



## An Investigation of "San Carlos Olivine": Comparing USNM-distributed Material with Commercially Available Material

John H. Fournelle

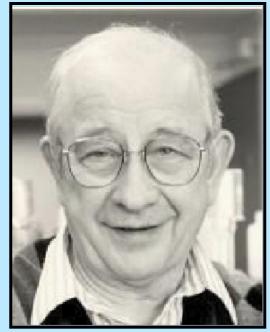
Eugene Cameron Electron Microprobe Lab Department of Geoscience University of Wisconsin Madison, Wisconsin In 1960-70s there was an explosion of e-probes being built and sold. Many early applications had been in metals and alloys. As it became tool of interest to geologists, the need for mineral and glass standards increased.



Gene Jarosewich and co-workers at the Dept of Mineral Sciences of the Smithsonian's Natural History Museum began a project to identify EPMA geological standards. Today many labs use the USNM San Carlos Fo90.1 standard which is distributed as USNM 111312/444.

There is common acceptance that this is an excellent standard.

Composition and statistics for this and other standards were published as Jarosewich et al, *Geostandards Newsletter* 4 (1980), 43; errata, 4 (1980) 257.



## Eugene Jarosewich 1926-2007

Reference Samples for Electron Microprobe Analysis

. JAROSEWICH, J.A. NELEN AND Julie A. NORBERS

Department of Mineral Sciences Smithsonian Institution, Washington, D.C. 2056

The observed insignee of turniy-siz winerale, four neuron jaceses, and one approximate plane prepared for use as eleroprobe reference applied any properties. Here indered any applies of published previously are included. Details of applie preparation are described and the herogemerky of the samples has been tested by the komogenety inice.

unhown is used because the matrix and possible wavlength shift forcis are ninsized and only accepted that, regulated, it is generally correction used, results convected by more than 10 percent should be viewed with caution officialises with correction procedores in the officialises with correction procedores in the officialises with correction procedores in the officialise with correction procedores in the percent definition of the processing of the percent matrix of the percent of the percent of the percent matrix of the percent of the percent of the percent matrix of the percent of the percent of the percent matrix of the percent of the percent of the percent matrix of the percent o

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several minerals that have been in use for a time are presented in Table 1. Much died mineral separates of the hypersthese from Johnstown meteorite and of the oliving from Springvater meteorite have been reanalyzed. TiOg content of the Kakanui hornblende has t redstarmined.

Newsletter, Vol. 4, Nº 1, Avril 1980, p. 43 à 47

Natural Forsterite-rich olivine, of mantle xenolith origin, is a standard for Mg and Si in many geoscience electron microprobe labs.

Forsterite (abbreviated Fo) is the  $Mg_2SiO_4$  component of olivine; Fo numbers are atomic %.



TAB	TABLE 1. Range of olivine compositions										
Fo#	Mg wt%	Fe wt%	Si wt%								
87	28.41	9.75	18.86								
88	28.85	9.04	18.94								
89	29.31	8.32	19.02								
90	29.76	7.60	19.11								
91	30.22	6.87	19.19								
92	30.69	6.13	19.27								

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## How this study came to be:

In 2008-9, a coincidence of two different researchers at the University of Wisconsin:

• A SIMS researcher measuring d<sup>18</sup>O of meteorite olivines, using "San Carlos olivine" as a well-characterized oxygen isotope reference material



## How this study came to be:

## And

A lunar researcher characterizing various silicate minerals for cosmic ray irradiation experiments, with a large number being described as San Carlos olivine – "Peridot" purchased from gem dealers





The EPMA compositions I found from the grains of "San Carlos olivine" being used as SIMS oxygen standards, mounted with the unknown olivines, differed enough from the published USNM values to make me wonder what was up.

Three 1-2 mm crystals from the vial supplying those used as SIMS oxygen standards were analyzed by EPMA for Si, Mg and Fe.

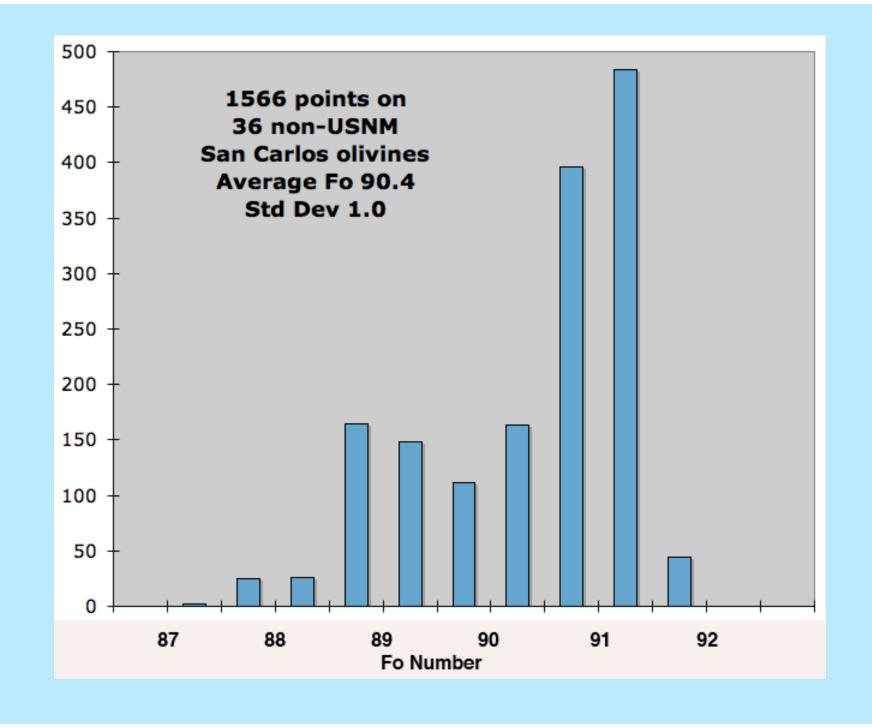
Wt% oxides	Published USNM	SIMS "San Carlos"
SiO <sub>2</sub>	40.81	40.66
MgO	49.42	48.72
FeO	9.55	10.49
"Fo #"	90.1	89.2

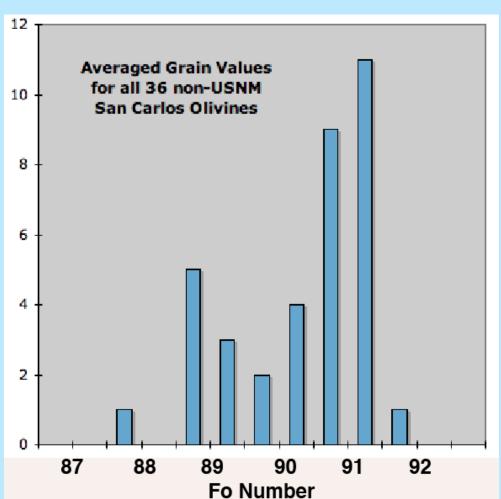
Study of the Gem "SC olivine" for lunar irradiation study

Thirty-six ~1 cm-size crystals acquired by the researcher from a commercial gem dealer were analyzed\* (1566 spot analyses; 30-40 points per crystal)

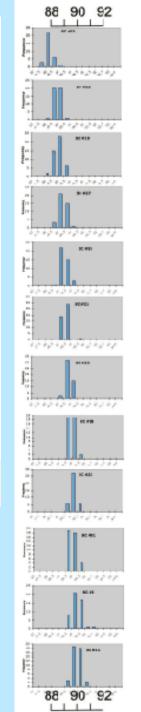
A range of compositions from <Fo88 to <Fo92 was found.

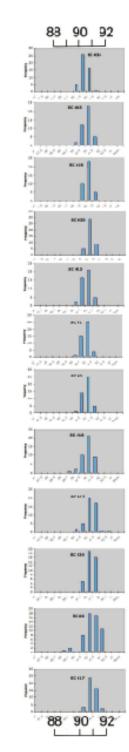
\*15 kV, 20 nA, fixed spot, 10 sec each bk & bkg, measuring Mg, Si, Ca, Mn, Fe, Ni with UW-Madison SX51

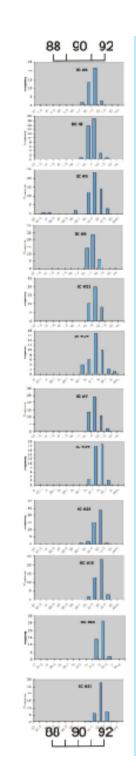


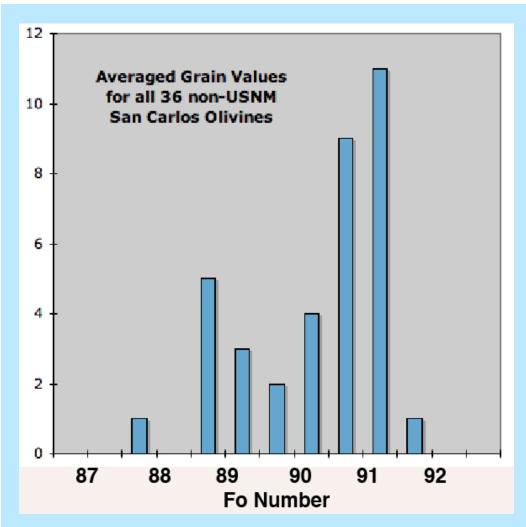


Plotting each grain average (above) or each grain histogram (right) shows while each grain fairly homogeneous, there is a significant range of compositions between grains









Plotting each grain average (above) or each grain histogram (right) shows while each grain fairly homogeneous, there is a significant range of compositions between grains The earlier crystals apparently are excellent oxygen isotope standards (though are Fo89)
Any of these could be used as EPMA

standards ONLY if they were first vetted carefully to determine each's chemical composition. A clear benefit, if shown to be homogeneous, is the large size. The range of compositions in the non-USNM San Carlos crystals lead to the logical question

"What is the range of variability possible in the individual grains of USNM San Carlos olivine reference material?"

This was a concern of Gene Jarosewich and co-workers:

## Reference Samples for Electron Microprobe Analysis.

E. JAROSEWICH, J.A. NELEN AND Julie A. NORBERS

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

The obmical analyses of twenty-siz mine-match from restance glasses, and one symbolic scales from restance glasses, and not symbolic sempler are presented. New chemical analyses of minerals and revised analyses of several minerals performed and the second neity of the samples has been tested by the homo-genetic states.

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 Lucies. As with all comparative instrumental techniques.

samples. Frime prerequisites for microprobe refe-rence samples are homogeneity at the micron level and availability in reasonable quantities for classical wet chemical analysis. Either prerequi-site is usually easily satisfied by itself but together are difficult to achieve.

tagether are difficult to anhieve. Lack of proper documentation is a serious problem with nome minerals used as microproble efference samples. Even if well-described minerals are from the same locality or are obtained from areliable source, they may vary in chemical compation. Therefore, a mineral sample chily selected and used only when smalytical isrs on the specific specient are available, Since netural materials fulfilling all the above requirements are not sluyag available, synthetic merstals and ginsee have costainally been requirements are not sluyag available, synthetic many and ginsee have costainally been requirements are not sluyag available, source these materials should be checked and chemical analyses performed. The assumption that a notinal composition is correct is certainly not sluyagy valid.

In general, the most reliable microprobe analyses are obtained when a reference sample of composition and structure close to that of the

Reprinted by permission of Smithaonian Institution Press From Smithaonian Institution Contributions to the Earth Sciences, Number 22: "Electron Microprobe Refe-rance Samples for Mineral Analyses", Rugene Garoawich, Joseph Nelm and Julie Norberg: pages 68-72. Washington, D.G.: Smithaonian Institution Press, 1979.

Geostandards Newsletter, Vol. 4, Nº 1, Avril 1

unknown is used because the matrix and possible wavelength shift effects are mininged and only meals corrections are meeded. It is generally generally and the shift of the shift of the shift of correction used, results corrected by more than 0.0 percent should be viewed with coation. Difficulties with correction procedures in the  $M(O^{-1}A(O^{-1}G))$  system have been pointed out by Bonce and Bolzwarth (1). Similar discrepancies have been cheaved by other probe users.

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

## PREPARATION OF REFERENCE SAMPLES

20 and 80 mes a heavy liq separator, or with a suital step, the ma ered microsoc are removed again checke (sigma ratios

Springwater a TiO<sub>2</sub> content

THEFARILUE OF RETRICES SAMPLES When a sufficient quantity (at least 2 g) of a mineral or giass is available for use as a microprobe reference sample, a thin section is prepared for microscopic examination. This microscopic to microscopic examination. This microscopic to microscopic examination of the theorem of the section of the homogeneity of several major cleants. If these preliminary results are favorable, the material is gonity cruthed, sized usually harmone 20 and 80 mms

1 corrections

### Geostandards Newsletter, Vol. 4, Nº 1, Avril 1980

(signs ratios Finally, a: methods (S.A) [Page 44] In Table 1 appearing in the paper "Reference samples for electron r that is to be larosewich, J.A. Helen and J.A. Norberg, the footnote'reference number S 112716". Starting from this "basilici" [Jar5". It should read as "Glass, B 112716". Starting from this "basilici" [Jar5". It should read as "Glass, B 112716". Starting from this "basilici" footnote numbering. Ito 14, is re units of the start of the sta

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standards Newsletter, Vol. 4, Nº 2, Octobre 1980, p. 257 à 258

Table 2. Sigma ratios (homogeneity indices) for all analyzed grains. Index for least homogeneous grain in parenthese

lineral	\$102	A1203	Fe0	MgD	CaO	Na <sub>2</sub> O	K20	T102	P205	MnD	Cr203	Zn
northite	0.96	0.81			0.92	1						
morthoclase	(1.51) 1.09	(1.26) 0.79	4	S	(1.23)	1.11						
spatite (Fluorapatite)	(1.60)	(1.38)			1.02	(1.57)			0.97			
lugite	0.99	0.97	0.84	0.94	(1.51)				(1.51)			
Senitoite		(1500)	(1.20)	(1.23)	(1.25)							
Chronite		1.00	1.01 (1.66)	1.11 (1.50)							1.12 (1.49)	
Corundum			(1100)	11.507							(1147)	
Diopside	1.07			0.97 (1.50)	0.95							
Fayalite	0.95		1.14 (2.32)							1.03 (1.58)		
Cahnite -		1.06										1
Garnet, 87375	0.89	1.01 (1.42)	1.06	1.01 (1.49)	0.86							
Garnet, 110752	0.88	0.94 (1.28)	0.90 (1.20)	1.00	0.87 (1.47)							
Glass, 111240/52 VG-2	0.94	0.89	0.86	0.96	1.00 (1.27)	1.05						
Class, 113498/1 VG-A99	0.94	1.10 (1.46)	1.07	0.92	0.93	1.15		0.97				
Glass, 113716	1.12	1.00	0.94 (1.34)	1.01 (1.36)	0.83	1.25						
Glass, 72854 VG-568	0.97	1.00				2.31 (3.45)	0.98					
Glass, 2213	1.05	0.87	1.01		1.05							
Hornblende, Arenal	1.07	0.97	1.12 (1.36)	1.11 (1.67)	1.01	0.98						
Hornblende, Kakanui	1.01 (1.38)	1.00 (1.24)	1.30 (1.67)	1.16 (2.38)	1.10 (1.73)	1.15 (2.15)	0.90 (1.29)	1.01 (1.49)				
Hyperstheme	1.07		1.10 (1.37)	0.93 (1.27)								
Ilmenite			1.72 (3.60)					1.34 (1.98)		1.21 (1.53)		
Magnetite			0.84									
Microcline	0.94 (1.13)	1.04 (1.52)	100				1.09 (1.59)					
Olivine (Fogg), San Carlos	0.81 (1.13)		0.90 (1.29)	1.00 (1.64)								
Olivine (Fogg), Springwater	0.96 (1.42)		1.06 (1.51)	0.99 (1.12)								
Omphacite	0.89 (1.23)	0.95 (1.64)	0.96 (1.87)	0.91 (1.30)	1.02 (1.51)	0.99 (1.31)						
Osumilite	0.96 (1.90)	1.27 (1.89)	1.20 (2.19)	1.00 (1.70)			1.13 (1.64)		Analy	vsts:		
Plagioclase (Labradorite)	1.09 (1.49)	0.95 (1.40)			1.04 (1.65)	0.91 (1.33)					1.2	
Pyrope	1.08 (1.46)	0.95 (1.20)	1.09 (1.59)	0.98 (1.21)	0.97 (1.18)					. Jaros mithson		
Quartz	-								2. J.	. Nele	n, De	par
Scapolite (Meionite)	0.99 (1.29)	0.95 (1.41)			0.91 (1.16)	0.96 (1.41)			3. J.	North	ian In erg, D	

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   E. Kiss, Department of Geophysids and Geoche-mistry, Australian National University
   J.J. Fahey and L.C. Peck, U.S. Geological Survey
- Survey

### Sources:

- 1. P. Desautels, J.S. White, Jr., and P.J. Dunn, Department of Mineral Sciences, Smithsonian
- Institution 2. B. Mason, Department of Mineral Sciences,

- B. Mason, Department of Mineral Sciences, Smithsonian Institution
   G. Switzer, Department of Mineral Sciences, Smithsonian Institution
   R.G. Dyeck, L.B. Wiggins and C.A. Francis, Harvard University
- 5. W.G. Melson, Department of Mineral Sciences,
- Smithsonian Institution 6. T.L. Wright, U.S. Geological Survey 7. H. Staudigel, Massachusetts Institute of Tech-
- R. S. Clarke, Jr., Department of Mineral Sciences, Saithconian Institution
   J.H. Berg, Northern Illinois University

Even after the most careful preparation of the reference sample, a grain of accessory mineral or matrix may remain in the sample, which, in the course of preparation of the reference sample discs, could be included with the reference sample. Occasional grains of the section of the sample discs, and the sample because of heterogeneity. These problems can never be totally eliminated. The user should be aware of the possible presence of such "impuri-ties" and make a through check for them. For example, occasional grains are found that are there in output and the sample of the sample of the insamgeness than usual in lake County Even after the most careful preparation of lower in sodium than usual in Lake County plagioclase. Infrequent inclusions in the glasses 72854, 111240/52, 113498/1 and 113716 are also found

The overall homogeneity of each sample was determined using the criterion given by Boyd et al. (5) whereby the sample is considered to be homogeneous if the ratio (homogeneity index) of homogeneous if the ratio (homogeneity index) of observed standard deviation to the standard diamed and the standard deviation of the statistics of the standard deviation of the randomly selected grains. Table 2 gives ratios for the ten ten-second counts on each of ten randomly selected grains. Table 2 gives ratios for the ten diames the order teness angle for major and some minor elements. The values in paronthese indicate the vorst ratio observed for parentineses indicate the worst ratio observed for an element in a single grain. This does not, however, imply a single worst grain as different grains may exhibit differing degrees of homo-geneity for each element present. When the criteria of these ratios are used as a measure of homogeneity, all the reference samples are very homogeneous provided a reasonably large number of

1. D.B. Stewart, G.W. Walker, T.L. Wright and J.J. Fahey (1966) Snithsonian Institution 3. J. Norberg, Department of Mineral Sciences, Snithsonian Institution 4. E.L. Musson, N.M. Conklin, J.N. Rosholt and I.C. Frost, U.S. Geological Survey, B. Witk, Geological Survey, Finland 6. U.S. Geological Survey, Geochemistry and Pe-trolory Branch J.J. Fahey (1966)
 HBysical properties of calcic labradorite from Lake County, Dregon, American Mineralogist, Si: 177-97.
 E.J. Young, A.T. Myers, E.L. Munson and N.M. Conklin (1999)
 Mineralogy and geochemistry of fluorapatite from Cerro de Mercado, Durango, Mexico, U.S. Geological Survey Professional Paper 6500: 84-93.

KEY TO TABLE 1 Analysts, Sources, References

> 3 B. Mason and R.O. Allen (1973)

References for previously published analyses:

B. Mason and R.O. Alien (1973) Minor and trace elements in augite, hornblende and pyrope megacrysts from Kakanui, New Zealand; New Zealand Journal of Geology and Antiper and State and

- 5. R.G. Dymek, L.B. Wiggins and C.A. Francis (1979)
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- cal Sciences, Harvard University.
   c. Jarosevich (1975)
   Chemical analysis of two microprobe standards, Smithsonian Contributions to the Earth Scien-
- ces, 14: 85-86. 7. E. Kiss (1970)
- Personal communication, Department of Geophy-sics and Geochemistry, Australian National niversity.
- Zealand; New Zealand Journal of Geology and Geophysics, 16(4): 935-947.
   E. Jarosewich (1972) Chemical analysis of five minerals for micro-probe standards, Smithsonian Contributions to the Earth Sciences, 9: 83-84.

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E. JAROSEWICH, J.A. NELEN AND Julie A. NORBERS

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### Lack of proper documentation is a serious

reference samples. Even if well-described minerals are from the same locality or are obtained from a reliable source, they may an chemical composition. Therefore, a mineral sample chained a reference sample should be care-olly de sample should be care-on the specific specime are evailable. Since

requirements are not always evailable, synthetic ninerals and glasses have occasionally been prepared as substitutes. Again, hongeneity of these materials should be checked and chemical mailyses performed. The assumption that a monimal 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

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## PREPARATION OF REFERENCE SAMPLES

a heavy liq separator.

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step, the ma ered microscc are removed again checke (sigma ratios

Springwater a TiO<sub>2</sub> content

recreasion of the triplets Several the anti-dense sufficient quantity (at least 2 g) of a mineral or giass is available for use as a microprobe reference sample, a thin section is prepared for sicrocopic exemination. This micropoid is the intraversed several times in the micropoid is the intraversed several times in the micropoid of the intraversed several migro cleansits. If these preliminary results are favorable, the material is gently crushed, sized usually harmone 20 and 80 mes

1 corrections

### Geostandards Newsletter, Vol. 4, Nº 1, Avril 1980

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 < Signa ratio for 10 grains - observed signs for all grains Signa ratio for least homogeneous grain = observed signs for this particular grain (in parentheses) signs predicted from counting statistics 
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 99.99 49.78 23.05 0.17 13.38 5.30 0.94 Bro 0.07; 8820; 1.43; 780; 0.02; 4430; 0.09; 120; 0.01; 00; 0.05; 8 CO2 not determined (insufficient eample); Cl 0.00; 7 0.01. 803 0.33: F 3.53; C1 0.41; sub-total: 101.52; 0 equivalent to C1, F -Synthetic glass prepared by Corning Class Company. 1.58; final total: 99.94. 9 New T10+ value: 4.72. 2 840 37.05. 10 magos 0.92. Total Te reported as 740. Freitminary values: Ng0 0.05; T10; 0.16; Nu0 +0.01; Cry0; 0.25. \* Entesten spectrometric analysis: \$1 0.03; Fe 0.003; Ng 0.007; 12 810 8.37. Ca 0.003; Na 0.005; E 0.003. analysis: A1 0.0005; Fe 0.01; Mg 0.005; Ca 0.001; Ma 0.001; X 0.0003. 5 ZnD 42.50. 14 002 2.5; 802 1.32; CL 1.43; aub-total: 190.18; 0 squivalent to 100.67. 2 053 S

7 Ci 0.13; ert-totel: 99.59; 0 ereivalent to Ci - 0.03; final total:

standards Newsletter, Vol. 4, Nº 2, Octobre 1980, p. 257 à 258

Table 2. Sigma ratios (homogeneity indices) for all analyzed grains. Index for least homogeneous grain in parenthese

ineral	\$102	A1203	Fe0	NgD	Ca0	Na <sub>2</sub> O	K20	T102	P205	MnD	Cr203	Zn
northite	0.96	0.81			0.92	1						
northoclase	(1.51) 1.09	(1.26) 0.79	- 6		(1.23)	1.11						
northoclase	(1.60)	(1.38)		- N		(1.57)	10					
patite (Fluorapatite)	(1100)	(11.20)			1.02	(ALCONY			0.97			
					(1.51)				(1.51)			
ugite	0.99	0.97	0.84	0.94	1.00							
enitoite	(1.37)	(1.66)	(1.26)	(1.23)	(1.25)							
		- d.										
hromite	1. N	1.00	1.01	1.11							1.12	
	· · · · · · · · · · · · · · · · · · ·	(1,47)	(1.66)	(1.50)							(1.49)	
forundum												
Dicpside	1.07			0.97	0.95							
	(1.37)			(1.50)	(1.50)							
ayalite	0.95		1.14							1.03		
ahnite -	(1.46)	1.06	(2.32)							(1.58)		
lahnite -	•	1.08										in
Jarnet, 87375	0.89	1.01	1.06	1.01	0.86							
Achec, 07375	(1.26)	(1.42)	(1.41)	(1.49)	(1.11)							
Garnet, 110752	0.88	0.94	0.90	1.00	0.87							
	(1.32)	(1.28)	(1.20)	(1.34)	(1.47)							
Glass, 111240/52 VG-2	0.94 (1.10)	0.89	0.86	0.96 (1.61)	1.00 (1.27)	1.05						
Class, 113498/1 VG-A99	0.94	1.10	1.07	0.92	0.93	1.15		0.97				
	(1.32)	(1.46)	(1.38)	(1.38)	(1.34)	(2.10)		(1.44)				
Glass, 113716	1.12	1.00	0.94	1.01	0.83	1.25						
	(1.42)	(1.30)	(1.34)	(1.36)	(1.19)	(2.39)						
Glass, 72854 VG-568	0.97 (1.61)	1.00 (1.47)				2.31 (3.45)	0.98 (1.36)					
Glass, 2213	1.05	0.87	1.01		1.05	(5.45)	(					
	(1.72)	(1.24)	(1.34)		(1.61)							
Hornblende, Arenal	1.07	0.97	1.12	1.11	1.01	0.98						
Hornblende, Kakanui	(1.67)	(1.66) 1.00	(1.36) 1.30	(1.67) 1.16	(1.27)	(1.32)	0.90	1.01				
Hornolende, Kakanul	1.01 (1.38)	(1.24)	(1.67)	(2.38)	(1.73)	(2.15)	(1.29)	(1.49)				
Hyperstheme	1.07	(Lines)	1.10	0.93	(11)31	(414.57		(				
	(1.55)		(1.37)	(1.27)								
Ilmenite			1.72					1.34		1.21		
			(3.60)					(1.98)		(1.53)		
Magnetite			0.84 (1.16)									
Microcline	0.94	1.04	(4.10)				1.09					
	(1.13)	(1.52)					(1.59)					
Olivine (Fogg), San Carlos	0.81		0.90	1.00								
	(1.13)		(1.29)	(1.64)								
Olivine (Fogg), Springwater	0.96 (1.42)		1.06 (1.51)	0.99 (1.12)								
Omphacite	0.89	0.95	0.96	0.91	1.02	0.99						
	(1.23)	(1.64)	(1.87)	(1.30)	(1.51)	(1.31)						
Osumilite	0.96	1.27	1.20	1.00			1.13					
Plagioclase (Labradorite)	(1.90)	(1.89) 0.95	(2.19)	(1.70)	1.04	0.91	(1.64)		Analy	sts:		
. reBrocress (PEDIAGOLICE)	(1.49)	(1.40)			(1.65)	(1.33)						
Pyrope	1.08	0.95	1.09	0.98	0.97				1. E.	Jaros	ewich,	Dep
	(1.46)	(1.20)	(1.59)	(1.21)	(1.18)					ithson		
Quartz									2. J.			part
Scapolite (Meionite)	0.99	0.95			0.91	0.96				ithson		
	(1.29)	(1.41)			(1.16)					Norbe		epar

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- Snithsonian Institution 3. J. Norberg, Department of Mineral Sciences, Smithsonian Institution 4. E.L. Musson, N.M. Conklin, J.N. Rosholt and I.C. Frost, U.S. Geological Survey, B. Wilk, Geological Survey, Finland 6. U.S. Geological Survey, Geochemistry and Pe-trology Branch

- 0.5. 062/02/CLI SUTVY, Geochemistry and re-trology Branch
   D. Mills, X-Ray Assay Laboratories, Ontario, Canada; J. Neing J. Korberg
   E. Kiss, Department of Geophysids and Geoche-mistry, Australian National University
   J.J. Fahey and L.C. Peck, U.S. Geological Survey
- Survey

## Sources:

- 1. P. Desautels, J.S. White, Jr., and P.J. Dunn, Department of Mineral Sciences, Smithsonian
- Institution 2. B. Mason, Department of Mineral Sciences,

- B. Mason, Department of Mineral Sciences, Smithsonian Institution
   G. Switzer, Department of Mineral Sciences, Smithsonian Institution
   R.G. Dyeck, L.B. Wiggins and C.A. Francis, Harvard University
- 5. W.G. Melson, Department of Mineral Sciences,
- Smithsonian Institution 6. T.L. Wright, U.S. Geological Survey 7. H. Staudigel, Massachusetts Institute of Tech-
- R. S. Clarke, Jr., Department of Mineral Sciences, Saithconian Institution
   J.H. Berg, Northern Illinois University

Even after the most careful preparation of the reference sample, a grain of accessory mineral or matrix may remain in the sample, which, in the course of preparation of the reference sample discs, could be included with the reference sample. Occasional grains of the section of the sample discs, and the sample because of heterogeneity. These problems can never be totally eliminated. The user should be aware of the possible presence of such "impuri-ties" and make a through check for them. For example, occasional grains are found that are there in output and the sample of the sample of the insamgeness than usual in lake County Even after the most careful preparation of lower in sodium than usual in Lake County plagioclase. Infrequent inclusions in the glasses 72854, 111240/52, 113498/1 and 113716 are also found

## References for previously published analyses:

KEY TO TABLE 1 Analysts, Sources, References

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J.J. Fahey (1966)
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3 B. Mason and R.O. Allen (1973)

B. Mason and R.O. Alien (1973) Minor and trace elements in augite, hornblende and pyrope megacrysts from Kakanui, New Zealand; New Zealand Journal of Geology and Antiper and State and

- Zealand; New Zealand Journal of Geology and Geophysics, 16(4): 935-947.
   E. Jarosewich (1972) Chemical analysis of five minerals for micro-probe standards, Smithsonian Contributions to the Earth Sciences, 9: 83-84.
- 5. R.G. Dymek, L.B. Wiggins and C.A. Francis (1979)
- Personal communication, Department of Geologi-
- cal Sciences, Harvard University.
   c. Jarosevich (1975)
   Chemical analysis of two microprobe standards, Smithsonian Contributions to the Earth Scien-
- ces, 14: 85-86. 7. E. Kiss (1970)
- Personal communication, Department of Geophy-sics and Geochemistry, Australian National niversity.

The overall homogeneity of each sample was determined using the criterion given by Boyd et al. (5) whereby the sample is considered to be homogeneous if the ratio (homogeneity index) of homogeneous if the ratio (homogeneity index) of observed standard deviation to the standard diamed and the standard deviation of the statistics of the standard deviation of the randomly selected grains. Table 2 gives ratios for the ten ten-second counts on each of ten randomly selected grains. Table 2 gives ratios for the ten diames the order teness angle for major and some minor elements. The values in paronthese indicate the vorst ratio observed for parentineses indicate the worst ratio observed for an element in a single grain. This does not, however, imply a single worst grain as different grains may exhibit differing degrees of homo-geneity for each element present. When the criteria of these ratios are used as a measure of homogeneity, all the reference samples are very homogeneous provided a reasonably large number of

"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."

## Reference Samples for Electron Microprobe Analysis.

E. JAROSEWICH, J.A. NELEN AND Julie A. NORBERS

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

The obmical analyses of twenty-siz mine-match from restance glasses, and one symbolic scales from restance glasses, and not symbolic sempler are presented. New chemical analyses of minerals and revised analyses of several minerals performed and the second neity of the samples has been tested by the homo-genetic states.

Microprobe analysis, a technique that is now well established, viely used, and capable of high-quality analyses, is an essential part of neutron interalogical and petrological Ludies. An observent, it requires well-characterized references samples. Frime perequisites for microprobe refe-rence samples are heavgeneity at the micron level and availability in reasonable quantities for citaleal wet hemical analysis. Either perequi-cisation are themical margins, Either perequi-tagether are difficult to achieve.

Lack of proper documention is a serious problem with some minorable with some minorable problem with some minorable with a serious problem of the source of the serious problem of the series of the obtained from a reliable source, they say vary in obtained from a reliable source, they say vary in child series of the prepared as substitutes, ignin, hengeneity of these series of the series of t

In general, the most reliable microprobe analyses are obtained when a reference sample of composition and structure close to that of the

Reprinted by permission of Smithaonian Institution Press From Smithaonian Institution Contributions to the Earth Sciences, Number 22: "Electron Microprobe Refe-rance Sample's for Mineria Analyses", Bagene Garcsweich, Joseph Nelm and Julie Horberg: pages 68-72. Washington, D.G.: Smithaonian Institution Frees, 1979.

Geostandards Newsletter, Vol. 4, Nº 1, Avril 1

unknown is used because the matrix and possible wavelength shift effects are mininged and only meals corrections are meeded. It is generally generally and the shift of the shift of the shift of the correction used, results corrected by more than 0.0 percent should be viewed with coation. Difficulties with correction procedures in the  $M(O^{-1}A(O^{-1}G))$  system have been pointed out by Bonce and Bolzwarth (1). Similar discrepancies have been cheaved by other probe users.

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

## PREPARATION OF REFERENCE SAMPLES

a heavy liq a heavy liq separator, or with a suital step, the ma ered microsoc are removed again checke (sigma ratios

Springwater a TiO<sub>2</sub> content

recreasion of the triplets Several the anti-dense sufficient quantity (at least 2 g) of a mineral or giass is available for use as a microprobe reference sample, a thin section is prepared for sicroscopic exemination. This micropost is too intraversed several times in the micropost is too intraversed several times in the micropost is too intraversed several migro cleansits. If these preliminary results are favorable, the material is gently crushed, sized usually harawane 20 and 80 mes

100.67.

1 corrections

### Geostandards Newsletter, Vol. 4, Nº 1, Avril 1980

(signs ratios Finally, as methods (3.4) [Page 44] In Table 1 appearing in the paper "Reference samples for electron r that is to be barosewith, 3.4. Melen and 3.4. Morbers, the footnotel reference number S 113716". Starting from this "baselie" in 1315. It should read as "Glass, Bi 113716". Starting from this "baselie" footnote numbering, 1 to 14, is rep Data for one unity. The whole Table 1 with correct footnote numbering, 1 to 14, is rep whiled an

published are the published and the published are the published are the published are published are publicle. (The pur time are pu not be representative of the entire USNM sample) mineral separ Johnstown met

5101 A3101 F6103, Fe0 Mg0 . Ce0 1 Xa20 E10 T102 P205 P 
 Image: Section 1, Sec Asorthite, Great Sickin Island, AL 44.00 38.03 0.62 +0.02 19.09 0.53 0.03 0.03 +0.05 99.29 3 2 Bornblende, Armai Volcano, Costa Hica USNE 111358 Rornblende, Kalkani, New Zealend <sup>9</sup> USNE 10495 USNE 10495 USNE 1049 USNE 1049 Hagnetice, Himan Mrss., Miani, USSE <sup>10</sup> USNE 1049 USNE 10497 USNE 10497 
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14 00: 2.3: 80: 1,32: CL 1.43: sub-total: 130.18: 0 equivalent to 2 053 S 7 Ci 0.13; ert-totel: 99.59; 0 ereivalent to Ci - 0.03; final total:

standards Newslatter, Vol. 4, N° 2, Octobre 1980, p. 257 à 258

Table 2. Sigma ratios (homogeneity indices) for all analyzed grains. Index for least homogeneous grain in parenthese

Mineral	\$102	A1203	Fe0	NgD	Ca0	Na <sub>2</sub> O	K20	T102	P205	MnD	Cr203	Zn
Anorthite	0.96	0.81			0.92							_
Anorthoclase	(1.51) 1.09 (1.60)	(1.26) 0.79 (1.38)	\$	5	(1.23)	1.11 (1.57)	ø					
Apatite (Fluorapatite)	(1100)	(11.50)			1.02	(1121)			0.97 (1.51)			
Augite	0.99 (1.37)	0.97	0.84	0.94	1.00 (1.25)							
Benitoite												
Chromite		1.00	1.01 (1.66)	1.11 (1.50)							1.12 (1.49)	
Corundum			(1100)	111307							(1147)	
Diopside	1.07			0.97	0.95							
Fayalite	0.95		1.14 (2.32)							1.03 (1.58)		
Gahnite -		1.06										0
Garnet, 87375	0.89	1.01	1.06	1.01	0.86							
Garnet, 110752	(1.26) 0.88	(1.42) 0.94	(1.41) 0.90	(1.49) 1.00	(1.11) 0.87							
Glass, 111240/52 VG-2	(1.32) 0.94	(1.28) 0.89	(1.20) 0.86	(1.34) 0.96	(1.47) 1.00	1.05						
Glass, 113498/1 VG-A99	(1.10) 0.94	(1.11) 1.10	(1.13) 1.07	(1.61) 0.92	(1.27) 0.93	(1.31) 1.15		0.97				
Glass, 113716	(1.32) 1.12	(1.46) 1.00	(1.38) 0.94	(1.38) 1.01	0.83	(2.10) 1.25		(1.44)				
Glass, 72854 VG-568	(1.42) 0.97	(1.30) 1.00	(1.34)	(1.36)	(1.19)	(2.39) 2.31	0.98					
Glass, 2213	(1.61) 1.05	(1.47) 0.87	1.01		1.05	(3.45)	(1.36)					
Hornblende, Arenal	(1.72) 1.07	(1.24) 0.97	(1.34) 1.12	1.11	(1.61) 1.01	0.98						
Hornblende, Kakanui	(1.67) 1.01	(1.66) 1.00	(1.36) 1.30	(1.67) 1.16	(1.27) 1.10	(1.32) 1.15	0.90	1.01				
Hyperstheme	(1.38)	(1.24)	(1.67) 1.10	(2.38) 0.93	(1.73)	(2.15)	(1.29)	(1.49)				
Ilmenite	(1.55)		(1.37) 1.72	(1.27)				1.34		1.21		
Hagnetite			(3.60) 0.84					(1.98)		(1.53)		
Microcline	0.94	1.04	(1.16)				1.09					
Oliving (Foso), San Carlos	(1.13) 0.81	(1.52)	0.90	1.00			(1.59)					
Olivine (Fogs), Springwater	(1.13)		(1.29) 1.06	(1.64) 0.99								
Omphacite	(1.42) 0.89	0.95	(1.51) 0.96	(1.12) 0.91	1.02	0.99						
Coumilite	(1.23) 0.96	(1.64) 1.27	(1.87) 1.20	(1.30) 1.00	(1.51)	(1.31)	1.13					
Plagioclase (Labradorite)	(1.90)	(1.89) 0.95	(2.19)	(1.70)	1.04	0.91	(1.64)		Analy	sts:		
Pyrope	(1.49) 1.08	(1.40) 0.95	1.09	0.98	(1.65)	(1.33)			1. E.	Jaros	ewich.	Der
Quartz	(1.46)		(1.59)						Sm	ithson	ian In	sti
Scapolite (Meionite)	0.99	0.95			0.91	0.96			2. J. Sn	Nele		par
scaporate (reionite)	(1.29)					(1.41)			3. J.		rg, D	

## Signa ratio for 10 grains - observed signs for all grains Signa ratio for least homogeneous grain = observed signs for this particular grain (in parentheses) signs predicted from counting statistics

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## KEY TO TABLE 1 Analysts, Sources, References

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- 3. J. Norberg, Department of Mineral Sciences,
- J. Norberg, Department of Mineral Sciences, Smithsonian Institution
   E.L. Munson, N.M. Conklin, J.N. Rosholt and I.C. Frost, U.S. Geological Survey
   B. Wilk, Geological Survey, Finland
   U.S. Geological Survey, Finland

- Survey

## Sources:

- 1. P. Desautels, J.S. White, Jr., and P.J. Dunn, Department of Mineral Sciences, Smithsonian

- nology 8. R.S. Clarke, Jr., Department of Mineral Sciences, Smithsonian Institution 9. J.H. Berg, Northern Illinois University

## Even after the most careful preparation of the reference sample, a grain of accessory mineral or matrix may remain in the sample, which, in the course of preparation of the

the reference sample. Occasional grains of the reference sample will differ in composition because of heterogeneity. These problems can never be totally eliminated. The user should be aware of the possible presence of such "impuri ties" and make a thorough check for them. For

lower in sodium and higher in potassium than usual in the reference sample microcline, lower in manganese than usual in Rockport fayalite, and lower in sodium than usual in Lake County plagioclase. Infrequent inclusions in the glasses 72854, 111240/52, 113498/1 and 113716 are also found

The overall homogeneity of each sample was determined using the criterion given by Boyd et al. (5) whereby the sample is considered to be homogeneous if the ratio (homogeneity index) of homogeneous if the ratio (homogeneity index) of observed standard deviation to the standard diamed and the standard deviation of the statistics of the standard deviation of the randomly selected grains. Table 2 gives ratios for the ten ten-second counts on each of ten randomly selected grains. Table 2 gives ratios for the ten diames the order teness angle for major and some minor elements. The values in paronthese indicate the vorst ratio observed for parentineses indicate the worst ratio observed for an element in a single grain. This does not, however, imply a single worst grain as different grains may exhibit differing degrees of homo-geneity for each element present. When the criteria of these ratios are used as a measure of homogeneity, all the reference samples are very homogeneous provided a reasonably large number of

## 0.5. 062/02/CLI SUTVY, Geochemistry and re-trology Branch D. Mills, X-Ray Assay Laboratories, Ontario, Canada; J. Neing J. Korberg E. Kiss, Department of Geophysids and Geoche-mistry, Australian National University J.J. Fahey and L.C. Peck, U.S. Geological Survey 3 Zealand; New Zealand Journal of Geology and Geophysics, 16(4): 935-947. E. Jarosewich (1972) Chemical analysis of five minerals for micro-probe standards, Smithsonian Contributions to the Earth Sciences, 9: 83-84.

- 5. W.G. Melson, Department of Mineral Sciences,
- Smithsonian Institution 6. T.L. Wright, U.S. Geological Survey 7. H. Staudigel, Massachusetts Institute of Tech-

- Institution 2. B. Mason, Department of Mineral Sciences,

- B. Mason, Department of Mineral Sciences, Smithsonian Institution
   G. Switzer, Department of Mineral Sciences, Smithsonian Institution
   R.G. Dyeck, L.B. Wiggins and C.A. Francis, Harvard University
  - - 7. E. Kiss (1970)
      - Personal communication, Department of Geophy-sics and Geochemistry, Australian National
- J.J. Fahey (1966)
   HBysical properties of calcic labradorite from Lake County, Dregon, American Mineralogist, Si: 177-97.
   E.J. Young, A.T. Myers, E.L. Munson and N.M. Conklin (1999)
   Mineralogy and geochemistry of fluorapatite from Cerro de Mercado, Durango, Mexico, U.S. Geological Survey Professional Paper 6500: 84-93. B. Mason and R.O. Allen (1973) B. Mason and K.O. Allen (1973) Kinor and trace elements in augite, hornblende and pyrope megacrysts from Kakanui, New Zealand; New Zealand Journal of Geology and

References for previously published analyses:

1. D.B. Stewart, G.W. Walker, T.L. Wright and J.J. Fahey (1966)

- - Personal communication, Department of Geologi-
- ces, 14: 85-86.
- 5. R.G. Dymek, L.B. Wiggins and C.A. Francis (1979)
- cal Sciences, Harvard University.
   c. Jarosevich (1975)
   Chemical analysis of two microprobe standards, Smithsonian Contributions to the Earth Scien-

  - niversity.

"Occasional grains of the reference sample will differ in composition because of heterogeneity. These problems can never be eliminated...

## Reference Samples for Electron Microprobe Analysis.

E. JAROSEWICH, J.A. NELEN AND Julie A. NORBERS

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

The obmical analyses of twenty-siz mine-match from restance glasses, and one symbolic scales from restance glasses, and not symbolic sempler are presented. New chemical analyses of minerals and revised analyses of several minerals performed and the second neity of the samples has been tested by the homo-genetic states.

Microprobe snalysis, a technique that is now well established, wiely used, and capable of high-quality and petrological inducts. As new provide the state of the state of the state new provide the state of the state of the state here of the state of the state of the state samples. Frime prerequisites for nicroprobe refe-nece samples are homogeneity at the nicron lavel and availability in reasonable quantities for cicles at wet homeist and prime is then perequi-cicles of the the state of the state of the together are difficult to achieve.

Lack of proper documention is a serious problem with some minorable with some minorable problem with some minorable with a serious problem of the some series of the series of problem of the series of the series of the series obtained from a reliable source, they say vary in obtained from a reliable source, they say vary in other series of the series of the series of the fully selected and used only when small the above matural materials fulfilling all the above matural materials fulfilling all

In general, the most reliable microprobe analyses are obtained when a reference sample of composition and structure close to that of the

Reprinted by permission of Smithaonian Institution Press From Smithaonian Institution Contributions to the Earth Sciences, Number 22: "Electron Microprobe Refe-rance Samples for Mineral Analyses", Rugene Garoawich, Joseph Nelm and Julie Norberg: pages 68-72. Washington, D.G.: Smithaonian Institution Press, 1979.

Geostandards Newsletter, Vol. 4, Nº 1, Avril 1

unknown is used because the matrix and possible wavelength shift effects are mininged and only meals corrections are meeded. It is generally generally and the shift of the shift of the shift of the correction used, results corrected by more than 0.0 percent should be viewed with coation. Difficulties with correction procedures in the  $M(O^{-1}A(O^{-1}G))$  system have been pointed out by Bonce and Bolzwarth (1). Similar discrepancies have been cheaved by other probe users.

All minerals and glasses described here, All minerals and glasses described here, except one, are of natural origin. Most specimes 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 gabnic have been published (2).

## PREPARATION OF REFERENCE SAMPLES

heavy liq a heavy liq separator, or with a suital step, the ma ered microsoc are removed again checke (sigma ratios

Springwater a TiO<sub>2</sub> content

recreasion of the triplets Several the anti-dense sufficient quantity (at least 2 g) of a mineral or giass is available for use as a microprobe reference sample, a thin section is prepared for sicroscopic exemination. This micropost is too intraversed several times in the micropost is too intraversed several times in the micropost is too intraversed several migro cleansits. If these preliminary results are favorable, the material is gently crushed, sized usually harawane 20 and 80 mes

., corrections

### Geostandards Newsletter, Vol. 4, Nº 1, Avril 1980

(signs ratios Finally, as methods (3.4) [Page 44] In Table 1 appearing in the paper "Reference samples for electron r that is to be barosewith, 3.4. Melen and 3.4. Morbers, the footnotel reference number S 113716". Starting from this "baselie" in 1315. It should read as "Glass, Bi 113716". Starting from this "baselie" footnote numbering, 1 to 14, is rep Data for one unity. The whole Table 1 with correct footnote numbering, 1 to 14, is rep whiled an

Data for bolland an Table 1. Chemical analyses of electron microprobe reference samples. (The pur ion are pro not be representative of the entire USNM sample) time are pr mineral separ Johnstown met

 
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 Signa ratio for 10 grains = observed signs for all grains Signa ratio for least homogeneous grain = observed signs for this particular grain (in parentheses) signs predicted from counting statistics 
 Description for fully, formation
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 Description
 Descripti 99.59 49.78 23.05 0.17 13.58 5.20 0<sub>5</sub>94 <sup>1</sup> Sto 0.07; \$520; 1.43; THO; 0.02; As;0; 0.09; \$20; 0.01; CO; 0.05; 8 CO2 not determined (insufficient eample); Cl 0.00; 7 0.01. 803 0.37: 7 3.53; Cl 0.41; sub-total: 101.52; 0 equivalent to Cl, 7 -Synthetic glass prepared by Corning Class Company. 1.58; final total: 99.94. 9 New T10+ value: 4.72. 2 840 37.05. 10 magos 0.92. Total Te reported as 740. Freitminary values: Ng0 0.05; T10; 0.16; Nu0 +0.01; Cry0; 0.25. \* Enterior epectrometric analysis: 51 0.03; Fe 0.003; Ng 0.007; 12 810 0.37. Ca 0.003; Na 0.005; E 0.003. analysis: Al 0.0005; Fe 0.01; Mg 0.005; Ca 0.001; Ma 0.001; X 0.0003. 5 Zn0 42.50. 14 00: 2.3: 80: 1.32; Cl 1.43; sub-total: 100.18; 0 equivalent to 100.67. 2 053 S 7 Ci 0.13; ert-totel: 99.59; 0 ereivalent to Ci - 0.03; final total:

standards Newslatter, Vol. 4, N° 2, Octobre 1980, p. 257 à 258

Mineral \$102 A1203 Fe0 NeD CaD Nas0 Ko0 T102 PoDe MnD Cra03 Zn 0.96 0.81 (1.51) (1.26) 1.09 0.79 (1.60) (1.38) Anorthite 0.92 ) Aporthorlase 1.11 (1.57) (1.60) (1.38) 1.02 (1.51) 0.99 0.97 0.84 0.94 1.00 (1.37) (1.66) (1.26) (1.23) (1.25) Apatite (Fluorapatite 0.97 (1.51) Augite Benitoite Chronite 1.00 1.01 1.11 (1.47) (1.66) (1.50) 1.12 Corundum Dicpside Favalite 1.03 (1.58) Cahnite 0 Garnet, 87375 Garnet, 110752 Glass, 111240/52 VG-2 Glass, 113498/1 VG-A99 Glass, 113716 Glass, 72854 VG-568 Glass, 2213 Hornblende, Arenal Hornblende, Kakanui Hypersthese Ilmenite 1.21 (1.53) Magnetite  $\begin{array}{c} (1,10)\\ 0.54 & 1.64\\ (1,10,1-32)\\ (1,10) & (1,20)\\ (1,10) & (1,20)\\ (1,10) & (1,20)\\ (1,10) & (1,20)\\ (1,20) & (1,20)\\$ Microcline Olivine (Fogg), San Carlos

## 1.13 (1.64) Analysts:

0.91 0.96 (1.16) (1.41)

- Smithsonian Institution 3. J. Norberg, Department of Mineral Sciences, Smithsonian Institution 4. E.L. Munson, N.M. Conklin, J.N. Rosholt and I.C. Frost, U.S. Geological Survey, B. Wilk, Geological Survey, Finland 6. U.S. Geological Survey, Geochemistry and Pe-trolory Prach.
- - Survey

- 1. P. Desautels, J.S. White, Jr., and P.J. Dunn, Department of Mineral Sciences, Smithsonian

Even after the most careful preparation of the reference sample, a grain of accessory mineral or matrix may remain in the sample, which, in the course of preparation of the reference sample discs, could be included with the reference sample. Occasional grains of the section of the sample discs, and the sample because of heterogeneity. These problems can never be totally eliminated. The user should be aware of the possible presence of such "impuri-ties" and make a through check for them. For example, occasional grains are found that are there in oution and higher in potasium than in manganese than usual in lake County Even after the most careful preparation of lower in sodium than usual in Lake County plagioclase. Infrequent inclusions in the glasses 72854, 111240/52, 113498/1 and 113716 are also found

The overall homogeneity of each sample was determined using the criterion given by Boyd et al. (5) whereby the sample is considered to be homogeneous if the ratio (homogeneity index) of homogeneous if the ratio (homogeneity index) of observed standard deviation to the standard delose deviation of the standard delose deviation of the standard standard deviation of the standard deviation by taking ten ten-second counts on aset of the randomly selected grains. Table 2 gives ratios for the ten grains of each reference sample for major and some minor elements. The values in paracheses indicate the vorst ratio observed for parentuleses indicate the worst ratio observed for an element in a single grain. This does not, however, imply a single worst grains as different grains may exhibit differing degrees of homo-geneity for each element present. When the criteria of these ratios are used as a measure of homogeneity, all the reference samples are very homogeneous provided a reasonably large number of

### Table 2. Sigma ratios (homogeneity indices) for all analyzed grains. Index for least homogeneous grain in narenthese

- E. Jarosewich, Department of Mineral Sciences, Smithsonian Institution
   J. Nelen, Department of Mineral Sciences, Smithsonian Institution

- 0.5. 062/02/CLI SUTVY, Geochemistry and re-trology Branch
   D. Mills, X-Ray Assay Laboratories, Ontario, Canada: J. Neing J. Korberg
   E. Kiss, Department of Geophysids and Geoche-mistry, Australian National University
   J.J. Fahey and L.C. Peck, U.S. Geological Survey

## Sources:

## Institution 2. B. Mason, Department of Mineral Sciences, B. Mason, Department of Mineral Sciences, Smithsonian Institution G. Switzer, Department of Mineral Sciences, Smithsonian Institution R.G. Dyeek, L.B. Wiggins and C.A. Francis, Harvard University 5. W.G. Melson, Department of Mineral Sciences, Smithsonian Institution 6. T.L. Wright, U.S. Geological Survey 7. H. Staudigel, Massachusetts Institute of Tech-

B. R.S. Clarke, Jr., Department of Mineral Sciences, Saithaonian Institution
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 E. Jarosewich (1972) Chemical analysis of five minerals for micro-probe standards, Smithsonian Contributions to the Earth Sciences, 9: 83-84.

KEY TO TABLE 1

Analysts, Sources, References

- 5. R.G. Dymek, L.B. Wiggins and C.A. Francis (1979)
- cal Sciences, Harvard University.
   c. Jarosevich (1975)
   Chemical analysis of two microprobe standards, Smithsonian Contributions to the Earth Scien-
- ces, 14: 85-86.

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B. Mason and R.O. Allen (1973)

References for previously published analyses:

D.B. Stewart, G.W. Walker, T.L. Wright and J.J. Fahey (1966)

Personal communication, Department of Geologi-

niversity.

Scapolite (Meionite)

Olivine (Fogs), Springwater

0.99 0.95

Omphacite

Osumilite

Pyrope

Quartz

Plantoclass (Labra

"The overall homogeneity of each sample was determined using the criterion given by Boyd el al whereby the sample is considered to be homogeneous if the ratio (homogeneity index) of observed standard deviation to the standard deviation predicted by counting statistics alone does not exceed 3. The ratios were obtained by taking ten 10-second counts on each of ten randomly selected grains...

... When the criteria of these 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)

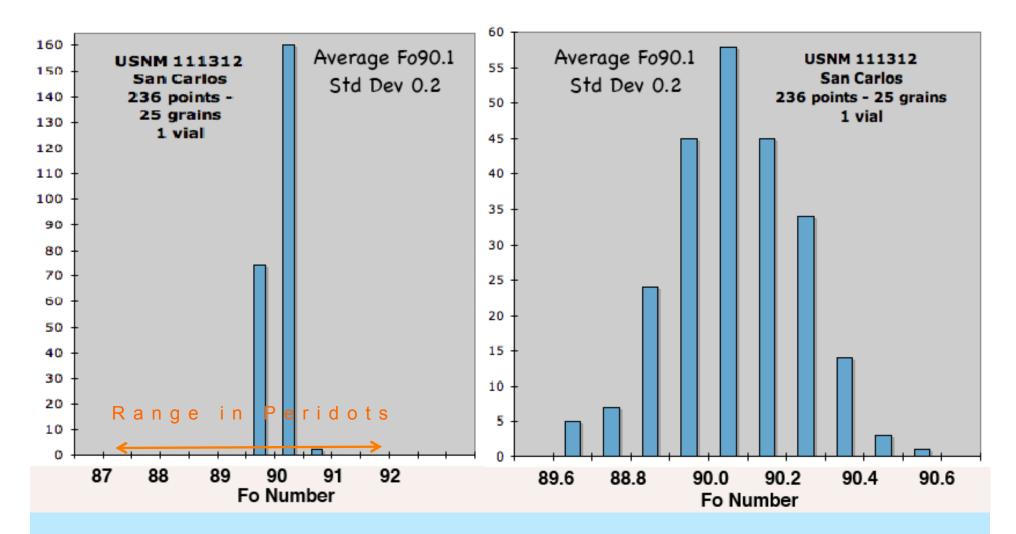


The Department of Mineral Sciences of the Smithsonian supplied me with 2 small vials of the USNM 111312 material (with at least 25 grains in each), which allowed me to look at the natural variability in the USNM San Carlos material

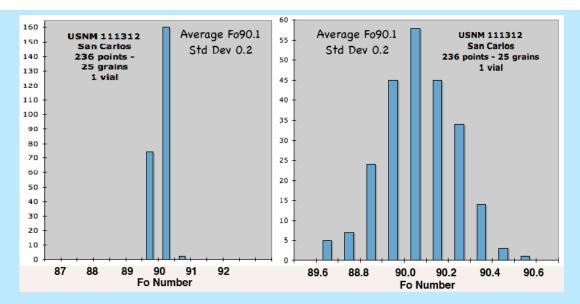


Here I report on EPMA measurements on 236 points in 25 small (200-300 um) grains from 1 vial, mounted in epoxy and polished.

The electron probe was operated similarly as above, with the exception that the mean atomic number background method was used.



These 2 histograms show the USNM 111312 standard material. It could be inferred from the very narrow range of composition that Jarosewich and co-workers selected only one ~cm-size crystal of the gemmy San Carlos material for their standard development.



Jarosewich et al calculated homogeneity indices with 100 total measurements on 10 grains (values <3 were considered OK). My 236 measurements on 25 grains of USNM 111312 show a bit wider range of heterogeneity in Si and Mg than reported in the 1980 paper:

Si 1.83 (vs 0.81), Mg 2.24 (vs 1.00) and Fe 1.08 (vs 0.9).

These current values, despite being larger than previously reported, are still indicative of a nicely homogeneous natural standard material. These "Boyd" numbers are to me less easy to comprehend than a simple "k-ratio"-like criteria, using peak counts on the standard one wishes to evaluate.

I find another possible approach to evaluation, using counting statistics sigma approach, to be simpler.

You want 99% of your actual standard counts to be equal or less than the counting statistical error spread.

(1) Determine total peak counts counts, with the average=exact value; using the count rate, determine 1 sigma, then look at **the real spread of the data**. Below, for Si, 1 sigma = a divergence of 0.5% from the measured average, and 50% of the measurements fall within this window. Two sigma is  $\pm 1\%$ , and contains 78% of the Si measurements; 3 sigma have 90% of values within 1.5% of the average. Or said another way, there is 1 chance in 10 that a Si measurement will be 1.5% different than the mean value.

Si	1 sigma	2 sigma	3 sigma
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: 4	120 cps x 10 seco	onds
	Mg count rate: 7	7030 cps x 10 sec	conds
	Fe count rate: 3	95 cps x 10 seco	nds

As Jarosewich said, if there are a large number of measurements of points on a large number of grains, then these values will be averaged out.

But not necessarily if there are a small number of measurements on 1 or 2 grains – which just so happen to vary some from the average value of the standard.

## Conclusions

(1) Crystals of "San Carlos olivine" (peridot) available from gem dealers cannot be assumed to be of the same composition as USNM 111312.

(2) There is a small but finite probability that EPMA users who assume that any ONE grain of USNM Carlos olivine is EXACTLY the published composition could be making an error of 2-3% in the characteristic X-ray intensity for Mg and Si, and 4-5% for Fe. EPMAers need to acquire "a reasonably large number of counts on a reasonably large number of grains" (Jarosewich et al, 1980).

(3) It is beneficial operating procedure for a lab to run several standards for an element and then compare the results for consistency.

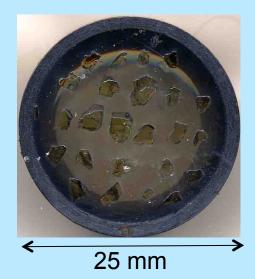
(4) Periodic use of applications such as "Evaluate" (Probe for EPMA software) provides one way to cross-check all standards and determine whether some grains of well known standards may not be exactly the published values and should perhaps have their compositions modified. QC Proposal: That a probe mount of at least 25 grains of USNM 111312 San Carlos olivine be made available to any EPMA lab for a short period of time, to run as a primary standard, to compare one's own few grains of olivine standard with and verify the composition of the lab's particular grains. Corollary: That potentially gem-dealer peridot San Carlos or Kilbourne Hole olivines be "qualified" as "second tier" olivine standards by use of such a QC mount.

One comment is that the small size of the USNM standard grains makes mounting and polishing/ repolishing a difficult procedure. Being able to "certify" larger crystals (using a "chain" approach?) is desirable.



Kilbourne Hole, NM





# Data for KH olivine: composition using SC USNM mount, and XRF data (JS Lackey, Pomona College)

Wt% oxide	XRF <sup>1</sup>	EPMA <sup>2</sup>	Theoretical
SiO <sub>2</sub>	39.88	40.66	40.60
MgO	49.56	49.26	49.04
FeO	9.72	9.74	9.71
CaO	0.10	0.10	
MnO	0.14	0.14	
NiO	0.38	0.38	
Total	99.94	100.29	
Fo #	90.0	90.0	

<sup>1</sup> Also: 0.14 wt% Al<sub>2</sub>O<sub>3</sub>; Cr 210 ppm; Zn 104 ppm; Na, K, P, Ti=0. <sup>2</sup> Using USNM San Carlos (26 grains averaged) as standard

## There may be Mg $K_{\alpha}$ Peak Shifts to watch out for

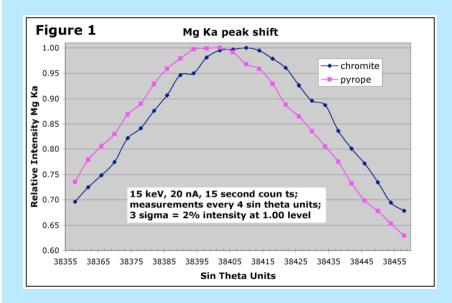


Table 2:	Relative	Relative
Mg Ka Peak	Counts on	Counts on
	Pyrope	Chromite
Pyrope Peak	1.000	0.968
Chromite Peak	0.956	1.000

In 2006 I reported on shifts in Mg Ka, using the SX51 as a poor-man's spectrometer. At AGU in December, Philippe Jonnard and I will report on high resolution spectrometer results corroborating this. So in some cases, a "good" standard may be a "bad" choice.

Table 1: S	Table 1: Shift in Mg Kα											
Mineral	Туре	Shift	Std									
			Dev									
Chromite	Spinel	-3.6	0.6									
MgAl2O4	Spinel	-5.1	0.5									
Kaersutite	Amphibole	-5.8	0.8									
MgO	Oxide	-6.0	0.5									
Enstatite	Pyroxene	-8.4	0.8									
Diopside	Pyroxene	-8.7	0.7									
Fo90	Olivine	-8.9	0.6									
Pyrope	Garnet	-13.3	0.7									

