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Validation of physical parameters in quantitative electron probe microanalysis (EPMA) Part II–mean ionization potential

Takenori KATO[1*], Mi-Jung JEEN[2] and Deung-Lyong CHO[3]

[1]Center for Chronological Research, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464–8602, Japan
[2]Center for Research Facilities, Pusan National University, 2, Busandehak-ro 63beon-gil, Geumjeong-gu, Busan 609–735, Republic of Korea
[3]Geological Mapping Department, Geological Research Division, Korea Institute of Geoscience and Mineral Resources, Gwahang-no 124, Yuseong-gu, Daejeon 305–350, Republic of Korea
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ABSTRACT

Approximations of the mean ionization potential have been compared with the latest dataset. Obtained chemical compositions are sensitive to the chosen model of the mean ionization potential. Selection of the mean ionization potential model causes about 5 % uncertainty of chemical compositions. However, Mg# (= Mg / (Mg + Fe)) and apparent U-Th-total Pb age are less sensitive to the mean ionization model, and uncertainty is less than 2 %. The conventional ZAF model is more sensitive to the mean ionization model than the double parabola model and surface-center Gaussian model.
Keywords. electron probe microanalysis, mean ionization potential, matrix correction, stopping power

INTRODUCTION

The true chemical compositions are obtained using the matrix correction procedure in quantitative EPMA. The matrix correction procedure converts X-ray intensities of the unknown target and standard materials, and chemical compositions of standard materials into the true chemical compositions of the unknown material. Correction factors of the unknown target and standard materials are used in this procedure. The correction factor is obtained from chemical compositions of the material, the energy of the incident electron and X-ray take-off angle using a variety of physical parameters. The correction factor can be divided into the four terms: electron backscattering, stopping power, X-ray absorption and fluorescence.

The stopping power term ($1/S$) in the matrix correction is obtained using the mean ionization potential (J), the averaged excitation potential per electron, in addition to other physical parameters. A variety of the mean ionization potential has been published by experimental and theoretical determination (c.f. summaries by Fano, 1960; Ahlen, 1980; Ziegler, 1980). Furthermore, approximations for the mean ioniza-

*Corresponding author, e-mail: kato@nanedai.nagoya-u.ac.jp

tion potential have been proposed (Bloch, 1933; Armstrong, 1991; Berger and Seltzer; 1964, Duncumb *et al.*, 1969; Joy and Luo, 1989; Ruste, 1979; Zeller and Ruste, 1976) and widely used in the matrix correction procedure.

This paper compares approximations of the mean ionization potential with the dataset by Hubbbell and Seltzer (1995) using the geological sample.

VALIDATION OF THE MEAN IONIZATION POTENTIAL

In the matrix correction procedure, an approximation for the mean ionization model is generally applied instead of experimental or theoretical values (c.f. Armstrong, 1995; Lavrant'ev *et al.*, 2004). The following seven approximations of the mean ionization potential (J in keV) were compared with the dataset by Hubbell and Seltzer (1995):

Armstrong (1991) $J = 10^{-3}Z[9.0(1 + Z^{-2/3}) + 0.03Z]$ $(Z < 30)$ (1)

$J = 10^{-3}Z(9.76 + 58.5 \cdot Z^{-1.10})$ $(Z > 29)$ (2)

Berger and Seltzer (1964) $J = 10^{-3}(9.76 \cdot Z + 58.5 \cdot Z^{-0.19})$ (3)

Bloch (1933) $J = 13.5 \cdot 10^{-3}Z$ (4)

Duncumb *et al.* (1969) $J = 10^{-3}Z\{14.0[1 - \exp(-0.1Z)] + 75.5/Z^{Z/7.5} - Z/(100 + Z)\}$ (5)

Joy and Luo (1989) $J = 11.5^{-3}Z$ $(Z < 13)$ (6)

$J = 10^{-3}Z(9.76 + 58.5 \cdot Z^{-1.19})$ $(Z > 12)$ (7)

Ruste (1979) $J = 0.00929(Z + 1.287Z^{1/3})$ (8)

Zeller and Ruste (1976) $J = 10^{-3}Z[10.04 + 8.25\exp(-Z/11.22)]$ (9)

Figure 1 shows the mean ionization potential by approximations and Hubbell and Seltzer (1995). Bloch (1933) and Duncumb *et al.* (1969) give higher values than other approximations and Hubbell and Seltzer (1995). Other approximations give the similar values to Hubbell and Seltzer (1995) in $Z = 10 - 30$. Berger and Seltzer (1964), Bloch (1933) and Duncumb *et al.* (1969) give higher mean ionization potential for $Z < 10$. Therefore, these approximations are unsuitable for ultra-light element analysis (e.g., B in tourmaline). The mean ionization potential obtained from an approximation is higher than that by Hubbell Seltzer (1995) in the range $Z = 51 - 70$ and $Z > 80$. Elements in these ranges are generally analyzed using L- or M- lines. This suggests that the stopping power part in the atomic number correction potentially has systematic uncertainty in quantitative EPMA using L- and M-lines (e.g., lanthanide, Pb, Th and U).

Table 1 – 3 demonstrate the effect of the mean ionization model for three $\varphi(\rho z)$ models: PAP (Pouchou and Pichoir, 1984 and 1991), surface-center Gaussian by Armstrong (1991) and conventional ZAF, respectively. Obtained chemical composi-

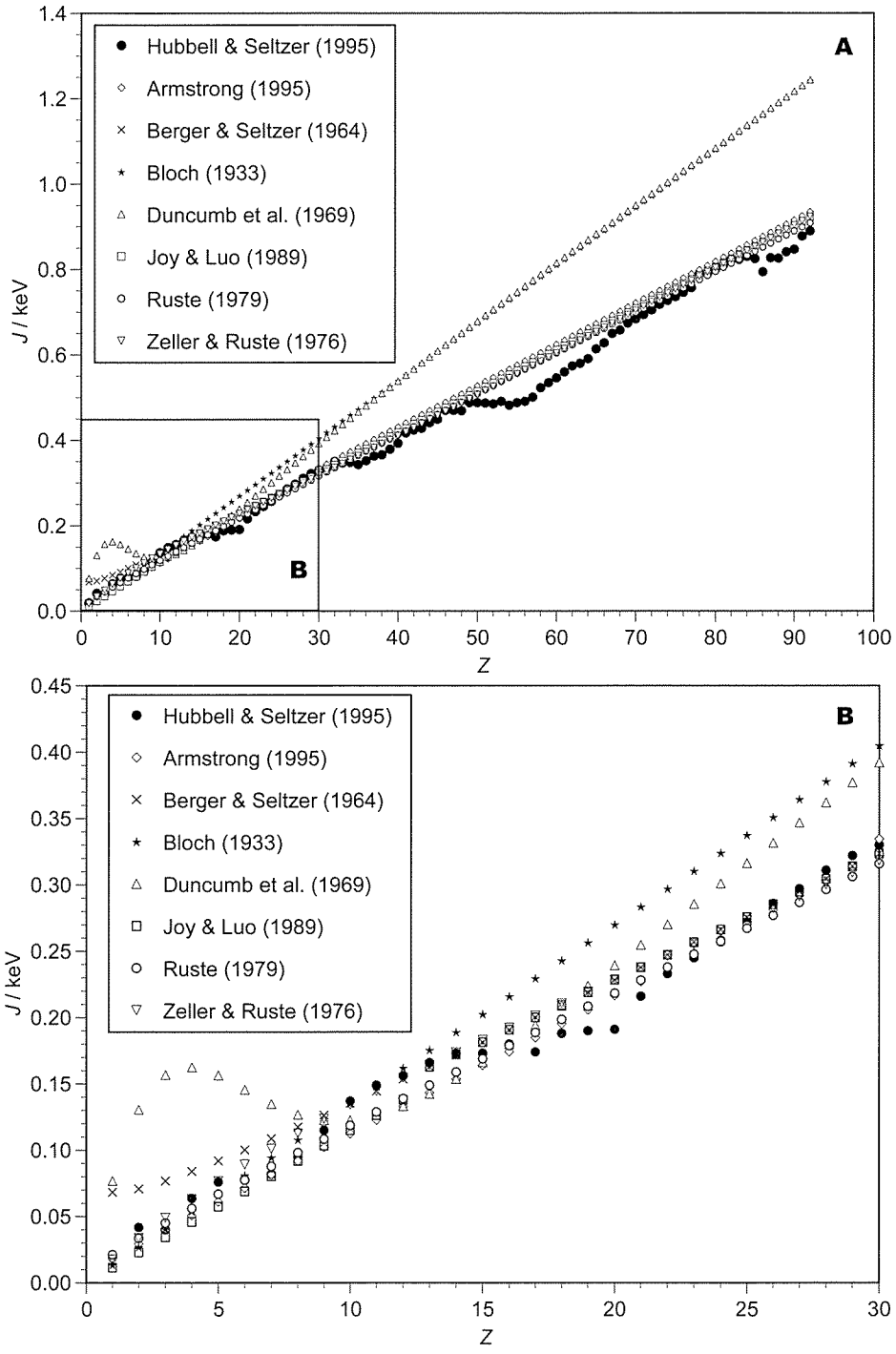

Figure 1. Mean ionization potentials by Hubbell and Seltzer (1995), Armstrong (1995), Berger and Seltzer (1964), Bloch (1933), Duncumb *et al.* (1969), Joy and Luo (1989), Ruste (1979) and Zeller and Ruste (1976).

Table 1. Results of matrix correction (PAP) using different mean ionization potential models.

J	Hubbell & Seltzer (1995)	Armstrong (1991)	Berger & Seltzer (1964)	Bloch (1933)	Duncumb et al. (1969)	Joy & Luo (1989)	Ruste (1979)	Zeller & Ruste (1976)	Average	%s.d.	max[a]	min[b]	100(a−b)/b
pyroxene													
SiO_2	50.3	50.1	50.4	50.1	50.0	50.2	50.2	50.4	50.21	0.29	50.4	50.0	0.8
TiO_2	0.10	0.10	0.10	0.11	0.11	0.10	0.10	0.10	0.10	4.52	0.11	0.10	10.0
Al_2O_3	1.51	1.49	1.51	1.51	1.50	1.50	1.50	1.51	1.50	0.49	1.51	1.49	1.3
FeO	24.4	24.7	24.2	24.8	25.1	24.5	24.5	24.2	24.55	1.25	25.1	24.2	3.7
MnO	0.61	0.62	0.61	0.62	0.63	0.62	0.61	0.61	0.62	1.21	0.63	0.61	3.3
MgO	22.4	22.2	22.5	22.4	22.3	22.2	22.3	22.4	22.34	0.47	22.5	22.2	1.4
CaO	0.64	0.66	0.65	0.66	0.66	0.66	0.66	0.66	0.66	1.13	0.66	0.64	3.1
Total	99.96	99.87	99.97	100.20	100.30	99.78	99.87	99.88	99.98	0.18	100.30	99.78	0.5
Mg#	0.621	0.616	0.624	0.617	0.613	0.618	0.619	0.623	0.619	0.58	0.624	0.613	1.8
monazite													
SiO_2	3.15	3.06	3.14	3.06	3.03	3.08	3.09	3.13	3.09	1.40	3.15	3.03	4.0
ThO_2	13.90	13.58	13.87	13.47	13.33	13.74	13.71	13.88	13.69	1.53	13.90	13.33	4.3
UO_2	0.409	0.399	0.408	0.396	0.392	0.404	0.403	0.408	0.402	1.54	0.409	0.392	4.3
Y_2O_3	0.27	0.26	0.27	0.26	0.26	0.27	0.27	0.27	0.266	1.94	0.27	0.26	3.8
La_2O_3	11.3	11.0	11.2	10.9	10.8	11.1	11.1	11.2	11.08	1.51	11.3	10.8	4.6
Ce_2O_3	29.2	28.6	29.1	28.2	27.9	28.9	28.8	29.1	28.72	1.62	29.2	27.9	4.7
Pr_2O_3	2.91	2.84	2.90	2.81	2.78	2.88	2.87	2.90	2.86	1.64	2.91	2.78	4.7
Nd_2O_3	10.4	10.1	10.3	9.99	9.88	10.2	10.2	10.3	10.17	1.70	10.4	9.88	5.3
Sm_2O_3	1.82	1.78	1.81	1.76	1.74	1.80	1.79	1.82	1.79	1.61	1.82	1.74	4.6
Gd_2O_3	0.69	0.68	0.69	0.67	0.66	0.68	0.68	0.69	0.68	1.57	0.69	0.66	4.5
Dy_2O_3	0.23	0.23	0.23	0.23	0.22	0.23	0.23	0.23	0.23	1.55	0.23	0.22	4.5
Er_2O_3	0.11	0.11	0.11	0.10	0.10	0.11	0.11	0.11	0.11	4.31	0.11	0.10	10.0
CaO	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.00	0.04	0.04	0.0
PbO	0.0435	0.0425	0.0433	0.0424	0.0420	0.0429	0.0429	0.0434	0.0435	1.24	0.0435	0.0420	3.6
P_2O_5	25.1	24.9	25.4	25.0	24.8	25.2	25.1	25.4	25.11	0.86	25.4	24.8	2.4
Total	99.57	97.62	99.51	96.93	95.97	98.68	98.44	99.52	98.28	1.36	99.57	95.97	3.8
Apparent age / Ma	68.0	68.0	67.9	68.4	68.5	67.9	68.0	68.0	68.1	0.34	68.5	67.9	0.9

Table 2. Results of matrix correction (surface-center Gaussian) using different mean ionization potential models.

J	Hubbell & Seltzer (1995)	Armstrong (1991)	Berger & Seltzer (1964)	Bloch (1933)	Duncumb et al. (1969)	Joy & Luo (1989)	Ruste (1979)	Zeller & Ruste (1976)	Average	%s.d.	max[a]	min[b]	100(a−b)/b
pyroxene													
SiO_2	51.6	51.5	51.7	51.4	51.3	51.5	51.6	51.7	51.50	0.27	51.7	51.3	0.8
TiO_2	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.00	0.10	0.10	0.0
Al_2O_3	1.57	1.56	1.57	1.56	1.56	1.57	1.56	1.57	1.57	0.34	1.57	1.56	0.6
FeO	24.0	24.2	23.9	24.4	24.6	24.1	24.1	23.9	24.20	1.01	24.6	23.9	2.9
MnO	0.61	0.61	0.60	0.62	0.62	0.61	0.61	0.60	0.61	1.24	0.62	0.60	3.3
MgO	23.5	23.3	23.5	23.4	23.2	23.2	23.4	23.5	23.40	0.55	23.5	23.2	1.3
CaO	0.64	0.65	0.65	0.66	0.65	0.66	0.65	0.65	0.65	0.98	0.66	0.64	3.1
Total	102.02	101.92	102.02	102.14	102.03	101.74	102.02	102.02	101.99	0.11	102.14	101.74	0.4
Mg#	0.636	0.632	0.637	0.631	0.627	0.632	0.634	0.637	0.633	0.53	0.637	0.627	1.6
monazite													
SiO_2	3.79	3.66	3.75	3.61	3.57	3.69	3.70	3.75	3.69	2.02	3.79	3.57	6.2
ThO_2	14.77	14.45	14.69	14.25	14.09	14.60	14.57	14.70	14.52	1.64	14.77	14.09	4.8
UO_2	0.439	0.429	0.437	0.423	0.419	0.434	0.433	0.437	0.431	1.66	0.439	0.419	4.8
Y_2O_3	0.30	0.30	0.30	0.29	0.29	0.30	0.30	0.30	0.30	1.56	0.30	0.29	3.4
La_2O_3	11.6	11.4	11.6	11.2	11.1	11.5	11.5	11.6	11.4	1.68	11.6	11.1	4.5
Ce_2O_3	30.1	29.5	29.9	29.0	28.7	29.7	29.7	29.9	29.6	1.63	30.1	28.7	4.9
Pr_2O_3	3.02	2.96	3.00	2.91	2.88	2.98	2.98	3.00	2.97	1.62	3.02	2.88	4.9
Nd_2O_3	10.7	10.5	10.6	10.3	10.2	10.6	10.5	10.6	10.5	1.61	10.7	10.2	4.9
Sm_2O_3	1.88	1.84	1.87	1.81	1.80	1.86	1.86	1.87	1.85	1.60	1.88	1.80	4.4
Gd_2O_3	0.72	0.70	0.71	0.69	0.68	0.71	0.71	0.71	0.70	1.85	0.72	0.68	5.9
Dy_2O_3	0.24	0.24	0.24	0.23	0.23	0.24	0.24	0.24	0.24	1.95	0.24	0.23	4.3
Er_2O_3	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.00	0.11	0.11	0.0
CaO	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.00	0.04	0.04	0.0
PbO	0.0478	0.0467	0.0474	0.0462	0.0457	0.0471	0.0470	0.0475	0.0469	1.49	0.0478	0.0457	4.6
P_2O_5	28.4	28.2	28.6	27.9	27.6	28.4	28.4	28.6	28.30	1.24	28.6	27.6	3.6
Total	106.16	104.38	105.89	102.81	101.75	105.21	105.09	105.90	104.65	1.52	106.16	101.75	4.3
Apparent age / Ma	70.3	70.2	70.1	70.4	70.4	70.1	70	70.2	70.2	0.21	70.4	70.0	0.6

Table 3. Results of matrix correction (conventional ZAF) using different mean ionization potential models.

J	Hubbell & Seltzer (1995)	Armstrong (1991)	Berger & Seltzer (1964)	Bloch (1933)	Duncumb et al. (1969)	Joy & Luo (1989)	Ruste (1979)	Zeller & Ruste (1976)	Average	%s.d.	max[a]	min[b]	100(a−b)/b
pyroxene													
SiO_2	50.9	50.5	51.1	50.3	50.2	50.6	50.8	51.1	50.70	0.68	51.1	50.2	1.8
TiO_2	0.10	0.11	0.10	0.11	0.10	0.11	0.10	0.10	0.10	4.99	0.11	0.10	10.0
Al2O3	1.58	1.56	1.58	1.56	1.56	1.58	1.57	1.58	1.57	0.63	1.58	1.56	1.3
FeO	25.9	26.5	25.3	26.9	26.3	26.1	26.0	25.3	26.00	2.12	26.9	25.3	6.3
MnO	0.62	0.64	0.61	0.64	0.63	0.63	0.63	0.61	0.63	1.90	0.64	0.61	4.9
MgO	24.0	23.8	23.9	23.8	23.6	23.6	23.9	23.9	23.80	0.61	24.0	23.6	1.7
CaO	0.63	0.65	0.65	0.65	0.65	0.66	0.65	0.65	0.65	1.29	0.66	0.63	4.8
Total	103.73	103.76	103.24	103.96	103.04	103.28	103.65	103.24	103.49	0.32	103.96	103.04	0.9
Mg#	0.623	0.616	0.627	0.612	0.615	0.617	0.621	0.627	0.620	0.93	0.627	0.612	2.5
monazite													
SiO_2	3.27	3.07	3.22	2.98	2.94	3.12	3.13	3.22	3.12	3.78	3.27	2.94	11.2
ThO_2	13.30	12.71	13.23	12.40	12.20	12.98	12.94	13.24	12.90	3.17	13.30	12.20	9.0
UO_2	0.395	0.376	0.392	0.367	0.361	0.385	0.384	0.393	0.380	3.29	0.395	0.361	9.4
Y_2O_3	0.27	0.26	0.26	0.25	0.25	0.26	0.26	0.26	0.26	2.48	0.27	0.25	8.0
La_2O_3	9.82	9.37	9.82	9.12	8.92	9.63	9.57	9.84	9.51	3.64	9.84	8.92	10.3
Ce_2O_3	25.2	24.0	25.2	23.3	22.8	24.7	24.5	25.2	24.40	3.78	25.2	22.8	10.5
Pr_2O_3	2.52	2.40	2.52	2.33	2.28	2.47	2.45	2.52	2.44	3.78	2.52	2.28	10.5
Nd_2O_3	8.84	8.38	8.82	8.15	7.96	8.64	8.58	8.83	8.53	3.91	8.84	7.96	11.1
Sm_2O_3	1.53	1.44	1.52	1.40	1.37	1.49	1.48	1.52	1.47	4.06	1.53	1.37	11.7
Gd_2O_3	0.57	0.54	0.57	0.52	0.51	0.56	0.55	0.57	0.55	4.29	0.57	0.51	11.8
Dy_2O_3	0.19	0.18	0.19	0.17	0.17	0.18	0.18	0.19	0.18	4.60	0.19	0.17	11.8
Er_2O_3	0.09	0.08	0.08	0.08	0.07	0.08	0.08	0.08	0.08	6.68	0.09	0.07	28.6
CaO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.00	0.03	0.03	0.0
PbO	0.0433	0.0415	0.0428	0.0406	0.0400	0.0422	0.0421	0.0429	0.0419	2.75	0.0433	0.0400	8.2
P_2O_5	25.1	24.6	25.3	24.1	23.5	25.0	25.0	25.4	24.80	2.64	25.4	23.5	8.1
Total	91.17	87.48	91.19	85.24	83.40	89.57	89.18	91.34	88.57	3.35	91.34	83.40	9.5
Apparent age / Ma	70.7	70.9	70.3	71.1	71.2	70.6	70.7	70.4	70.7	0.45	71.2	70.3	1.3

tions of pyroxene and monazite are shown in those tables. The Mg# (= Mg / (Mg + Fe)) of pyroxene and the apparent age (c.f. Suzuki and Adachi, 1991a and 1991b; Suzuki and Kato, 2008) of monazite are also shown. Chemical compositions are sensitive to chosen mean ionization potential model in all matrix correction models, and the conventional ZAF model is more sensitive than other models. Monazite is more sensitive to the mean ionization potential model than pyroxene in those tables because monazite contains lanthanide and actinide. Selection of the mean ionization model possibly causes about 5 % uncertainty in obtaining chemical compositions of monazite. The Mg# and apparent age are less sensitive to the mean ionization model and the standard deviations are less than 1 %.

SUMMARY

Seven approximations for the mean ionization potential were compared with the latest dataset in Hubbell and Seltzer (1995). Chemical compositions are sensitive to chosen mean ionization potential model and selection of the mean ionization model causes about 5 % uncertainty in obtaining chemical compositions. On the contrary, the Mg# and apparent U-Th-total Pb age is less sensitive to the mean ionization model. The conventional ZAF is more sensitive to the mean ionization potential than PAP and surface-center Gaussian by Armstrong (1991).

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