Reprinted from Smithsonian Contributions to the Earth Sciences,
No. 22, R. F. Fudali, Ed., 1979.

Electron Microprobe Reference Samples for Mineral Analyses

Eugene Jarosewich, Joseph A. Nelen, and Julie A. Norberg

ABSTRACT

A table is presented containing compositional data for 25 minerals, four natural glasses, and one synthetic glass prepared and analyzed for use as microprobe reference samples at the Smithsonian Institution. The table includes new chemical analyses of minerals and some updated analyses of minerals published previously.

Detailed descriptions of sample preparation and evaluation of homogeneity are given.

Introduction

Microprobe analyses are an essential part of present-day mineralogical and petrological studies. It can be said that the application of the microprobe to mineral studies and material sciences in general is one of the most significant advances since the first use of the petrographic microscope in the middle of the last century. The technique is now well established, widely used, and capable of high-quality analyses. As with all comparative instrumental techniques, however, it requires well-characterized reference samples. Prime prerequisites for microprobe reference samples are homogeneity at the micrometer level and availability in reasonable quantities for standard chemical analyses. Either prerequisite is usually easily satisfied by itself but together are difficult to achieve.

One of the problems with some minerals used as microprobe reference samples is a lack of proper documentation. Even if well-described minerals are from the same locality and/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 this particular 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 the precalculated 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 Si-Al-Mg system have been pointed out by Bence and Holzwarth (1977). Similar discrepancies have been observed by other probe users.

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

ACKNOWLEDGMENTS.—We wish to acknowledge those curators and others listed in Table 1 who provided us with samples for use as microprobe reference samples. Brian Mason's careful examination and assistance in separation of minerals is also greatly appreciated.

Preparation of Reference Samples

When a sufficient quantity (at least 2 g) of a mineral or glass is available for use as a microprobe

Eugene Jarosewich, Joseph A. Nelen, and Julie A. Norberg, Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, D.C. 20560.

reference sample, a thin section is prepared for microscopic examination. Next, a microprobe analysis for composition and homogeneity is performed. If 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 or a Franz magnetic separator or both. In some instances cleaning with a suitable acid is also useful. As a final step, the material is examined under a low-powered microscope and most 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 (Peck, 1964; Hillebrand et al., 1953) is performed on the same separate that is to be used as the reference sample.

Discussion

In Table 1 are presented the data for newly analyzed minerals, earlier published analyses, and updated analyses for several minerals that have been in use for some time. Johnstown meteorite hypersthene and Springwater meteorite olivine have been re-analyzed using what we believe to be much cleaner separates. Kakanui hornblende has been re-analyzed for TiO_2.

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 standard discs, could be included with the reference sample. Occasional grains of the standard itself will be "off composition," due to inhomogeneity. 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 criteria given by Boyd et al. (1967) whereby the sample is considered to be homogeneous if the sigma ratio (homogeneity index) of observed standard deviation (sigma) to the standard deviation predicted from counting statistics alone does not exceed 3. The sigma ratios were calculated with reference to ten ten-second counts on each of ten randomly selected grains. Table 2 gives sigma ratios for the ten grains of each reference sample for major and some minor elements. The values in parentheses indicate the worst sigma 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 criterion of sigma ratios is used as a measure of homogeneity, all the reference samples prove to be 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.

These samples were prepared in only small quantities, but they can be judiciously made available to microprobe users interested in the analysis of geologic materials. Potential users should remember that the purified samples differ in bulk chemistry from the specimens from which they were separated and should be very specific in their requests—i.e., the requests should be made for *microprobe standard* USNM no. *n* rather than simply material from specimen USNM no. *n*.

Literature Cited

Bence, A. E., and W. Holzwarth
1977. Non-Linearities of Electron Microprobe Matrix Corrections in the System MgO-Al_2O_3-SiO_2. *Proceedings of the Eighth International Conference on X-Ray Optics and Microanalysis and Twelfth Annual Conference of the Microbeam Analysis Society*, page 38.

Boyd, F. R., L. W. Finger, and F. Chayes
1967. Computer Reduction of Electron-Probe Data. *Carnegie Institution Year Books*, 67:210–215.

Hillebrand, W. G., G.E.F. Lundell, H. A. Bright, and J. I. Hoffman
1953. *Applied Inorganic Analysis*. 2nd edition, 1034 pages. New York: John Wiley and Sons.

Peck, L. C.
1964. Systematic Analysis of Silicates. *U.S. Geological Survey Bulletin*, 1170:66.

KEY TO TABLE 1
Analysts, Sources, References

Analysts:

1. E. Jarosewich, Dept. of Mineral Sciences, Smithsonian Institution
2. J. Nelen, Dept. of Mineral Sciences, Smithsonian Institution
3. J. Norberg, Dept. 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, Dept. 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, Dept. of Mineral Sciences, Smithsonian Institution
2. B. Mason, Dept. of Mineral Sciences, Smithsonian Institution
3. G. Switzer, Dept. of Mineral Sciences, Smithsonian Institution
4. W. G. Melson, Dept. of Mineral Sciences, Smithsonian Institution
5. T. L. Wright, U.S. Geological Survey
6. H. Staudigel, Massachusetts Institute of Technology
7. R. S. Clarke, Jr., Dept. of Mineral Sciences, Smithsonian Institution
8. J. H. Berg, Northern Illinois University

References for previously published analyses:

1. Stewart, D. B., 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. Young, E. J., 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. Mason, B., 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. Jarosewich, E.
   1972. Chemical Analysis of Five Minerals for Microprobe Standards. *In* William G. Melson, editor, Mineral Sciences Investigations, 1969–1971. *Smithsonian Contributions to the Earth Sciences,* 9:83–84.
5. Jarosewich, E.
   1975. Chemical Analysis of Two Microprobe Standards. *In* George S. Switzer, editor, Mineral Sciences Investigations, 1972–1973. *Smithsonian Contributions to the Earth Sciences,* 14:85–86.

TABLE 1.—Chemical analyses of electron microprobe reference samples; analysts, sources, and references identified in "Key to Table 1" on facing page; these purified samples all differ, to greater or lesser degree, from the bulk chemistry of the USNM specimens from which they were separated (see text).

Mineral	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	H_2O	Total	Analyst	Source	Reference
Anorthite, Great Sitkin Island, AL USNM 137041	44.00	36.03		0.62	<0.02	19.09	0.53	0.03	0.03					100.33	1	1	
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	7.86	3.69	3.45	16.65	15.82	1.27	0.00	0.74		0.13		0.04	100.38	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 6578		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	
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[5] 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[6] 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[7] 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[8] 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[9] USNM 96189			11.6	36.1	0.31				45.7		4.77			99.40	7	1	
Magnetite, Minas Gerais, Brazil[10] 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_{89}), San Carlos, Gila Co., AZ[11] 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[12] USNM R17701	99.99													99.99	1	1	
Scapolite (Meionite), Brazil[13] 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] S 0.12; sub-total: 100.13; O equivalent to S = 0.06; final total: 100.07.

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

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

[8] New TiO_2 value: 4.72.

[9] Nb_2O_5 0.92.

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

[11] NiO 0.37.

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

[13] 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 of each reference sample (sigma ratio for n grains = $\frac{\text{observed sigma for } n \text{ grains}}{\text{sigma predicted from counting statistics}}$; least homogeneous grain in parentheses; dashes = not evaluated)

Mineral	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3
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)	
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)					

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

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