Seeking Compositional Truth: EDS vs. WDS to Evaluate New Standard Materials

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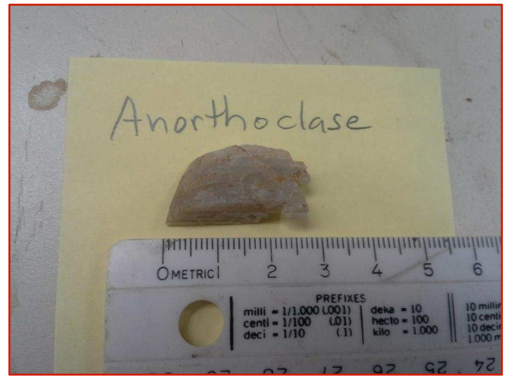
Two Questions, Three Materials

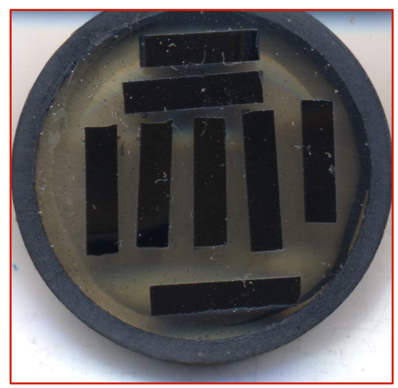
Q1: How well can quantitative energy dispersive spectrometry (EDS) analysis compare with the “gold standard” of wavelength dispersive spectrometry (WDS) analysis?

Q2: Could the materials we tested (two minerals and a glass) become new candidates for microanalysis standard materials?



Kakanui Anorthoclase Megacryst

Kakanui Augite Megacryst



NIST K530 Glass

Analytical Approach and Parameters

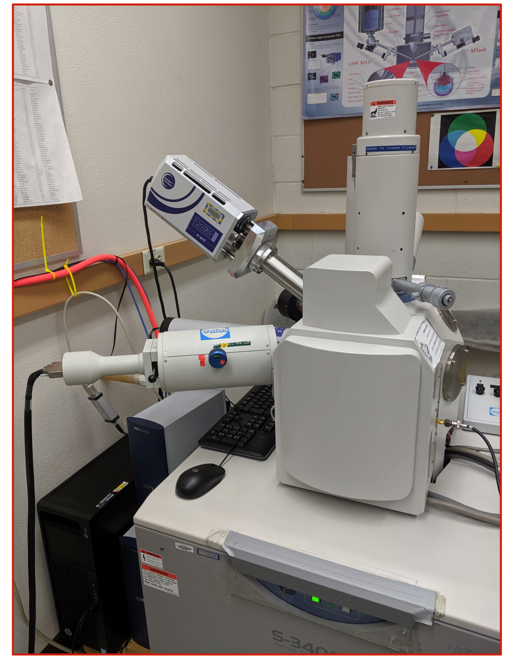
Cameca SX51

SEM Conditions
- E0= 15 kV
- Current set to Deadtime 30-40%

Probe Conditions

Anorthoclase
- E0 = 15 kV
- Current = 10 nA
- Defocused beam = 10 um

Augite & K530
- E0 = 15 kV
- Current = 20 nA
- Focused beam = 0 um


Hitachi S3400N

- **EDS 'normalized' compositions** were used due to observed beam drift on Co standard.
- **'WDS composition'** was calculated based on the use of standards that yielded analytical totals between 99% and 101%.

Beam Drift on EDS

Method

- Measurements were taken on Oxford Instrument's suggested metal standard (Co) at the beginning and end of each SEM run.

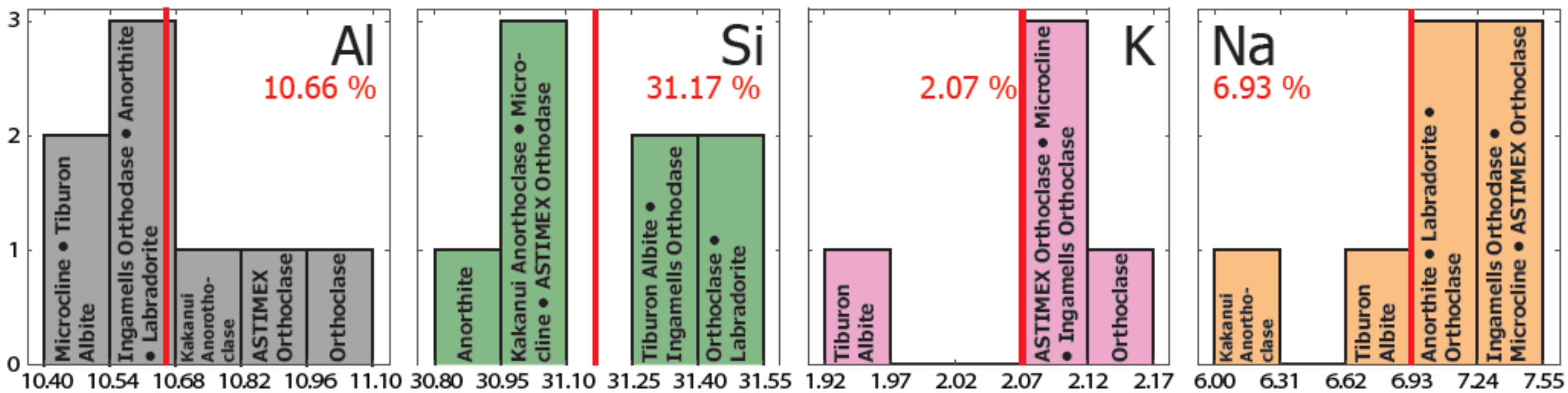
Observations

- Drift of 2-8% was observed over the three SEM runs, which were 1-1.5 hours in length.

Implications for the work

- As a result of this observation, 'normalized' EDS data was used for the comparative part of this work.

Q1: EDS vs. WDS Results (Anorthoclase)

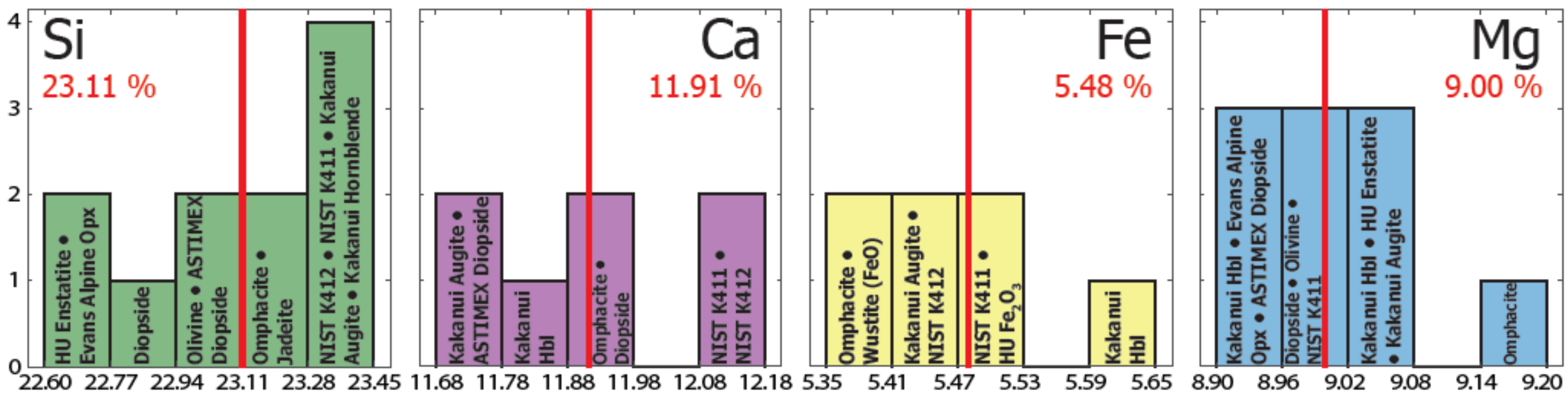


New Kakanui Anorthoclase Analyses								
Element	**Si**	**Al**	**Na**	**K**	**Ca**	**Fe**	**O**	**Total**
Wet Chem.*	31.06	10.65	6.91	1.95	0.62	0.16	51.35	99.32
EDS	31.41	10.69	6.81	2.09	0.43	0.12	48.33	100.00
WDS	31.17	10.66	6.93	2.07	0.43	0.10	48.12	99.68
EDS/WDS	1.01	1.00	0.98	1.01	1.00	1.20	1.00	1.00

• EDS/WDS ratios <1.25 indicate that EDS performs comparably to the ‘gold standard’ of WDS.

*Wet chemistry composition of existing Smithsonian Kakanui Anorthoclase standard

Q1: EDS vs. WDS Results (Augite)

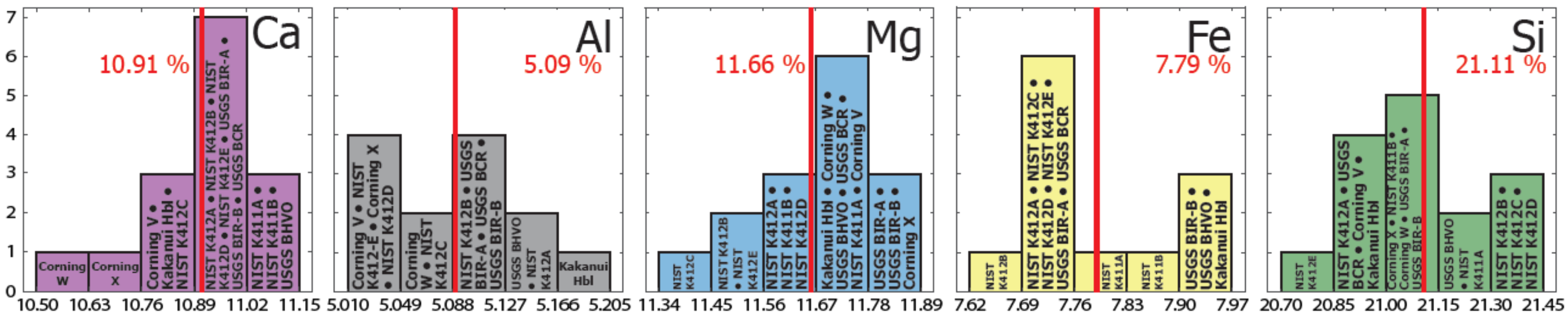


New Kakanui Augite Analyses									
Element	Si	Al	Na	Mg	Ca	Fe	Ti	O	Total
Wet Chem.*	23.74	4.62	0.94	10.04	11.31	4.93	0.44	44.60	100.38
EDS	23.36	4.60	1.09	8.86	11.84	5.81	0.67	43.76	100.00
WDS	23.11	4.68	1.13	9.00	11.91	5.48	0.67	43.63	99.61
EDS/WDS	1.01	0.98	0.96	0.98	0.99	1.06	1.00	1.00	1.00

• EDS/WDS ratios <1.06 indicate that EDS performs comparably to the ‘gold standard’ of WDS.

*Wet chemistry composition of existing Smithsonian Kakanui Augite standard

Q1: EDS vs. WDS Results (NIST K530)



NIST K530 Glass Analyses

Element	Si	Al	Mg	Ca	Fe	O	Total
K412	21.20	4.91	11.66	10.90	7.74	43.60	100.09
EDS	21.51	5.10	11.52	10.68	8.01	43.18	100.00
WDS	21.11	5.09	11.66	10.91	7.79	42.93	99.49
EDS/WDS	1.02	1.00	0.99	0.98	1.03	1.01	1.01

- EDS/WDS ratios <1.05 indicate that EDS performs comparably to the ‘gold standard’ of WDS.

Q1: EDS vs. WDS Discussion

EDS vs. WDS

- EDS/WDS ratios < 1.25 for all major elements in all three materials indicate that EDS 'normalized' quantitative analysis is comparable to WDS quantitative analysis
- The largest differences occurred in Fe for Augite and K530 (6% and 3% respectively)—this could possibly be resolved by more over voltage (higher count rate).

Effect of WDS Standards

- Using different standards gave a range of WDS compositions, and in some cases a bimodal distribution (e.g. SiO2 on Augite).
- This indicates that standard choice is non-negligible when performing analysis, and the average of several analyses with good standards may be best practice

Q2: Possible Standard? Homogeneity

- Homogeneity was determined after *Jarosewich et al* whereby a sample is considered homogeneous if the 'homogeneity index' (ratio of observed standard deviation to that obtained from counting statistics) is less than 3.

- All three of the materials we tested yield indices <2, indicating homogeneity on the scale of analysis

New Kakanui Anorthoclase Homogeneity						
Element	**Si**	**Al**	**Na**	**K**	**Ca**	**Fe**
WDS Std. Dev	20.20	11.90	7.30	2.60	1.50	1.00
1 sigma	19.50	10.90	5.20	3.70	1.90	0.80
Stdev/sigma	1.04	1.09	1.40	0.70	0.79	1.25

New Kakanui Augite Homogeneity							
Element	**Si**	**Al**	**Na**	**Mg**	**Ca**	**Fe**	**Ti**
WDS Std. Dev	37.40	12.90	2.60	13.50	13.90	5.20	3.20
1 sigma	23.70	9.70	2.90	11.10	13.20	5.30	3.00
Stdev/sigma	1.58	1.33	0.90	1.22	1.05	0.98	1.07

K530 Homogeneity					
Element	**Si**	**Al**	**Mg**	**Ca**	**Fe**
WDS Std. Dev	38.10	7.70	7.40	11.20	5.50
1 sigma	21.40	10.00	9.90	12.80	6.30
Stdev/sigma	1.78	0.77	0.75	0.88	0.87

Q2: Possible Standard? Characterization

New Kakanui Anorthoclase Stoichiometry				
	WDS		EDS	
	2+K+Na	1+Ca	2+K+Na	1+Ca
Expected	2.94	1.03	2.93	1.03
Observed	2.96	1.05	2.98	1.06
E/O	0.99	0.98	0.98	0.97

New Kakanui Augite Stoichiometry								
	Na	Mg	Si	Al	Ca	Ti	Fe	O (stoic)	Total
WDS	0.11	0.81	1.81	0.38	0.65	0.03	0.22	6	10.02
EDS	0.10	0.80	1.82	0.37	0.65	0.03	0.23	6	10.01

Approach

Stoichiometric relationships were examined for the two geologic minerals as a mark of 'good' characterization by WDS and EDS.

Anorthoclase

Stoichiometry was assessed using the relationships **Si = 2+K+Na** and **Al = 1+Ca**, assuming 8 Oxygens.

Augite

Stoichiometry was assessed assuming 6 Oxygens, producing cation totals of 10 as expected.

Q2: Possible Standards? Discussion

Homogeneity & Characterization

- All three of the materials we tested yield indices <2, indicating homogeneity on the scale of analysis

$$HI = std.\,dev / \sigma$$

- Inclusions in the geologic minerals were avoided via use of high resolution SEM images.

Advantages of Megacryst Standards

- Ease of mounting and polishing
- Large amount of material available for use
- Ability to exclude heterogeneities visually/ analytically via the use of high resolution SEM images

Conclusions

1) Attempting to use Oxford Instrument's internal beam correction on pure metal (Co), beam drift of 5-10% was observed over the course of the hour + long EDS quantitative analysis (**Q1**)

2) Using 'normalized' EDS data resolves the above issue, and compares very well (most within ~1.5%) with 'gold standard' WDS analysis.(**Q1**)

3) Each of the three materials analyzed is homogeneous on the scale of analysis and are well characterized by both EDS and WDS, and could be considered for use as standards by the community. (**Q2**)

Future Work

Q1: EDS vs. WDS

- An improvement could be made by integrating a beam drift correction into the Oxford software—tagging the Co with a timestamp and calculating drift to apply a correction, a la current microprobe practice
- Higher overvoltage might help resolve discrepancies in Fe by producing higher count rates

Q2: Homogeneity & Standard Characterization

- We have measured these potential new reference materials with many different standards via WDS—a pseudo ‘round robin’.
- We propose the use of these materials by a focused interest group or others interested in the documentation and development of new standard materials

References & Acknowledgements

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References

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