P&H Developments Ltd.

Calibration Standards for Electron Probe Microanalysis

Geological Standards for Silicates and Oxide Minerals

Geo Block MkII No. GeoII/ 40

P&H Developments Ltd.

e-mail info@pandhdevelopments.com www.pandhdevelopments.com

INTRODUCTION

The standards mounted in this block have primarily been chosen for their suitability for calibrating Electron Probe Microanalysers or Analytical Electron Microscopes equipped with Wavelength Dispersive Spectrometers (WDS), but could be of use for machines equipped with an Energy Dispersive Spectrometer (EDS). It is imperative that the instructions contained in the section CARE OF THE STANDARDS BLOCK are followed if the quality of the polish on the standard's surface and carbon coating are to be maintained.

THE STANDARDS

The 27 standard materials contained in this block have been carefully chosen for their suitability for use as standard reference materials and comprise of naturally found minerals, synthetic compounds and pure metals. In particular they have been chosen to fulfil the following requirements:

1. Have a major characteristic x-ray peak for calibration clear of interference from other x- ray peaks (this is particularly relevant when calibrating EDS systems).
2. Able to be highly polished.
3. To remain stable in air, while under vacuum and while being electron bombarded.
4. To be of accurately known chemical composition, homogeneous on a micron scale and inclusion free.

Four of the standards, Olivine, Kyanite, Almandine and Diopside have been added as secondary standards to test the quality of the quantitative analysis achieved after calibration.
The standards are coated with approximately 200 angstroms of carbon to render the surface electrically conductive.

THE PLAN OF THE STANDARD BLOCK

The included diagram shows the layout of the standards in the block as viewed from above.

STANDARDS CERTIFICATION

This manual contains information on the chemical compositions and the source of the materials used in this standard block so that they are fully traceable. Most of this information is provided by the supplier of the standard materials.

SECONDARY STANDARDS

Four secondary standards are provided (Diopside, Olivine, Almandine and Kyanite) so that the quality of the instrument calibration can be tested. Each mineral has been accurately analysed by EPMA and the average chemical analysis given along with the corresponding mineral formulae and cation ratios. If the instrument calibration is correct and functioning correctly then the analysis results obtained from the secondary standards should be very similar to those listed.

CARE AND USE OF THE STANDARDS BLOCK

The standards are epoxy resin mounted in a brass block, polished to quarter micron diamond finish and carbon coated. Every care is taken during manufacture to ensure that there are no gaps between the brass block, epoxy resin and standards which could harbour polishing oil. It is important that the surface of the standards are never touched or wiped even with a soft tissue as some of the materials in the block are extremely soft and could easily be scratched. If airborne dust settles on the standards surface this can be removed by using a gentle air jet.
Care must be taken in selecting areas on the surface of the standards for analysis or calibration.

NEVER SUBJECT THE STANDARD BLOCK TO ULTRASONIC CLEANING!

It is strongly advised that the standards are kept permanently inside the specimen chamber of the SEM/Microprobe, kept under vacuum or placed in a desiccator immediately after use. The standard block contains Sodium Chloride (NaCl) which is water soluble so if the standards are re-polished they should

never come into contact with water. Sodium Chloride is not soluble in alcohol. After carbon coating Sodium Chloride should keep in good condition almost indefinitely.

CHEMICAL HAZARDS

Some of the materials contained in this standard block are known to be toxic. The standards do not offer any significant hazard to the user due to the small amounts of materials being used and the fact that they are encapsulated in epoxy resin. The standard block should be handled with care such that the surface of the standard materials are not touched, kept in a dry atmosphere, and not allowed to get damp or wet. If repolishing is attempted by the user it is recommended that only an oil based polishing medium is used and that the standards never come into contact with water.

STANDARDS RENOVATION SERVICE

In the event of the standards becoming damaged or requiring re-coating, P&H Developments are able to provide a standards renovation service. If the standard block is returned a quotation will be issued for the cost of reinstating the standard block to its original condition.

Key to the Geo MkII Standard Block and Source of Materials

1	Andradite #	Natural andradite, Stanley Butte, Arizona USA
2	Zircon #	Natural Zirconium Silicate, $ZrSiO_4$, Peixe, Goias, Brazil
3	Periclase	Magnesium Oxide, MgO, synthetic, 99.999%
4	Caesium glass	P&H Developments special glass, see analysis details
5	Apatite	Natural Fluo-Apatite, Durango, Mexico
6	Albite	Natural $NaAlSi_3O_8$, Amelia County, Virginia, USA
7	Rutile	Titanium Oxide, TiO_2, synthetic, 99.999, PI-KEM Ltd. UK.
8	Baryte	Natural Barium Sulphate, $BaSO_4$, Cow Green Mine, Harwood Fell, UK.
9	Cobalt	Metal, 99.998%, NewMet K1075
10	Wollastonite	Natural Calcium Pyroxenoid, $CaSiO_3$, Leeds University, England
11	Haematite	Natural Ferric Oxide, Fe_2O_3, Elba, Italy
12	Orthoclase	Natural Potassium Feldspar, $KAlSi_3O_8$, Lucerne, Switzerland
13	Vanadium	Metal, 99.5%, JM batch 31310
14	Pyrite	Natural Iron Sulphide, FeS_2, Silver Valley Mine, N.S.W. Australia
15	Halite	Natural Sodium Chloride, NaCl
16	Fluorite	NaturalCalcium Fluoride, CaF_2, County Durham, UK
17	Olivine*	Natural Peridot, Forsteritic, $(Mg, Fe)SiO_4$, Sumput, Kohisthan, Parkistan
18	Rb glass	P&H Developments special glass, see analysis details.
19	Rhodonite	Natural Manganese Pyroxenoid, North Mine, Broken Hill, NSW, Australia
20	Kyanite*	Natural Al_2SiO_5, Collinsville, Connecticut, USA
21	Sphalerite	Zinc Sulphide, ZnS, synthetic, 99.995%, Earth Jewelry Co. Japan
22	Celestine	Natural Strontium Sulphate, $SrSO_4$, Yate , Bristol, UK.
23	Nickel	Metal, 99.999%, Alfa, JM batch 043762
24	Chromium Oxide	Cr_2O_3, synthetic, >99.99%, Earth Jewelry Co. Japan
25	Almandine*	Natural $Fe_3Al_2Si_3O_{12}$, Roxbury, Connecticut, USA
26	Copper	Metal, 99.999%, JM batch 854
27	Diopside*	Natural $CaMgSi_2O_6$, Dog Lake, Ontario, Canada
28	Corundum	Aluminium Oxide, Al_2O_3, synthetic, 99.9999%

Utility Standards #
In addition to the twenty six standards for Quantitative Microanalysis, two *UTILITY* standards are provided.

1. Andradite containing Si, Ca, Fe & O is provided to calibrate (*VERI*fication) the positions of the Wavelength Dispersive Spectrometers (WDS).

2. Zircon, is provided for observing, aligning and focusing the electron beam (this Zirconium silicate exhibits very strong cathodoluminescence). Although not intended as a primary standards for Zr analysis this Zircon could be used as a standard. Most Zircons contain a small amount of Hf but less than 0.2wt% is estimated to be present in this zircon.

* Secondary Standard Mineral
JM – Johnson Matthey GmbH, Karlsruhe, Germany

Table showing which Standard is suitable for calibrating which Element

Std.No.	Standard	Calibration Element
1	Andradite #	
2	Zircon #	Zr
3	Periclase	Mg
4	Caesium glass	Cs
5	Apatite	P
6	Albite	Na
7	Rutile	Ti
8	Baryte	Ba
9	Cobalt	Co
10	Wollastonite	Si & Ca
11	Haematite	Fe
12	Orthoclase	K
13	Vanadium	V
14	Pyrite	S
15	Halite	Cl
16	Fluorite	F
17	Olivine*	
18	Rb glass	Rb
19	Rhodonite	Mn
20	Kyanite*	
21	Sphalerite	Zn
22	Celestine	Sr
23	Nickel	Ni
24	Chromium Oxide	Cr
25	Almandine*	
26	Copper	Cu
27	Diopside*	
28	Corundum	Al

\# Utility Standards
* Secondary Standard Mineral

CHEMICAL COMPOSITIONS OF THE STANDARDS

The chemical compositions of the standard minerals and compounds are given in the following tables. All chemical compositions are reported as wt% element and are normalised to 100%, it is recommended that these are the composition values used in any quantitative micoanalysis program used by an EDS or EPMA manufacturer. The EPMA chemical analysis details for the minerals used as standards are given in the tables from page 9 to 14 titled: Chemical analysis details by EPMA of the minerals used as standards.

NATURAL MINERAL AND SYNTHETIC COMPOUND STANDARDS

	Albite	Wollastonite	Orthoclase	Rhodonite
Si	32.44	23.99	30.43	22.17
Ti		0.01	0.01	
Al	10.06		9.82	
Fe		0.15	0.02	0.79
Mn		0.49	0.01	32.93
Mg		0.01		1.12
Ca	0.07	34.17	0.01	5.11
Na	8.53	0.01	1.01	
K	0.08		12.19	
Sr			0.04	
Ba			0.13	
O	48.84	41.17	46.28	37.88
Tot.	100.00	100.00	99.95	100.00

	Barite		Celestine		Fluorite
Ba	58.84	Sr	47.70	Ca	51.33
S	13.74	S	17.45	F	48.67
O	27.42	O	34.85		
Tot.	100.00		100.00		100.00

	Periclase		Corundum		Rutile		Chromium Oxide
Mg	60.30	Al	52.92	Ti	59.95	Cr	68.42
O	39.70	O	47.08	O	40.05	O	31.58
Tot.	100.00		100.00		100.00		100.00

	Haematite		Halite		Zircon (excluding Hf content)
Fe	69.94	Na	39.34	Zr	49.77
O	30.06	Cl	60.66	Si	15.33
				O	34.90
Tot.	100.00		100.00		100.00

Apatite (Durango, Mexico) as quoted in Deer, Howie and Zussman vol 5B, table 39 analysis 9, page 306

	Oxide wt%	Elmt wt%	Oxygen wt%
SiO2	0.34	0.16	0.18
Al2O3	0.07	0.037	0.033
Fe2O3	0.06	0.042	0.018
MnO	0.01	0.007	0.003
MgO	0.01	0.006	0.004
CaO	54.02	38.61	15.41
SrO	0.07	0.06	0.01
Na2O	0.23	0.17	0.06
K2O	0.01	0.008	0.002
P2O5	**40.78**	**17.8**	**22.98**
SO3	0.37	0.15	0.22
CO2	0.05	0.014	0.036
F	3.53	3.53	
Cl	0.41	0.41	
H2O+	0.01	0.001	0.009
ThO2	0.02	0.018	0.002
REE2O3	1.43	1.22	0.21
As2O5	0.09	0.06	0.03
V2O5	0.01	0.006	0.004
total	101.52	62.309	39.211
O=F	-1.486		-1.486
O=Cl	-0.093		-0.093
Total	**99.941**	**62.309**	**37.632**

*Calculated REE_2O_3 assuming all is Ce_2O_3

Sulphide compositions:-

	Sphalerite		Pyrite
Zn	67.10	Fe	46.55
S	32.90	S	53.45
Tot.	100.00		100.00

P&H Developments Rubidium and Caesium Glass Chemical Compositions

Caesium 10wt% in Si-Al-Ca glass

Oxide	Theoretical wt% oxide	Elmt.	Theoretical wt% Elmt.	Chemical Analysis wt% oxide	wt% Elmt.
SiO_2	55.43	Si	25.91	55.21	25.81
Al_2O_3	12.96	Al	6.86	13.08	6.92
CaO	21.01	Ca	15.02	21.07	15.06
Cs_2O	10.60	Cs	10.00	10.50	9.90
		O	42.21		42.86
Tot.	100.00		100.00	99.86	99.86

Rubidium 10wt% in Ge-Al-Ca glass

Oxide	Theoretical wt% oxide	Elmt.	Theoretical wt% Elmt	Chemical Analysis wt% oxide	wt% Elmt.
GeO_2	55.22	Ge	38.33	54.09	37.54
Al_2O_3	12.91	Al	6.83	13.54	7.17
CaO	20.93	Ca	14.96	22.03	15.74
Rb_2O	10.94	Rb	10.00	10.41	9.52
		O	29.88		30.10
Tot.	100.00			100.07	100.07

Periclase, Corundum, Rutile, Sphalerite, and Chromium Oxide, are very high purity synthetic compounds, verified by electron probe microanalysis.

Wollastonite, Zircon, Pyrite, Haematite, Celestine, Apatite, Albite, Fluorite, Barite, Orthoclase, Halite, Rhodonite, Kyanite, Almandine, Diopside, and Olivine are natural minerals, the compositions of which have been checked by rigourous EPMA.

The Rubidium and Caesium glasses were checked by EPMA to be Homogenous.
The melt compositions and independent chemical analysis by a NAMAS accredited analytical laboratory are given in the analysis table above. The chemical analysis was performed by the XRF method which is thought to give good accurate analytical data. The enclosed TEST REPORTS from CERAM Research, a NAMAS approved analytical laboratory, give the chemical analysis for each glass standard.

Chemical analysis details by EPMA of the minerals used as standards.

Rhodonite ($MnSiO_3$)

These data were obtained under the following analysis conditions.
Average of 12 analysis points taken at random
15kV at 20 nA probe currant

	Conc.	Oxides	Cations	
	Ave.	S.D.	Ave.	dev.
SiO_2	47.307	0.218	1.001	0.002
Al_2O_3	0.000	0.000	0.000	0.000
MgO	1.860	0.022	0.059	0.001
CaO	7.135	0.058	0.162	0.001
MnO	42.417	0.124	0.760	0.003
FeO	1.017	0.016	0.018	0.000
O				
Tot.	99.736		1.999	

Haematite (Fe_2O_3)

These data were obtained under the following analysis conditions.
Average of 50 analysis points taken at random
20kV at 20 nA probe currant
Counting times, for Fe 30sec peak and 15sec backgroundat each position, all other elements 20sec peak 10 sec background at each position.

Element	Ave.	S.D.	Min.	Max
SiO_2	0.01	0.01	0.00	0.04
TiO_2	0.01	0.01	0.00	0.04
Al_2O_3	0.01	0.02	0.00	0.09
V_2O_3	0.01	0.01	0.00	0.03
Cr_2O_3	0.01	0.01	0.00	0.05
Fe_2O_3	100.65	0.23	99.97	101.01
MnO	0.02	0.02	0.00	0.07
MgO	0.04	0.22	0.00	1.53
NiO	0.02	0.02	0.00	0.09
ZnO	0.03	0.04	0.00	0.18
Tot.	100.81			

Cations to 1 oxygen

Si	0.000
Ti	0.000
Al	0.000
V_3	0.000
Cr	0.000
Fe_3	0.666
Mn	0.000
Mg	0.000
Ni	0.000
Zn	0.000
Tot.	0.667

Wollastonite ($CaSiO_3$)

These data were obtained under the following analysis conditions.
Average of 60 analysis points taken at random
15kV at 15 nA probe currant
Counting times, all elements 30sec at each peak position and 15sec background at each position

Element	Ave	S.D.	Cations to 3 oxygen atoms
SiO_2	50.96	0.28	0.995
TiO_2	0.01	0.01	0.000
Al_2O_3	0.00	0.00	0.000
Fe_2O_3	0.22	0.08	0.003
MnO	0.63	0.08	0.010
MgO	0.01	0.01	0.000
CaO	47.48	0.15	0.993
Na_2O	0.01	0.01	0.000
K_2O	0.00	0.00	0.000
Tot.	99.32		2.003

Chemical analysis details of the four Secondary Standard Minerals

1. Diopside $CaMgSi_2O_6$

The average of 46 random analysis points are given below. These data were obtained under the following analysis conditions.
15kV at 20 nA probe currant
Na, Mn, Cr, and Ti 20 sec peak at each peak position and 10 sec background counting time at each position.
Si, Al, Fe, Mg, and Ca 30 sec peak at each position and 15 sec background counting time at each position.

Element	Ave.	S.D.	Min.	Max.
SiO_2	55.36	0.16	55.00	55.68
TiO_2	0.05	0.02	0.00	0.11
Al_2O_3	0.06	0.23	0.00	1.55
Cr_2O_3	0.01	0.01	0.00	0.04
Fe_2O_3	0.12	0.09	0.00	0.23
FeO	0.79	0.10	0.62	1.05
MnO	0.09	0.03	0.02	0.15
MgO	17.98	0.08	17.78	18.13
CaO	25.72	0.08	25.59	25.91
Na_2O	0.07	0.01	0.04	0.10
Tot.	100.25			
Fe asFeO	*0.90*			

Cations to 6 Oxygen Atoms

	Ave
Si	1.998
Ti	0.001
Al	0.002
Cr	0.000
Fe_3	0.003
Fe_2	0.024
Mn	0.003
Mg	0.968
Ca	0.995
Na	0.005
Tot.	4.000

Cation Ratios etc.

Ca	49.93
Mg	48.57
Fe[t] +Mn	1.49
Mg#	97.02
Jadeite	0.24
Acmite	0.25
Fe_3CaTs	0.04
CrCaTs	0.01
TiCaTs	0.00
CaTs	0.00
Woll	49.75
En	48.42
Fs	1.28
% allocation	99.95

Fe_3+ by Sum VI ions = Al(IV)+Na. End-members by method of Cawthorn and Collerson (Am.Min.,1974)
Mg# = Mg*100/(Mg+Fe[t]+Mn)

2. Olivine $(Mg,Fe)SiO_4$ (Peridot)

The average of 72 random analysis points are given below. These data were obtained under the following analysis conditions.
15kV at 20 nA probe currant
All elements at 30 sec peak, 15 sec background counting time at each position.

Element	Ave.	S.D.	Min.	Max.
SiO_2	41.84	0.14	41.50	42.11
TiO_2	0.01	0.01	0.00	0.04
Al_2O_3	0.00	0.00	0.00	0.01
FeO	4.44	0.13	4.12	4.72
MnO	0.15	0.03	0.09	0.23
MgO	52.66	0.14	52.25	52.98
CaO	0.01	0.01	0.00	0.03
NiO	0.21	0.05	0.10	0.34

Tot. 99.33

Cations to 6 Oxygen Atoms

	Ave.
Si	1.007
Ti	0.000
Al	0.000
Fe_2	0.089
Mn	0.003
Mg	1.889
Ca	0.000
Ni	0.004

Tot. 2.993

Cation Ratios etc.
Mg# 95.33
Mg# = Mg*100/(Mg+Fe[t]+Mn)

3. Almandine $Fe_3Al_2Si_3O_{12}$

This almandine contains inclusions of very small mineral grains, these should be avoided when choosing positions for analysis. The average of 49 random analysis points are given below. These data were obtained under the following analysis conditions.
15kV at 20 nA probe currant
All elements 30 sec peak, 15 sec background counting time at each position.

Element	Ave.	S.D.	Min.	Max.
SiO_2	37.17	0.17	36.76	37.46
TiO_2	0.07	0.03	0.00	0.12
Al_2O_3	21.01	0.08	20.75	21.19
Cr_2O_3	0.02	0.02	0.00	0.07
Fe_2O_3	0.14	0.14	0.00	0.52
FeO	35.13	0.23	34.72	35.63
MnO	0.20	0.03	0.14	0.26
MgO	2.35	0.04	2.24	2.43
CaO	3.94	0.20	3.54	4.29
Tot.	100.03			
Fe asFeO	*35.26*			

Cations to 12 Oxygen Atoms

	Ave.
Si	2.993
Ti	0.004
Al	1.994
Cr	0.001
Fe_3	0.009
Fe_2	2.365
Mn	0.014
Mg	0.282
Ca	0.340
Tot.	8.001

Cation ratios etc.

	Ave.
Mg#	10.64

Goldmanite	0.00
Uvarovite	0.06
Knorringite	0.00
Andradite	0.44
Pyrope	9.41
Spessartine	0.46
Grossular	10.86
Almandine	78.78
Schorlomite	0.00
% allocation	99.75

4. Kyanite Al_2SiO_5

The average of 50 random analysis points are given below. These data were obtained under the following analysis conditions.
15kV at 20 nA probe currant
All elements 20 sec peak, 10 sec background counting time at each position.

Element	Ave.	S.D.	Min.	Max.
SiO_2	37.80	0.13	36.54	37.10
TiO_2	0.01	0.02	0.00	0.08
Al_2O_3	62.75	0.16	62.30	63.03
Fe_2O_3	0.15	0.04	0.08	0.25
MnO	0.01	0.01	0.00	0.04
MgO	0.01	0.01	0.00	0.03
CaO	0.01	0.01	0.00	0.05
Na_2O	0.00	0.01	0.00	0.04
K_2O	0.00	0.01	0.00	0.02
Tot.	99.74			

Cations to 5 Oxygen Atoms

	Ave.
Si	0.996
Ti	0.000
Al	2.001
Fe_3	0.003
Mn	0.000
Mg	0.000
Ca	0.000
Na	0.000
K	0.000
Tot.	3.002

Method of Manufacture of the Rubidium, and Caesium Glasses

These glasses were made by mixing chemical reagents by hand in a porcelaine mortar followed by mechanical shaking, the base compositions being, SiO_2=62.0% or GeO_2=62.0%, Al_2O_3=14.5%, CaO=23.5%.

The starting materials where as follows:

SiO_2	99.9% <325 mesh,	supplied by Johnson Matthey
Al_2O_3	99.99% (alpha alumina),	" " " "
$CaCO_3$	99.5% AR Grade,	" " " "
GeO_2	99.999% Puratronic,	" " " "
Rb	Rb_2CO_3, 99.9%,	" " " "
Cs	Cs_2CO_3, 99.99% Specpure,	" " " "

The weighed powders were mixed for longer than one hour using a standard mechanical mixer, melted in a Pt basin at 1450 - 1500^{o}c for sixteen hours and then annealed.

Acknowledgement

P&H Developments would like to thank Dr. Eric Condliffe of the Earth Sciences Department, Leeds University for advice on which standards would be suitable to use in Standard block and for checking the chemical compositions by Electron Probe Microanalysis (EPMA).

GEO MK II Block Layout