UNLIMITED SCOPE

Analysis and Classification of Environmental Samples Using ASPEX Automated P-SEM

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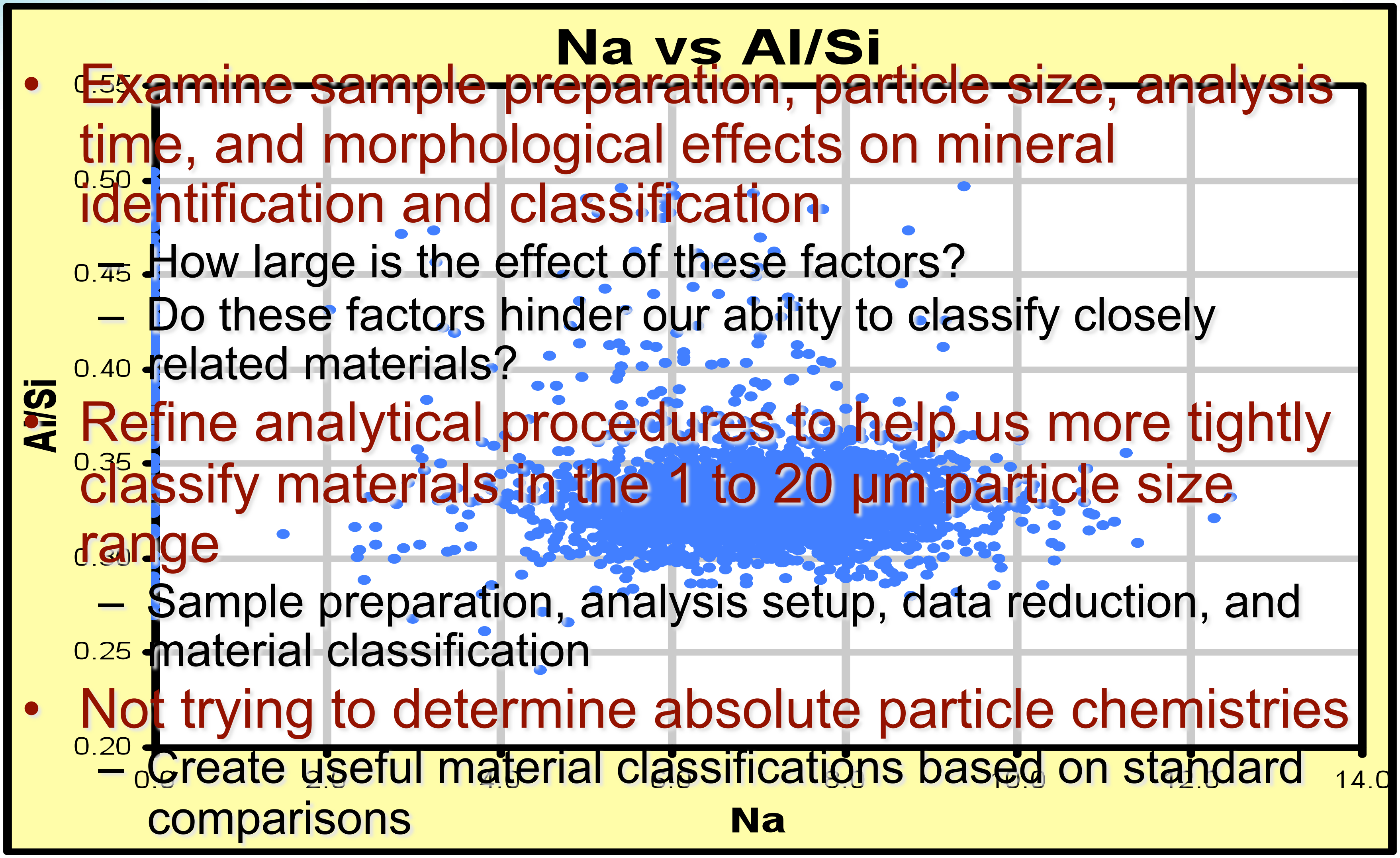
Purpose of Research



- Examine sample preparation, particle size, analysis time, and morphological effects on mineral identification and classification
  - How large is the effect of these factors?
  - Do these factors hinder our ability to classify closely related materials?
- Refine analytical procedures to help us more tightly classify materials in the 1 to 20 µm particle size range
  - Sample preparation, analysis setup, data reduction, and material classification
- Not trying to determine absolute particle chemistries
  - Create useful material classifications based on standard comparisons

Mineral Identification
PLM vs. ASPEX

PLM

- Identify biological materials
- Can differentiate polymorphs
- Need a skilled optical mineralogist
- Time consuming
- Subjective
- Harder to find 'needle in haystack'

ASPEX

- Overcome possible analysis biases
- Analyze all particles on stub within set thresholds
- Outputs all chemical and morphological parameters
- Not as labor intensive as a manual analysis
- Good at recognizing opaque heavy minerals
- SPEED!

ASPEX SEM/EDS

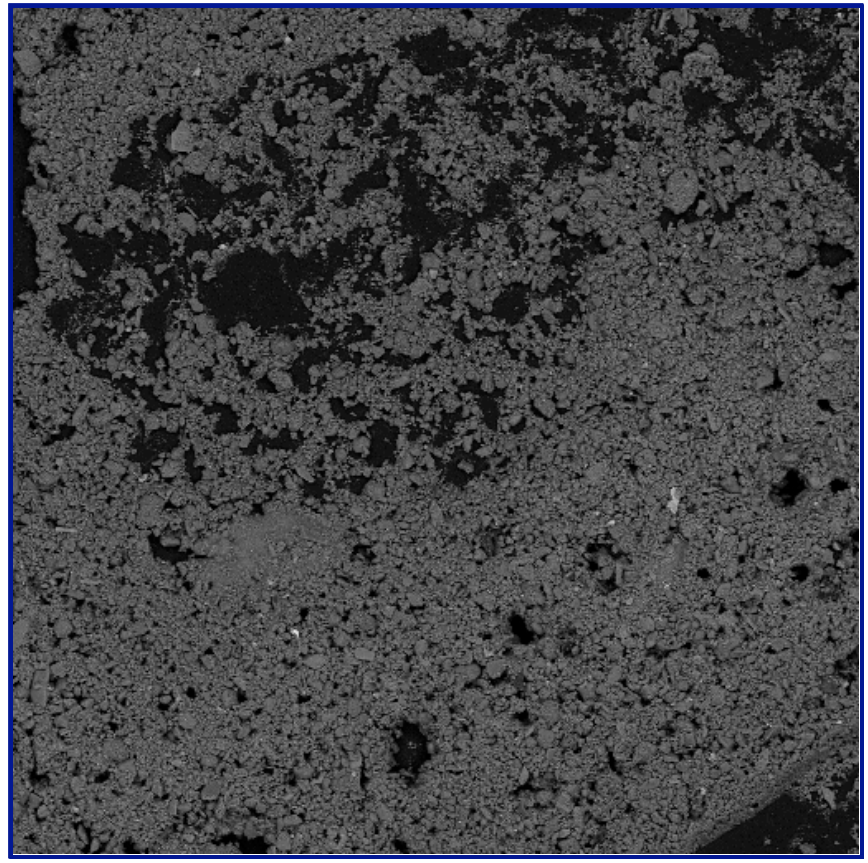
- Developed for high-speed automated elemental analyses of environmental and industrial materials
  - Determine general populations of materials
  - High sample throughput
- Our typical ASPEX automated analysis
  - Analyze particle dispersions for specific materials of interest
  - Perform the analysis in a time frame of several hours
- We are currently developing procedures to bin the remaining materials into useful material classifications, while maintaining our high sample throughput

Samples Analyzed

- Analyzed five silicate minerals
  - Thre
    - Al
    - Ar
    - La
  - Two erals
    - Bi
    - Al

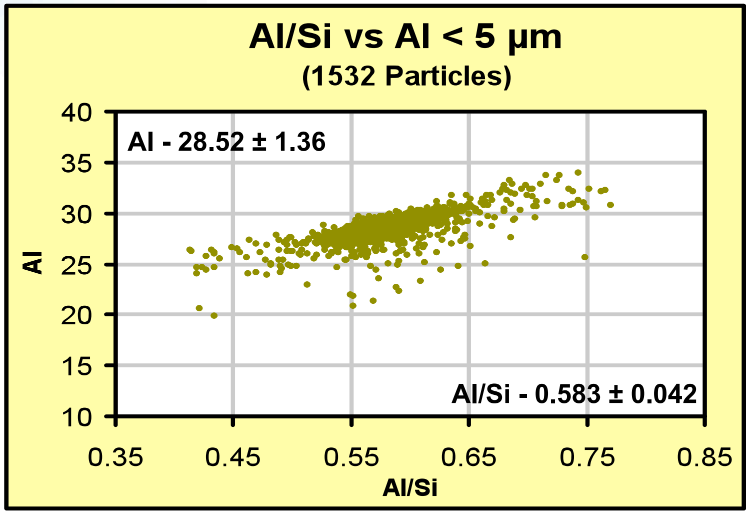
Sample Preparation

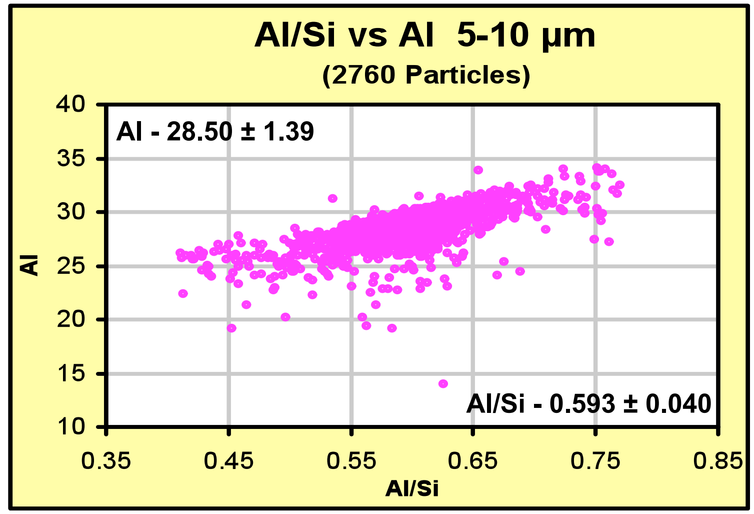
- Need to avoid touching and overlapping particles
- Preferable to have small, uniform, size range
  - Can do several analyses at different size ranges to see variability of materials
- Reverse sieving technique
  - Back sieve samples onto a GSR stub

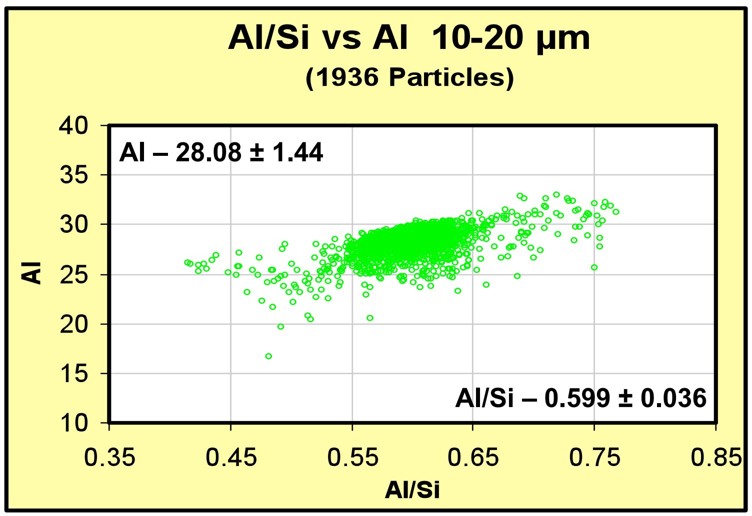


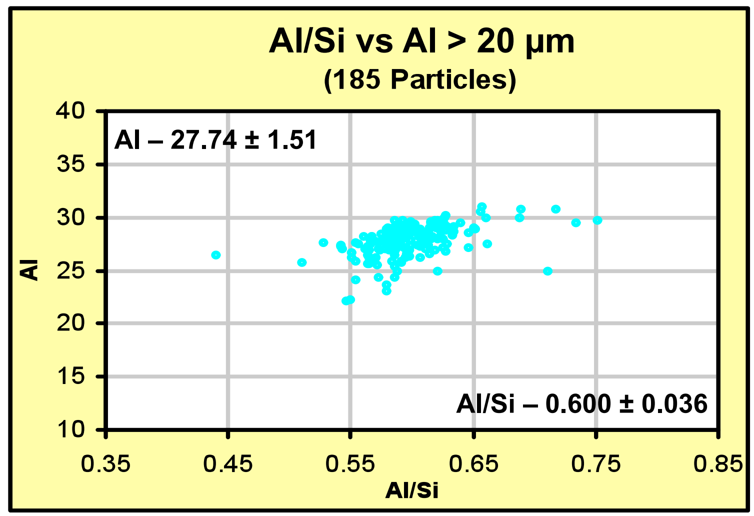
Size Effect – Labradorite

$(Ca,Na)(Al,Si)_4O_8$









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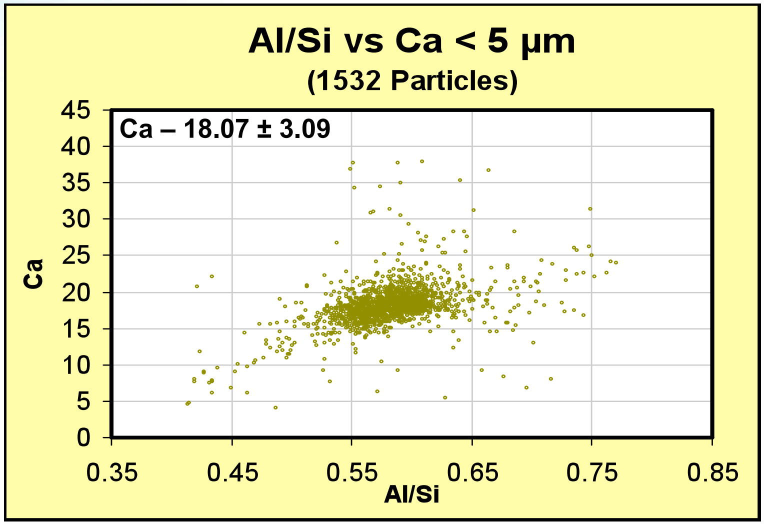

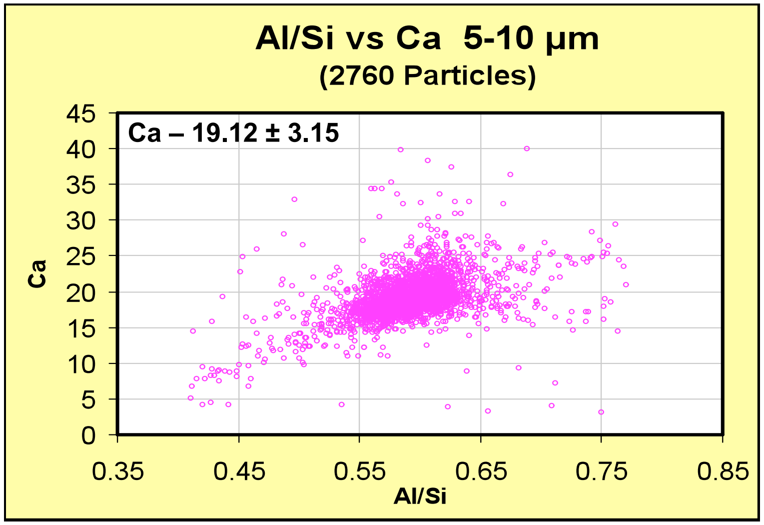

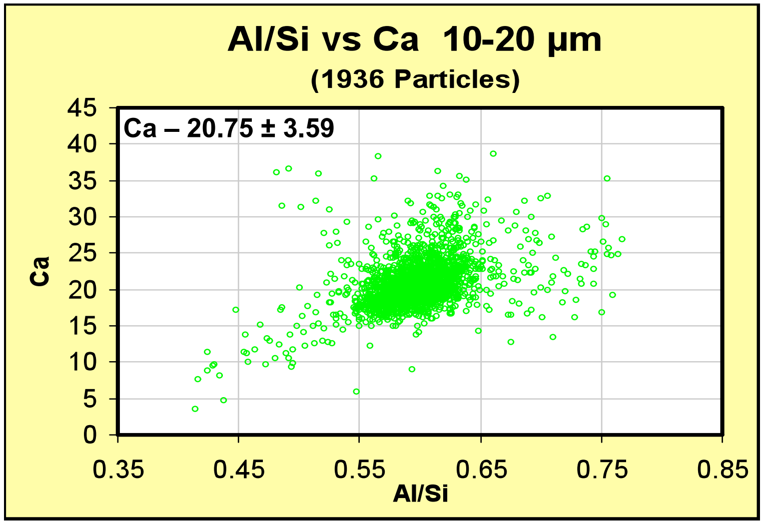

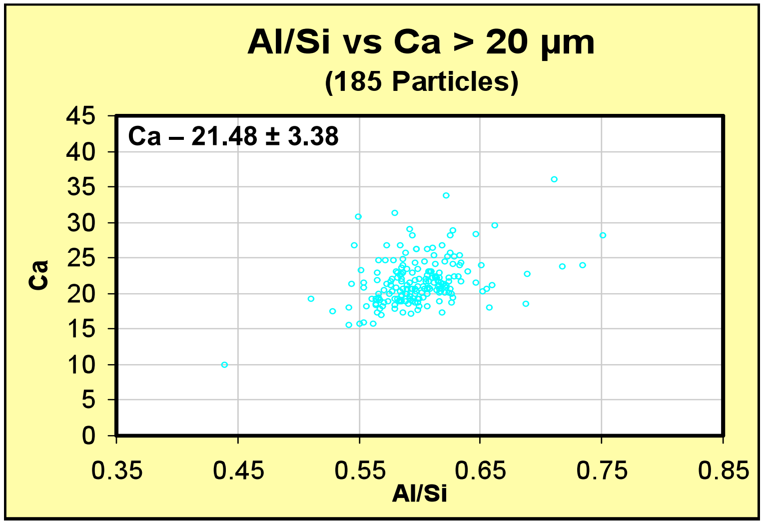

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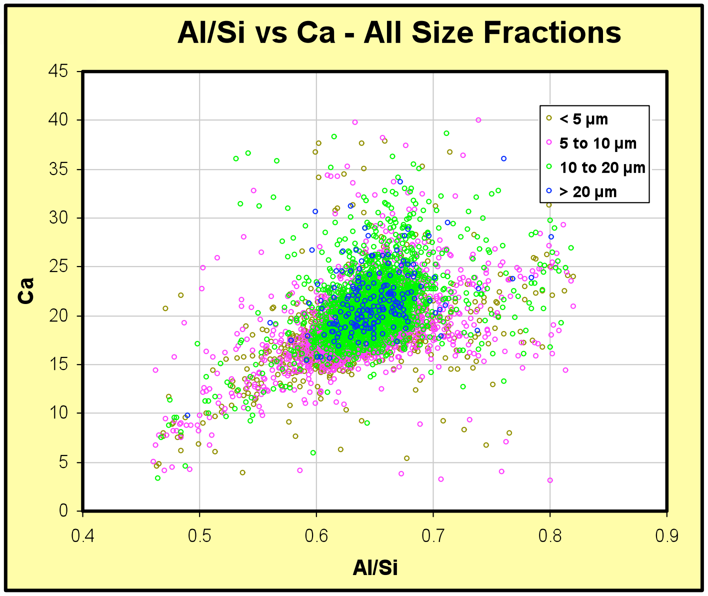
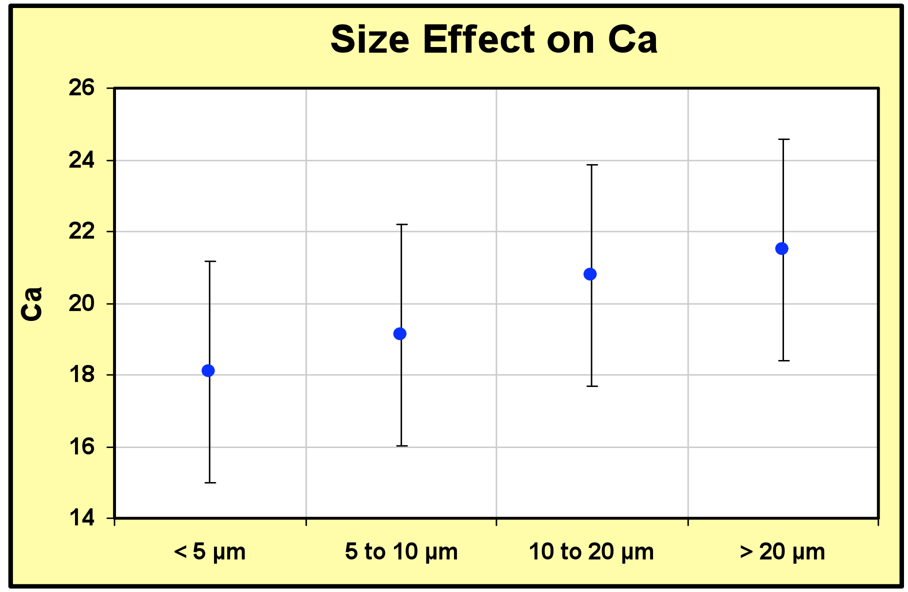
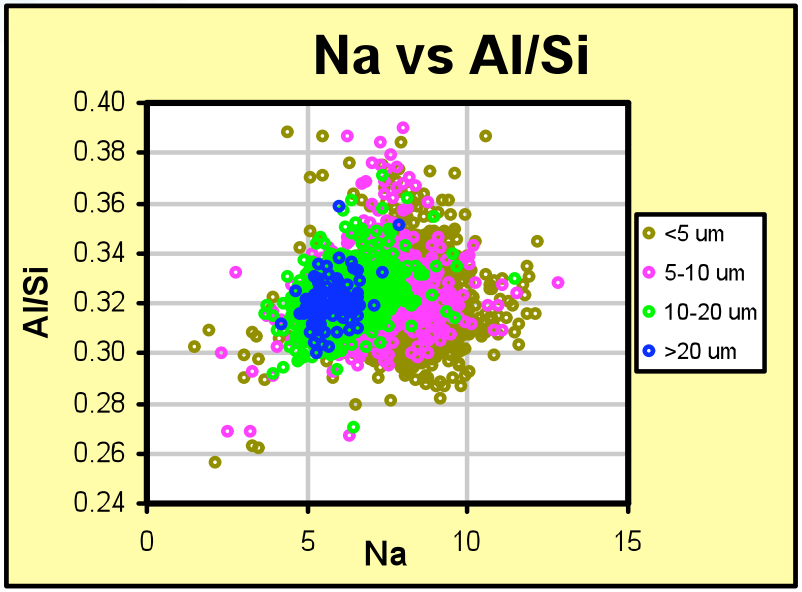
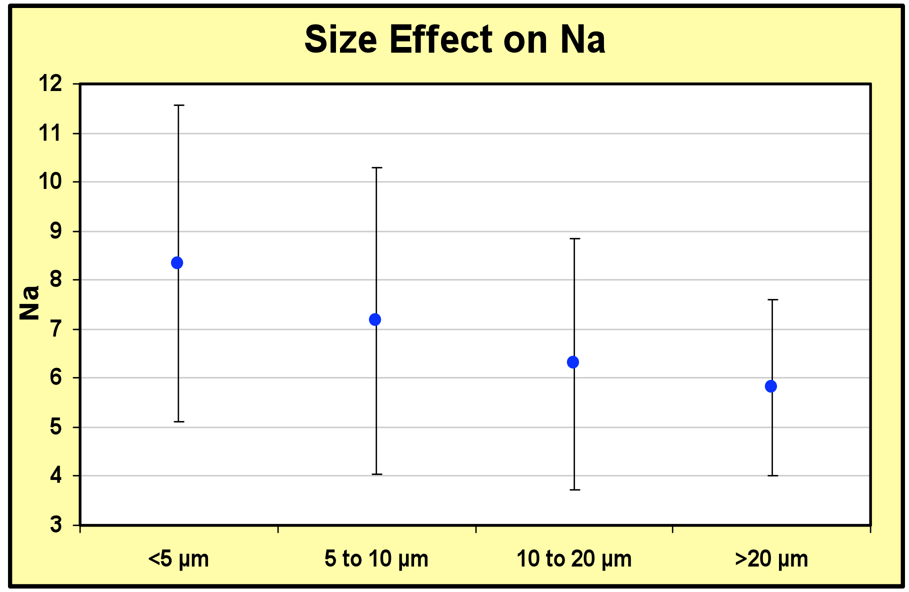




- Ca content increases with size
  - Artifact of Size???
  - Due to normalization???

Size Effects – Na Migration??
Albite ($NaAlSi_3O_8$)

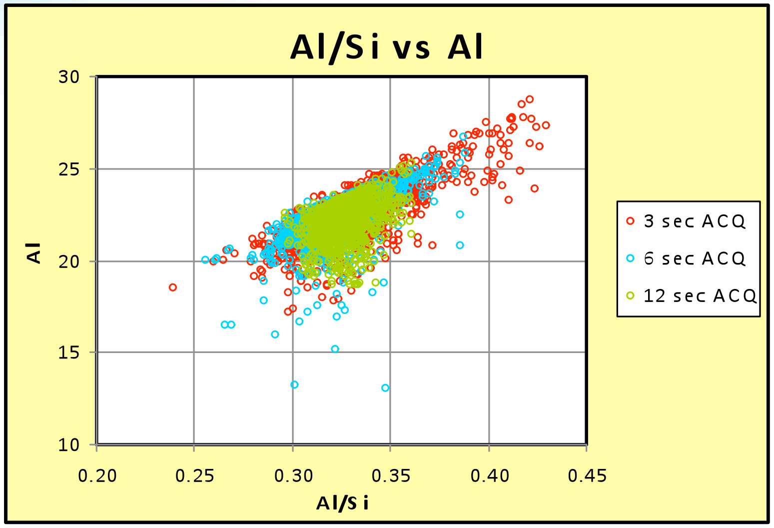


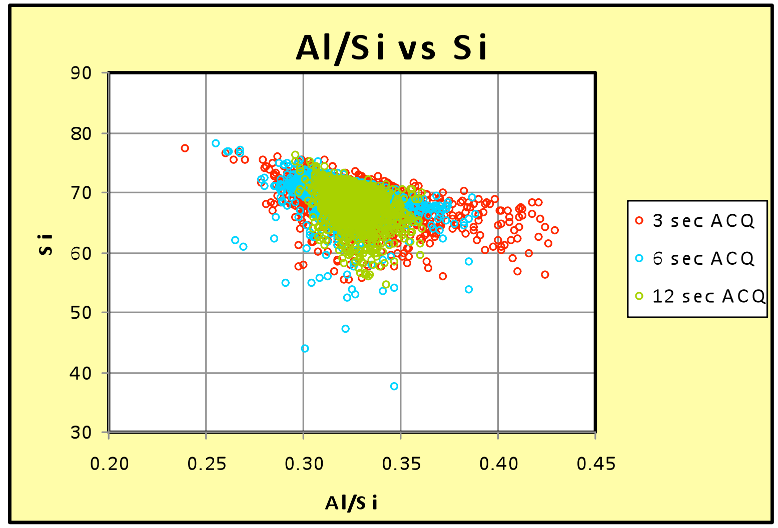


- Na content decreases with size
  - Is this due to sodium migration??
  - How does this effect other elemental data due to normalization??

Time Effects on Particle Analysis

Albite ($NaAlSi_3O_8$)

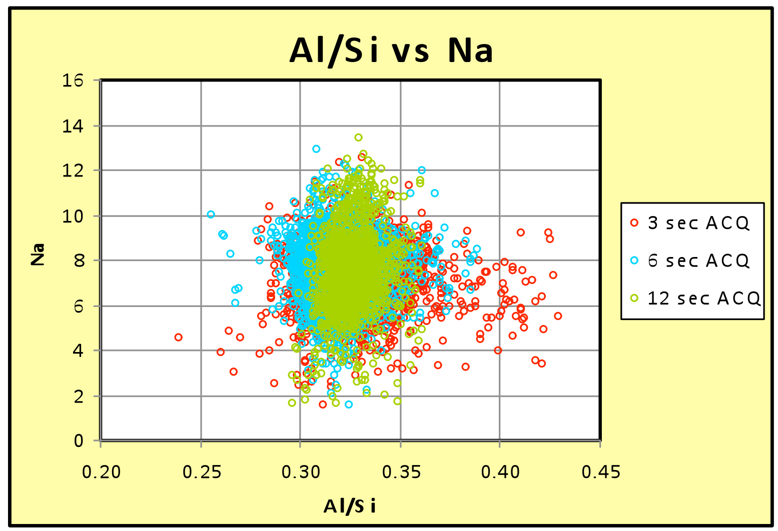




Al/Si

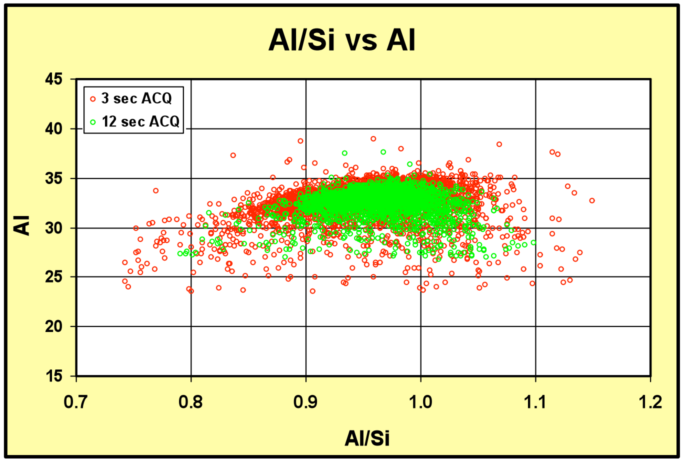
Na Al Si

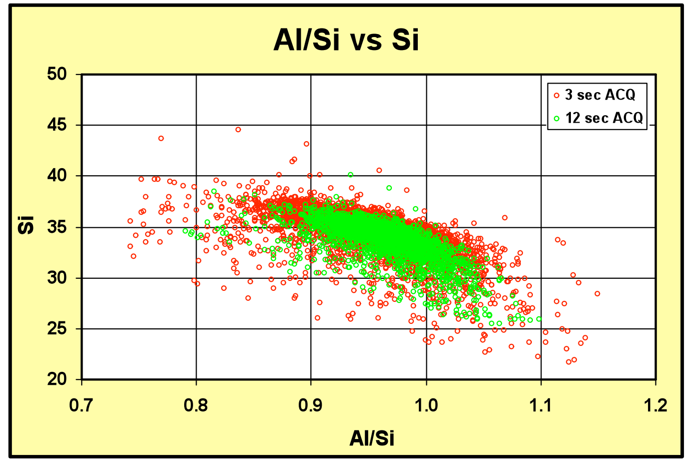
•3 Sec Analysis					
	•Average	0.329	7.086	22.629	68.896
	•S.D.	0.018	1.208	1.095	2.447
•6 Sec Analysis					
	•Average	0.321	7.398	22.349	69.693
	•S.D.	0.012	1.325	0.842	2.095
•12 Sec Analysis					
	•Average	0.326	7.379	22.218	68.095
	•S.D.	0.009	1.546	0.870	2.661

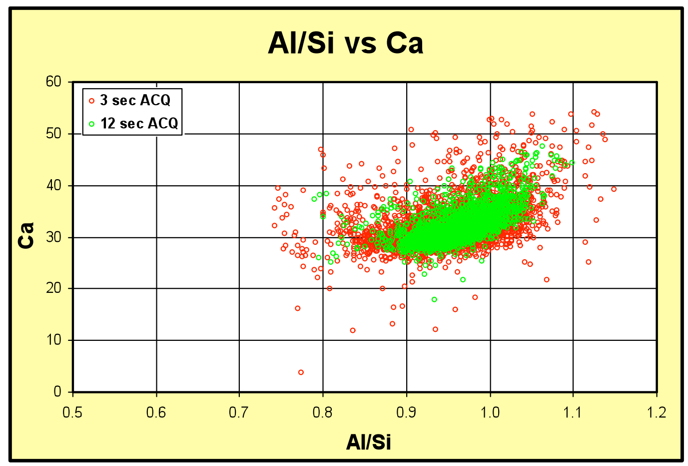


Time Effects on Particle Analysis

Anorthite ($CaAl_2Si_2O_8$)





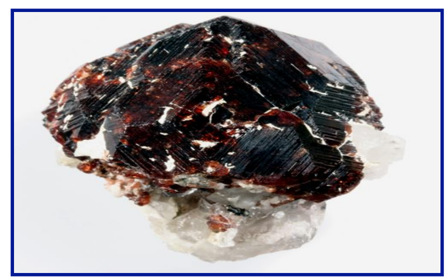


Ca		Al	Si		Al/Si
•3 Sec Analysis					
	•Average	0.954	32.02	32.50	34.58
	•S.D.	0.054	4.18	1.88	2.36
•12 Sec Analysis					
	•Average	0.962	31.90	32.32	33.64
	•S.D.	0.039	3.33	1.40	1.93

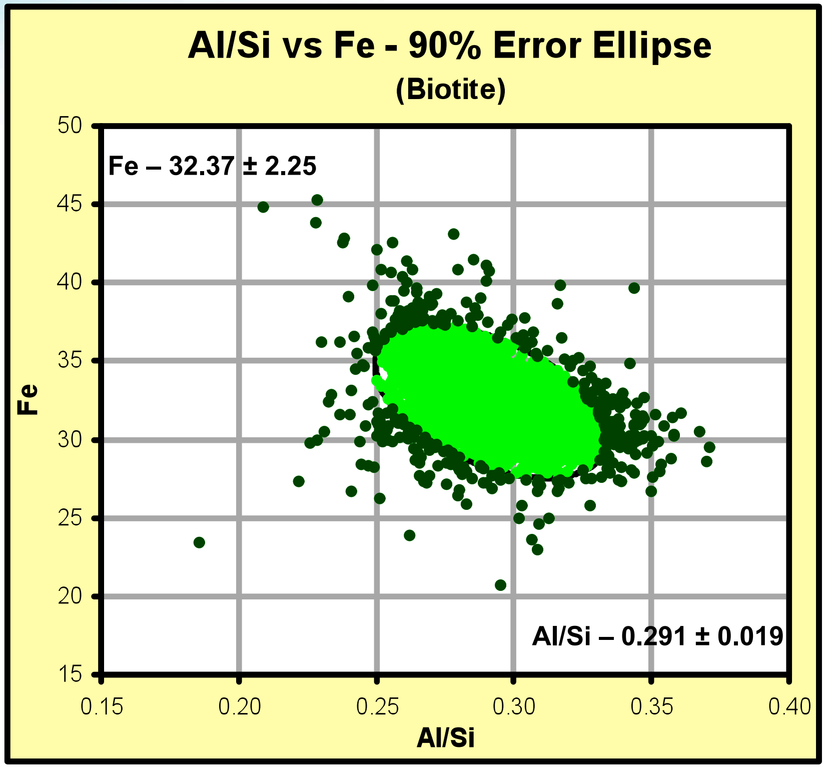
Morphology Effects

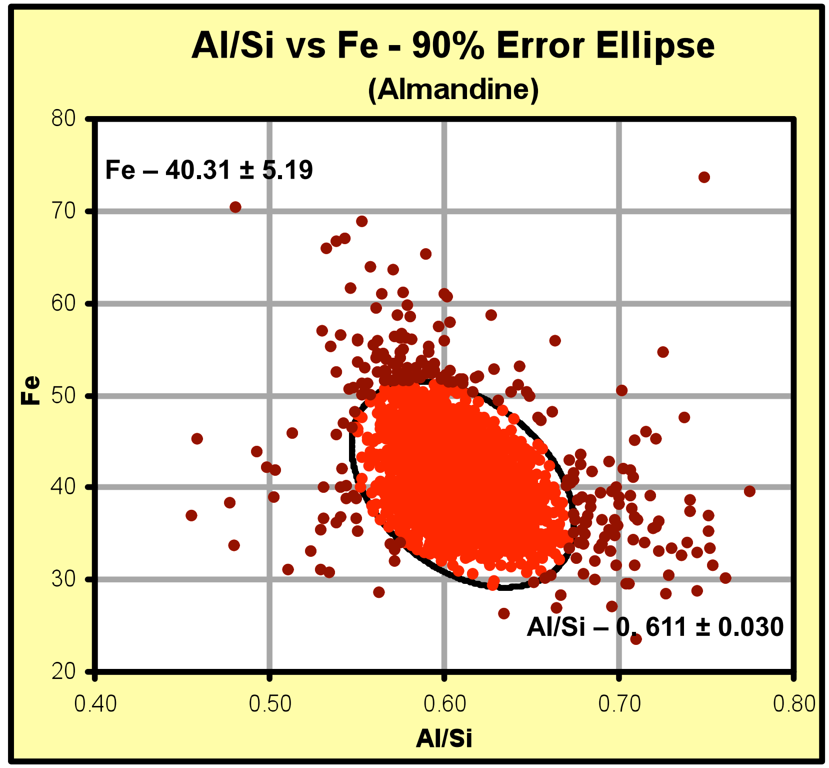
- Analyzed two minerals with similar elemental compositions but different morphologies
  - Biotite - $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$
    - Monoclinic mica
    - Phyllosilicate (sheet silicate)
      - results in infinitely extending flat sheets

  - Almandine – $Fe_3Al_2Si_3O_{12}$
    - Isometric garnet (Cubic)
    - Nesosilicate (single silicate)
      - Independent tetrahedral SiO_4 groups (cleavage absent)



Morphology Effects





Less than 5 µm – 123 Particles

5 to 10 µm – 1,650 Particles

10 to 20 µm – 1,614 Particles

Greater than 20 µm – 1039 Particles

Less than 5 µm – 2,089 Particles

5 to 10 µm – 534 Particles

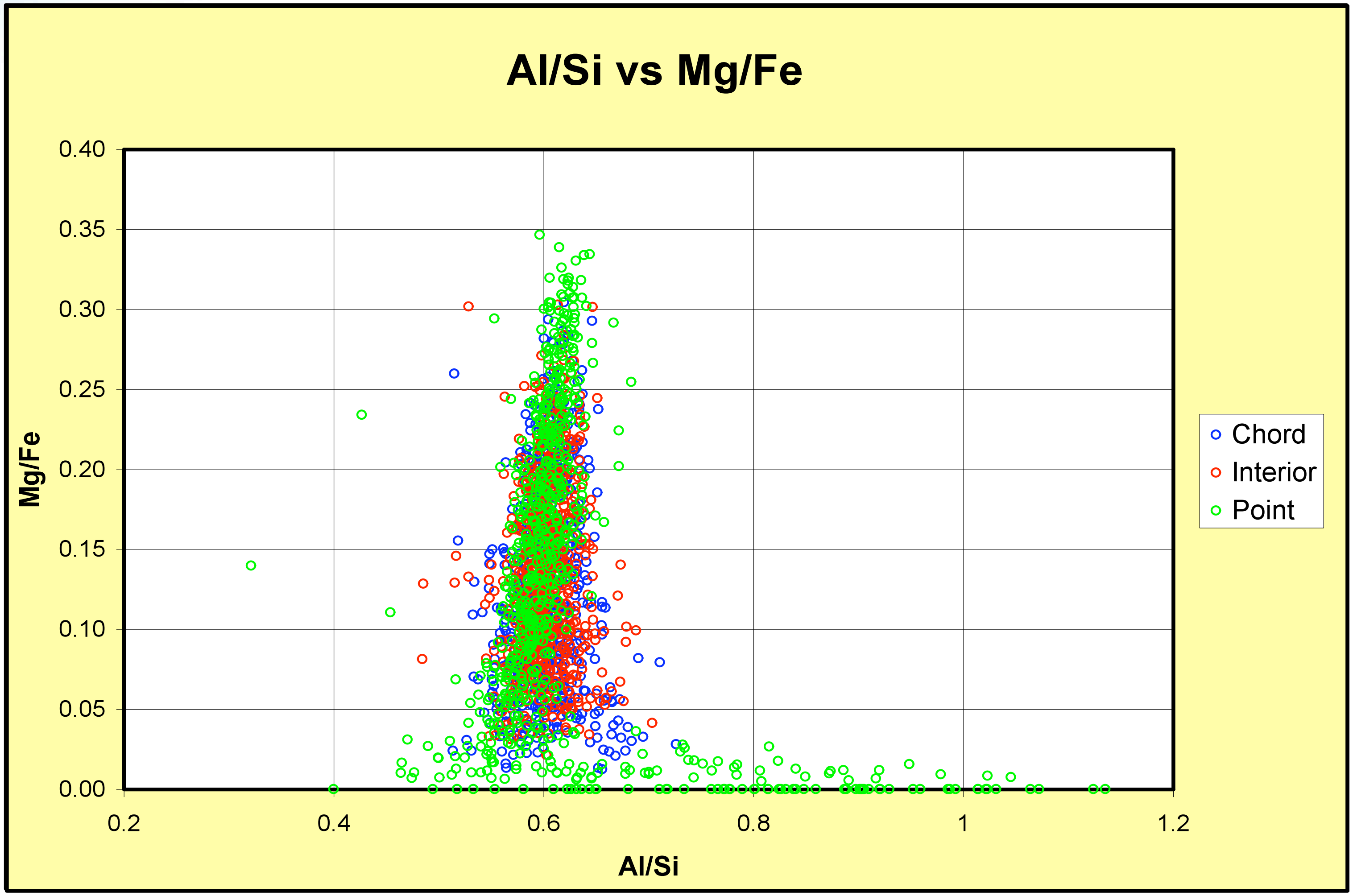
10 to 20 µm – 147 Particles

Greater than 20 µm – 9 Particles

Raster Effects

- Investigated effects of three different beam raster modes
  - Chord Raster
    - Beam is rastered over the particle along the 16 chords used to measure particle dimensions
  - Point Raster
    - Beam sits on the centroid of the particle
  - Interior Raster
    - Beam rastered over entire particle

Raster Effects – Almandine (>50um)



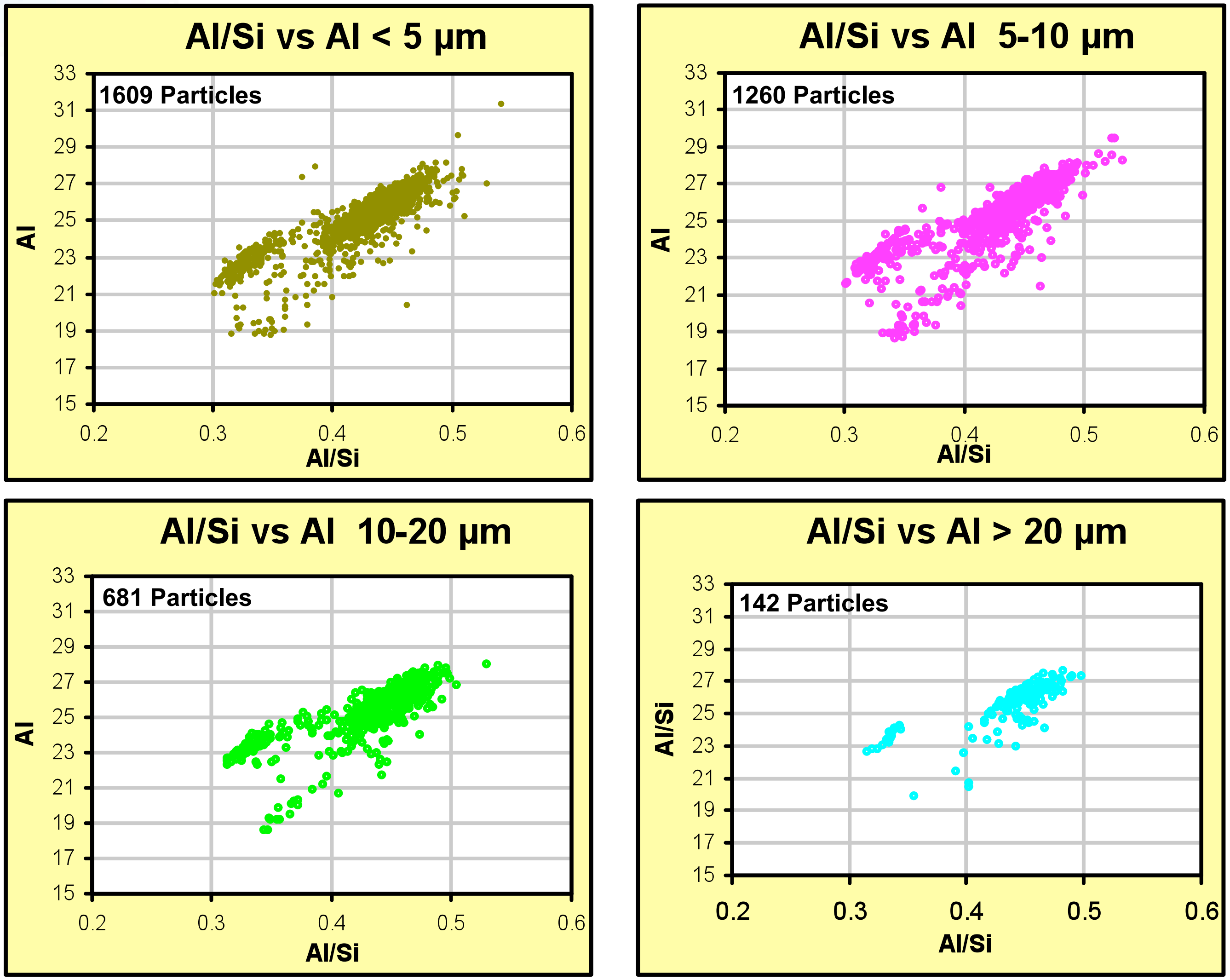
Raster Effects – Garnet (>50um)

- Statistics
  - Point Raster (678 particles)
    - Al/Si – 0.626 ± 0.098 (3 sigma RSD – 47.2%)
  - Chord Raster (697 particles)
    - Al/Si – 0.600 ± 0.042 (3 sigma RSD – 21.2%)
  - Interior Raster (695 particles)
    - Al/Si – 0.602 ± 0.024 (3 sigma RSD – 11.8%)
- Interior and chord raster provide similar average; interior has smaller S.D.
- Point raster provides worst data for this sample
  - Affected most by elemental heterogeneity and particle morphology
  - May result in overlapping rule files

Albite Sample Showing Three Groupings of Particles

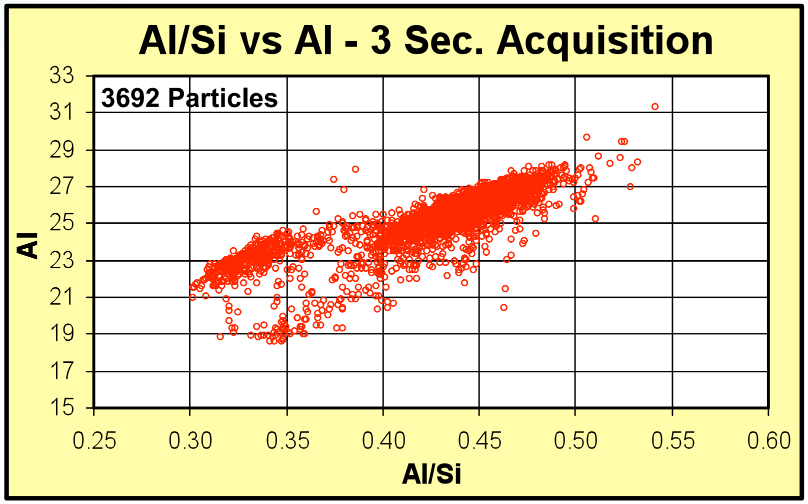
- Cargille ‘albite’ reference standard analyzed
- Results show three separate groupings present in the plots
- Can these three phases be distinguished regardless of:
  - Particle size
  - Particle analysis time
  - Raster type

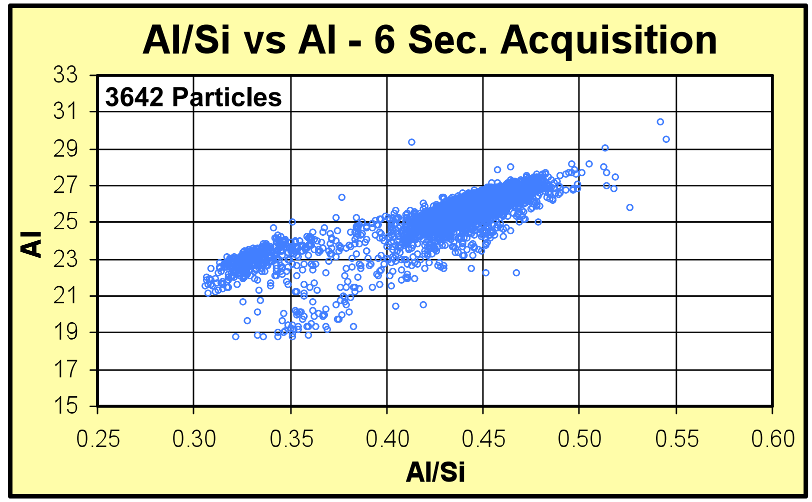
Size Effects – 'Albite'
(6 Sec. Chord Raster)

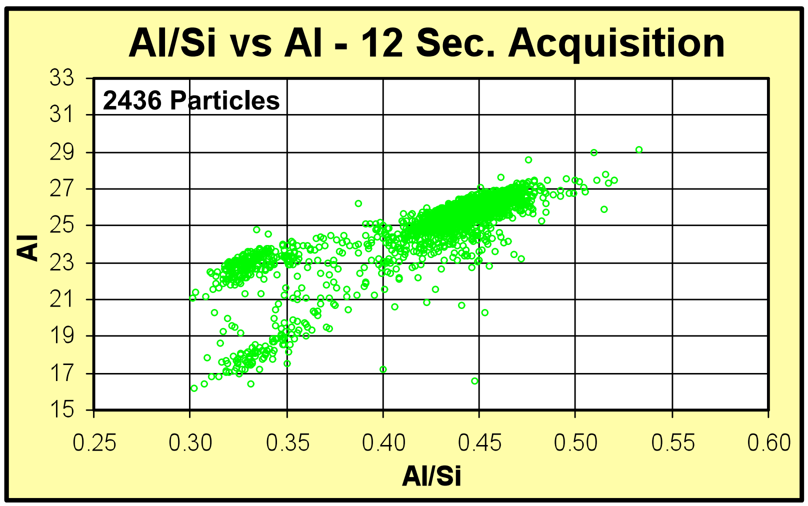


Time Effect – ‘Albite’

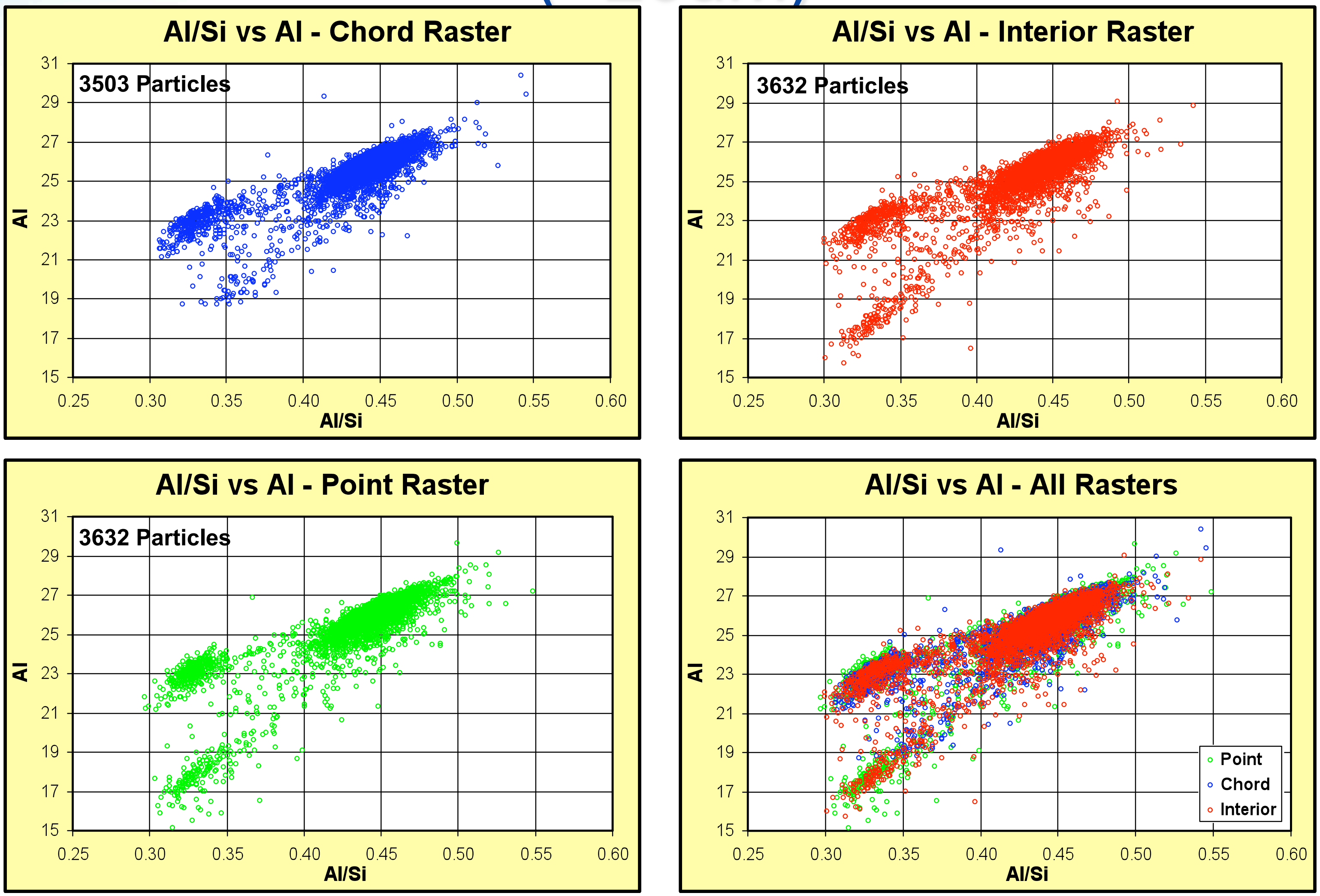
(Chord Raster)



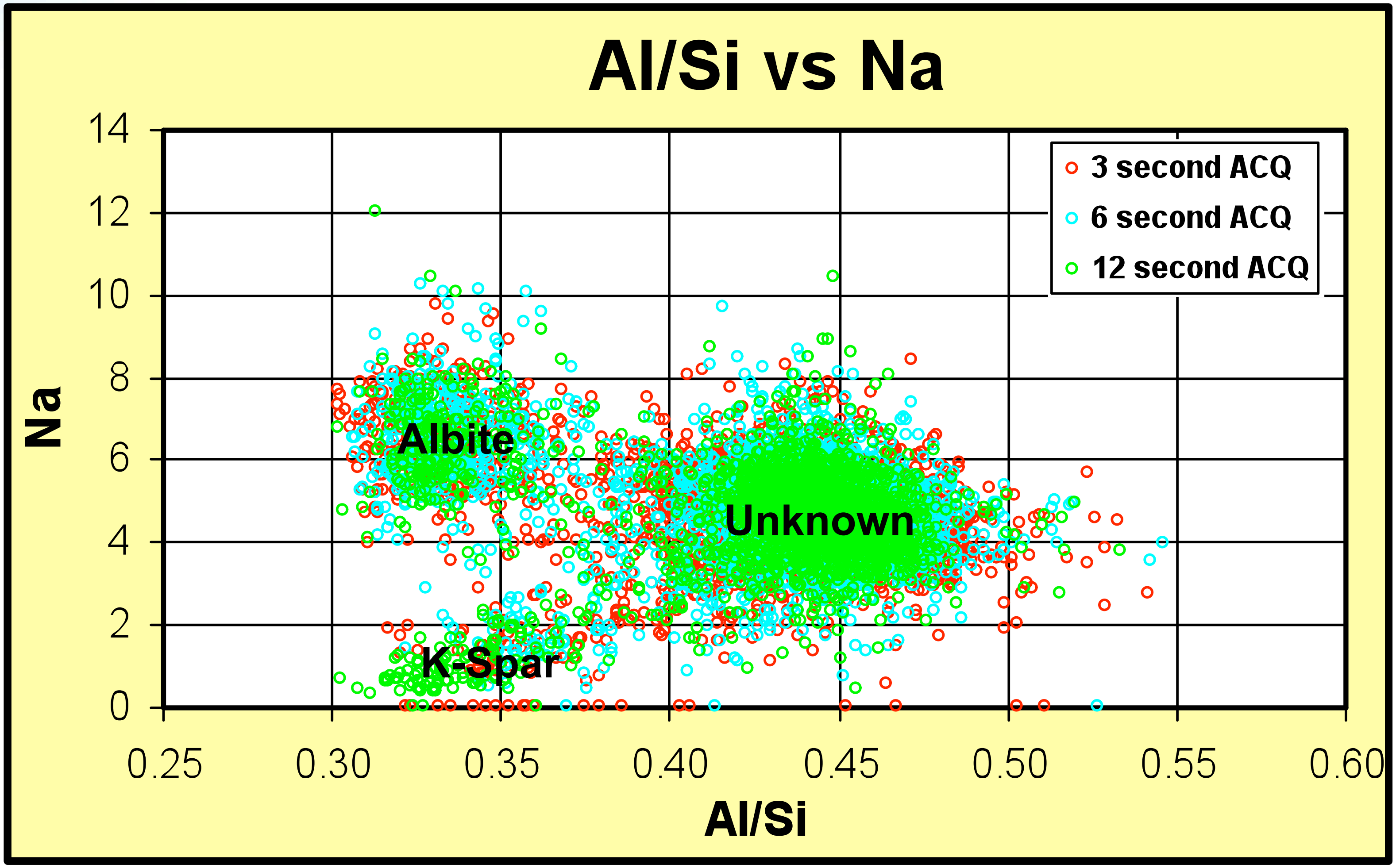




Raster Effects – 'Albite' Sample (<20um)

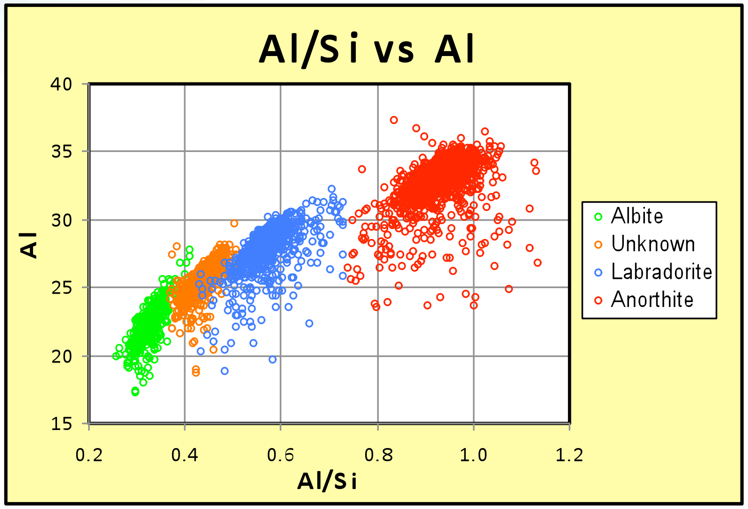


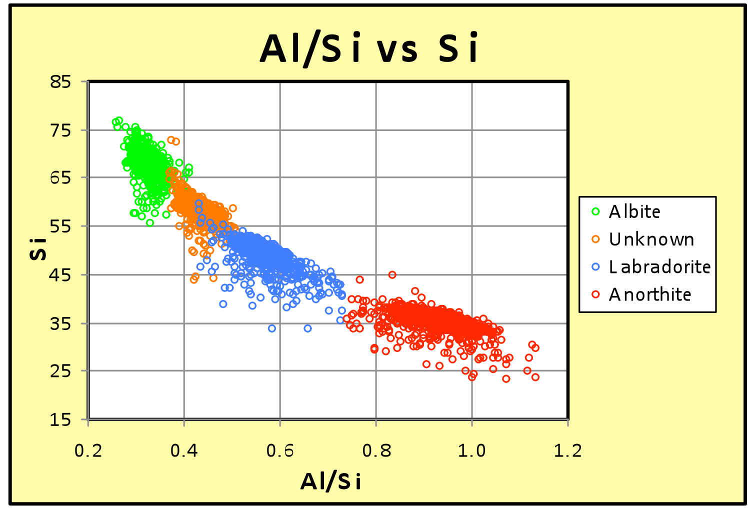
Unknown Plagioclase Feldspar

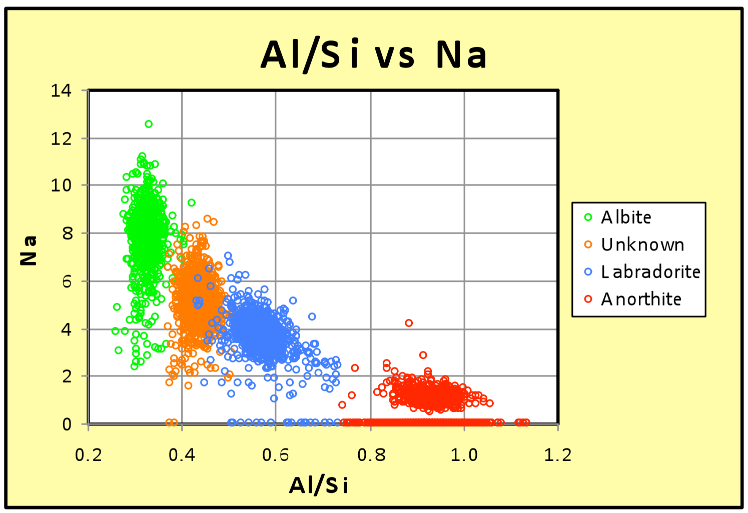


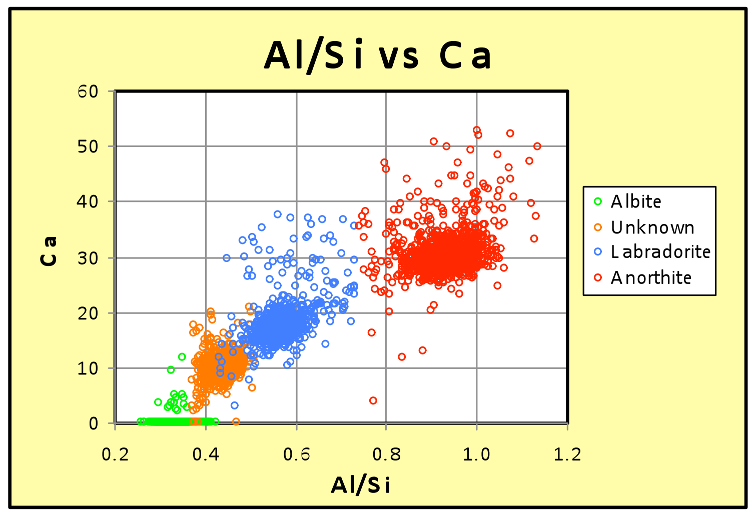
Particle Classification

Plagioclase Feldspars – (3 Sec. < 5µm)

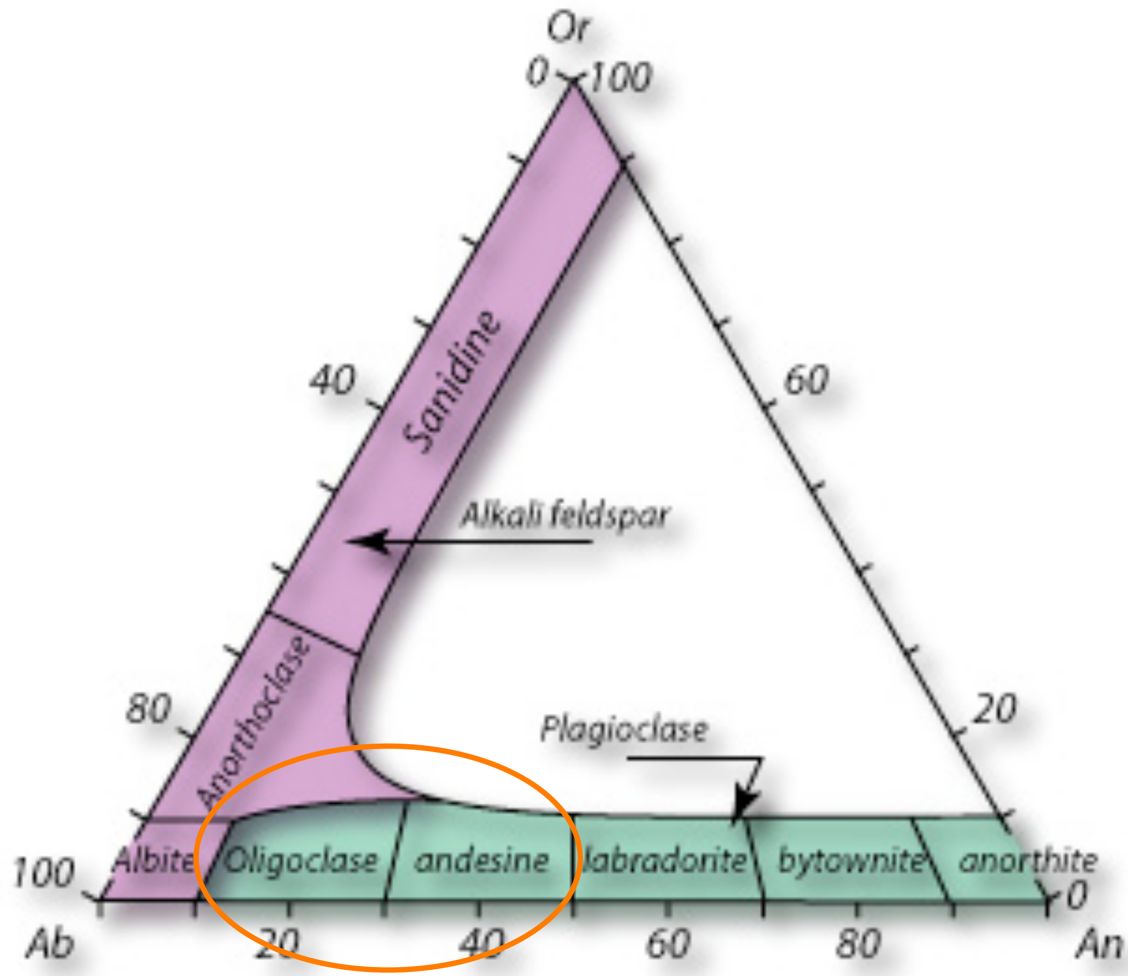








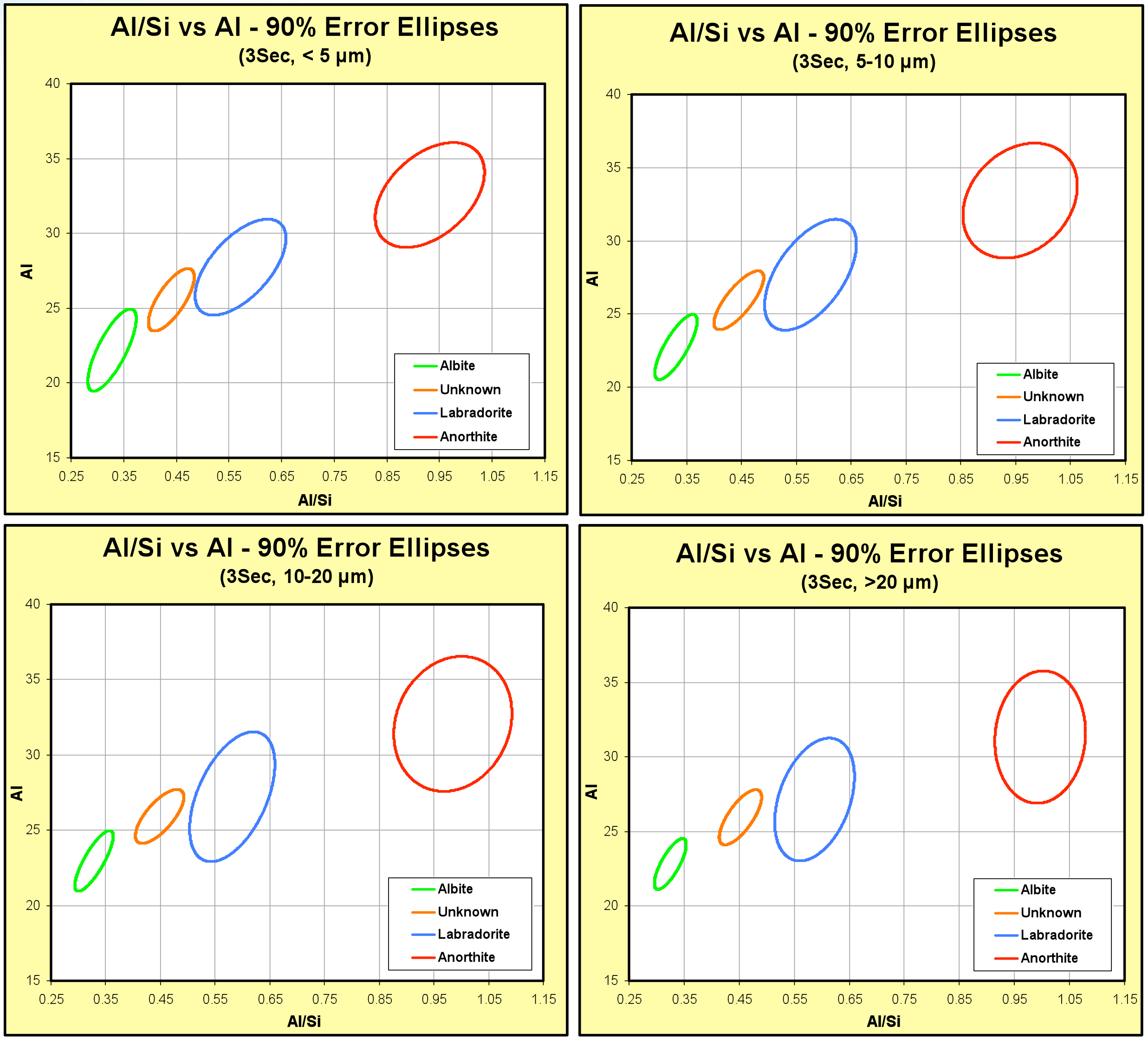
Unknown Feldspar Phase



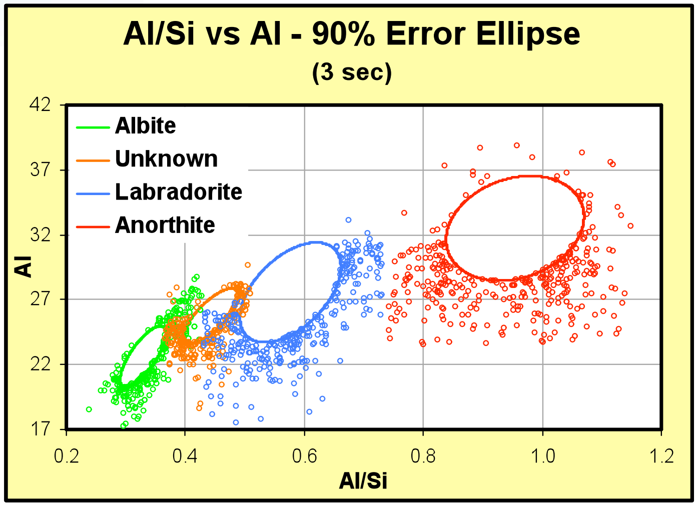
90% Error Ellipse – Albite

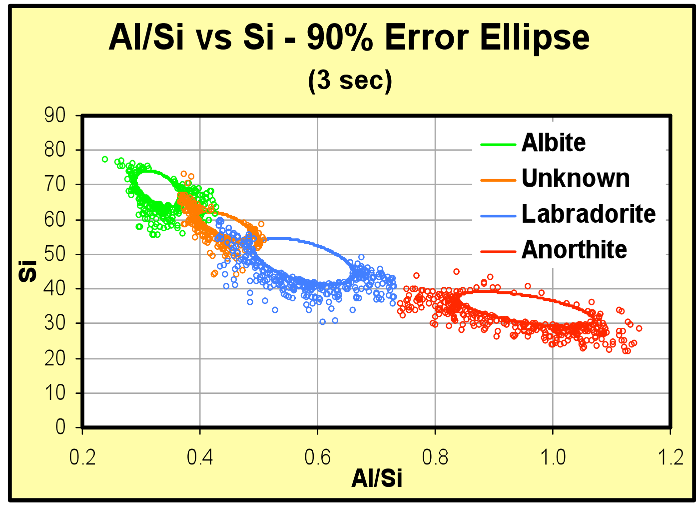
($NaAlSi_3O_8$)

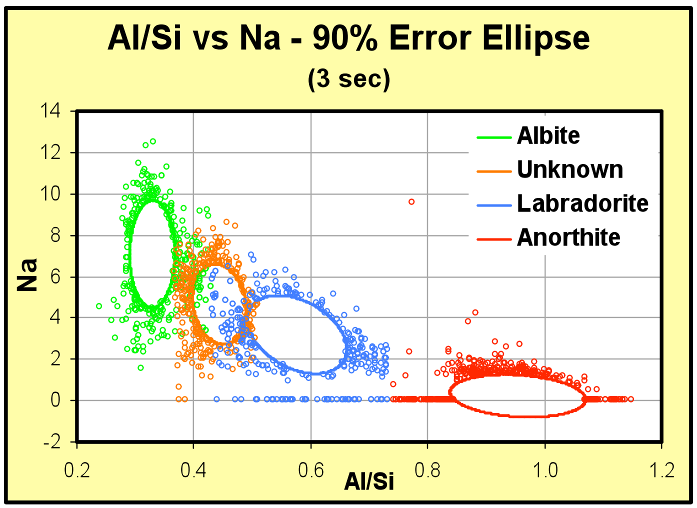
Size Effects – Plagioclase Feldspars 90% Error Ellipses

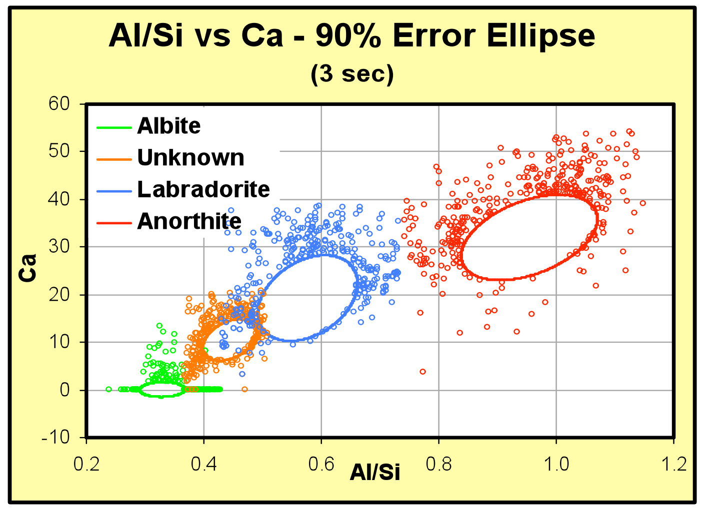


90% Error Ellipses – 3 Sec. Analysis Plagioclase Feldspars

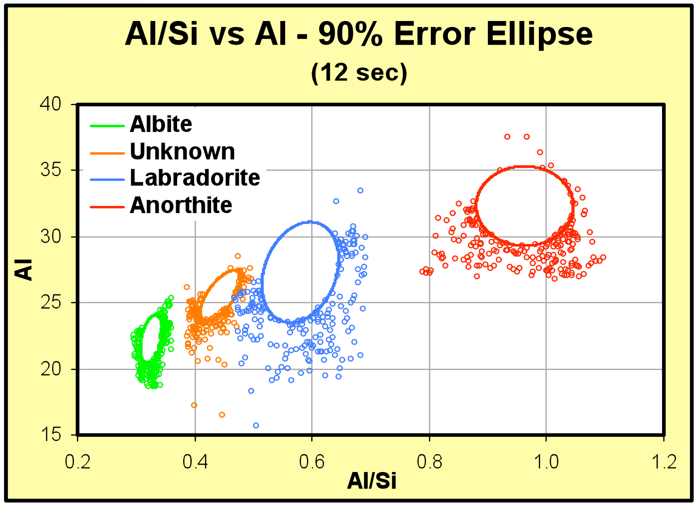


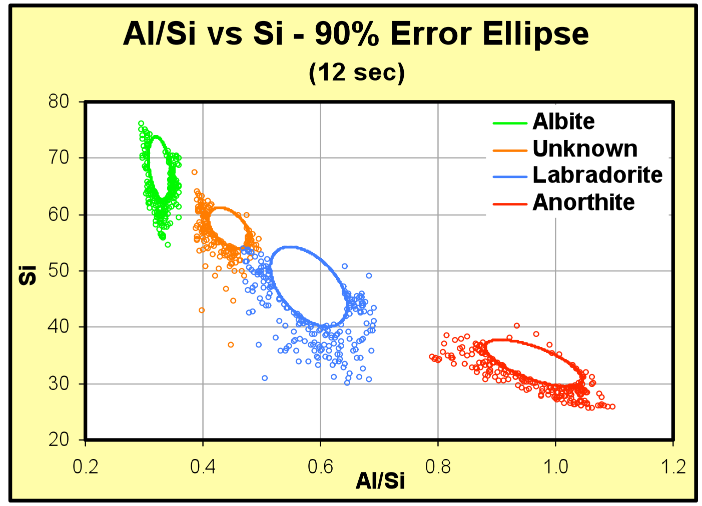


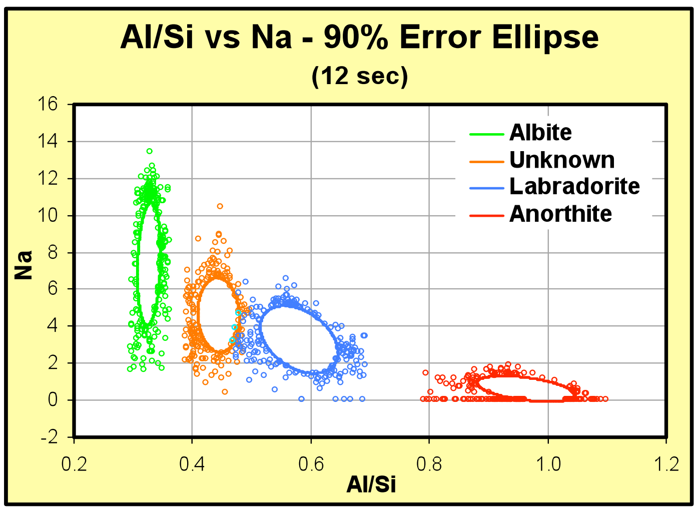


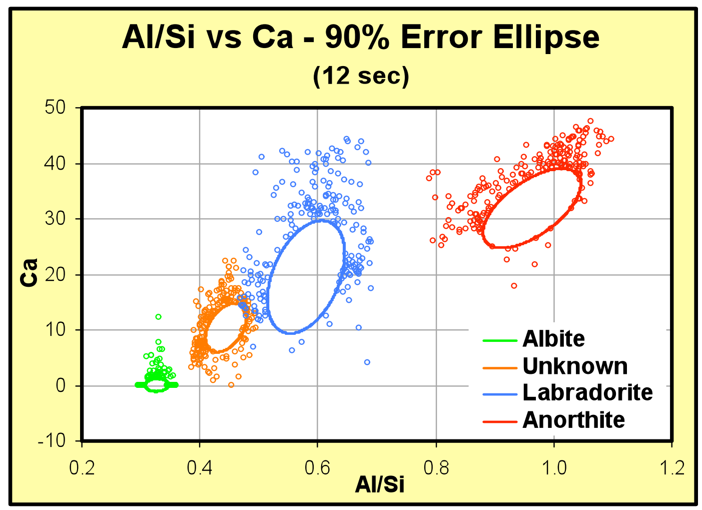


90% Error Ellipses – 12 Sec. Analysis
Plagioclase Feldspars

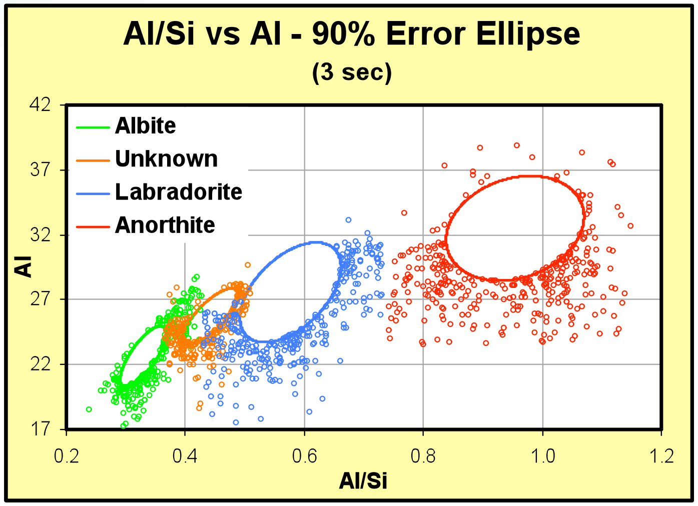


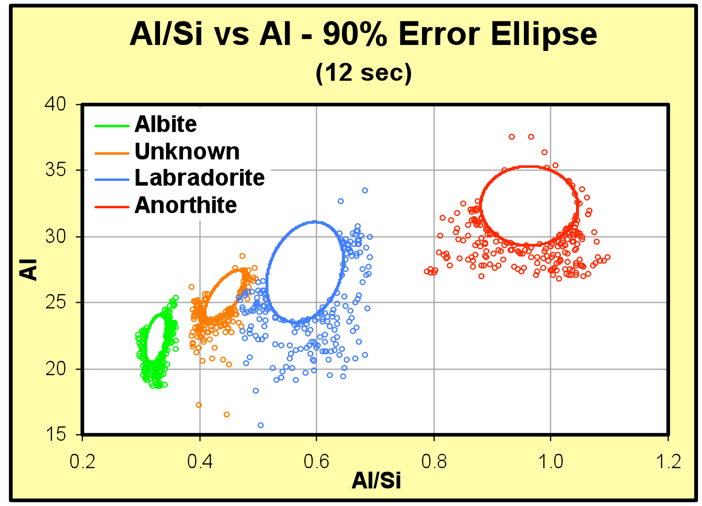






Comparison – 3 Sec. vs. 12 Sec. Plagioclase Feldspar

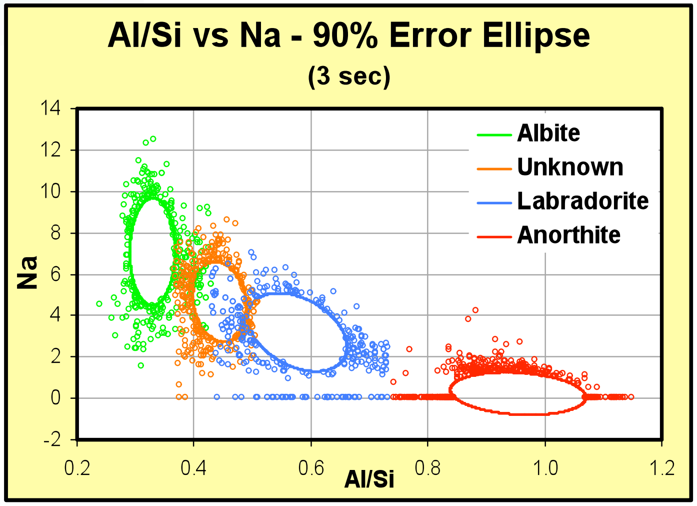


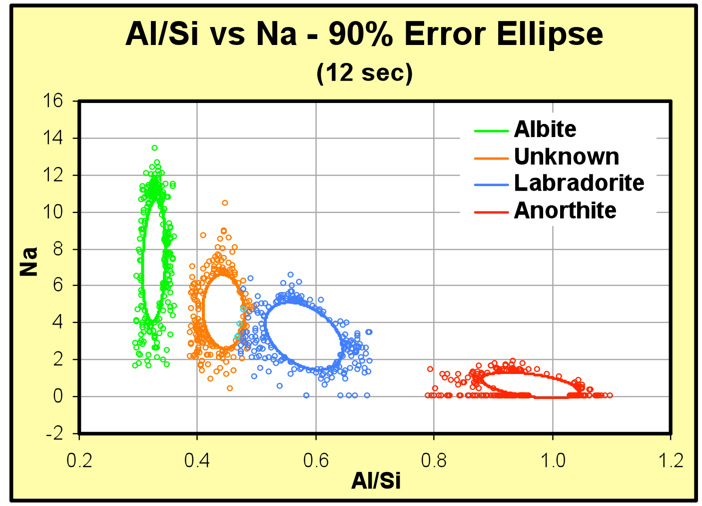


- Albite (3236 particles)
  - 10 particles fall within another ellipse (< 0.33%)
- Unknown (3077 particles)
  - 10 particles fall within another ellipse (< 0.33%)
- Labradorite (2872 particles)
  - 13 particles fall within another ellipse (< 0.5%)
- Anorthite (3599 particles)
  - 0 particles fall within another ellipse

- No particles from any of the mineral groups fall within another mineral's error ellipse.

Comparison – 3 Sec. vs. 12 Sec.



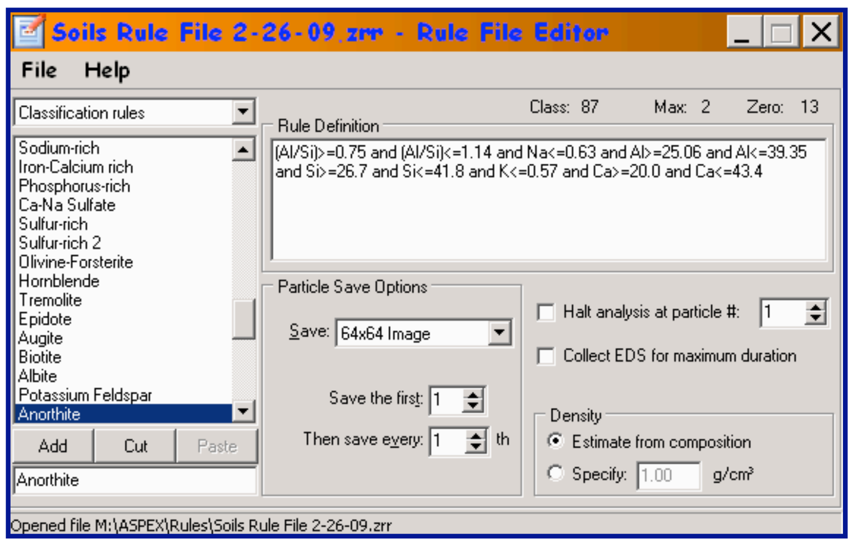


- Albite (3236 particles)
  - 14 particles fall within another ellipse (< 0.45%)
- Unknown (3077 particles)
  - 14 particles fall within another ellipse (< 0.50%)
- Labradorite (2872 particles)
  - 35 particles fall within another ellipse (1.2%)
- Anorthite (3599 particles)
  - 0 particles fall within another ellipse

- Albite (2069 particles)
  - 0 particles fall within another ellipse
- Unknown (2040 particles)
  - 0 particles fall within another ellipse
- Labradorite (1850 particles)
  - 3 particles fall within another ellipse (< 0.2%)
- Anorthite (2211 particles)
  - 0 particles fall within another ellipse

Current Material Classification Method

- Rule File Editor
  - Contains a set of user-defined classifications as logical rules
    - Can use chemical and/or morphological properties for classifying material
    - Designed to work with normalized k-ratio values
  - Top-down method
    - Search through list from top to bottom
      - Each rule is evaluated until ALL criteria are met
      - No additional rules will be evaluated
    - Labeled as unclassified if it doesn't fit in any group



Conclusions

- Size, analysis time, raster type, morphology
  - Small effects relative to the overall scatter of the data
    - May lead to a small percentage of mineral misclassification
  - Makes rule file setup complex and time consuming
    - Updating of elemental ranges in specific rule files due to particle effects, not necessarily new materials
- Sample Prep - Overlapping/touching particles
  - Can never fully solve this problem
    - Reverse sieving technique helps to alleviate it
- Other complementary techniques will still be needed for soil/mineral classification
  - Polarized Light Microscopy, X-Ray Diffraction, Raman

Future Research Plans

- Analyze additional mineral standards
  - Further develop rule classifications
- Continue to improve sample preparations techniques
  - Reverse sieving
  - Vacuum impaction
- Start analyzing mixtures of materials
  - Mixed mineral standards
    - Test for reproducibility and reliability

Future Research Plans

- Investigate other material classification techniques
  - Is the Rule File method the best way to classify data
    - Clustering techniques (diluvian, density, hierarchical)
      - Still need to provide useful names to these clusters
    - Distance function (delta value determination) to previously determined mineral groups
- Test usefulness in other industries

Acknowledgements

- Dr. Kris Ingeneri
- Dr. John Hoff
- Dr. Kent Rhodes
- Richard Bisbing
- Carol Injerd