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

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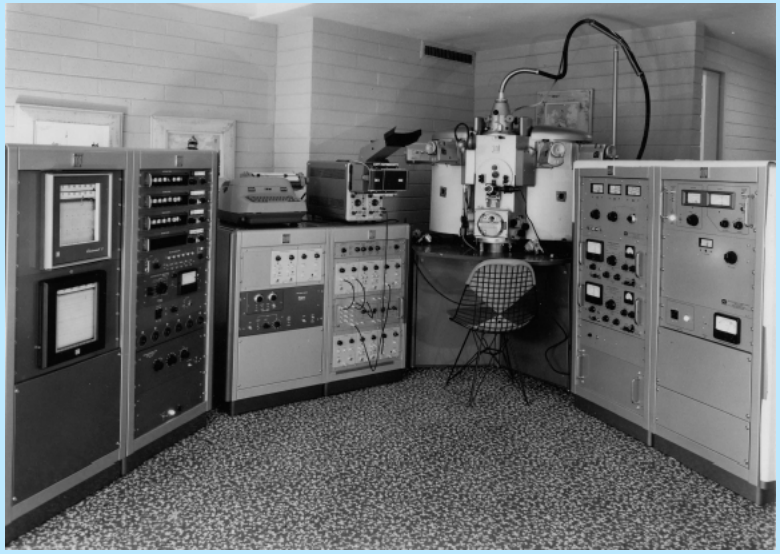
In 1960-70s there was an explosion of e-probes being built and sold. Many early applications had been in metals and alloys. As it became tool of interest to geologists, the need for mineral and glass standards increased.

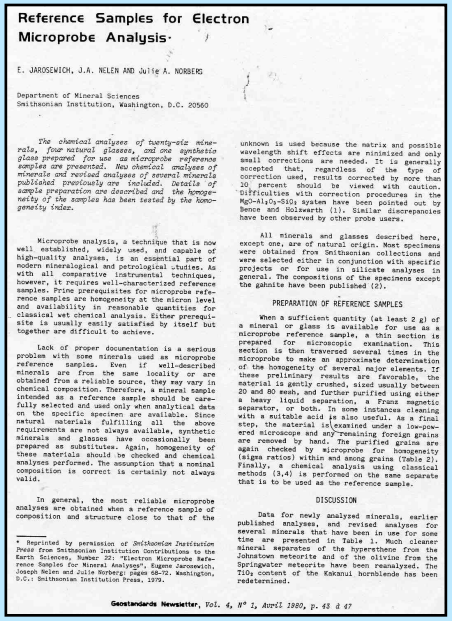


Gene Jarosewich and co-workers at the Dept of Mineral Sciences of the Smithsonian's Natural History Museum began a project to identify EPMA geological standards. Today many labs use the USNM San Carlos Fo90.1 standard which is distributed as USNM 111312/444 .

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*

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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 Frantz 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.

* Reprinted by permission of *Smithsonian Institution Press* from Smithsonian Institution Contributions to the Earth Sciences, Number 22: 'Electron Microprobe Reference Samples for Mineral Analyses', Eugene Jarosewich, Joseph Nelen and Julie Norberg; pages 68-72. Washington, D.C.: Smithsonian Institution Press, 1979.

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 %.

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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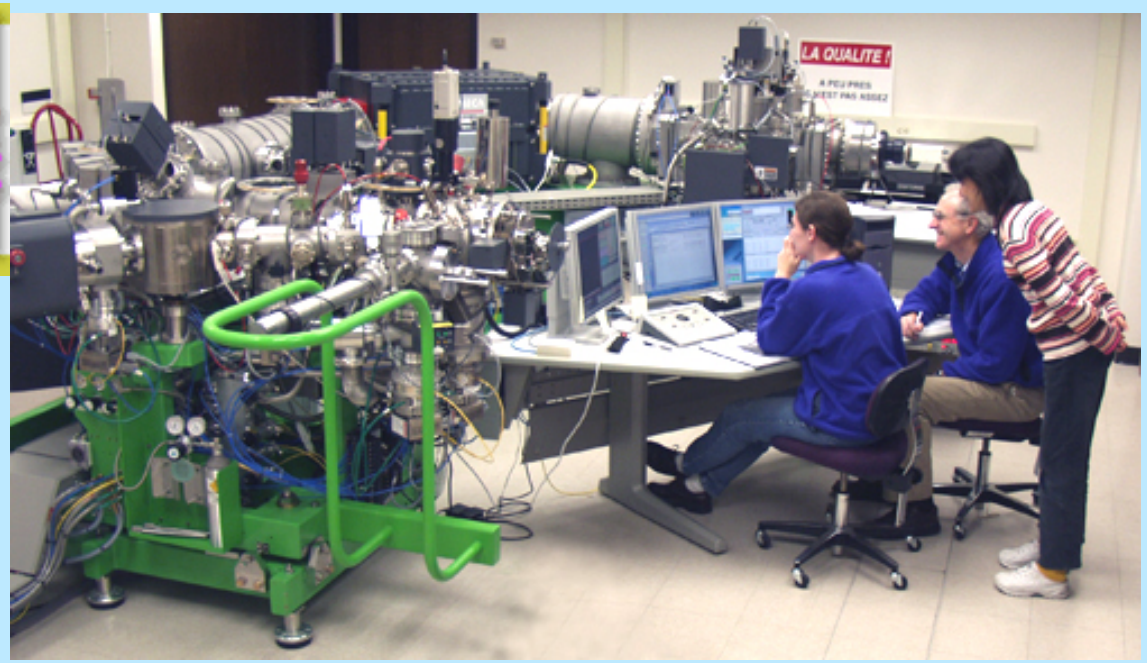
How this study came to be:

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

• A SIMS researcher measuring d^{18}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.

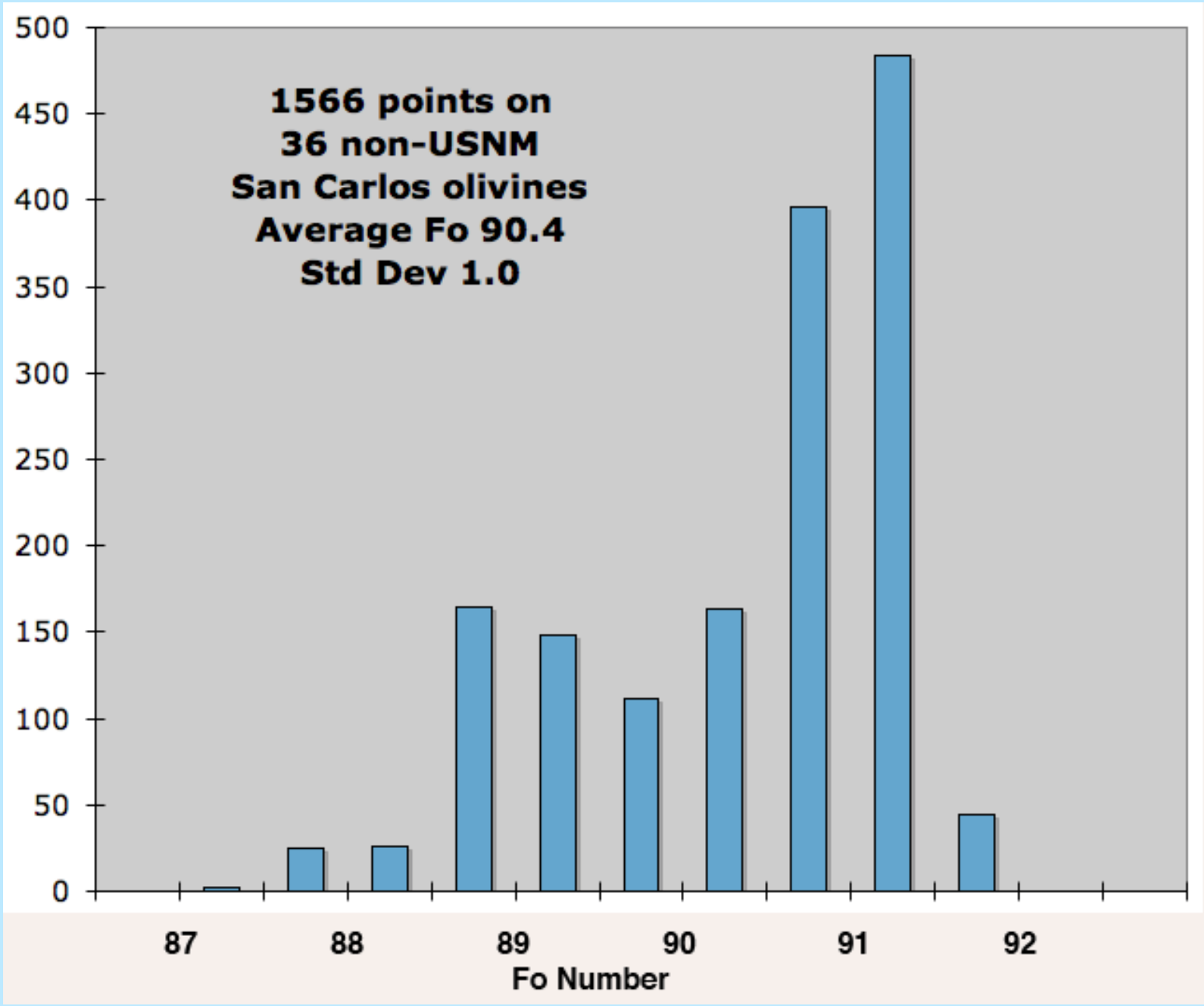
Wt% oxides	Published USNM	SIMS “San Carlos”
SiO_2	40.81	40.66
MgO	49.42	48.72
FeO	9.55	10.49
“Fo #”	90.1	89.2

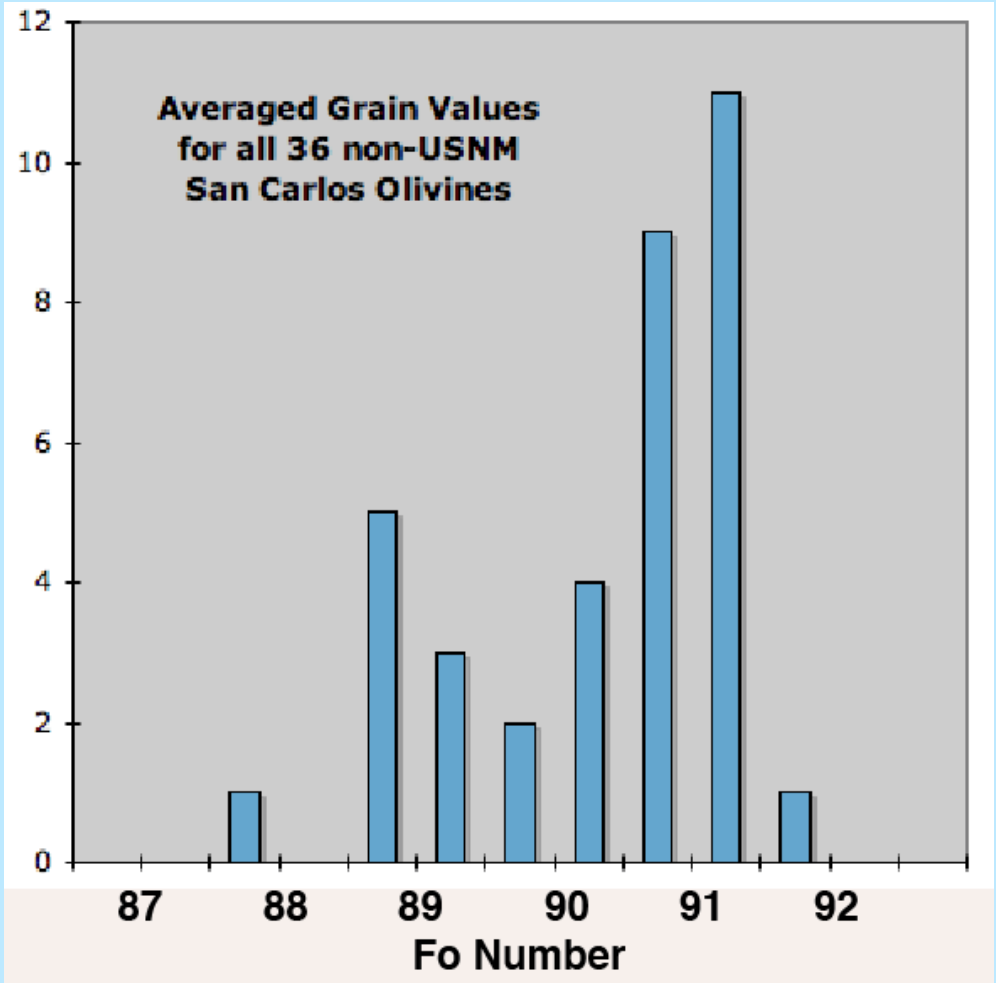
Study of the Gem "SC olivine" for lunar irradiation study

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)

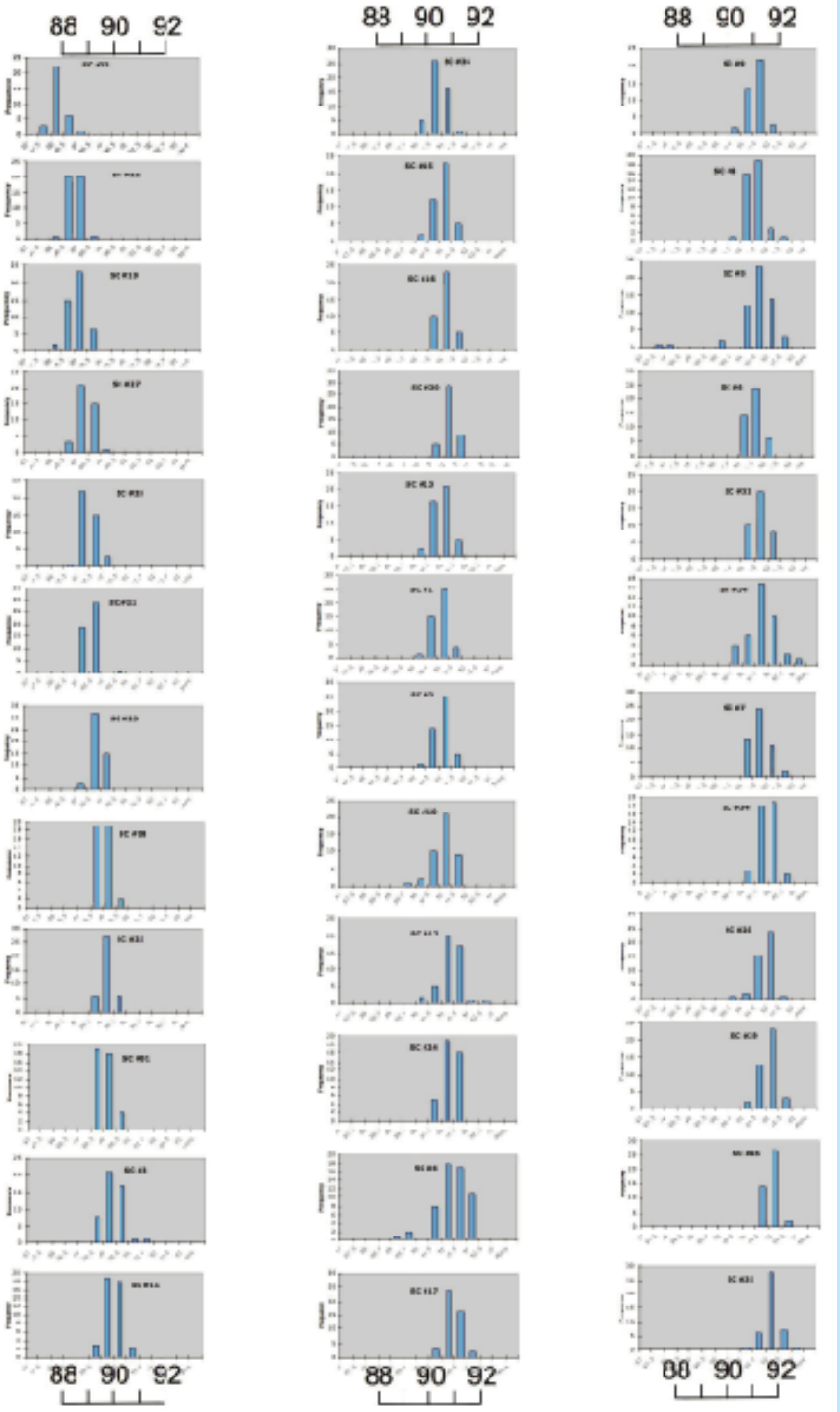
A range of compositions from <Fo88 to <Fo92 was found.

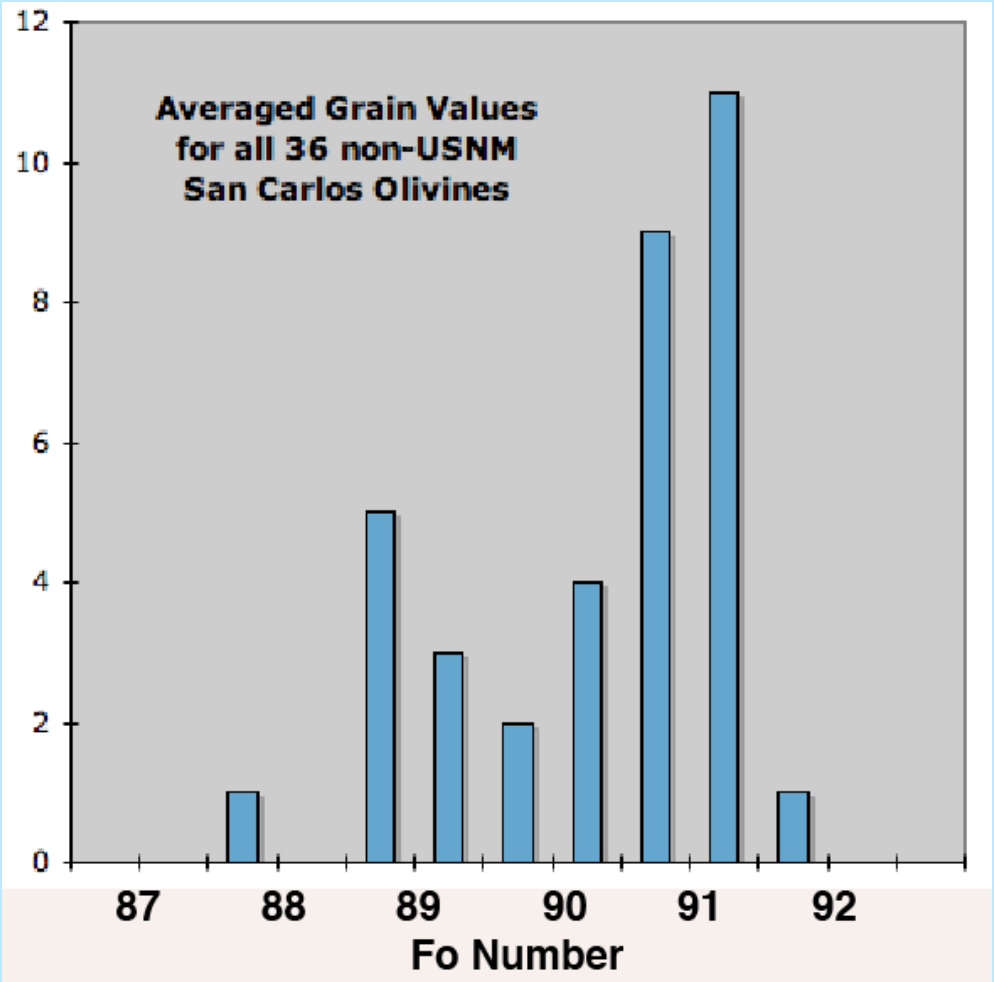
*15 kV, 20 nA, fixed spot, 10 sec each bk & bkg, measuring Mg, Si, Ca, Mn, Fe, Ni with UW-Madison SX51


1566 points on
36 non-USNM
San Carlos olivines
Average Fo 90.4
Std Dev 1.0
500
450
400
350
300
250
200
150
100
50
0
87
88
89
90
91
92
Fo Number



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





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- 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:

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Data for … published an… several miner… time are pr… mineral separ… Johnstown met… Springwater m… TiO_2 content … redetermined.

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corrections

Geostandards Newsletter, *Vol. 4, N° 1, Avril 1980*

|Page 44| In Table 1 appearing in the paper "Reference samples for electron m… Jarosewich, J.A. Nelen and J.A. Norberg, the footnote reference number 5 … "Glass, Basaltic, Indian Ocean[5], USNM 113716". It should read as "Glass, Ba… 113716". Starting from this "basaltic" sample, all further sequential footn… one unity. The whole Table 1 with correct footnote numbering, 1 to 14, is rep…

Table 1. Chemical analyses of electron microprobe reference samples. (The pur… not be representative of the entire USNM sample)

Mineral	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5							
Anorthite, Great Sitkin Island, AL USNM 137041	44.00	36.03		0.62	<0.02	19.09	0.53	0.03	0.03								
Anorthoclase, Kakanui, New Zealand USNM 133868	66.44	20.12		0.20		0.87	9.31	2.35					<0.05	99.29	3	2	
Apatite (Fluorapatite), Durango, Mexico[1] USNM 104021	0.34	0.07	0.06	0.00	0.01	54.02	0.23	0.01		40.78	0.01		0.01	99.94	4	1	2
Augite, Kakanui, New Zealand USNM 122142	50.73				16.65	15.82	1.27	0.00	0.74		0.13		0.04	100.[illegible]	5	2	3
Benitoite, San Benito County, CA[2] USNM 86539	43.75								19.35					100.15	2	1	
Chromite, Tiebaghi Mine, New Caledonia[3] USNM 117075		9.92		13.04	15.20	0.12					0.11	60.5		98.89	2	1	
Corundum, synthetic[4] USNM 6575		99.99												99.99	1	1	
Diopside, Natural Bridge, NY USNM 117733	54.87	0.11		0.24	18.30	25.63	0.34				0.04			99.53	2	1	
Fayalite, Rockport, MA USNM 85276	29.22		1.32	66.36					0.04		2.14		0.1	99.18	2	1	
Gahnite, Brazil[5] USNM 145883		55.32		1.97							0.38			100.13	2		
Garnet, Roberts Victor Mine, South Africa USNM 87375	39.47	22.27	2.77	13.76	6.55	14.39			0.39		0.59		<0.01	100.19	1	3	4
Garnet, Roberts Victor Mine, South Africa USNM 110752	40.16	22.70	2.17	9.36	7.17	18.12			0.35		0.19		<0.01	100.22	1	3	4
Glass, Basaltic, Juan de Fuca Ridge USNM 111240/52 VG-2	50.81	14.06	2.21	9.83	6.71	11.12	2.62	0.19	1.85	0.20	0.22		0.02	99.86	1	4	5
Glass, Basaltic, Makaopuhi Lava Lake, HI USNM 113498/1 VG-A99	50.94	12.49	1.87	11.62	5.08	9.30	2.66	0.82	4.06	0.38	0.15		0.02	99.39	3	5	
Glass, Basaltic, Indian Ocean[6] USNM 113716	51.52	15.39	1.12	8.12	8.21	11.31	2.48	0.09	1.30	0.12	0.17		0.18	100.07	3	6	
Glass, Rhyolitic, Yellowstone Nat. Pk., WY[7] USNM 72854 VG-568	76.71	12.06	0.48	0.80	<0.1	0.50	3.75	4.89	0.12	<0.01	0.03		0.12	99.56	3	4	
Glass, Tektite, synthetic[8] USNM 2213	75.75	11.34	0.64	4.32	1.51	2.66	1.06	1.88	0.50	0.00	0.11		0.10	99.88	6	7	
Hornblende, Arenal Volcano, Costa Rica USNM 111356	41.46	15.47	5.60	6.43	14.24	11.55	1.91	0.21	1.41	<0.01	0.15		1.21	99.64	1	4	5
Hornblende, Kakanui, New Zealand[9] USNM 143965	40.37	14.90	3.30	7.95	12.80	10.30	2.60	2.05	4.72	0.00	0.09		0.94	100.02	1	2	4
Hypersthene, Johnstown meteorite USNM 746	54.09	1.23		15.22	26.79	1.52	<0.05	<0.05	0.16		0.49	0.75	0.00	100.25	3	7	
Ilmenite, Ilmen Mtns., Miask, USSR[10] USNM 96189			11.6	36.1	0.31				45.7		4.77			99.40	7	1	
Magnetite, Minas Gerais, Brazil[11] USNM 114887			67.5	30.2										98.16	3	1	
Microcline, location unknown USNM 143966	64.24	18.30	0.00	0.04	0.03	0.02	1.30	15.14	0.01		0.04			99.12	8	3	
Olivine (Fo_{90}), San Carlos, Gila Co., AZ[12] USNM 111312/444	40.81			9.55	49.42	<0.05				0.00	0.14			100.29	1	2	
Olivine (Fo_{83}), Springwater meteorite USNM 2566	38.95			16.62	43.58						0.30	0.02	<0.05	99.47	3	7	
Omphacite, Roberts Victor Mine, So. Africa USNM 110607	55.42	8.89	1.35	3.41	11.57	13.75	5.00	0.15	0.37		0.10		0.02	100.03	1	3	4
Osumilite, Main, Labrador USNM 143967	60.20	22.60		6.38	5.83	<0.03	0.39	4.00	0.18				0.02	99.60	1	8	
Plagioclase (Labradorite), Lake County, OR USNM 115900	51.25	30.91	0.34	0.15	0.14	13.64	3.45	0.18	0.05		0.01		0.05	100.17	9	1	1
Pyrope, Kakanui, New Zealand USNM 143968	41.46	23.73		10.68	18.51	5.17			0.47		0.28		<0.01	100.30	1	2	4
Quartz, Hot Springs, AR[13] USNM R17701	99.99													99.99	1	1	
Scapolite (Meionite), Brazil[14] USNM R6600-1	49.78	25.05		0.17		13.58	5.20	0.94					0.21	99.86	2	1	

[1] SrO 0.07; RE_2O_3 1.43; ThO_2 0.02; As_2O_3 0.09; V_2O_5 0.01; CO_2 0.05; SO_3 0.37; F 3.53; Cl 0.41; sub-total: 101.52; O equivalent to Cl, F = 1.58; final total: 99.94.

[2] BaO 37.05.

[3] Total Fe reported as FeO.

[4] Emission spectrometric analysis: Si 0.03; Fe 0.003; Mg 0.007; Ca 0.003; Na 0.005; K 0.005.

[5] ZnO 42.50.

[6] S 0.12; sub-total: 100.13; O equivalent to S = 0.06; final total: 100.07.

[7] Cl 0.13; sub-total: 99.59; O equivalent to Cl = 0.03; final total: 99.56.

[8] CO_2 not determined (insufficient sample); Cl 0.00; F 0.01. Synthetic glass prepared by Corning Glass Company.

[9] New TiO_2 value: 4.72.

[10] Nb_2O_5 0.92.

[11] Preliminary values: MgO 0.05; TiO_2 0.16; MnO <0.01; Cr_2O_3 0.25.

[12] NiO 0.37.

[13] Emission spectrometric analysis: Al 0.0005; Fe 0.01; Mg 0.005; Ca 0.001; Na 0.001; K 0.0003.

[14] CO_2 2.5; SO_3 1.32; Cl 1.43; sub-total: 100.18; O equivalent to Cl = 0.32; final total: 99.86.

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

Mineral	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	Zn
Anorthite	0.96 (1.51)	0.81 (1.26)			0.92 (1.23)							
Anorthoclase	1.09 (1.60)	0.79 (1.38)				1.11 (1.57)						
Apatite (Fluorapatite)					1.02 (1.51)				0.97 (1.51)			
Augite	0.99 (1.37)	0.97 (1.66)	0.84 (1.26)	0.94 (1.23)	1.00 (1.25)							
Benitoite	----------											
Chromite		1.00 (1.47)	1.01 (1.66)	1.11 (1.50)							1.12 (1.49)	
Corundum	----------											
Diopside	1.07 (1.37)			0.97 (1.50)	0.95 (1.50)							
Fayalite	0.95 (1.46)		1.14 (2.32)							1.03 (1.58)		
Gahnite		1.06 (1.36)										1 (1)
Garnet, 87375	0.89 (1.26)	1.01 (1.42)	1.06 (1.41)	1.01 (1.49)	0.86 (1.11)							
Garnet, 110752	0.88 (1.32)	0.94 (1.28)	0.90 (1.20)	1.00 (1.34)	0.87 (1.47)							
Glass, 111240/52 VG-2	0.94 (1.10)	0.89 (1.11)	0.86 (1.13)	0.96 (1.61)	1.00 (1.27)	1.05 (1.31)						
Glass, 113498/1 VG-A99	0.94 (1.32)	1.10 (1.46)	1.07 (1.38)	0.92 (1.38)	0.93 (1.34)	1.15 (2.10)		0.97 (1.44)				
Glass, 113716	1.12 (1.42)	1.00 (1.30)	0.94 (1.34)	1.01 (1.36)	0.83 (1.19)	1.25 (2.59)						
Glass, 72854 VG-568	0.97 (1.61)	1.00 (1.47)				2.31 (3.45)	0.98 (1.36)					
Glass, 2213	1.05 (1.72)	0.87 (1.24)	1.01 (1.34)		1.05 (1.61)							
Hornblende, Arenal	1.07 (1.67)	0.97 (1.66)	1.12 (1.36)	1.11 (1.67)	1.01 (1.27)	0.98 (1.32)						
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)				
Hypersthene	1.07 (1.55)		1.10 (1.37)	0.93 (1.27)								
Ilmenite			1.72 (3.60)					1.34 (1.98)		1.21 (1.53)		
Magnetite			0.84 (1.16)									
Microcline	0.94 (1.13)	1.04 (1.52)					1.09 (1.59)					
Olivine (Fo_{90}), San Carlos	0.81 (1.13)		0.90 (1.29)	1.00 (1.64)								
Olivine (Fo_{83}), 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)					
Plagioclase (Labradorite)	1.09 (1.49)	0.95 (1.40)			1.04 (1.65)	0.91 (1.33)						
Pyrope	1.08 (1.46)	0.95 (1.20)	1.09 (1.59)	0.98 (1.21)	0.97 (1.18)							
Quartz	----------											
Scapolite (Meionite)	0.99 (1.29)	0.95 (1.41)			0.91 (1.16)	0.96 (1.41)						

$$\text{Sigma ratio for 10 grains} = \frac{\text{observed sigma for all grains}}{\text{sigma predicted from counting statistics}}$$

$$\text{Sigma ratio for least homogeneous grain (in parentheses)} = \frac{\text{observed sigma for this particular grain}}{\text{sigma predicted from counting statistics}}$$

KEY TO TABLE 1
Analysts, Sources, References

Analysts:

1. E. Jarosewich, Department of Mineral Sciences, Smithsonian Institution
2. J. Nelen, Department of Mineral Sciences, 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
5. B. Wiik, Geological Survey, Finland
6. U.S. Geological Survey, Geochemistry and Petrology Branch
7. D. Mills, X-Ray Assay Laboratories, Ontario, Canada; J. Nelen; J. Norberg
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Sources:

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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 observed standard deviation to the standard deviation predicted from counting statistics alone does not exceed 3. The ratios were obtained by taking ten ten-second counts on each of ten randomly selected grains. Table 2 gives ratios for the ten grains of each reference sample for major and some minor elements. The values in parentheses 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 homogeneity 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

“Prime prerequisites for microprobe reference samples are homogeneity at the micron level and availability in reasonable quantities for classical wet chemical analysis”

Reference Samples for Electron Microprobe Analysis*

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

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.

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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
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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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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
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corrections

Geostandards Newsletter, *Vol. 4, N° 1, Avril 1980*

[Page 44] In Table 1 appearing in the paper "Reference samples for electron m
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"Glass, Basaltic, Indian Ocean[5], USNM 113716". It should read as "Glass, Ba
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Table 1. Chemical analyses of electron microprobe reference samples. (The pur
not be representative of the entire USNM sample)

Mineral	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	M						
Anorthite, Great Sitkin Island, AL USNM 137041	44.00	36.03		0.62	<0.02	19.09	0.53	0.03	0.03								
Anorthoclase, Kakanui, New Zealand USNM 133868	66.44	20.12		0.20		0.87	9.31	2.35					<0.05	99.29	3	2	
Apatite (Fluorapatite), Durango, Mexico[1] USNM 104021	0.34	0.07	0.06	0.00	0.01	54.02	0.23	0.01		40.78	0.01		0.02	99.94	4	1	2
Augite, Kakanui, New Zealand USNM 122142	50.73	8.73	1.08	5.37	16.65	15.82	1.27	0.00	0.74		0.13		0.04	100.[illegible]	5	2	3
Benitoite, San Benito County, CA[2] USNM 86539	43.75								19.35					100.15	2	1	
Chromite, Tiebaghi Mine, New Caledonia[3] USNM 117075		9.92		13.04	15.20	0.12					0.11	60.5		98.89	2	1	
Corundum, synthetic[4] USNM 6575		99.99												99.99	1	1	
Diopside, Natural Bridge, NY USNM 117733	54.87	0.11		0.24	18.30	25.63	0.34				0.04			99.53	2	1	
Fayalite, Rockport, MA USNM 85276	29.22		1.32	66.36					0.04		2.14		0.1	99.18	2	1	
Gahnite, Brazil[5] USNM 145883		55.32		1.97							0.38			100.13	2		
Garnet, Roberts Victor Mine, South Africa USNM 87375	39.47	22.27	2.77	13.76	6.55	14.39			0.39		0.59		<0.01	100.19	1	3	4
Garnet, Roberts Victor Mine, South Africa USNM 110752	40.16	22.70	2.17	9.36	7.17	18.12			0.35		0.19		<0.01	100.22	1	3	4
Glass, Basaltic, Juan de Fuca Ridge USNM 111240/52 VG-2	50.81	14.06	2.23	9.83	6.71	11.12	2.62	0.19	1.85	0.20	0.22		0.02	99.86	1	4	5
Glass, Basaltic, Makaopuhi Lava Lake, HI USNM 113498/1 VG-A99	50.94	12.49	1.87	11.62	5.08	9.30	2.66	0.82	4.06	0.38	0.15		0.02	99.39	3	5	
~~Glass, Basaltic, Indian Ocean[6]~~ USNM 113716	51.52	15.39	1.12	8.12	8.21	11.31	2.48	0.09	1.30	0.12	0.17		0.18	100.07	3	6	
Glass, Rhyolitic, Yellowstone Nat. Pk., WY[7] USNM 72854 VG-568	76.71	12.06	0.48	0.80	<0.1	0.50	3.75	4.89	0.12	<0.01	0.03		0.12	99.56	3	6	
Glass, Tektite, synthetic[8] USNM 2213	75.75	11.34	0.64	4.32	1.51	2.66	1.06	1.88	0.50	0.00	0.11		0.10	99.88	6	7	
Hornblende, Arenal Volcano, Costa Rica USNM 111356	41.46	15.47	5.60	6.43	14.24	11.55	1.91	0.21	1.41	<0.01	0.15		1.21	99.64	1	4	5
Hornblende, Kakanui, New Zealand[9] USNM 143965	40.37	14.90	3.30	7.95	12.80	10.30	2.60	2.05	4.72	0.00	0.09		0.94	100.02	1	2	4
Hypersthene, Johnstown meteorite USNM 746	54.09	1.23		15.22	26.79	1.52	<0.05	<0.05	0.16		0.49	0.75	0.00	100.25	3	7	
Ilmenite, Ilmen Mtns., Miask, USSR[10] USNM 96189			11.6	36.1	0.31				45.7		4.77			99.40	7	1	
Magnetite, Minas Gerais, Brazil[11] USNM 114887			67.5	30.2										98.16	3	1	
Microcline, location unknown USNM 143966	64.24	18.30	0.00	0.04	0.03	0.02	1.30	15.14	0.01		0.04			99.12	8	3	
Olivine (Fo_{90}), San Carlos, Gila Co., AZ[12] USNM 111312/444	40.81			9.55	49.42	<0.05				0.00	0.14			100.29	1	2	
Olivine (Fo_{83}), Springwater meteorite USNM 2566	38.95			16.62	43.58						0.30	0.02	<0.05	99.47	3	7	
Omphacite, Roberts Victor Mine, So. Africa USNM 110607	55.42	8.89	1.35	3.41	11.57	13.75	5.00	0.15	0.37		0.10		0.02	100.03	1	3	4
Osumilite, Nain, Labrador USNM 143967	60.20	22.60		6.38	5.83	<0.03	0.39	4.00	0.18				0.02	99.60	1	8	
Plagioclase (Labradorite), Lake County, OR USNM 115900	51.25	30.91	0.34	0.15	0.14	13.64	3.45	0.18	0.05		0.01		0.05	100.17	9	1	1
Pyrope, Kakanui, New Zealand USNM 143968	41.46	23.73		10.68	18.51	5.17			0.47		0.28		<0.01	100.30	1	2	4
Quartz, Hot Springs, AR[13] USNM R17701	99.99													99.99	1	1	
Scapolite (Meionite), Brazil[14] USNM R6600-1	49.78	25.05		0.17		13.58	5.20	0.94					0.21	99.86	2	1	

[1] SrO 0.07; RE_2O_3 1.43; ThO_2 0.02; As_2O_3 0.09; V_2O_5 0.01; CO_2 0.05; SO_3 0.37; F 3.53; Cl 0.41; sub-total: 101.52; O equivalent to Cl, F = 1.58; final total: 99.94.

[2] BaO 37.05.

[3] Total Fe reported as FeO.

[4] Emission spectrometric analysis: Si 0.03; Fe 0.003; Mg 0.007; Ca 0.003; Na 0.005; K 0.005.

[5] ZnO 42.50.

[6] S 0.12; sub-total: 100.13; O equivalent to S = 0.06; final total: 100.07.

[7] Cl 0.13; sub-total: 99.59; O equivalent to Cl = 0.03; final total: 99.56.

[8] CO_2 not determined (insufficient sample); Cl 0.00; F 0.01. Synthetic glass prepared by Corning Glass Company.

[9] New TiO_2 value: 4.72.

[10] Nb_2O_5 0.92.

[11] Preliminary values: MgO 0.05; TiO_2 0.16; MnO <0.01; Cr_2O_3 0.25.

[12] NiO 0.37.

[13] Emission spectrometric analysis: Al 0.0005; Fe 0.01; Mg 0.005; Ca 0.001; Na 0.001; K 0.0003.

[14] CO_2 2.5; SO_3 1.32; Cl 1.43; sub-total: 100.18; O equivalent to Cl = 0.32; final total: 99.86.

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

Mineral	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	Zn
Anorthite	0.96 (1.51)	0.81 (1.26)			0.92 (1.23)							
Anorthoclase	1.09 (1.60)	0.79 (1.38)				1.11 (1.57)						
Apatite (Fluorapatite)					1.02 (1.51)				0.97 (1.51)			
Augite	0.99 (1.37)	0.97 (1.66)	0.84 (1.26)	0.94 (1.23)	1.00 (1.25)							
Benitoite	----------											
Chromite		1.00 (1.47)	1.01 (1.66)	1.11 (1.50)							1.12 (1.49)	
Corundum	----------											
Diopside	1.07 (1.37)			0.97 (1.50)	0.95 (1.50)							
Fayalite	0.95 (1.46)		1.14 (2.32)							1.03 (1.58)		
Gahnite		1.06 (1.36)										1 (1)
Garnet, 87375	0.89 (1.26)	1.01 (1.42)	1.06 (1.41)	1.01 (1.49)	0.86 (1.11)							
Garnet, 110752	0.88 (1.32)	0.94 (1.28)	0.90 (1.20)	1.00 (1.34)	0.87 (1.47)							
Glass, 111240/52 VG-2	0.94 (1.10)	0.89 (1.11)	0.86 (1.13)	0.96 (1.61)	1.00 (1.27)	1.05 (1.31)						
Glass, 113498/1 VG-A99	0.94 (1.32)	1.10 (1.46)	1.07 (1.38)	0.92 (1.38)	0.93 (1.34)	1.15 (2.10)		0.97 (1.44)				
Glass, 113716	1.12 (1.42)	1.00 (1.30)	0.94 (1.34)	1.01 (1.36)	0.83 (1.19)	1.25 (2.59)						
Glass, 72854 VG-568	0.97 (1.61)	1.00 (1.47)				2.31 (3.45)	0.98 (1.36)					
Glass, 2213	1.05 (1.72)	0.87 (1.24)	1.01 (1.34)		1.05 (1.61)							
Hornblende, Arenal	1.07 (1.67)	0.97 (1.66)	1.12 (1.36)	1.11 (1.67)	1.01 (1.27)	0.98 (1.32)						
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)				
Hypersthene	1.07 (1.55)		1.10 (1.37)	0.93 (1.27)								
Ilmenite			1.72 (3.60)					1.34 (1.98)		1.21 (1.53)		
Magnetite			0.84 (1.16)									
Microcline	0.94 (1.13)	1.04 (1.52)					1.09 (1.59)					
Olivine (Fo_{90}), San Carlos	0.81 (1.13)		0.90 (1.29)	1.00 (1.64)								
Olivine (Fo_{83}), 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)					
Plagioclase (Labradorite)	1.09 (1.49)	0.95 (1.40)			1.04 (1.65)	0.91 (1.33)						
Pyrope	1.08 (1.46)	0.95 (1.20)	1.09 (1.59)	0.98 (1.21)	0.97 (1.18)							
Quartz	----------											
Scapolite (Meionite)	0.99 (1.29)	0.95 (1.41)			0.91 (1.16)	0.96 (1.41)						

$$\text{Sigma ratio for 10 grains} = \frac{\text{observed sigma for all grains}}{\text{sigma predicted from counting statistics}}$$

$$\text{Sigma ratio for least homogeneous grain (in parentheses)} = \frac{\text{observed sigma for this particular grain}}{\text{sigma predicted from counting statistics}}$$

KEY TO TABLE 1
Analysts, Sources, References

Analysts:

1. E. Jarosewich, Department of Mineral Sciences, Smithsonian Institution
2. J. Nelen, Department of Mineral Sciences, Smithsonian Institution
3. J. Norberg, Department of Mineral Sciences, Smithsonian Institution
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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 mes
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Geostandards Newsletter, *Vol. 4, N° 1, Avril 1980*

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not be representative of the entire USNM sample)

Mineral	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	M						
Anorthite, Great Sitkin Island, AL USNM 137041	44.00	36.03		0.62	<0.02	19.09	0.53	0.03	0.03								
Anorthoclase, Kakanui, New Zealand USNM 133868	66.44	20.12		0.20		0.87	9.31	2.35					<0.05	99.29	3	2	
Apatite (Fluorapatite), Durango, Mexico[1] USNM 104021	0.34	0.07	0.06	0.00	0.01	54.02	0.23	0.01		40.78	0.01		0.01	99.94	4	1	2
Augite, Kakanui, New Zealand USNM 122142	50.73	8.73	1.08	5.37	16.65	15.82	1.27	0.00	0.74		0.13		0.04	100.[illegible]	5	2	3
Benitoite, San Benito County, CA[2] USNM 86539	43.75								19.35					100.15	2	1	
Chromite, Tiebaghi Mine, New Caledonia[3] USNM 117075		9.92		13.04	15.20	0.12					0.11	60.5		98.89	2	1	
Corundum, synthetic[4] USNM 6575		99.99												99.99	1	1	
Diopside, Natural Bridge, NY USNM 117733	54.87	0.11		0.24	18.30	25.63	0.34				0.04			99.53	2	1	
Fayalite, Rockport, MA USNM 85276	29.22		1.32	66.36					0.04		2.14		0.1	99.18	2	1	
Gahnite, Brazil[5] USNM 145883		55.32		1.97							0.38			100.13	2		
Garnet, Roberts Victor Mine, South Africa USNM 87375	39.47	22.27	2.77	13.76	6.55	14.39			0.39		0.59		<0.01	100.19	1	3	4
Garnet, Roberts Victor Mine, South Africa USNM 110752	40.16	22.70	2.17	9.36	7.17	18.12			0.35		0.19		<0.01	100.22	1	3	4
Glass, Basaltic, Juan de Fuca Ridge USNM 111240/52 VG-2	50.81	14.06	2.23	9.83	6.71	11.12	2.62	0.19	1.85	0.20	0.22		0.02	99.86	1	4	5
Glass, Basaltic, Makaopuhi Lava Lake, HI USNM 113498/1 VG-A99	50.94	12.49	1.87	11.62	5.08	9.30	2.66	0.82	4.06	0.38	0.15		0.02	99.39	3	5	
Glass, Basaltic, Indian Ocean[6] USNM 113716	51.52	15.39	1.12	8.12	8.21	11.31	2.48	0.09	1.30	0.12	0.17		0.18	100.07	3	6	
Glass, Rhyolitic, Yellowstone Nat. Pk., WY[7] USNM 72854 VG-568	76.71	12.06	0.48	0.80	<0.1	0.50	3.75	4.89	0.12	<0.01	0.03		0.12	99.56	3	4	
Glass, Tektite, synthetic[8] USNM 2213	75.75	11.34	0.64	4.32	1.51	2.66	1.06	1.88	0.50	0.00	0.11		0.10	99.88	6	7	
Hornblende, Arenal Volcano, Costa Rica USNM 111356	41.46	15.47	5.60	6.43	14.24	11.55	1.91	0.21	1.41	<0.01	0.15		1.21	99.64	1	4	5
Hornblende, Kakanui, New Zealand[9] USNM 143965	40.37	14.90	3.30	7.95	12.80	10.30	2.60	2.05	4.72	0.00	0.09		0.94	100.02	1	2	4
Hypersthene, Johnstown meteorite USNM 746	54.09	1.23		15.22	26.79	1.52	<0.05	<0.05	0.16		0.49	0.75	0.00	100.25	3	7	
Ilmenite, Ilmen Mtns., Miask, USSR[10] USNM 96189			11.6	36.1	0.31				45.7		4.77			99.40	7	1	
Magnetite, Minas Gerais, Brazil[11] USNM 114887			67.5	30.2										98.16	3	1	
Microcline, location unknown USNM 143966	64.24	18.30	0.00	0.04	0.03	0.02	1.30	15.14	0.01		0.04			99.12	8	3	
Olivine (Fo_{90}), San Carlos, Gila Co., AZ[12] USNM 111312/444	40.81			9.55	49.42	<0.05				0.00	0.14			100.29	1	2	
Olivine (Fo_{83}), Springwater meteorite USNM 2566	38.95			16.62	43.58						0.30	0.02	<0.05	99.47	3	7	
Omphacite, Roberts Victor Mine, So. Africa USNM 110607	55.42	8.89	1.35	3.41	11.57	13.75	5.00	0.15	0.37		0.10		0.02	100.03	1	3	4
Osumilite, Nain, Labrador USNM 143967	60.20	22.60		6.38	5.83	<0.03	0.39	4.00	0.18				0.02	99.60	1	8	
Plagioclase (Labradorite), Lake County, OR USNM 115900	51.25	30.91	0.34	0.15	0.14	13.64	3.45	0.18	0.05		0.01		0.05	100.17	9	1	1
Pyrope, Kakanui, New Zealand USNM 143968	41.46	23.73		10.68	18.51	5.17			0.47		0.28		<0.01	100.30	1	2	4
Quartz, Hot Springs, AR[13] USNM R17701	99.99													99.99	1	1	
Scapolite (Meionite), Brazil[14] USNM R6600-1	49.78	25.05		0.17		13.58	5.20	0.94					0.21	99.86	2	1	

[1] SrO 0.07; RE_2O_3 1.43; ThO_2 0.02; As_2O_3 0.09; V_2O_5 0.01; CO_2 0.05; SO_3 0.37; F 3.53; Cl 0.41; sub-total: 101.52; O equivalent to Cl, F = 1.58; final total: 99.94.

[2] BaO 37.05.

[3] Total Fe reported as FeO.

[4] Emission spectrometric analysis: Si 0.03; Fe 0.003; Mg 0.007; Ca 0.003; Na 0.005; K 0.005.

[5] ZnO 42.50.

[6] S 0.12; sub-total: 100.13; O equivalent to S = 0.06; final total: 100.07.

[7] Cl 0.13; sub-total: 99.59; O equivalent to Cl = 0.03; final total: 99.56.

[8] CO_2 not determined (insufficient sample); Cl 0.00; F 0.01. Synthetic glass prepared by Corning Glass Company.

[9] New TiO_2 value: 4.72.

[10] Nb_2O_5 0.92.

[11] Preliminary values: MgO 0.05; TiO_2 0.16; MnO <0.01; Cr_2O_3 0.25.

[12] NiO 0.37.

[13] Emission spectrometric analysis: Al 0.0005; Fe 0.01; Mg 0.005; Ca 0.001; Na 0.001; K 0.0003.

[14] CO_2 2.5; SO_3 1.32; Cl 1.43; sub-total: 100.18; O equivalent to Cl = 0.32; final total: 99.86.

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

Mineral	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	Zn
Anorthite	0.96 (1.51)	0.81 (1.26)			0.92 (1.23)							
Anorthoclase	1.09 (1.60)	0.79 (1.38)				1.11 (1.57)						
Apatite (Fluorapatite)					1.02 (1.51)				0.97 (1.51)			
Augite	0.99 (1.37)	0.97 (1.66)	0.84 (1.26)	0.94 (1.23)	1.00 (1.25)							
Benitoite	----------											
Chromite		1.00 (1.47)	1.01 (1.66)	1.11 (1.50)							1.12 (1.49)	
Corundum	----------											
Diopside	1.07 (1.37)			0.97 (1.50)	0.95 (1.50)							
Fayalite	0.95 (1.46)		1.14 (2.32)							1.03 (1.58)		
Gahnite		1.06 (1.36)										1 (1)
Garnet, 87375	0.89 (1.26)	1.01 (1.42)	1.06 (1.41)	1.01 (1.49)	0.86 (1.11)							
Garnet, 110752	0.88 (1.32)	0.94 (1.28)	0.90 (1.20)	1.00 (1.34)	0.87 (1.47)							
Glass, 111240/52 VG-2	0.94 (1.10)	0.89 (1.11)	0.86 (1.13)	0.96 (1.61)	1.00 (1.27)	1.05 (1.31)						
Glass, 113498/1 VG-A99	0.94 (1.32)	1.10 (1.46)	1.07 (1.38)	0.92 (1.38)	0.93 (1.34)	1.15 (2.10)		0.97 (1.44)				
Glass, 113716	1.12 (1.42)	1.00 (1.30)	0.94 (1.34)	1.01 (1.36)	0.83 (1.19)	1.25 (2.59)						
Glass, 72854 VG-568	0.97 (1.61)	1.00 (1.47)				2.31 (3.45)	0.98 (1.36)					
Glass, 2213	1.05 (1.72)	0.87 (1.24)	1.01 (1.34)		1.05 (1.61)							
Hornblende, Arenal	1.07 (1.67)	0.97 (1.66)	1.12 (1.36)	1.11 (1.67)	1.01 (1.27)	0.98 (1.32)						
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)				
Hypersthene	1.07 (1.55)		1.10 (1.37)	0.93 (1.27)								
Ilmenite			1.72 (3.60)					1.34 (1.98)		1.21 (1.53)		
Magnetite			0.84 (1.16)									
Microcline	0.94 (1.13)	1.04 (1.52)					1.09 (1.59)					
Olivine (Fo_{90}), San Carlos	0.81 (1.13)		0.90 (1.29)	1.00 (1.64)								
Olivine (Fo_{83}), 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)					
Plagioclase (Labradorite)	1.09 (1.49)	0.95 (1.40)			1.04 (1.65)	0.91 (1.33)						
Pyrope	1.08 (1.46)	0.95 (1.20)	1.09 (1.59)	0.98 (1.21)	0.97 (1.18)							
Quartz	----------											
Scapolite (Meionite)	0.99 (1.29)	0.95 (1.41)			0.91 (1.16)	0.96 (1.41)						

$$\text{Sigma ratio for 10 grains} = \frac{\text{observed sigma for all grains}}{\text{sigma predicted from counting statistics}}$$

$$\text{Sigma ratio for least homogeneous grain (in parentheses)} = \frac{\text{observed sigma for this particular grain}}{\text{sigma predicted from counting statistics}}$$

KEY TO TABLE 1
Analysts, Sources, References

Analysts:

1. E. Jarosewich, Department of Mineral Sciences, Smithsonian Institution
2. J. Nelen, Department of Mineral Sciences, 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
5. B. Wiik, Geological Survey, Finland
6. U.S. Geological Survey, Geochemistry and Petrology Branch
7. D. Mills, X-Ray Assay Laboratories, Ontario, Canada; J. Nelen; J. Norberg
8. E. Kiss, Department of Geophysics and Geochemistry, Australian National University
9. J.J. Fahey and L.C. Peck, U.S. Geological 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, Smithsonian Institution
3. G. Switzer, Department of Mineral Sciences, Smithsonian Institution
4. R.G. Dymek, 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 Technology
8. R.S. Clarke, Jr., Department of Mineral Sciences, Smithsonian Institution
9. J.H. Berg, Northern Illinois University

References for previously published analyses:

1. D.B. Stewart, G.W. Walker, T.L. Wright and J.J. Fahey (1966)
Physical properties of calcic labradorite from Lake County, Oregon, American Mineralogist, 51: 177-197.
2. E.J. Young, A.T. Myers, E.L. Munson and N.M. Conklin (1969)
Mineralogy and geochemistry of fluorapatite from Cerro de Mercado, Durango, Mexico, U.S. Geological Survey Professional Paper 650D: 84-93.
3. B. Mason and R.O. Allen (1973)
Minor and trace elements in augite, hornblende and pyrope megacrysts from Kakanui, New Zealand; New Zealand Journal of Geology and Geophysics, 16(4): 935-947.
4. E. Jarosewich (1972)
Chemical analysis of five minerals for microprobe 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 Geological Sciences, Harvard University.
6. E. Jarosewich (1975)
Chemical analysis of two microprobe standards, Smithsonian Contributions to the Earth Sciences, 14: 85-86.
7. E. Kiss (1970)
Personal communication, Department of Geophysics and Geochemistry, Australian National 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 "impurities" and make a thorough check for them. For
…are found that are 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 observed standard deviation to the standard deviation predicted from counting statistics alone does not exceed 3. The ratios were obtained by taking ten ten-second counts on each of ten randomly selected grains. Table 2 gives ratios for the ten grains of each reference sample for major and some minor elements. The values in parentheses 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 homogeneity 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

“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. NORBERG

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
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* Reprinted by permission of *Smithsonian Institution Press* from Smithsonian Institution Contributions to the Earth Sciences, Number 22: "Electron Microprobe Reference Samples for Mineral Analyses", Eugene Jarosewich, Joseph Nelen and Julie Norberg: pages 68-72. Washington, D.C.: Smithsonian Institution Press, 1979.

corrections

Geostandards Newsletter, *Vol. 4, N° 1, Avril 1980*

|Page 44| In Table 1 appearing in the paper "Reference samples for electron m
Jarosewich, J.A. Nelen and J.A. Norberg, the footnote reference number 5
"Glass, Basaltic, Indian Ocean[5], USNM 113716". It should read as "Glass, Ba
113716". Starting from this "basaltic" sample, all further sequential foot
one unity. The whole Table 1 with correct footnote numbering, 1 to 14, is rep

Table 1. Chemical analyses of electron microprobe reference samples. (The pur
not be representative of the entire USNM sample)

Mineral	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	M						
Anorthite, Great Sitkin Island, AL USNM 137041	44.00	36.03		0.62	<0.02	19.09	0.53	0.03	0.03								
Anorthoclase, Kakanui, New Zealand USNM 133868	66.44	20.12		0.20		0.87	9.31	2.35					<0.05	99.29	3	2	
Apatite (Fluorapatite), Durango, Mexico[1] USNM 104021	0.34	0.07	0.06	0.00	0.01	54.02	0.23	0.01		40.78	0.01		0.01	99.94	4	1	2
Augite, Kakanui, New Zealand USNM 122142	50.73	[illegible]	[illegible]	[illegible]	16.65	15.82	1.27	0.00	0.74		0.13		0.04	100.[illegible]	5	2	3
Benitoite, San Benito County, CA[2] USNM 86539	43.75								19.35					100.15	2	1	
Chromite, Tiebaghi Mine, New Caledonia[3] USNM 117075		9.92		13.04	15.20	0.12					0.11	60.5		98.89	2	1	
Corundum, synthetic[4] USNM 6575		99.99												99.99	1	1	
Diopside, Natural Bridge, NY USNM 117733	54.87	0.11		0.24	18.30	25.63	0.34				0.04			99.53	2	1	
Fayalite, Rockport, MA USNM 85276	29.22		1.32	66.36					0.04		2.14		0.1	99.18	2	1	
Gahnite, Brazil[5] USNM 145883		55.32		1.97							0.38			100.13	2		
Garnet, Roberts Victor Mine, South Africa USNM 87375	39.47	22.27	2.77	13.76	6.55	14.39			0.39		0.59		<0.01	100.19	1	3	4
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Glass, Basaltic, Makaopuhi Lava Lake, HI USNM 113498/1 VG-A99	50.94	12.49	1.87	11.62	5.08	9.30	2.66	0.82	4.06	0.38	0.15		0.02	99.39	3	5	
~~Glass, Basaltic, Indian Ocean[6] USNM 113716~~	51.52	15.39	1.12	8.12	8.21	11.31	2.48	0.09	1.30	0.12	0.17		0.18	100.07	3	6	
Glass, Rhyolitic, Yellowstone Nat. Pk., WY[7] USNM 72854 VG-568	76.71	12.06	0.48	0.80	<0.1	0.50	3.75	4.89	0.12	<0.01	0.03		0.12	99.56	3	4	
Glass, Tektite, synthetic[8] USNM 2213	75.75	11.34	0.64	4.32	1.51	2.66	1.06	1.88	0.50	0.00	0.11		0.10	99.88	6	7	
Hornblende, Arenal Volcano, Costa Rica USNM 111356	41.46	15.47	5.60	6.43	14.24	11.55	1.91	0.21	1.41	<0.01	0.15		1.21	99.64	1	4	5
Hornblende, Kakanui, New Zealand[9] USNM 143965	40.37	14.90	3.30	7.95	12.80	10.30	2.60	2.05	4.72	0.00	0.09		0.94	100.02	1	2	4
Hypersthene, Johnstown meteorite USNM 746	54.09	1.23		15.22	26.79	1.52	<0.05	<0.05	0.16		0.49	0.75	0.00	100.25	3	7	
Ilmenite, Ilmen Mtns., Miask, USSR[10] USNM 96189			11.6	36.1	0.31				45.7		4.77			99.40	7	1	
Magnetite, Minas Gerais, Brazil[11] USNM 114887			67.5	30.2										98.16	3	1	
Microcline, location unknown USNM 143966	64.24	18.30	0.00	0.04	0.03	0.02	1.30	15.14	0.01		0.04			99.12	8	3	
Olivine (Fo_{90}), San Carlos, Gila Co., AZ[12] USNM 111312/444	40.81			9.55	49.42	<0.05				0.00	0.14			100.29	1	2	
Olivine (Fo_{83}), Springwater meteorite USNM 2566	38.95			16.62	43.58						0.30	0.02	<0.05	99.47	3	7	
Omphacite, Roberts Victor Mine, So. Africa USNM 110607	55.42	8.89	1.35	3.41	11.57	13.75	5.00	0.15	0.37		0.10		0.02	100.03	1	3	4
Osumilite, Main, Labrador USNM 143967	60.20	22.60		6.38	5.83	<0.03	0.39	4.00	0.18				0.02	99.60	1	8	
Plagioclase (Labradorite), Lake County, OR USNM 115900	51.25	30.91	0.34	0.15	0.14	13.64	3.45	0.18	0.05		0.01		0.05	100.17	9	1	1
Pyrope, Kakanui, New Zealand USNM 143968	41.46	23.73		10.68	18.51	5.17			0.47		0.28		<0.01	100.30	1	2	4
Quartz, Hot Springs, AR[13] USNM R17701	99.99													99.99	1	1	
Scapolite (Meionite), Brazil[14] USNM R6600-1	49.78	25.05		0.17		13.58	5.20	0.94					0.21	99.86	2	1	

[1] SrO 0.07; RE_2O_3 1.43; ThO_2 0.02; As_2O_3 0.09; V_2O_5 0.01; CO_2 0.05; SO_3 0.37; F 3.53; Cl 0.41; sub-total: 101.52; O equivalent to Cl, F = 1.58; final total: 99.94.

[2] BaO 37.05.

[3] Total Fe reported as FeO.

[4] Emission spectrometric analysis: Si 0.03; Fe 0.003; Mg 0.007; Ca 0.003; Na 0.005; K 0.005.

[5] ZnO 42.50.

[6] S 0.12; sub-total: 100.13; O equivalent to S = 0.06; final total: 100.07.

[7] Cl 0.13; sub-total: 99.59; O equivalent to Cl = 0.03; final total: 99.56.

[8] CO_2 not determined (insufficient sample); Cl 0.00; F 0.01. Synthetic glass prepared by Corning Glass Company.

[9] New TiO_2 value: 4.72.

[10] Nb_2O_5 0.92.

[11] Preliminary values: MgO 0.05; TiO_2 0.16; MnO <0.01; Cr_2O_3 0.23.

[12] NiO 0.37.

[13] Emission spectrometric analysis: Al 0.0005; Fe 0.01; Mg 0.005; Ca 0.001; Na 0.001; K 0.0003.

[14] CO_2 2.5; SO_3 1.32; Cl 1.43; sub-total: 100.18; O equivalent to Cl = 0.32; final total: 99.86.

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

Mineral	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	Zn
Anorthite	0.96 (1.51)	0.81 (1.26)			0.92 (1.23)							
Anorthoclase	1.09 (1.60)	0.79 (1.38)				1.11 (1.57)						
Apatite (Fluorapatite)					1.02 (1.51)				0.97 (1.51)			
Augite	0.99 (1.37)	0.97 (1.66)	0.84 (1.26)	0.94 (1.23)	1.00 (1.25)							
Benitoite	----------											
Chromite		1.00 (1.47)	1.01 (1.66)	1.11 (1.50)							1.12 (1.49)	
Corundum	----------											
Diopside	1.07 (1.37)			0.97 (1.50)	0.95 (1.50)							
Fayalite	0.95 (1.46)		1.14 (2.32)							1.03 (1.58)		
Gahnite		1.06 (1.36)										1 (1)
Garnet, 87375	0.89 (1.26)	1.01 (1.42)	1.06 (1.41)	1.01 (1.49)	0.86 (1.11)							
Garnet, 110752	0.88 (1.32)	0.94 (1.28)	0.90 (1.20)	1.00 (1.34)	0.87 (1.47)							
Glass, 111240/52 VG-2	0.94 (1.10)	0.89 (1.11)	0.86 (1.13)	0.96 (1.61)	1.00 (1.27)	1.05 (1.31)						
Glass, 113498/1 VG-A99	0.94 (1.32)	1.10 (1.46)	1.07 (1.38)	0.92 (1.38)	0.93 (1.34)	1.15 (2.10)		0.97 (1.44)				
Glass, 113716	1.12 (1.42)	1.00 (1.30)	0.94 (1.34)	1.01 (1.36)	0.83 (1.19)	1.25 (2.59)						
Glass, 72854 VG-568	0.97 (1.61)	1.00 (1.47)				2.31 (3.45)	0.98 (1.36)					
Glass, 2213	1.05 (1.72)	0.87 (1.24)	1.01 (1.34)		1.05 (1.61)							
Hornblende, Arenal	1.07 (1.67)	0.97 (1.66)	1.12 (1.36)	1.11 (1.67)	1.01 (1.27)	0.98 (1.32)						
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)				
Hypersthene	1.07 (1.55)		1.10 (1.37)	0.93 (1.27)								
Ilmenite			1.72 (3.60)					1.34 (1.98)		1.21 (1.53)		
Magnetite			0.84 (1.16)									
Microcline	0.94 (1.13)	1.04 (1.52)					1.09 (1.59)					
Olivine (Fo_{90}), San Carlos	0.81 (1.13)		0.90 (1.29)	1.00 (1.64)								
Olivine (Fo_{83}), 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)					
Plagioclase (Labradorite)	1.09 (1.49)	0.95 (1.40)			1.04 (1.65)	0.91 (1.33)						
Pyrope	1.08 (1.46)	0.95 (1.20)	1.09 (1.59)	0.98 (1.21)	0.97 (1.18)							
Quartz	----------											
Scapolite (Meionite)	0.99 (1.29)	0.95 (1.41)			0.91 (1.16)	0.96 (1.41)						

$$\text{Sigma ratio for 10 grains} = \frac{\text{observed sigma for all grains}}{\text{sigma predicted from counting statistics}}$$

$$\text{Sigma ratio for least homogeneous grain (in parentheses)} = \frac{\text{observed sigma for this particular grain}}{\text{sigma predicted from counting statistics}}$$

KEY TO TABLE 1
Analysts, Sources, References

Analysts:

1. E. Jarosewich, Department of Mineral Sciences, Smithsonian Institution
2. J. Nelen, Department of Mineral Sciences, 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
5. B. Wiik, Geological Survey, Finland
6. U.S. Geological Survey, Geochemistry and Petrology Branch
7. D. Mills, X-Ray Assay Laboratories, Ontario, Canada; J. Nelen; J. Norberg
8. E. Kiss, Department of Geophysics and Geochemistry, Australian National University
9. J.J. Fahey and L.C. Peck, U.S. Geological 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, Smithsonian Institution
3. G. Switzer, Department of Mineral Sciences, Smithsonian Institution
4. R.G. Dymek, 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 Technology
8. R.S. Clarke, Jr., Department of Mineral Sciences, Smithsonian Institution
9. J.H. Berg, Northern Illinois University

References for previously published analyses:

1. D.B. Stewart, G.W. Walker, T.L. Wright and J.J. Fahey (1966) Physical properties of calcic labradorite from Lake County, Oregon, American Mineralogist, 51: 177-197.
2. E.J. Young, A.T. Myers, E.L. Munson and N.M. Conklin (1969) Mineralogy and geochemistry of fluorapatite from Cerro de Mercado, Durango, Mexico, U.S. Geological Survey Professional Paper 650D: 84-93.
3. B. Mason and R.O. Allen (1973) Minor and trace elements in augite, hornblende and pyrope megacrysts from Kakanui, New Zealand; New Zealand Journal of Geology and Geophysics, 16(4): 935-947.
4. E. Jarosewich (1972) Chemical analysis of five minerals for microprobe 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 Geological Sciences, Harvard University.
6. E. Jarosewich (1975) Chemical analysis of two microprobe standards, Smithsonian Contributions to the Earth Sciences, 14: 85-86.
7. E. Kiss (1970) Personal communication, Department of Geophysics and Geochemistry, Australian National University.

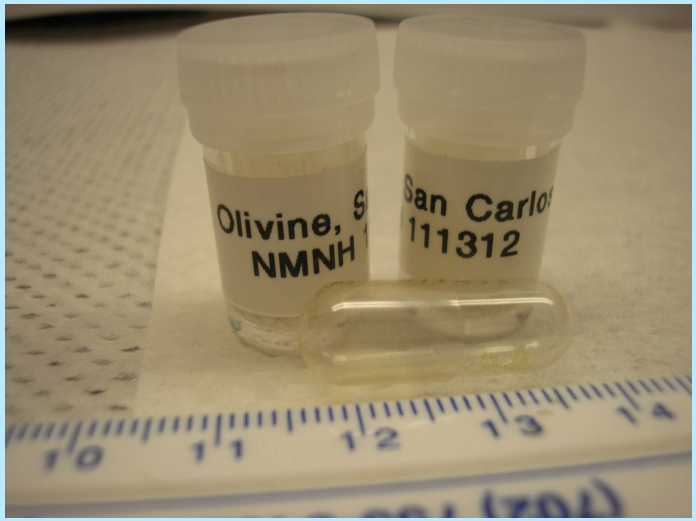
Even after the most careful preparation of the reference sample, a grain of accessory mineral or matrix may remain in the sample, which, in the course of preparation of the reference sample discs, could be included with the reference sample. Occasional grains of the reference sample will differ in composition because of heterogeneity. These problems can never be totally eliminated. The user should be aware of the possible presence of such "impurities" and make a thorough check for them. For example, occasional grains are found that are 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 observed standard deviation to the standard deviation predicted from counting statistics alone does not exceed 3. The ratios were obtained by taking ten ten-second counts on each of ten randomly selected grains. Table 2 gives ratios for the ten grains of each reference sample for major and some minor elements. The values in parentheses 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 homogeneity 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

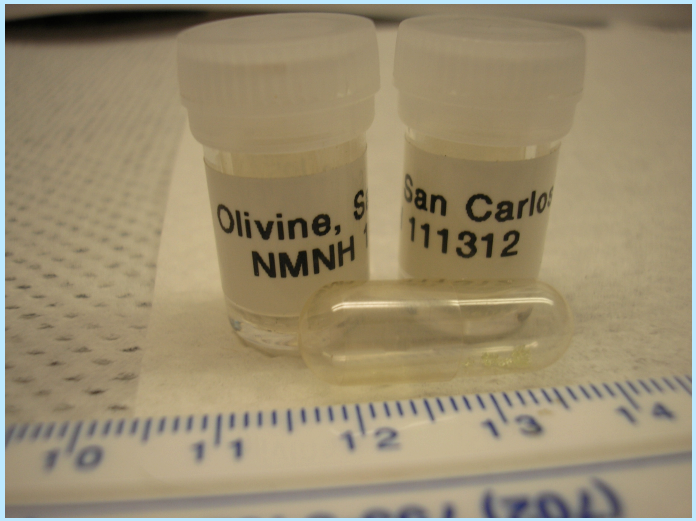
“The overall homogeneity of each sample was determined using the criterion given by Boyd el al whereby the sample is considered to be homogeneous if the ratio (homogeneity index) of observed standard deviation to the standard deviation predicted by counting statistics alone does not exceed 3. The ratios 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)

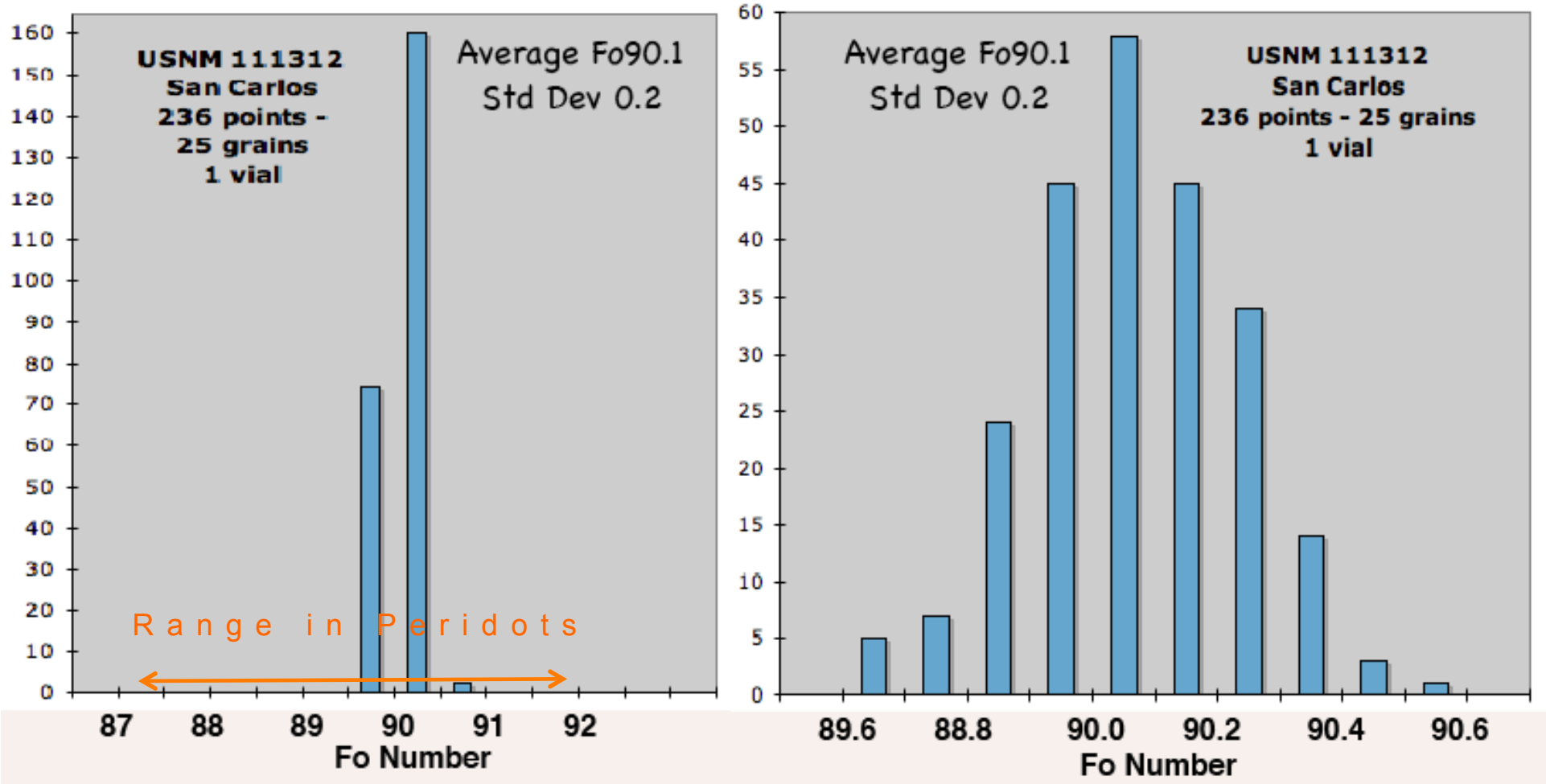


The Department of Mineral Sciences of the Smithsonian supplied me with 2 small vials of the USNM 111312 material (with at least 25 grains in each), which allowed me to look at the natural variability in the USNM San Carlos material

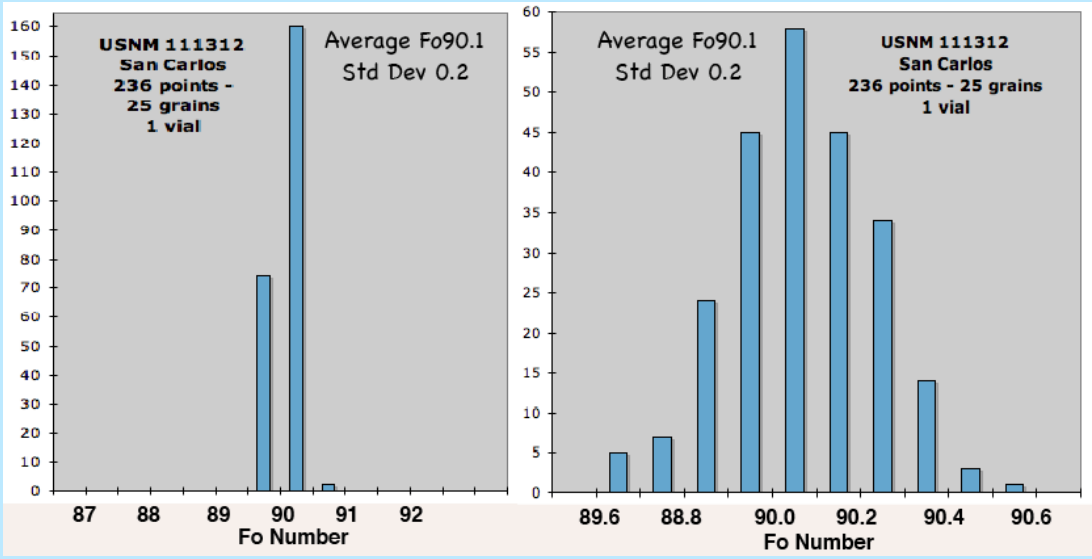


Here I report on EPMA measurements on 236 points in 25 small (200-300 um) grains from 1 vial, mounted in epoxy and polished.

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 ±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.

	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

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

Kilbourne Hole xenolith

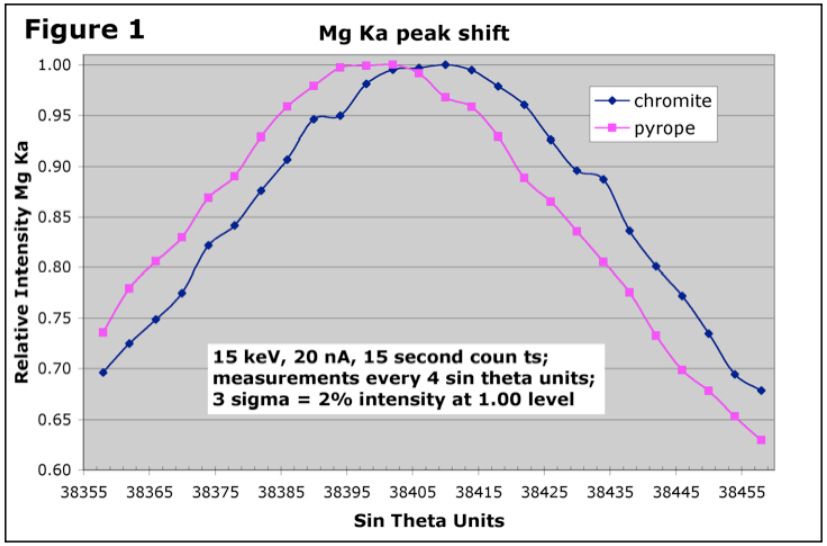
25 mm

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

Wt% oxide	XRF[1]	EPMA[2]	Theoretical
SiO_2	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	

[1] Also: 0.14 wt% Al_2O_3; Cr 210 ppm; Zn 104 ppm; Na, K, P, Ti=0.
[2] Using USNM San Carlos (26 grains averaged) as standard

There may be Mg K_α Peak Shifts to watch out for



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

Table 1: Shift in Mg Kα

Mineral	Type	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