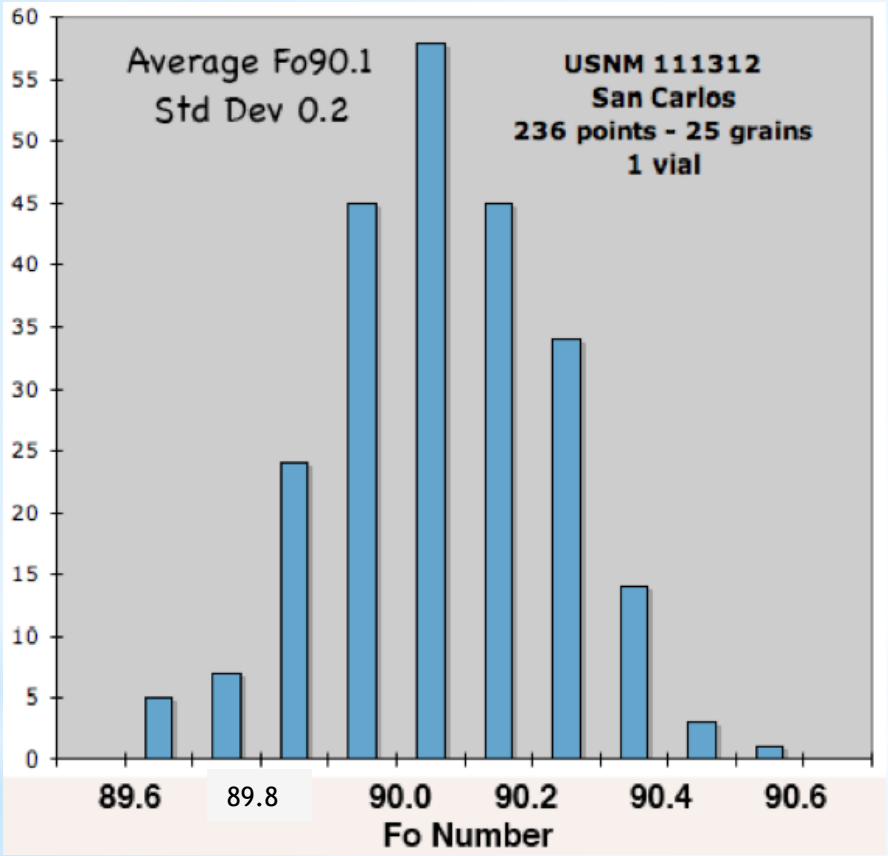
2 different researchers, over 2 months, brought in “San Carlos olivine” which was NOT from the Smithsonian. I analyzed them all…..

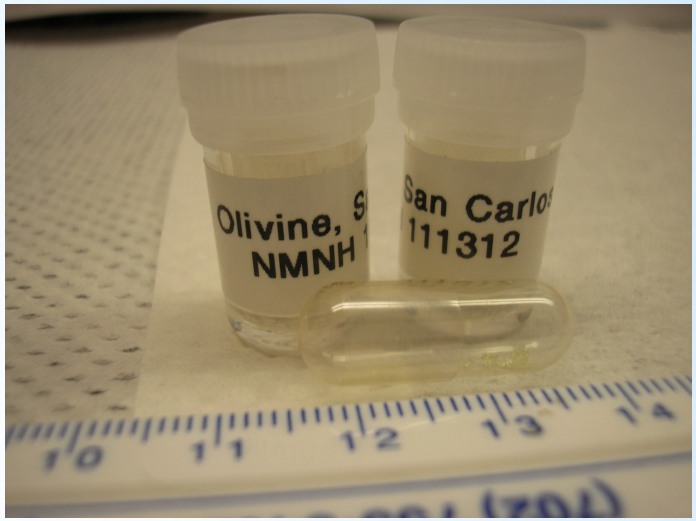


Plotting grain averages (above) or each grain histogram (right) shows while each grain fairly homogeneous, there is wide range of compositions between grains.



…resulted in an evaluation of 25 grains of the NMNH 111312 San Carlos olivine

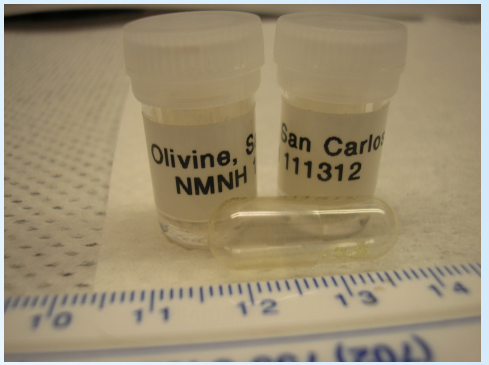




Olivine – San Carlos – NMNH 111312

	1 sigma	2 sigma	3 sigma
Si			
counts/(ave cts)	0.995-1.005	0.99-1.01	0.985-1.015
% of samples	50%	78%	90%
Mg			
counts/(ave cts)	0.996-1.004	0.992-1.008	0.989-1.011
% of samples	40%	67%	88%
Fe			
counts/(ave cts)	0.984-1.016	0.968-1.032	0.952-1.048
% of samples	66%	94%	100%

Si count rate: 4120 cps x 10 seconds
Mg count rate: 7030 cps x 10 seconds
Fe count rate: 395 cps x 10 seconds



Two ways to look at these numbers:

→ Not exactly a normal distribution for Si and Mg: 1σ should be >68, 2σ>95, 3σ>99

→There is a finite probability that 1 of 10 grains will have Si and Mg contents > 1% different from the nominal/mean value.

"... When the criteria of these [std dev/sigma] ratios are used as a measure of homogeneity, all the reference samples are very homogeneous **provided a reasonably large number of counts are taken on a reasonably large number of grains**. *In practice, however, fewer counts and grains are normally used for standardization, and under these circumstances a grain having a slightly different composition may influence the microprobe results adversely.* For this reason, grains showing some discrepancy in composition should be avoided. The percentages of these "impurities" in the whole samples are minimal and the effects on the bulk analyses of the samples are negligible."

--Jarosewich, Nelen and Norberg, 1980 (my emphasis added)

This immediate pyroxene project

In November 2011, a graduate student at another university was having difficulty with EPMA of experimental orthopyroxene:

“high totals >101 with decent stoichiometries, 3.99-4.01. But with other pyroxenes, decent totals but high stoichiometries (>4.01).”

After ruling out common instrumental gotchas (e.g., PHA, peaking), I asked what standards were used and was told:

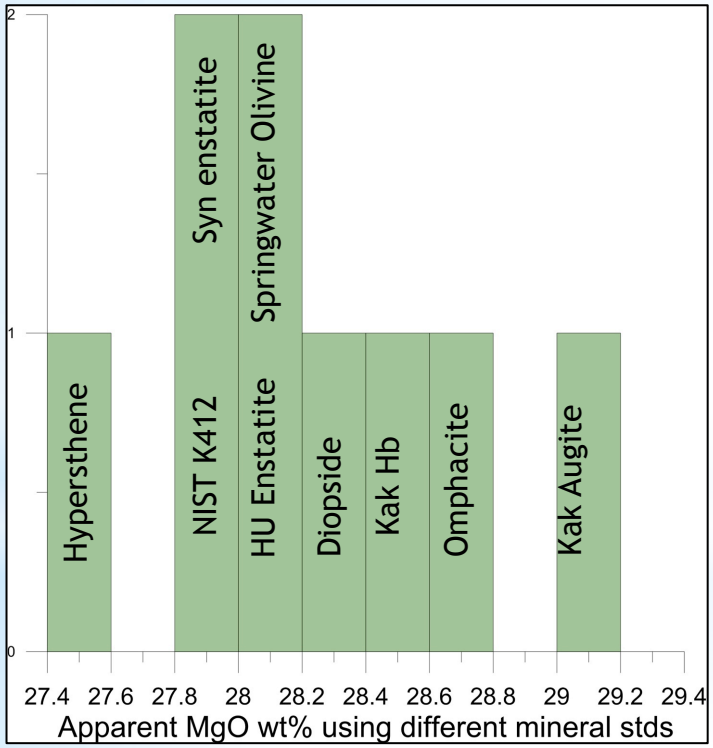
NMNH hypersthene for Si, Mg, Fe
NMNH Cr augite for Ca, Cr
and also tried
NMNH Kakanui augite for Fe
Harvard Sri Lanka enstatite for Si, Mg
but no difference

I volunteered to try my hand at it….

…. And I had similar problems!

The problem clearly is Si and Mg as all other elements are minor.

I acquired many different standards and then processed the same K-ratio with different standards, yielding the histogram below, with almost 2 wt% differences in MgO and SiO2 using common standards

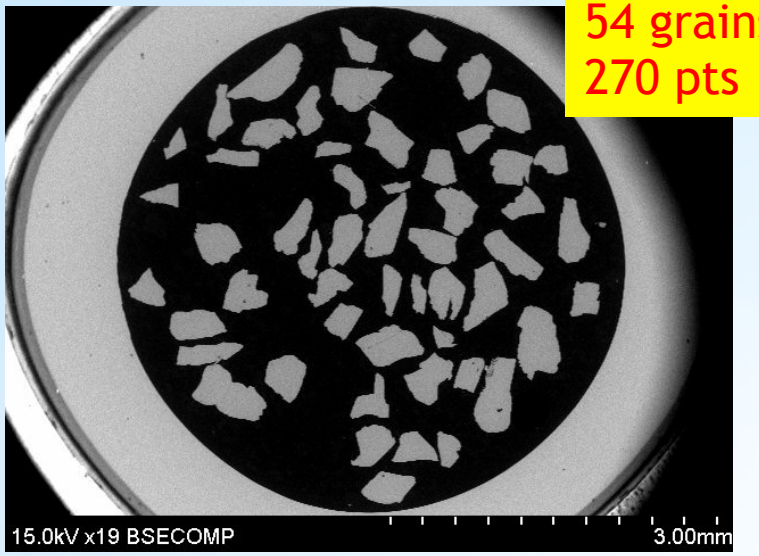


NMNH Diopside (Mg, Si)
NMNH Hypersthene (Mg, Si)
NMNH Kak augite (Mg, Si)
NMNH Kak hornblende (Mg, Si
NMNH omphacite (Mg, Si)
NMNH Springwater olivine (Mg,Si)
Harvard enstatite (Mg, Si)
NIST K412 silicate glass (Mg, Si)
Synthetic enstatite (Mg, Si)
UW jadeite (Si)

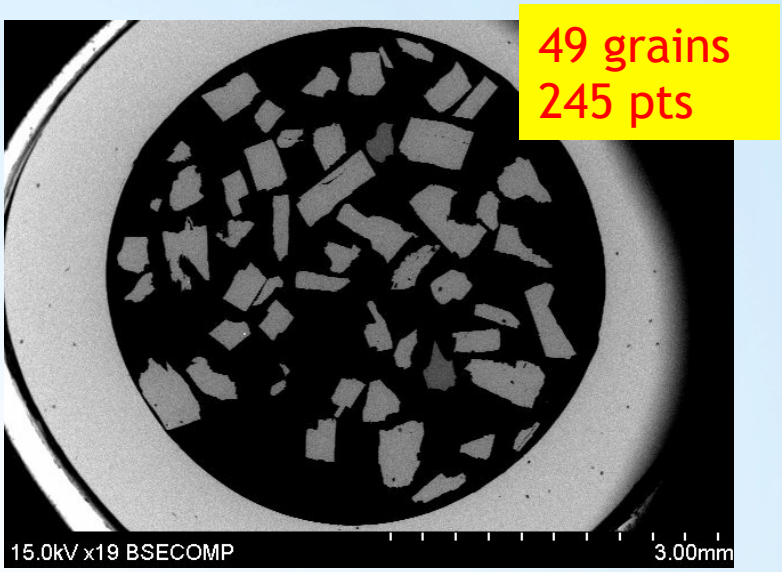
Proposal to Tim Rose @ Smithsonian: he send me many grains of 4 NMNH pyroxene standards, and I would evaluate them as I had the San Carlos olivine.

Hypothesis = the wet chemical analysis of grains was correct, but that natural variability intragrain may produce inaccuracies IF a small number (1? 2? 3?) grains are used for calibration.

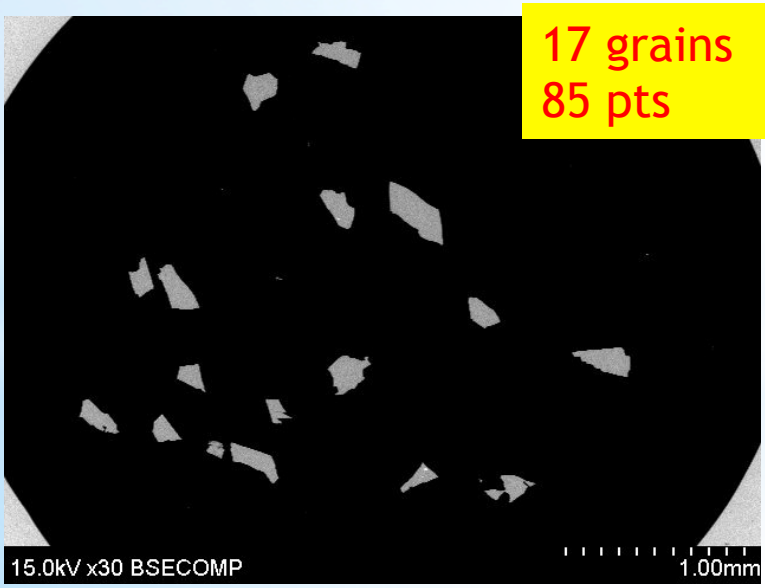
Goal = examine as large a number of grains as are available and document the variability.



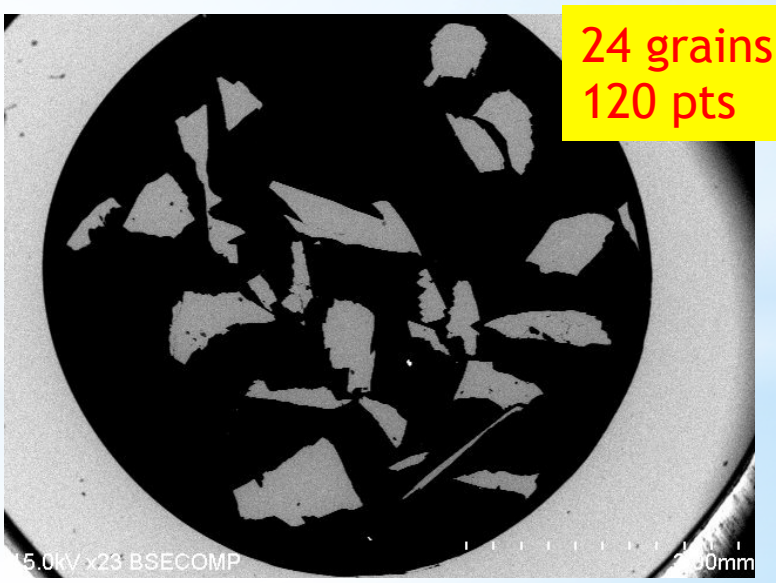
Kakanui Augite, NMNH 122142



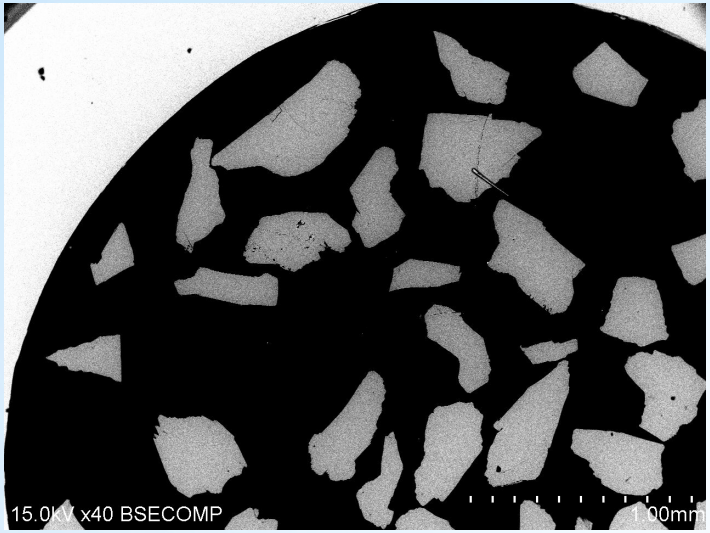
Natural Bridge Diopside, NMNH 117733



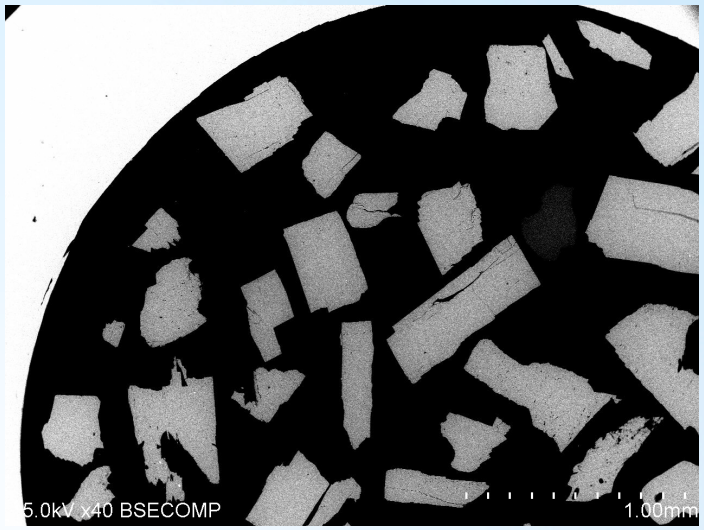
Johnstown Hypersthene, NMNH 744



Black Rock Summit Flow, Chromian Augite, NMNH 164905

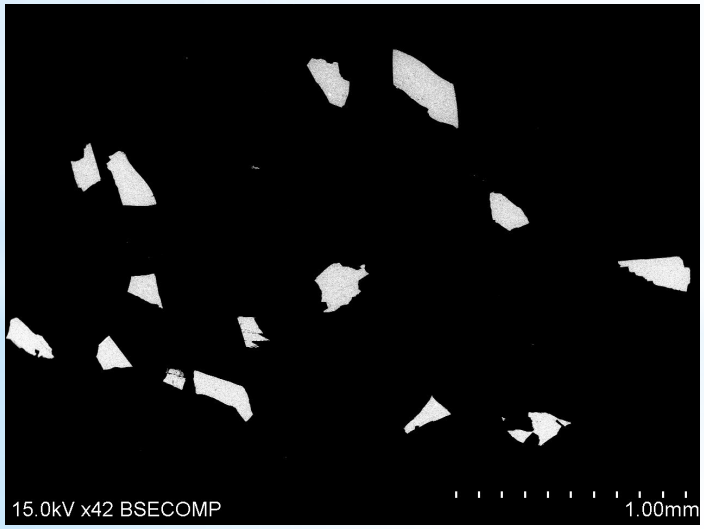


Kakanui Augite, NMNH 122142



Natural Bridge Diopside, NMNH 117733

Grains are typically a couple hundred microns in size; free of zoning



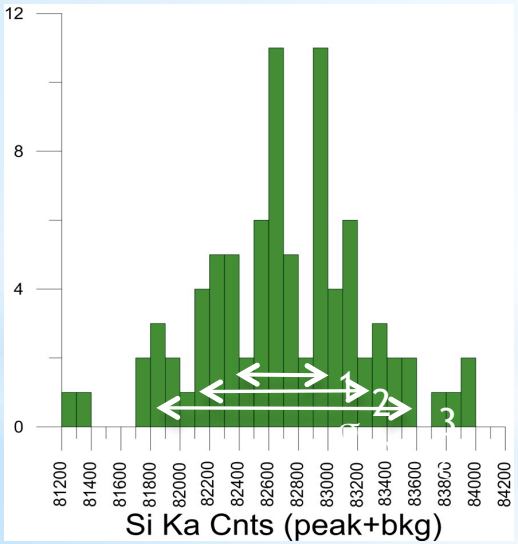
Johnstown Hypersthene, NMNH 744

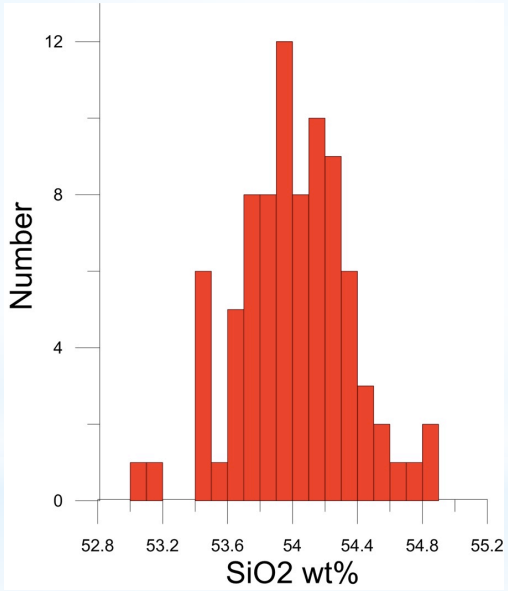
Black Rock Summit Flow, Chromian Augite, NMNH 164905

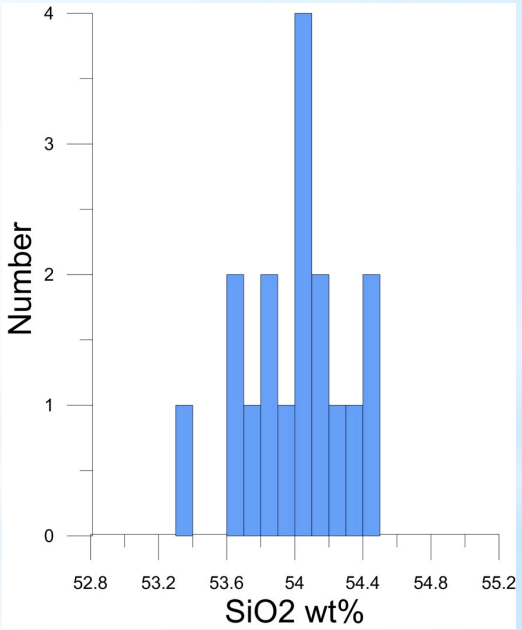
Roadmap for following slides:

For each of the 4 NMNH pyroxene reference materials

- Green Histogram of 10 second counts (P+B) w/ σ
- Red Histogram of all measurements wt% oxides
- Blue Histogram of averaged compositions of all grains



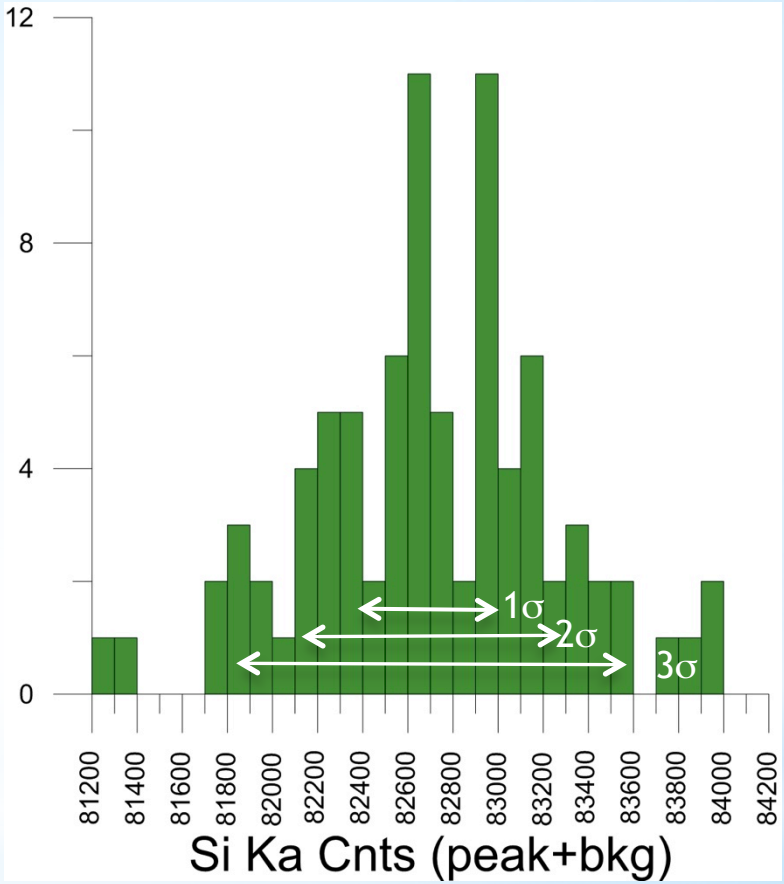




A comment about the use of these histograms:

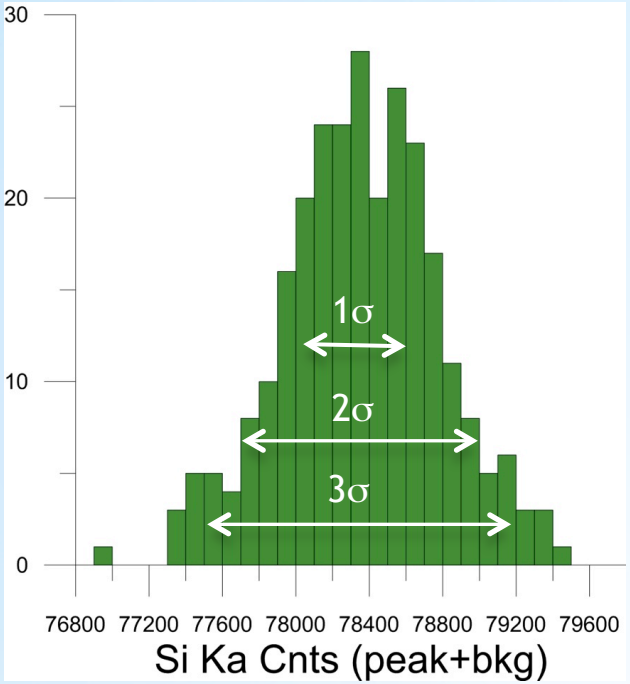
- Optimally the distribution of grains should be “normal” with the wet chemical analysis representing the mean value.
- 68.2% of random analytical points should be within 1 sigma of the chemical analysis
- 95.4% within 2 sigma
- 99.6% within 3 sigma

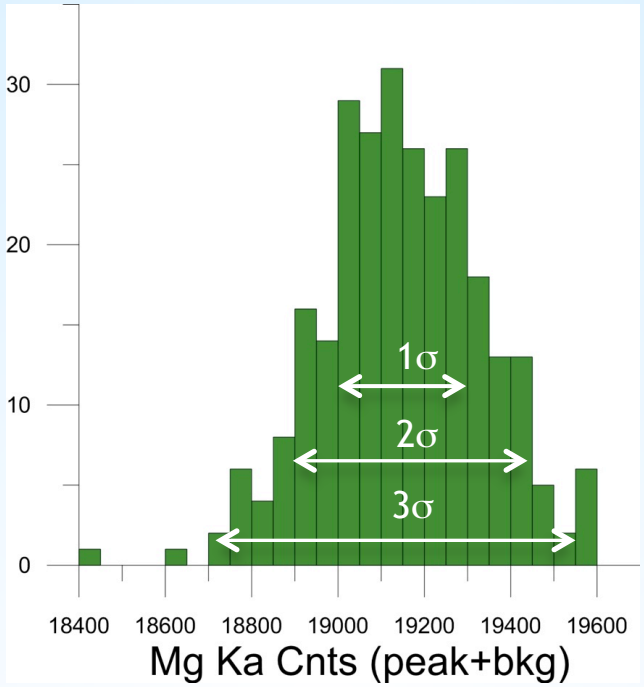
The histogram to the right differs from the above ideal case (e.g. only 44% of the analytical points fall within 1 sigma of the mean), suggesting at least for this element in this suite of grains, the distribution is more complex and more care is needed in assuming any grain is representation of the mean.

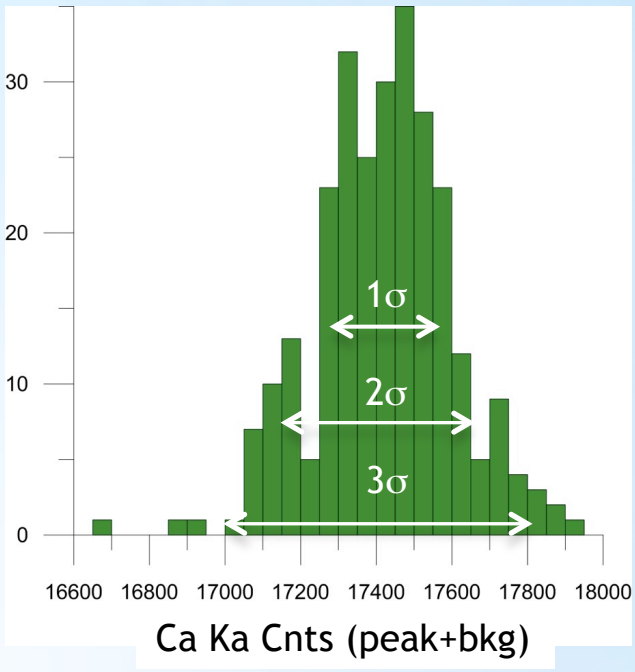


Relative to mean (82709)
1 sigma: 37 of 84 (44%)
2 sigma: 61 of 84 (73%)
3 sigma: 75 of 84 (89%)

NMNH Kakanui Augite - 54 grains -- 270 analyses





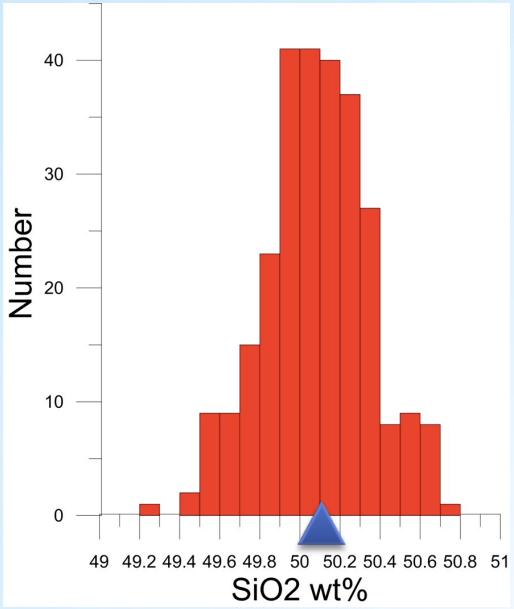


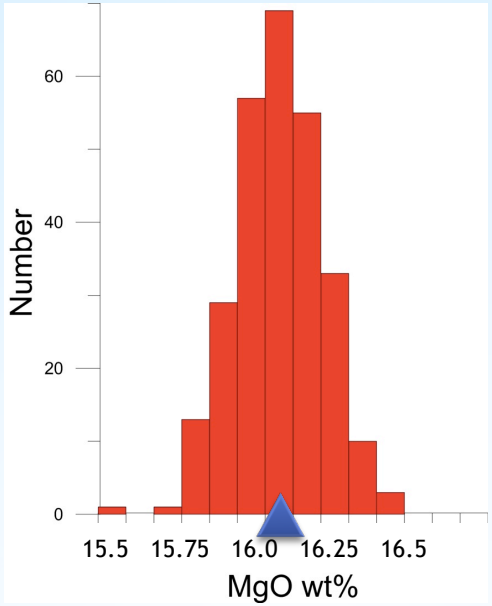
Relative to mean (78353)
1 sigma: 140 of 270 (52%)
2 sigma: 222 of 270 (82%)
3 sigma: 255 of 270 (94%)

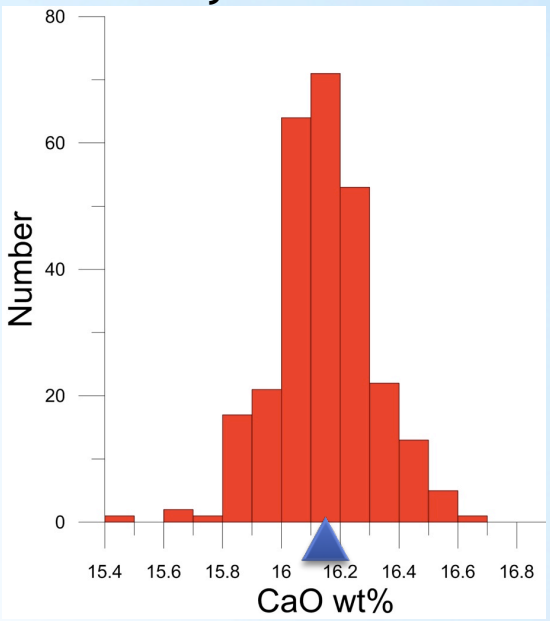
Relative to mean (19150)
1 sigma: 149 of 270 (55%)
2 sigma: 231 of 270 (86%)
3 sigma: 263 of 270 (99%)

Relative to mean (17418)
1 sigma: 160 of 270 (59%)
2 sigma: 231 of 270 (86%)
3 sigma: 262 of 270 (97%)

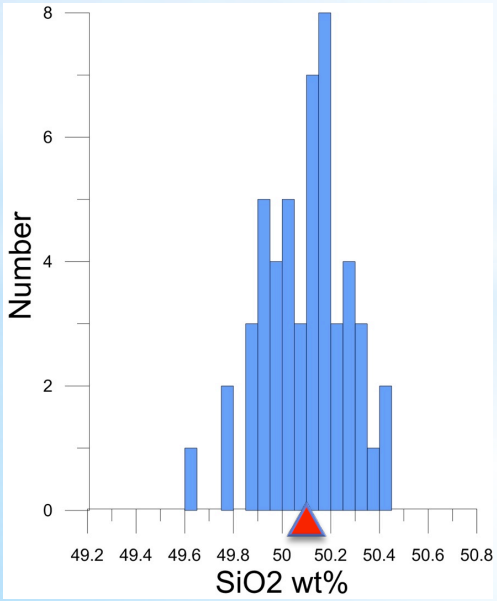
NMNH Kakanui Augite - 54 grains -- 270 analyses

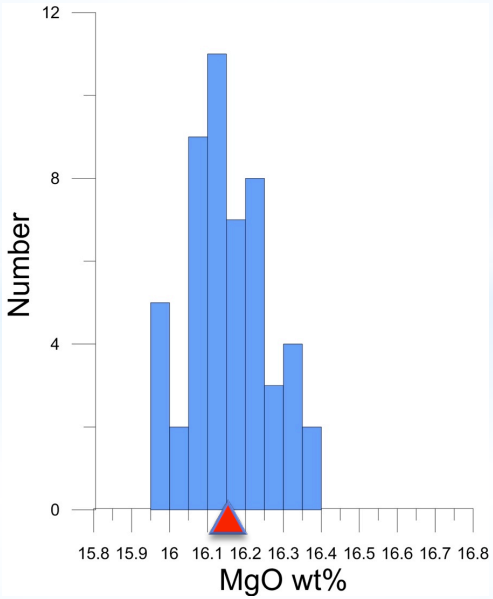


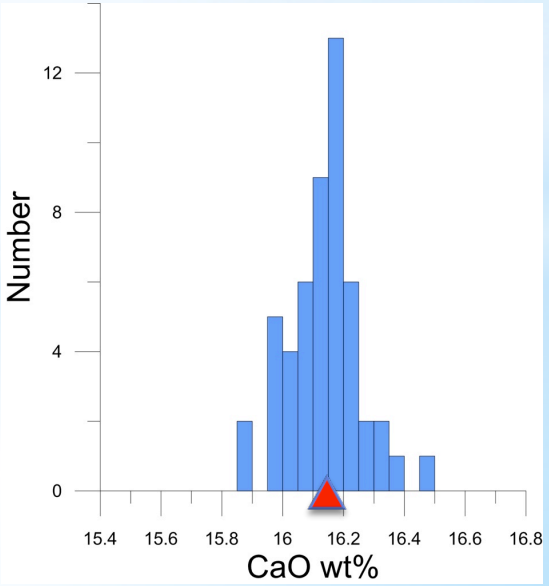




NMNH Kakanui Augite - 54 grains – averages of grains (below)



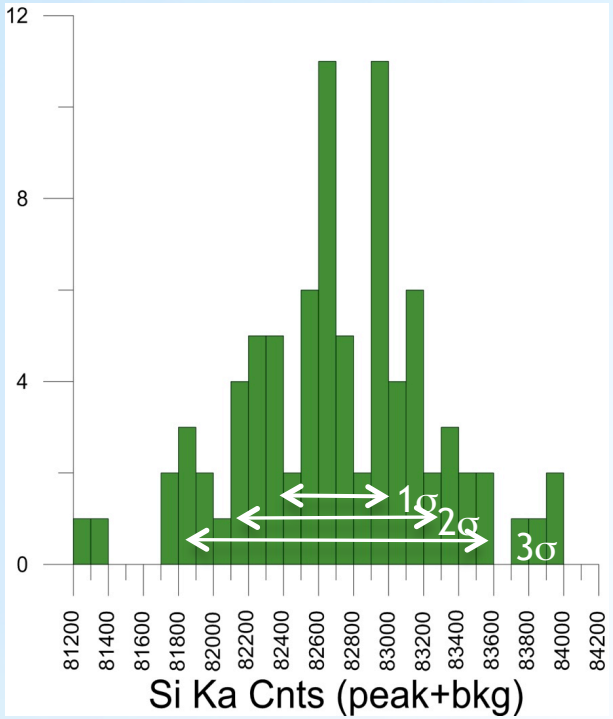


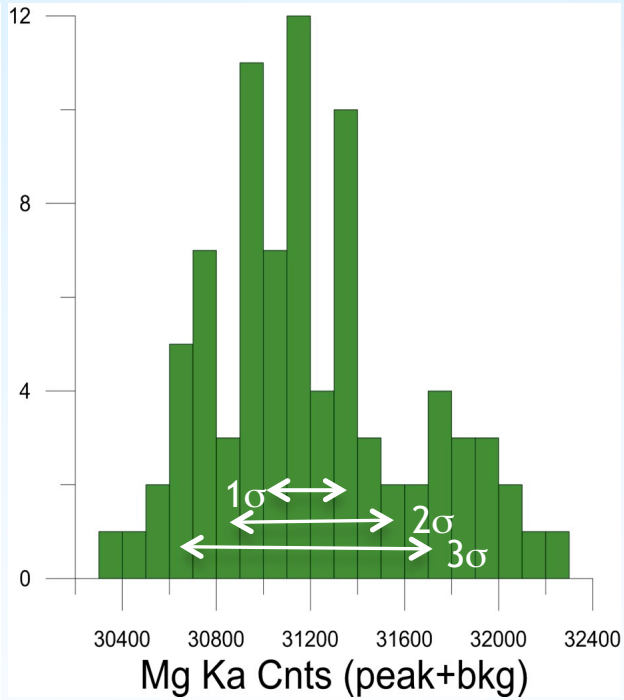


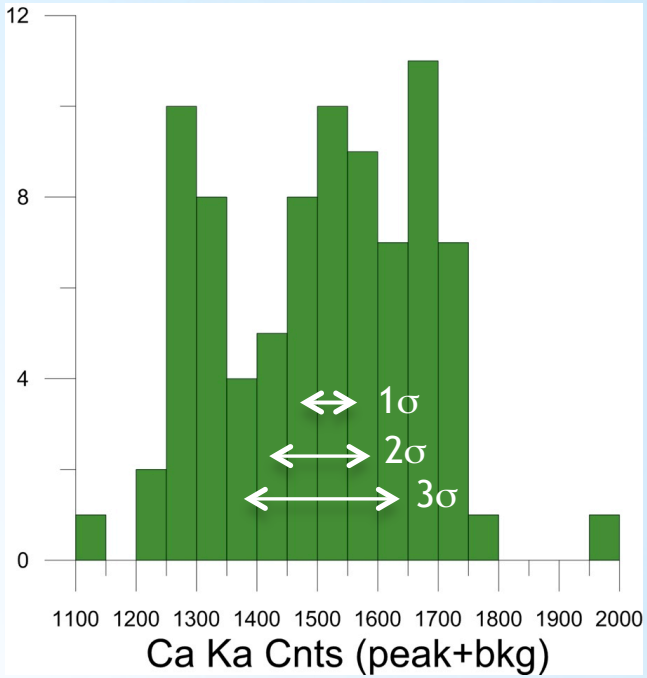
		NMNH Kakanui Augite			54 grains		
	wet chem	wet chem	EPMA	EPMA	EPMA		
	Mason '66	NMNH '80	USGS '85	GeoREM '05	UW2012	UW stds	
→	SiO2	50.73	50.73	49.85	50.39	50.08	K411
	TiO2	0.74	0.74	0.84	0.78	0.81	NMNH Ilm
→	Al2O3	7.86	8.73	8.50	8.72	8.34	K412
	Cr2O3		0.12		0.15	0.15	UW Cr2O3
	FeO	6.77	6.34	6.35	6.31	6.29	UW Fe2O3
	MnO	0.13	0.13	0.08	0.14	0.15	UW Tephro.
→	MgO	16.65	16.65	16.48	16.45	16.15	K411
→	CaO	15.82	15.82	16.07	15.89	16.14	UW Woll.
	Na2O	1.27	1.27	1.45	1.25	1.32	UW Jadeite
		100.38	100.56	99.62	100.08	99.48	
						10.015	on 6 oxygens (all Fe as FeO)

Huebner & Woodruff: "The classical/wet chem analyses have sums that are slightly high…preferred analysis can be recalculated to perfect stoich px. Kak Px is homogeneous [average of 18 pts] wrt all major elements. Should be excellent std and superior known-unknown for major elements in px. It has not been used as much as it deserves."

NMNH Johnstown Hypersthene- 17 grains -- 84 analyses





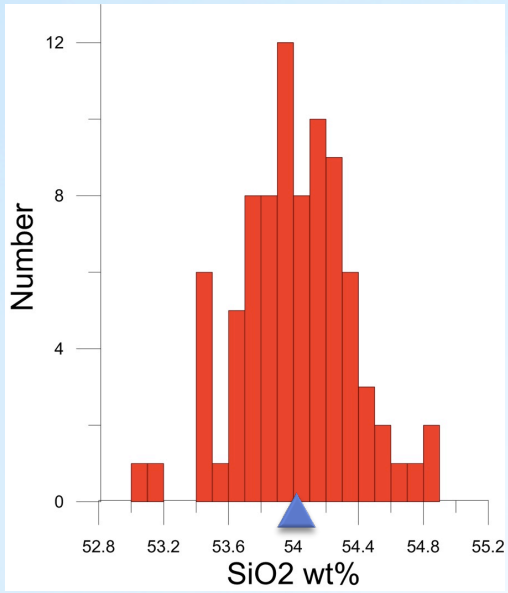


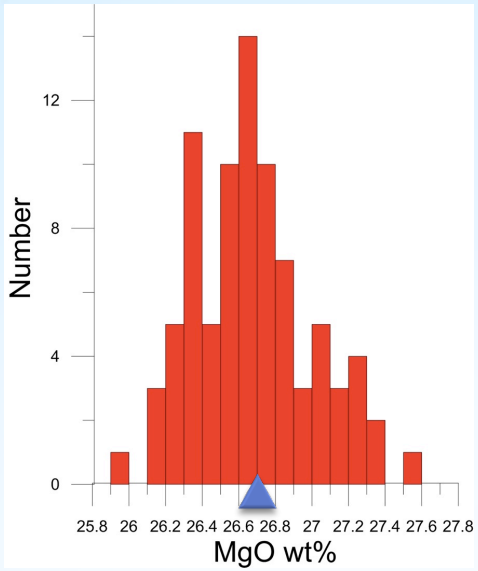
Relative to mean (82709)
1 sigma: 37 of 84 (44%)
2 sigma: 61 of 84 (73%)
3 sigma: 75 of 84 (89%)

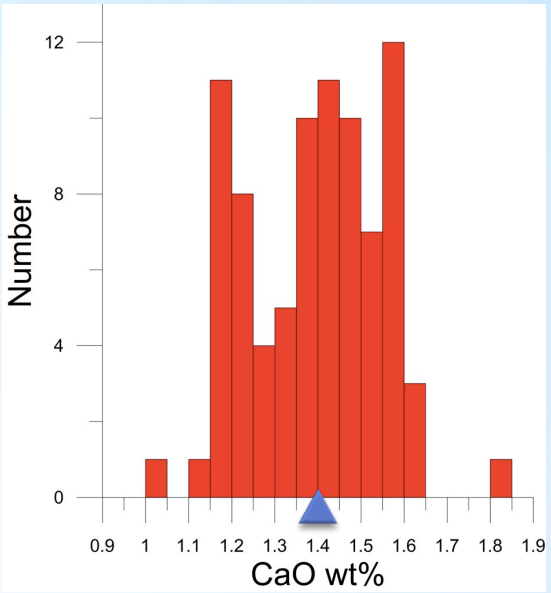
Relative to mean (31195)
1 sigma: 30 of 84 (36%)
2 sigma: 50 of 84 (60%)
3 sigma: 63 of 84 (75%)

Relative to mean (1507)
1 sigma: 16 of 84 (19%)
2 sigma: 27 of 84 (32%)
3 sigma: 37 of 84 (44%)

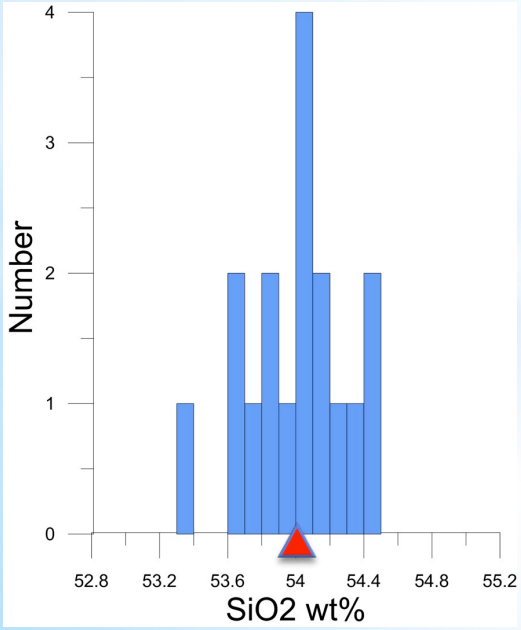
NMNH Johnstown Hypersthene- 17 grains -- 84 analyses

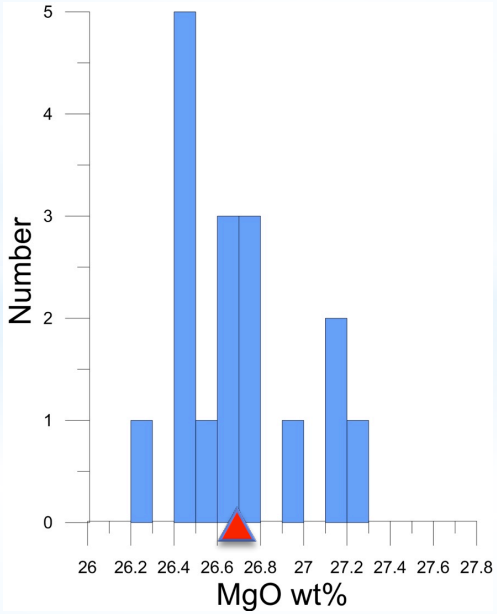


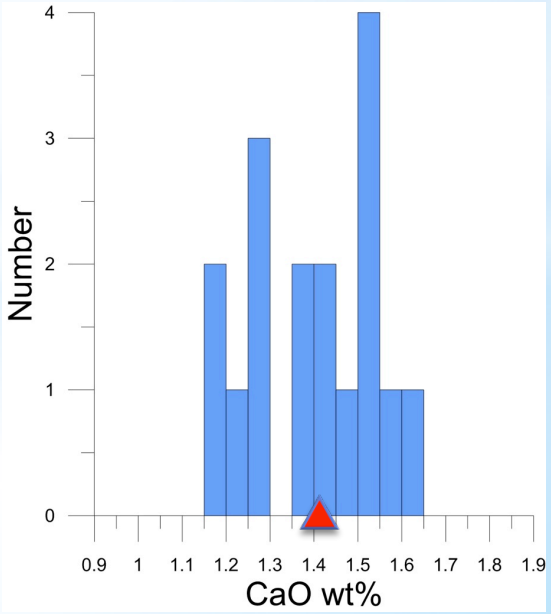




NMNH Johnstown Hypersthene- 17 grains – average of each grain (below)





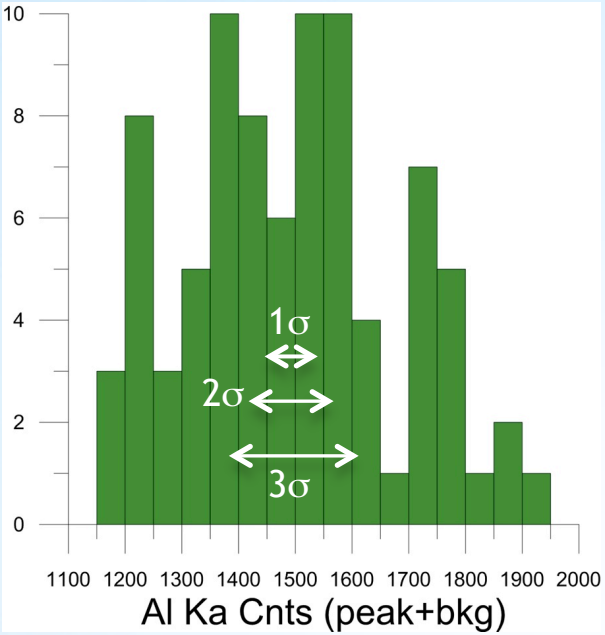


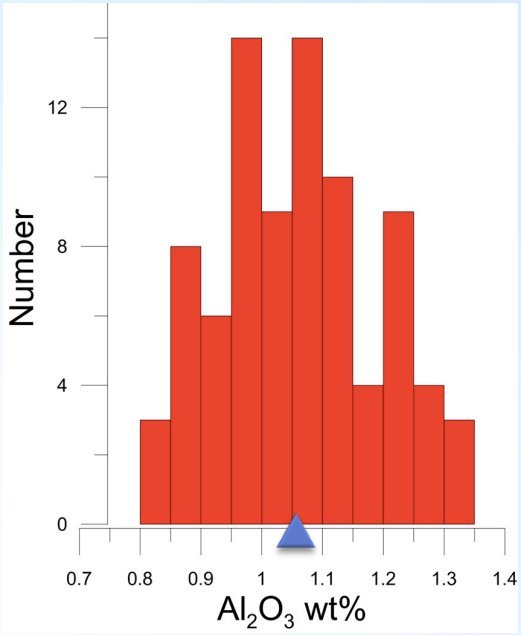
		NMNH Hypersthene			
	Mason '71	NMNH '80	USGS '85	UW 2012	UW stds
SiO2	53.63	54.09	53.19	54.01	K411
TiO2	0.21	0.16	0.09	0.11	NMNH Ilm
Al2O3	0.33	1.23	0.96	1.06	K412
Cr2O3	0.81	0.75	0.74	0.74	UW Cr2O3
FeO	15.66	15.22	14.72	14.90	UW Fe2O3
MnO	0.50	0.49	0.51	0.51	UW Tephro.
MgO	27.23	26.79	26.53	26.68	K411
CaO	1.39	1.52	1.28	1.40	UW Woll.
Na2O	0.13	<.05	0.05	0.01	UW Jadeite
	99.97	100.25	98.10	99.41	

Huebner & Woodruff: "…is very homogeneous [5 pts] wrt Si & only slightly less homogeneous wrt Mg and Fe. Should be a good std for Ca-poor px and may serve to check standardizations for Cr2O3 in silicates, provided sufficient # of pts is collected."

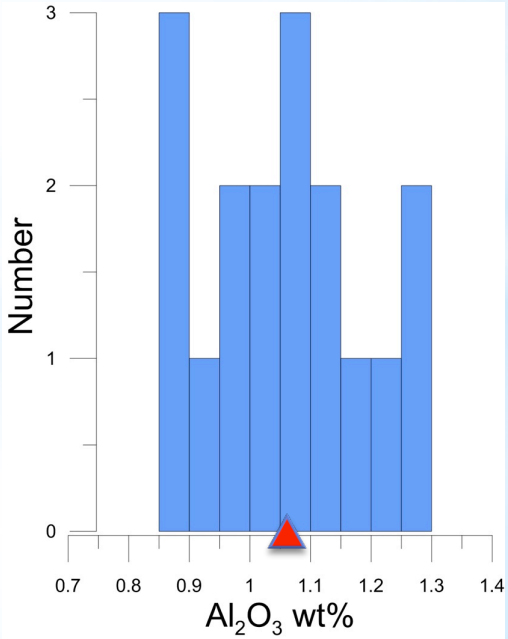
From the NMNH microanalysis standards web page: a caution regarding the NMNH hypersthene: use of Al and Ca may produce "inferior results".

NMNH Johnstown Hypersthene- 17 grains -- 84 analyses

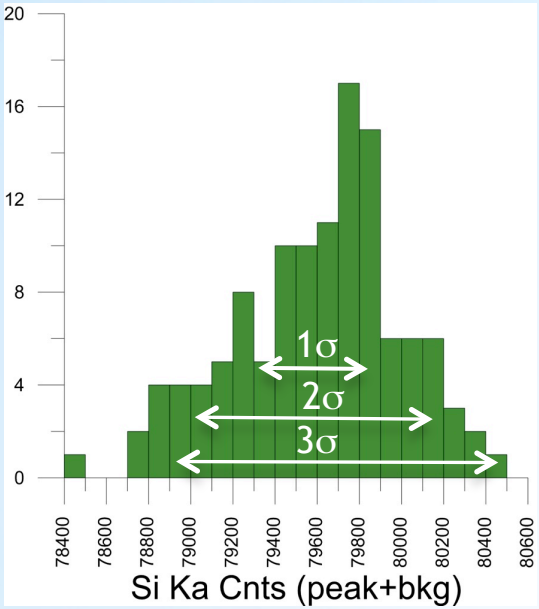


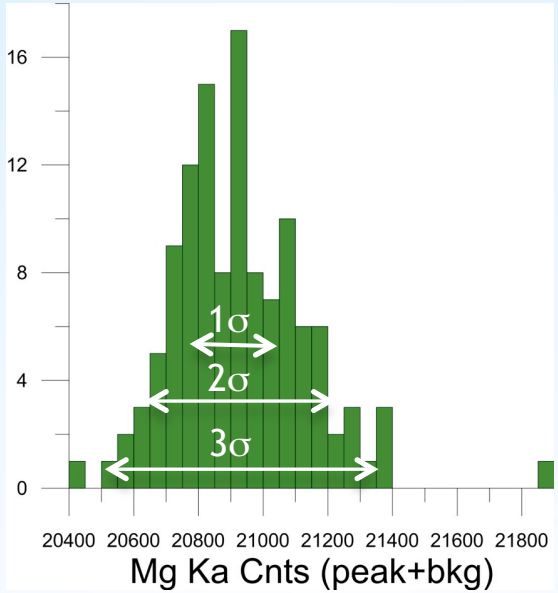


NMNH Johnstown Hypersthene- 17 grains – average of each grain (below)



NMNH Chrome Augite - 24 grains -- 120 analyses

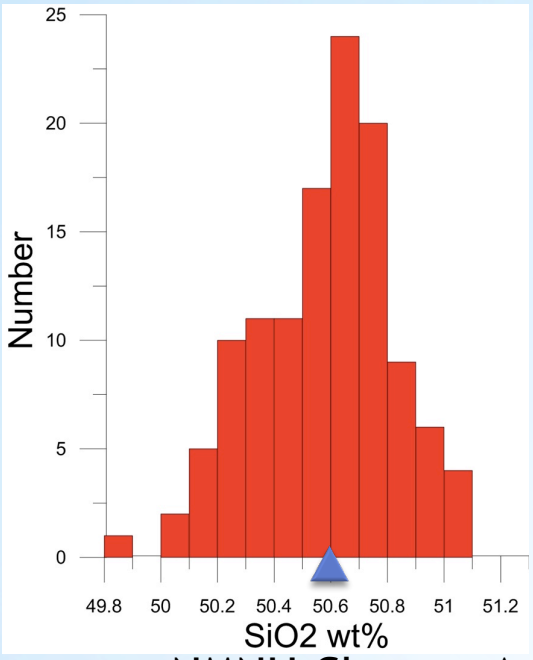


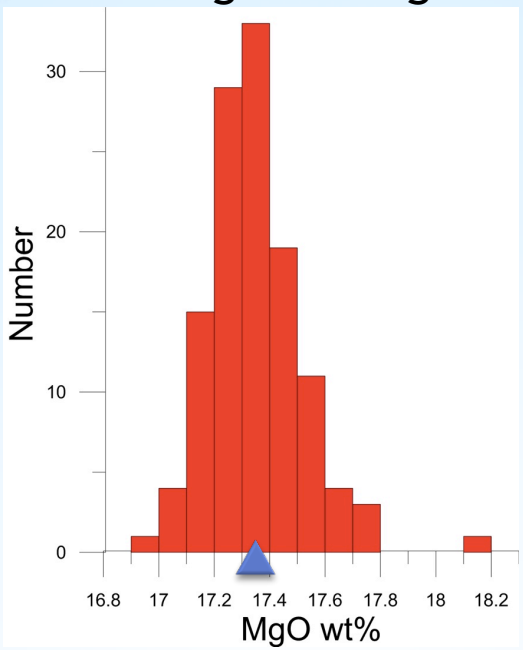


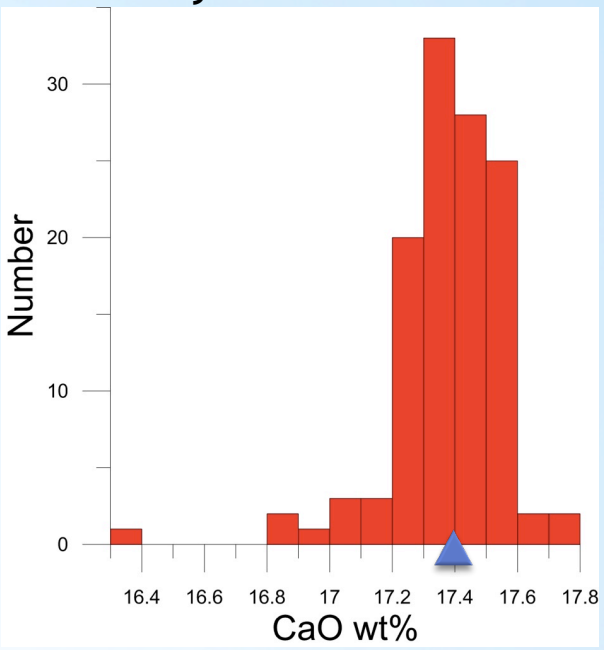
Relative to mean (79604)
1 sigma: 64 of 120 (53%)
2 sigma: 99 of 120 (83%)
3 sigma: 118 of 120 (98%)

Relative to mean (20927)
1 sigma: 62 of 120 (52%)
2 sigma: 105 of 120 (88%)
3 sigma: 115 of 120 (96%)

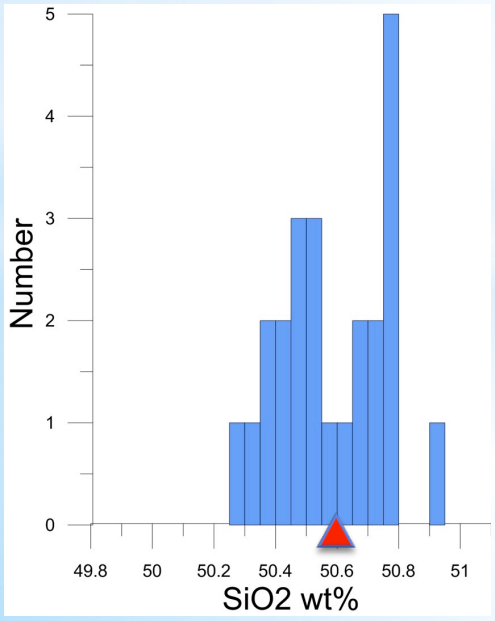
NMNH Chrome Augite - 24 grains -- 120 analyses

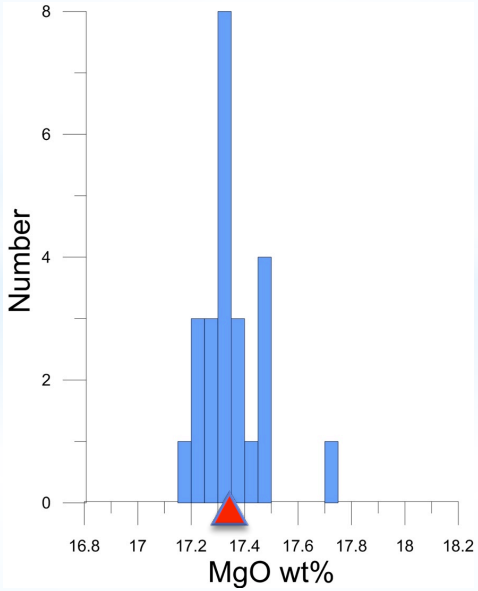


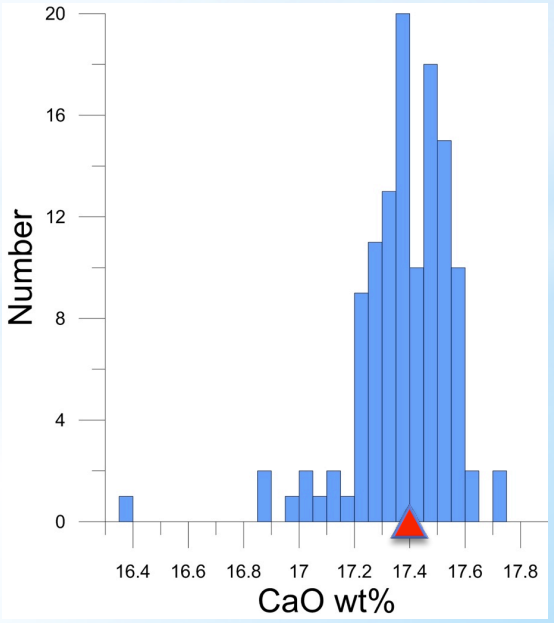




NMNH Chrome Augite - 24 grains – averages of grains (below)

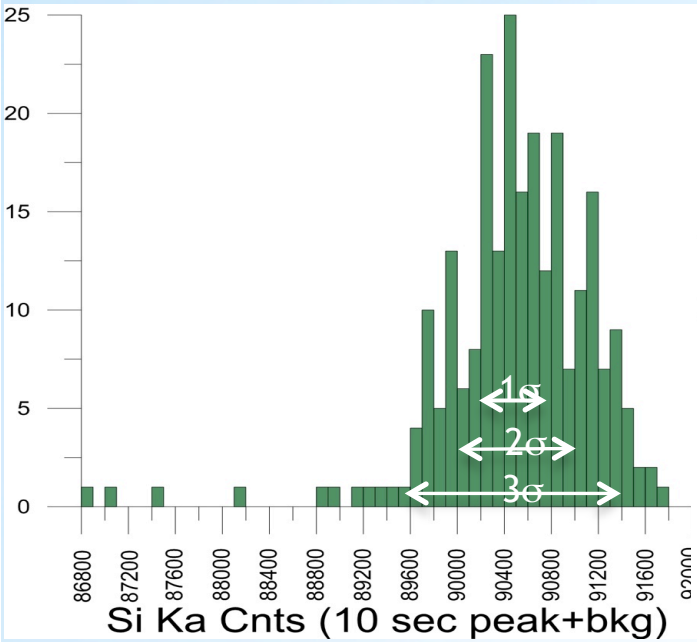


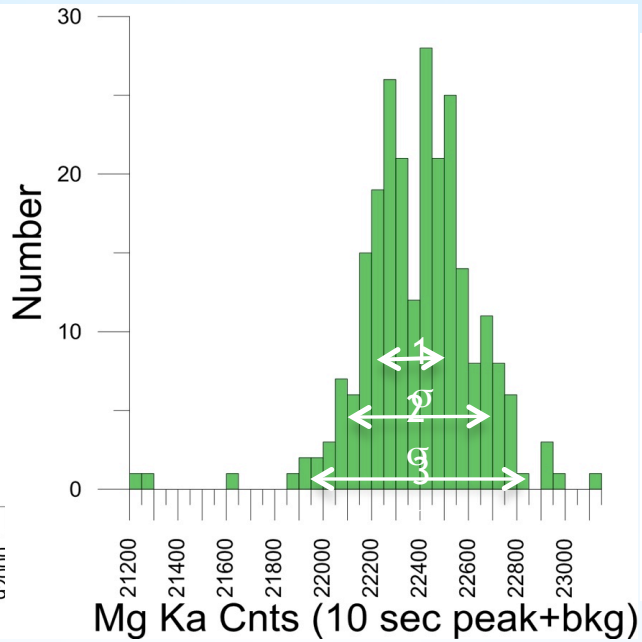


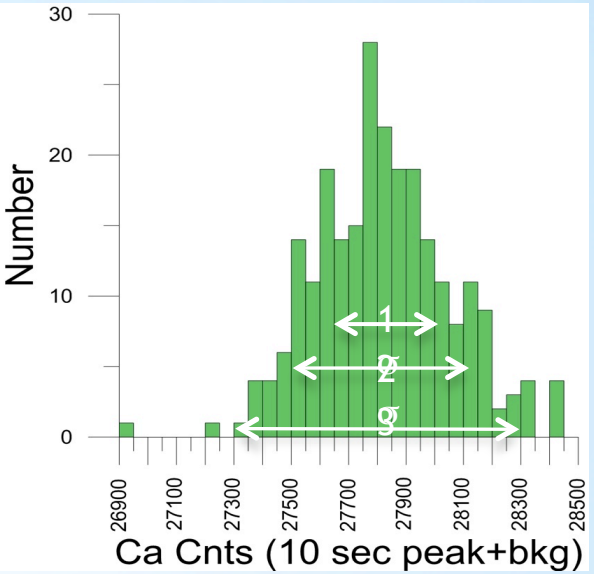


		NMNH Cr Augite	
		24 grains	
	wet chem	EPMA	
	NMNH '87	UW 2012	UW stds
SiO2	50.48	50.58	K411
TiO2	0.51	0.46	NMNH Ilm
Al2O3	8.03	7.60	K412
Cr2O3	0.85	0.90	UW Cr2O3
FeO	4.71	4.65	UW Fe2O3
MnO	0.12	0.13	UW Tephro.
MgO	17.32	17.35	K411
CaO	17.30	17.38	UW Woll.
Na2O	0.84	0.85	UW Jadeite
	100.26	99.96	
		10.001	on 6 oxygens

NMNH Natural Bridge Diopside - 49 grains -- 245 analyses





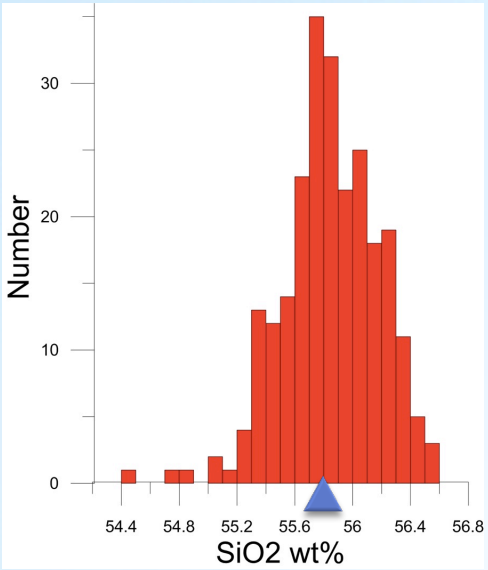


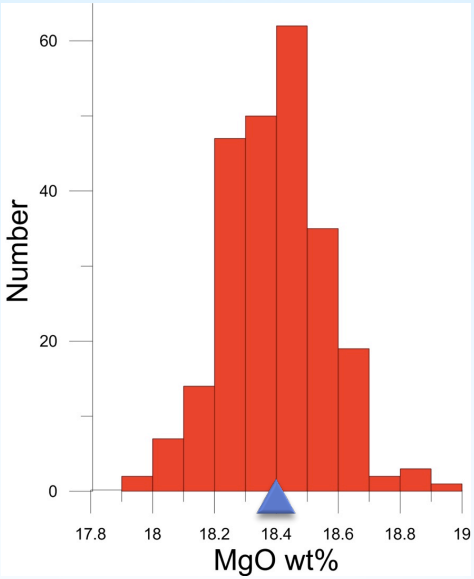
Relative to mean (90498)
1 sigma: 108 of 245 (44%)
2 sigma: 160 of 245 (65%)
3 sigma: 234 of 245 (96%)

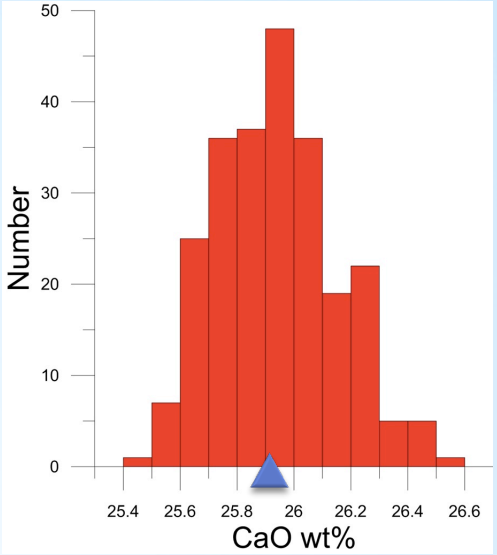
Relative to mean (22394)
1 sigma: 132 of 245 (54%)
2 sigma: 209 of 245 (85%)
3 sigma: 234 of 245 (96%)

Relative to mean (27820)
1 sigma: 119 of 245 (49%)
2 sigma: 210 of 245 (86%)
3 sigma: 237 of 245 (97%)

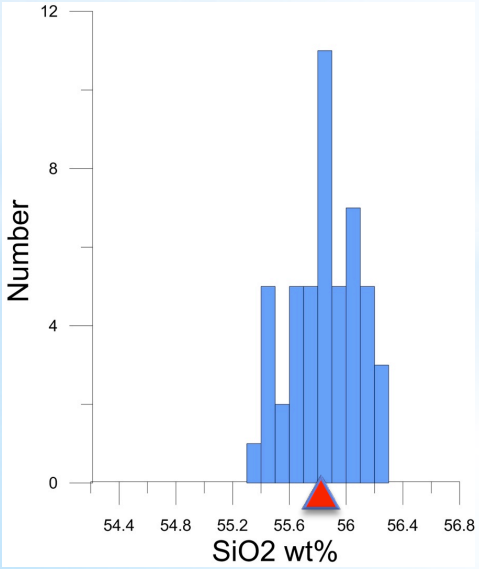
NMNH Natural Bridge Diopside - 49 grains -- 245 analyses

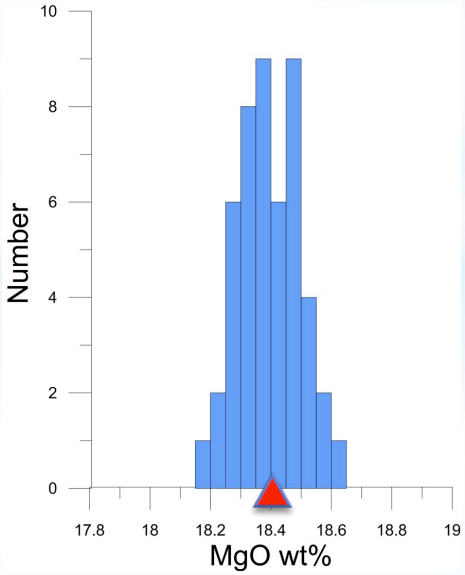


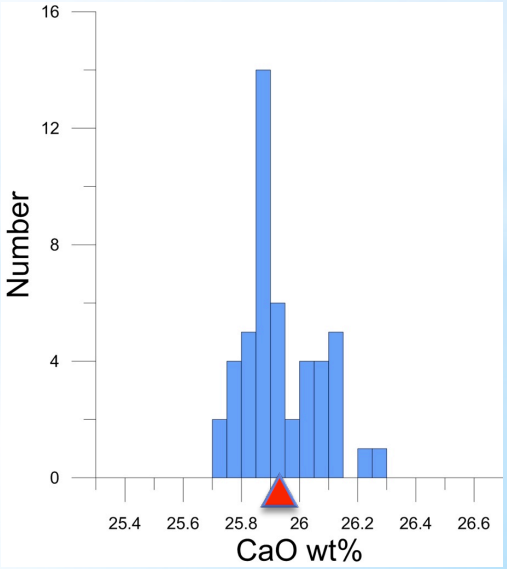




NMNH Natural Bridge Diopside - 49 grains – average of each







		NMNH Diopside		49 grains	
	wet chem	EPMA	EPMA	EPMA	
	NMNH '80	USGS '85A	USGS' 85B	UW 2012	UW stds
SiO2	54.87	55.12	55.06	55.82	K411
Al2O3	0.11		0.16	0.27	K412
FeO	0.24	0.26	0.22	0.23	UW Fe2O3
MnO	0.04		0.02	0.04	UW Tephro.
MgO	18.30	18.07	18.25	18.39	K411
CaO	25.63	26.52	25.76	25.93	UW Woll.
Na2O	0.34		0.17	0.18	UW Jadeite
	99.53	99.97	99.68	100.89	
				10.004	on 6 oxygens

Huebner & Woodruff: "…Despite [this diopside's] successful use as a reference material, inspection of formula suggests Si value too low. However, addition of Si would cause wt% summation to rise to 101% and create excess of tetrahedral cations, suggesting Si alone is not the only problem with the analysis. Pending reanalysis, the diopside should be used only with caution."

Concluding thoughts:

That it is ill advised to

Use a small number of grains (1!) of NMNH pyroxene reference materials assuming they are exactly the published chemical composition…

UNLESS those specific grains in one's standard mount have been "checked"

How would one check them????

→ Acquire ~100 counts off of ~20 grains of the standard in question, to determine the precise composition of the one grain of that standard in your mount. This might be considered "traceability" to the original reference material.

For this to happen, a mechanism for loaning out for short periods of time a block of said grains…. With a deposit of $ to ensure it's return within a reasonable period of time (10 days?).

See me if you are interested.

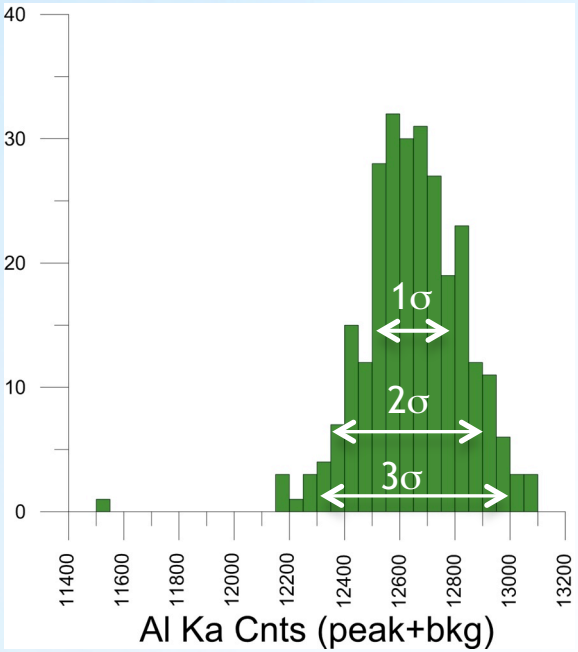
Some next steps for this specific project

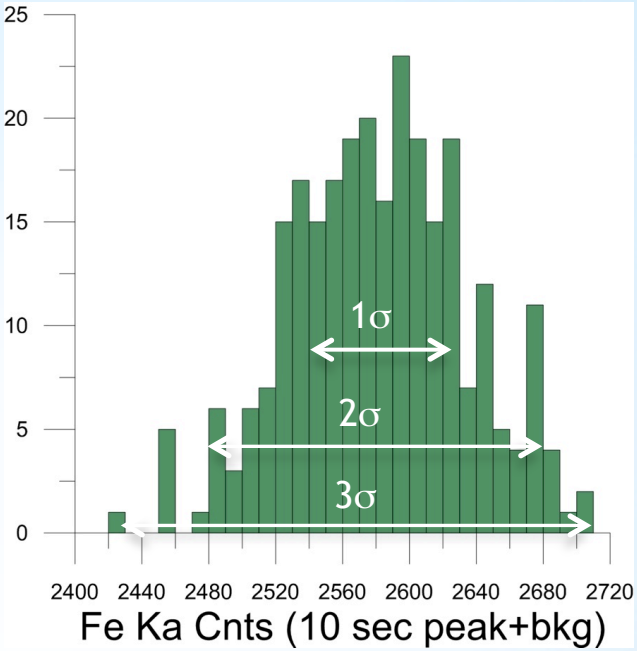
1. Increase counts by 4-9x to double-triple precision

2. Use same process of evaluation for K411 and K412 glasses (which are virtual pyroxene compositions)


NO
PARKING

NMNH Kakanui Augite - 54 grains -- 270 analyses

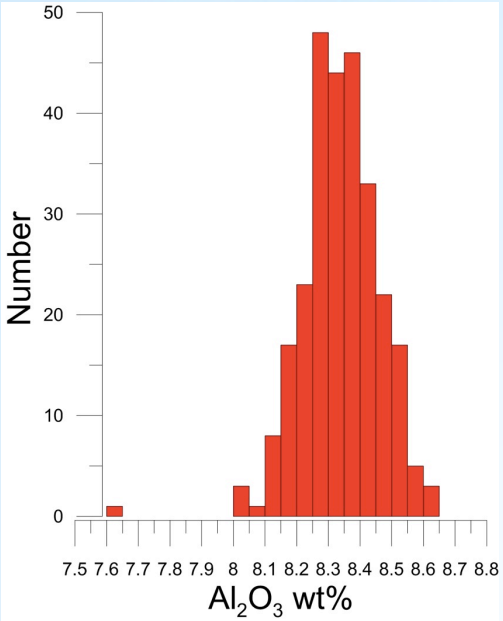


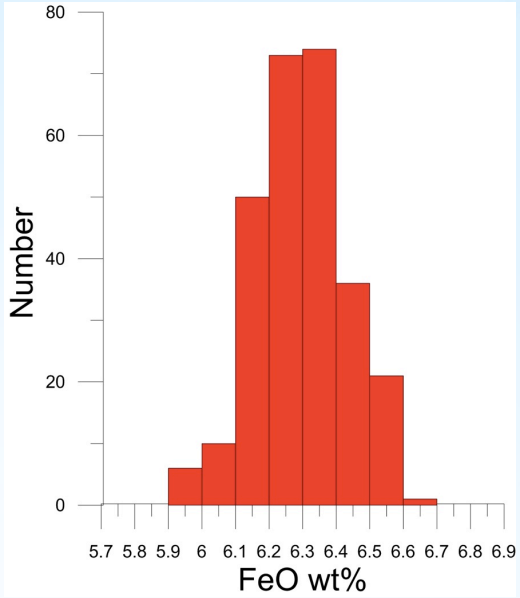


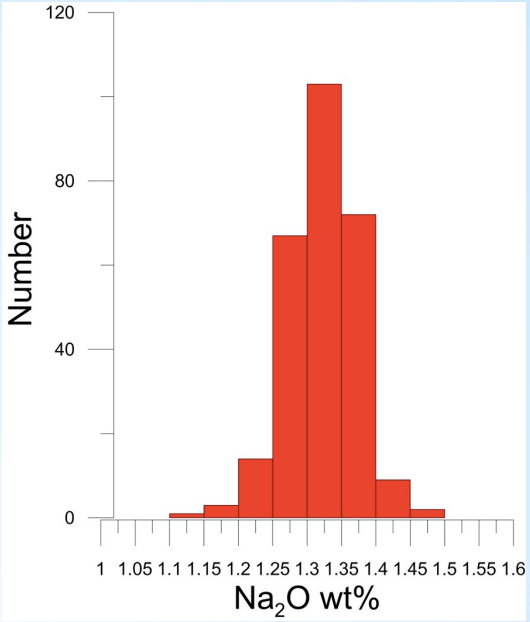
Relative to mean (12649)
1 sigma: 132 of 270 (49%)
2 sigma: 218 of 270 (81%)
3 sigma: 255 of 270 (94%)

Relative to mean (2582)
1 sigma: 182 of 270 (67%)
2 sigma: 259 of 270 (96%)
3 sigma: 270 of 270 (94%)

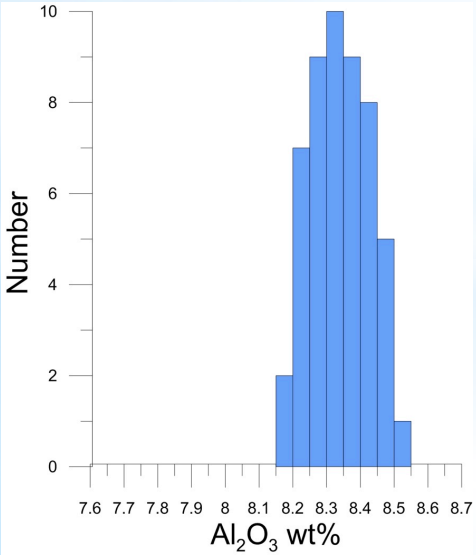
NMNH Kakanui Augite - 54 grains -- 270 analyses

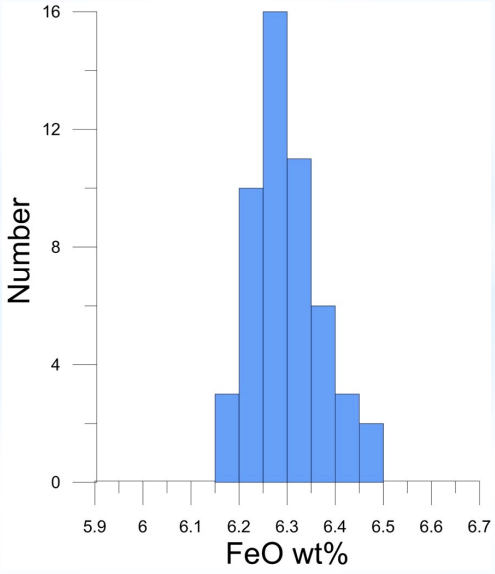


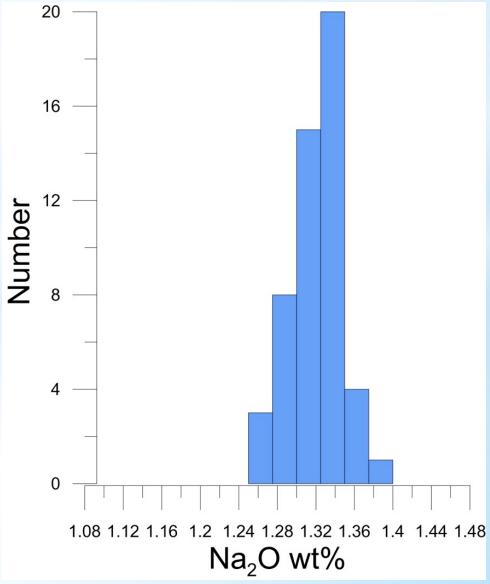




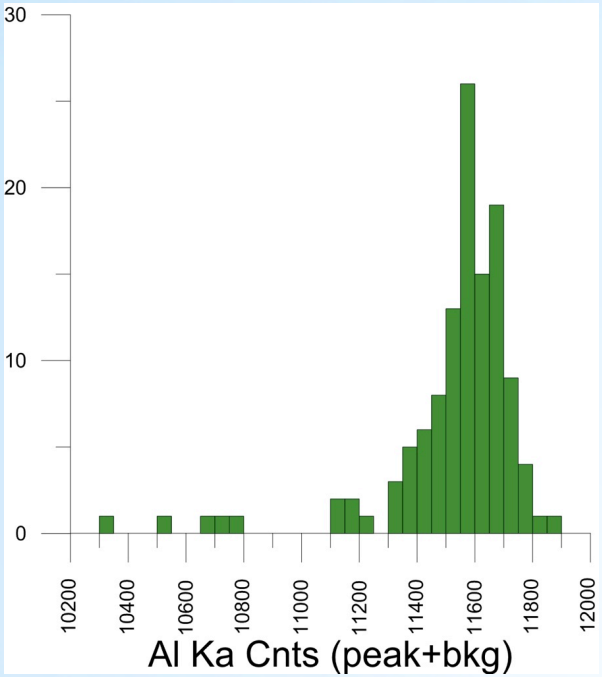
NMNH Kakanui Augite - 54 grains – averages of grains (below)

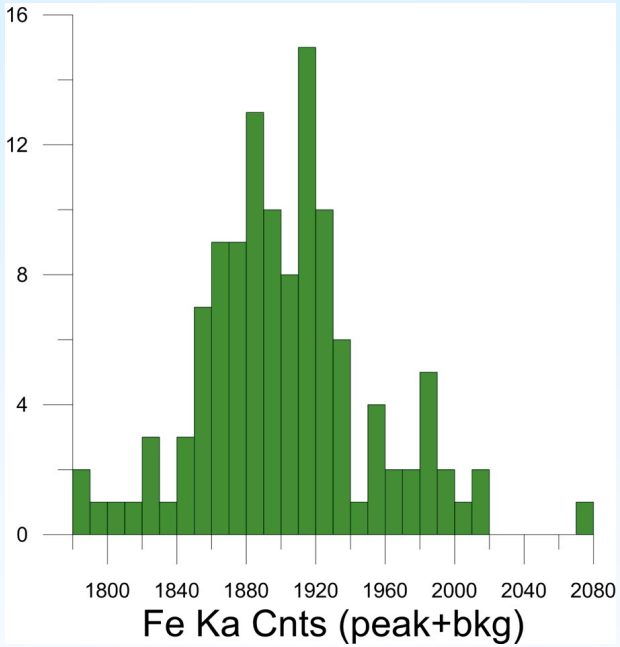


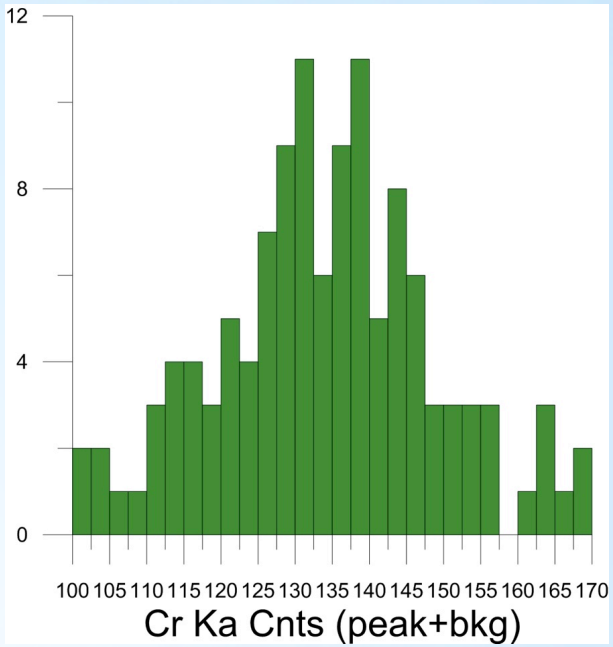




NMNH Chrome Augite - 24 grains -- 120 analyses







Relative to mean (11530)
1 sigma: 66 of 120 (55%)
2 sigma: 103 of 120 (86%)
3 sigma: 110 of 120 (92%)

Relative to mean (1905)
1 sigma: 81 of 120 (68%)
2 sigma: 110 of 120 (92%)
3 sigma: 118 of 120 (98%)

Pyroxenes are one of key rock forming minerals, and Eugene Jarosewich and NMNH co-workers developed several standards in 1970s.

Reference Samples for Electron Microprobe Analysis*

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Department of Mineral Sciences
Smithsonian Institution, Washington, D.C. 20560

The chemical analyses of twenty-six minerals, four natural glasses, and one synthetic glass prepared for use as microprobe reference samples are presented. New chemical analyses of minerals and revised analyses of several minerals published previously are included. Details of sample preparation are described and the homogeneity of the samples has been tested by the homogeneity index.

Microprobe analysis, a technique that is now well established, widely used, and capable of high-quality analyses, is an essential part of modern mineralogical and petrological studies. As with all comparative instrumental techniques, however, it requires well-characterized reference samples. Prime prerequisites for microprobe reference samples are homogeneity at the micron level and availability in reasonable quantities for classical wet chemical analysis. Either prerequisite is usually easily satisfied by itself but together are difficult to achieve.

Lack of proper documentation is a serious problem with some minerals used as microprobe reference samples. Even if well-described minerals are from the same locality or are obtained from a reliable source, they may vary in chemical composition. Therefore, a mineral sample intended as a reference sample should be carefully selected and used only when analytical data on the specific specimen are available. Since natural materials fulfilling all the above requirements are not always available, synthetic minerals and glasses have occasionally been prepared as substitutes. Again, homogeneity of these materials should be checked and chemical analyses performed. The assumption that a nominal composition is correct is certainly not always valid.

In general, the most reliable microprobe analyses are obtained when a reference sample of composition and structure close to that of the unknown is used because the matrix and possible wavelength shift effects are minimized and only small corrections are needed. It is generally accepted that, regardless of the type of correction used, results corrected by more than 10 percent should be viewed with caution. Difficulties with correction procedures in the $MgO-Al_2O_3-SiO_2$ system have been pointed out by Bence and Holzwarth (1). Similar discrepancies have been observed by other probe users.

All minerals and glasses described here, except one, are of natural origin. Most specimens were obtained from Smithsonian collections and were selected either in conjunction with specific projects or for use in silicate analyses in general. The compositions of the specimens except the gahnite have been published (2).

PREPARATION OF REFERENCE SAMPLES

When a sufficient quantity (at least 2 g) of a mineral or glass is available for use as a microprobe reference sample, a thin section is prepared for microscopic examination. This section is then traversed several times in the microprobe to make an approximate determination of the homogeneity of several major elements. If these preliminary results are favorable, the material is gently crushed, sized usually between 20 and 80 mesh, and further purified using either a heavy liquid separation, a Franz magnetic separator, or both. In some instances cleaning with a suitable acid is also useful. As a final step, the material is examined under a low-powered microscope and any remaining foreign grains are removed by hand. The purified grains are again checked by microprobe for homogeneity (sigma ratios) within and among grains (Table 2). Finally, a chemical analysis using classical methods (3,4) is performed on the same separate that is to be used as the reference sample.

DISCUSSION

Data for newly analyzed minerals, earlier published analyses, and revised analyses for several minerals that have been in use for some time are presented in Table 1. Much cleaner mineral separates of the hypersthene from the Johnstown meteorite and of the olivine from the Springwater meteorite have been reanalyzed. The TiO_2 content of the Kakanui hornblende has been redetermined.

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