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Seeking Compositional Truth Continued: Comparisons of EDS Analytical Results with WDS

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Following the initial investigations of utilizing energy-dispersive spectrometry (EDS) and wavelength-dispersive spectrometry (WDS) to evaluate new standard materials [1], we have continued our studies to further compare EDS and WDS at different kVs and using different manufacturers' EDS systems. Despite EDS being often considered a less robust method for quantitative analysis (in comparison to WDS), our previous findings suggested EDS can be a fast and useful tool, and comparable to WDS. In this study, we continue to investigate quantitative differences **1)** across different instruments including Oxford EDS and Thermo EDS and **2)** comparing the EDS values relative to the WDS compositions of the studied materials.

We used the same three samples as our previous experiment; this includes the new Kakanui Anorthoclase, new Kakanui Augite, and the National Institute of Technology and Standards (NIST) K530 glass [2]. The Kakanui samples were >1-2 mm crystals from the same eastern New Zealand locality as corresponding Smithsonian standards [3], donated by James Scott (University of Otago, NZ) [4]. We acquired reference values on these three materials by WDS on a CAMECA SX51, and EDS values by Oxford AZtec on a Hitachi S3400 VP SEM and by Thermo Scientific Pathfinder on a SXFive FE electron probe, all housed at the University of Wisconsin-Madison Department of Geoscience. **Table 1** shows comparisons between EDS (by Oxford and Thermo systems) and WDS (by CAMECA SX51)**.**

The original intention of this project was to compare EDS with WDS EPMA results on this small number of reference materials. Over time, the project has expanded, to consider (1) possible effect of a different accelerating voltage, (2) possible differences in analytical results from different analytical sessions spread over ~10 months on the same instrument and same EDS system, and (3) any differences in analyses resulting from using different manufacturers' EDS systems. When sampling and quantifying a given reference material (assumed to be robust under the electron beam), it is assumed to have constant elemental abundances that do not vary over time. However, these materials may have some degree of heterogeneity, demonstrated in our earlier study [1]. We utilized the new Kakanui mineral and K530 glass samples by re-analyzing them through our Hitachi S3400N (Oxford EDS) at 15 and 20 kV as well and comparing EDS values from data taken over a year ago (**Table 2**).

Different accelerating voltages: Originally, the Fe contents for the new Kakanui augite were significantly higher (by 6%) compared with the WDS. It was suggested by Oxford that we attempt the measurement at 20 kV, as the Oxford factory calibration is done at this voltage. However, EDS reanalysis at 20 kV did not improve the fit between EDS and WDS, and the difference in measured iron content for the new Kakanui Augite and NIST K530 glass both increased by 2%.

Different analytical sessions: Typically, most samples are measured once. Here, as the project has spanned almost a year, we have acquired EDS measurements on the same system at two times, separated by ~10 months. We show in Table 2 the variation in the measurements over time. We note that there was one slight change in procedure. Based upon feedback from Oxford at the 2019 QMA topical conference at the University of Minnesota, we revised the sample positioning, to modifying the physical working distance to achieve optical focus at a nominal value of 10.0 mm (versus before, setting the physical Z working distance and then adjusting the objective lense). Whether a small difference of a few hundred microns made a difference, we cannot be certain. For most elements, composition varied by only 1-2% from the initial measurements. Si varied the least, increasing in the second analysis by only 0.14% at most. Na showed the most variation, decreasing in the second analysis by ~5% for both new Kakanui mineral samples.

Different EDS systems: We have now 3 sets of data on the same materials from Oxford AZtec EDS and one set of data from Thermo Pathfinder EDS. Both systems work well for most elements, compared with given WDS determined compositions. We note some possible systematic issues, though, using a benchmark of relative values compared to WDS of ±2% relative (0.98-1.02) to be acceptable, and outside that, to be representing a possible analytical issue:

Si and Al: for these major elements, both systems gave acceptable values relative to WDS.

Mg: this major element in 2 of the materials showed a different trend: the Oxford values were on the low side, while the Thermo were within the desired range.

Ca: here a major element in the K530 glass and augite, there was a reversal: Oxford came in within 1% of the WDS value, whereas Thermo was 3-6% low.

Fe: a major element in the K530 and augite, and here both systems had difficulties; Oxford was 4-8% high, while Thermo was either 3% high or 5% low.

Na: for low abundance Na in augite, Oxford is significantly low, (8-10%) whereas Thermo is 7% high; in high abundance anorthoclase, Oxford is similarly low (9%), with Thermo now 4% low.

Some trends seem clear, some not so clear. We hope to discuss these findings with each manufacturer and try to understand what particular issues there might be (e.g., for lowish energy elements like Na and Mg, could there be some physical issue (dirty window?). Clearly, running some reference standards and doing the traditional standards-based EPMA might shed light on these issues [5].

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	WDS (2019)	Oxford EDS (2019)		Oxford EDS (2020)		Oxford EDS (2020)		Thermo EDS (2020)	
K' Augite	15 kV	15 kV	EDS/ WDS	15 kV	EDS/ WDS	20 kV	EDS/ WDS	15kV	EDS/ WDS
Si	23.11	23.36	1.01	23.37	1.01	23.27	1.01	23.13	1.00
Ti	0.71	-	-	0.69	0.97	0.70	0.99	0.64	0.90
Al	4.68	4.60	0.98	4.59	0.98	4.58	0.98	4.73	1.01
Fe	5.48	5.81	1.06	5.87	1.07	5.93	1.08	5.22	0.95
Mg	9.00	8.86	0.98	8.73	0.97	8.64	0.96	9.15	1.02
Ca	11.91	11.84	0.99	11.89	1.00	12.08	1.01	11.58	0.97
Na	1.13	1.09	0.97	1.04	0.92	1.02	0.90	1.21	1.07
"O by stoch"	43.63	43.76	1.00	43.73	1.00	43.65	1.00	44.31	1.02
NIST K530	15 kV	15 kV	EDS/ WDS	15 kV	EDS/ WDS	20 kV	EDS/ WDS	15 kV	EDS/ WDS
Si	21.11	21.51	1.02	21.54	1.02	21.44	1.02	21.02	1.00
Al	5.09	5.10	1.00	5.05	0.99	5.02	0.99	5.11	1.00
Fe	7.79	8.01	1.03	8.13	1.04	8.19	1.05	8.01	1.03
Mg	11.66	11.52	0.99	11.30	0.97	11.24	0.96	11.67	1.00
Ca	10.91	10.68	0.99	10.83	0.99	11.01	1.01	10.27	0.94
"O by stoch"	42.93	43.18	1.01	43.13	1.00	43.05	1.00	43.77	1.02
K' Anorthoclase	15kV	15 kV	EDS/ WDS	15 kV	EDS/ WDS	20 kV	EDS/ WDS	15kV	EDS/ WDS
Si	31.17	31.49	1.01	31.61	1.01	-	-	31.40	1.01
Al	10.66	10.69	1.00	10.64	1.00	-	-	10.89	1.02
Fe	0.10	-	-	0.28	2.80	-	-	0.13	1.30
Ca	0.43	0.43	1.00	0.45	1.05	-	-	0.52	1.21
Na	7.13	6.83	0.95	6.47	0.91	-	-	6.87	0.96
K	2.07	2.10	1.01	2.12	1.02	-	-	1.67	0.81
"O by stoch"	48.12	48.45	1.01	48.42	1.01	-	-	48.48	1.01

Figure 1. Table 1. EDS, WDS, and EDS/WDS composition ratios from varying kV (15 and 20) and EDS manufacturer, including data from previous study (2019) and this study (2020). K' = Kakanui.

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	WDS (2019)	EDS (2019)	EDS (2020)	
K' Augite	15 kV	15 kV	15 kV	% Change
Si	23.11	23.36	23.37	0.04
Ti	0.71	-	0.69	-
Al	4.68	4.6	4.59	-0.22
Fe	5.48	5.81	5.87	1.03
Mg	9.00	8.86	8.73	-1.47
Ca	11.91	11.84	11.89	0.42
Na	1.13	1.09	1.04	-4.59
"O by stoch"	43.63	43.76	43.73	-0.07
NIST K530	15 kV	15 kV	15 kV	% Change
Si	21.11	21.51	21.54	0.14
Al	5.09	5.1	5.05	-0.98
Fe	7.79	8.01	8.13	1.5
Mg	11.66	11.52	11.3	-1.91
Ca	10.91	10.68	10.83	1.4
"O by stoch"	42.93	43.18	43.13	-0.12
K' Anorthoclase	15 kV	15 kV	15 kV	% Change
Si	31.17	31.49	31.61	0.38
Al	10.66	10.69	10.64	-0.47
Fe	0.10	-	0.28	-
Ca	0.43	0.43	0.45	4.65
Na	7.13	6.83	6.47	-5.27
K	2.07	2.1	2.12	0.95
"O by stoch"	48.12	48.45	48.42	-0.06

Figure 2. Table 2. EDS comparison from previous study (2019) and this study (2020), from varying kV (15 and 20) and EDS manufacturer (Oxford and Thermo). K' = Kakanui.

References

[1] Barshi, N., Bruck, B., Mixon, E., Valenca Villa, A., Kotsakis, G., Kumar, A. and Fournelle, J., 2019, Abstracts of MAS Quantitative Microanalysis Topical Conference

[2] Doug Meier (personal communication, October 2015)

[3] Jarosewich, E., Nelen, J. A., and Norberg, J. A. (1980) *Geo-standards Newsletter* 4, p. 257-258.

[4] Fournelle, J. and Scott, J., 2017, *Microscopy and Microanalysis* 23.S1 (2017): 502-503.

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