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?
Analytical Approach and Parameters

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

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)**

- 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)

- 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)

- 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.
Q2: Possible Standard? Characterization

**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 $\text{Si} = 2+\text{K+Na}$ and $\text{Al} = 1+\text{Ca}$, assuming 8 Oxygens.

**Augite**
Stoichiometry was assessed assuming 6 Oxygens, producing cation totals of 10 as expected.
### Q2: Possible Standards? Discussion

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<tr>
<th>Homogeneity &amp; Characterization</th>
<th>Advantages of Megacryst Standards</th>
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<tr>
<td>• All three of the materials we tested yield indices &lt;2, indicating homogeneity on the scale of analysis</td>
<td>• Ease of mounting and polishing</td>
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<td>• Large amount of material available for use</td>
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<td>• Ability to exclude heterogeneities visually/analytically via the use of high resolution SEM images</td>
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\[ HI = \frac{\text{std. dev}}{\sigma} \]

• Inclusions in the geologic minerals were avoided via 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
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References