SEM Imaging Clinker and Cement

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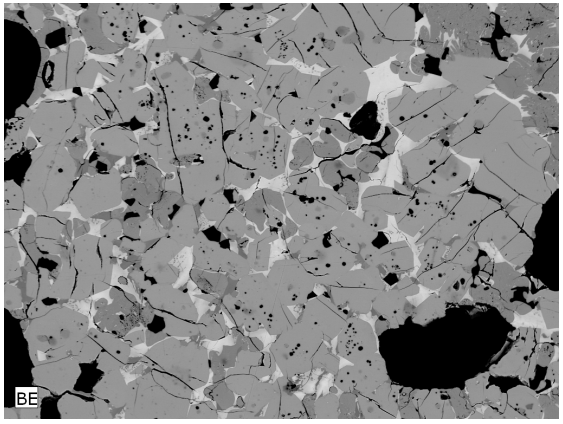
Sample Preparation

- Provides a clear definition of microstructure features without altering the sample with preparation-induced artifacts
  - simplifies identification of constituents
  - facilitates description of features
  - eases interpretation

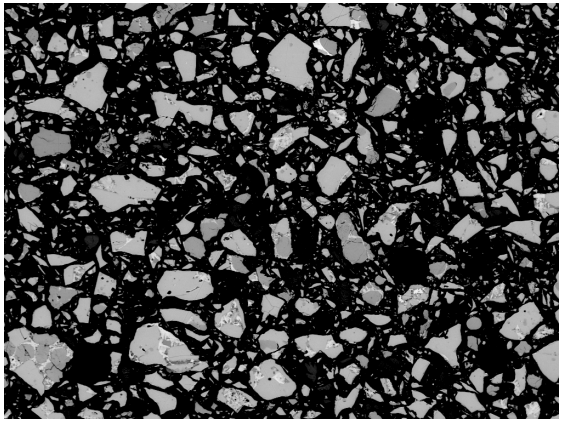
The preparation processes are essentially the same for different materials – clinker, cement, fly ash, slag, cement paste, concrete: grinding using progressively finer grits then polishing with diamond pastes to remove the surface damage from the previous step

Time spent preparing the sample properly is more than regained in the ease of description and interpretation of features !

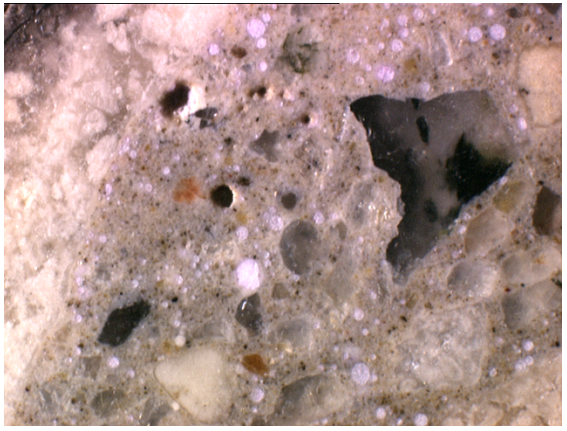
Cement Clinker



Cement (ground clinker)



Hardened Concrete



Ideal surface – flat with well-defined phases, chip, and scratch-free

Polished Sections:
Potting, Cutting, Grinding, and Polishing

Polished specimens are typically potted in an epoxy or resin, serving multiple purposes

- Fills voids to support microstructure
- Appears dark in SEM imaging (or could be stained for thin sections)
- Provides a specimen that is easily handled for the cutting and polishing

•Cutting and Grinding expose a fresh surface, diamond blade slab or wafering saws are suitable. Cutting fluids may include alcohols (ethanol, isopropyl) or propylene glycol

•Abrasives of 220, 400, 600, and 1200 silicon carbide removes damage produced by the previous grit. After the 1200 grit grind, the surface is smooth enough for polishing with the diamond pastes. (start with the finest grit possible to cut a planer surface)

•Polishing removes the damage imparted by the sawing and grinding operations through use of a sequence of successively finer particle size diamond polishing pastes ranging from 6 μm to 0.25 μm, and a lap wheel covered with a low-relief polishing cloth.

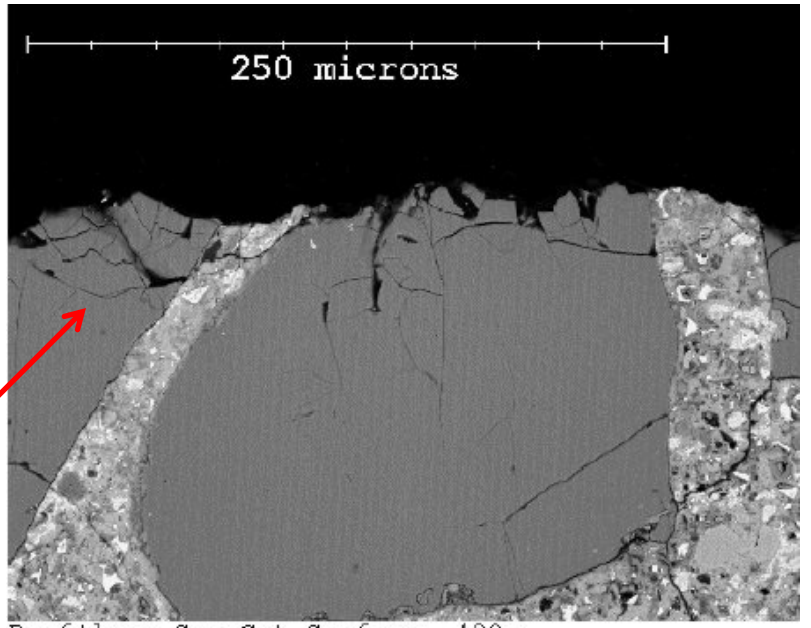
•The goal is to prepare a smooth, scratch-free, low-relief surface of particles surrounded and permeated by epoxy, presenting the ideal surface for SEM imaging and X-ray microanalysis

Cut and lapped surfaces are not suitable for SEM imaging because of the substantial surface damage.

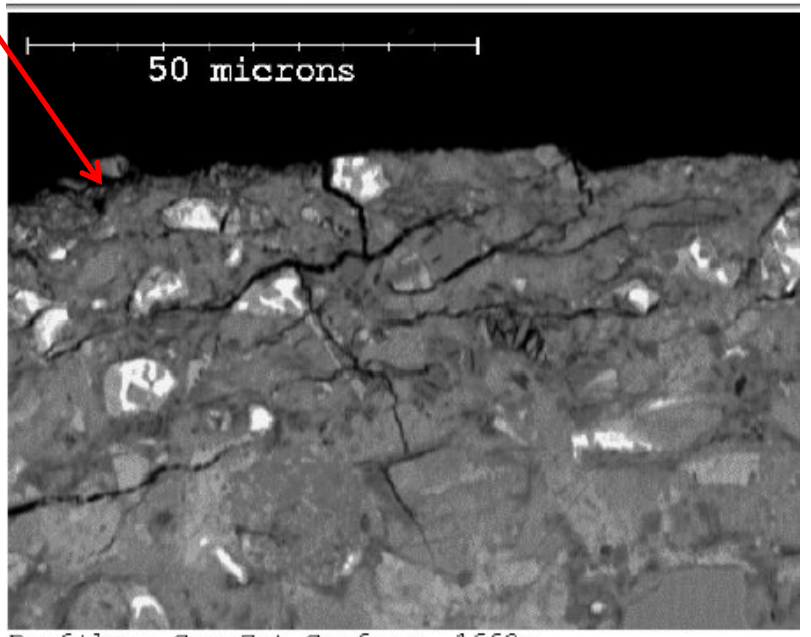
In the example, a cross-section of a saw-cut preparation (now epoxy impregnated and polished) shows the depth of damage from a small lab diamond blade saw (≈50 µm).

Damage of the sample is due to cutting and subsequent drying shrinkage-related cracking of the paste.

Epoxy embedding will stabilize the specimen while polishing will remove the surface damage that prevents viewing clean, unaltered microstructure (unaltered at the microscope resolution, that is)

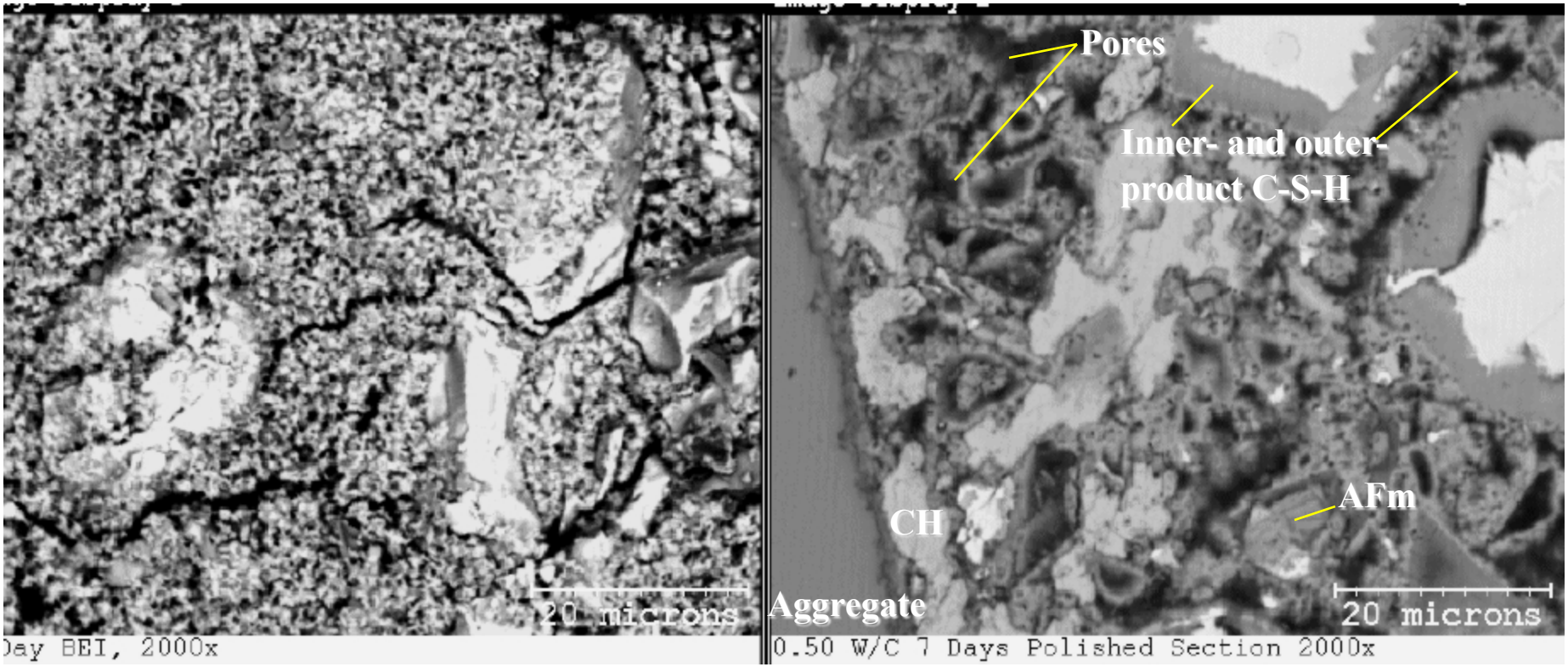


Profile - Saw Cut Surface, 400x



Profile - Saw Cut Surface, 1660x

0.50 W/C, 7-day Old Cement Paste: Saw-cut vs. epoxy & polish preparation



Map-view images of samples taken from the same core clearly illustrate the improved feature definition with the epoxy-impregnated, polished sections

Materials

Item	Purpose
Diamond blade slab saw	large-sized sample slabbing
Diamond blade wafering saw	cutting of thin (mm-sized) sections
Propylene glycol	diamond saw cutting lubricant
Alcohol: 200 proof ethanol	cutting lubricant, cleaning aid
Ultrasonic bath or probe	specimen cleaning
Specimen jars and lids	for replacement steps
Potting epoxies (medium and low viscosity)	for powders and hardened pastes
Dye, blue or red, alcohol miscible	to estimate alcohol replacement depth
Refrigerator	epoxy storage
Vacuum chamber and pump	vacuum impregnation
Drying / curing oven	capable of at least 65 °C
Glass plate (400 x 400 mm)	smooth surface for grinding
Lapidary wheel	grinding and polishing
Mold cups	potting specimens
Aluminum foil (heavy duty)	for forming odd-sized specimen molds
Mold release	facilitates removal of specimen / epoxy
Diamond pen	label engraving
Abrasive papers (silicon carbide)	coarse to fine grinding, 100 to 600 grit
Polishing cloths (low-relief)	for 6 μm and finer polishing
Diamond paste for polishing	6, 3, 1, 0.25 μm in non-aqueous suspension
Lint-free cloths	specimen handling and cleaning
Compressed air	specimen cleaning and drying
Vacuum dessiccators	specimen storage

Epoxies / Embedding Media

Epotek 353 ND*
Higher-viscosity (like honey)
2-component
high-temperature epoxy
Beam-stable for SEM
Works well for powders

Physical Properties:	
*Color: Part A: Clear (Gardner <5) Part B: Amber (Gardner <18)	Weight Loss:
*Consistency: Pourable liquid	@ 200°C: 0.22%
*Viscosity (@ 50 RPM/23°C): 3,000 – 5,000 cPs	@ 250°C: 0.39%
Thixotropic Index: N/A	@ 300°C: 0.87%
*Glass Transition Temp.(Tg): ≥ 90°C (Dynamic Cure 20—200°C /ISO 25 Min; Ramp -10—200°C @ 20°C/Min)	Operating Temp:
	Continuous: - 55°C to 250°C
Coefficient of Thermal Expansion (CTE):	Intermittent: - 55°C to 350°C
Below Tg: 54 x 10^{-6} in/in/°C	Storage Modulus @ 23°C: 516,912 psi
Above Tg: 206 x 10^{-6} in/in/°C	Ions: Cl^- 329 ppm
Shore D Hardness: 85	Na^+
Lap Shear Strength @ 23°C: > 2,000 psi	NH_4^+ 409 ppm
Die Shear Strength @ 23°C: ≥ 15 Kg / 5,100 psi	K^+ 5 ppm
Degradation Temp. (TGA): 412°C	Particle Size: N/A
Optical Properties @ 23°C:	
Refractive Index @ 23°C (uncured): 1.5694 @ 589 nm	Spectral Transmission: > 50% @ 550 nm; > 98% @ 800-1000 nm > 95% @ 1100 - 1600 nm
Electrical & Thermal Properties:	
Thermal Conductivity: N/A	Volume Resistivity @ 23°C: ≥ 1.8 x 10^{13} Ohm-cm
Dielectric Constant @ 23°C (1 KHz): 3.17	Dissipation Factor @ 23°C (1 KHz): 0.005

***Certain commercial equipment or materials are identified to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.**

Epoxies / Embedding Media

L.R. White Resin*
Ultra Low-viscosity (like water)
Retains low viscosity when refrigerated
Single component, low toxicity
Cure with accelerator or at 60 °C
Beam-stable for SEM
Works well for cement paste and concrete

Used in the biological community and is available from most microscopy suppliers. I use the hard grade as it polishes better.

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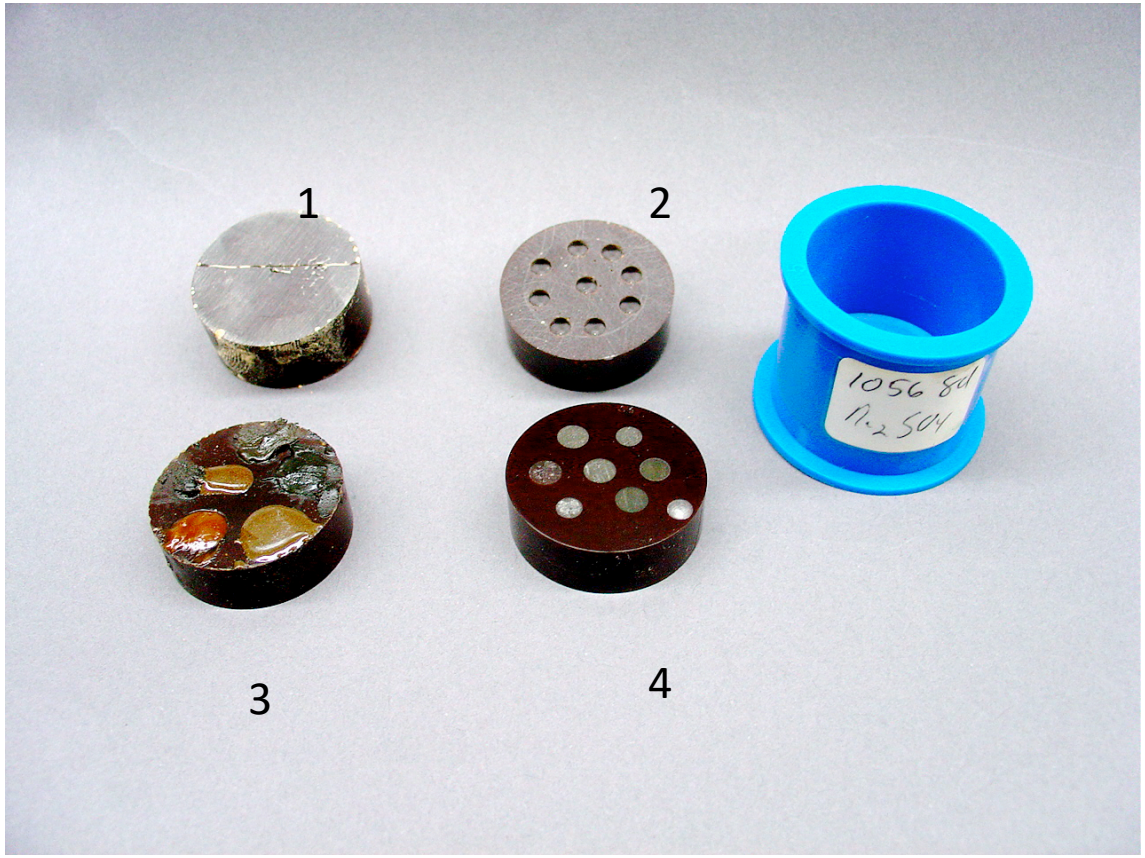
Potting Powders



1) Cast Blanks

- cure overnight

2) Drill holes

3) Mix Powders to a modeling clay consistency for cements and slightly runny for fly ash and slag*

- Cure

4) Grind and Polish

5) Carbon-coat for SEM**

* Take a few drops of epoxy, blend in cement until it forms a thick paste. If it cracks and breaks on mixing, it is too dry.

** Carbon works best for SEM backscattered and X-ray imaging as it does not adversely affect signal intensity and contrast and will not interfere with X-ray signals of interest (for example, another popular specimen coating, Au characteristic X-rays overlaps those from S)

Grinding
- do as little as possible !

Dry grind to reduce the possibility of softening the resin (L.R. White primarily), resulting in particle plucking.

Clean with a cloth or compressed air under a fume hood

Polishing - 1200 grit and 6 um polish are critical in removing cutting and grinding damage!

The specimen is polished on the outer portion, and then cleaned of polishing residue in the center of the cloth. There are many different types of polishing cloths and plates, I use these cotton SEM cleaning cloths, which are used once and then discarded.

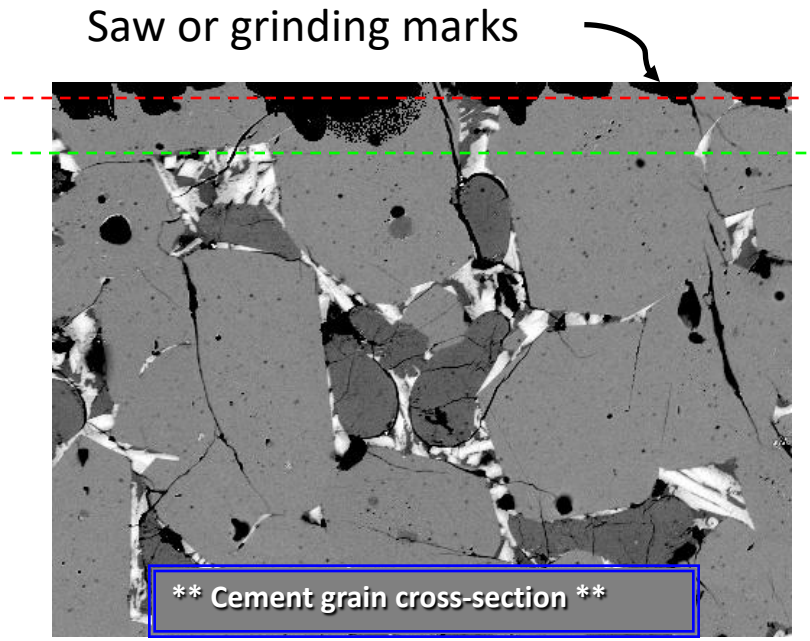
Grinding & Polishing

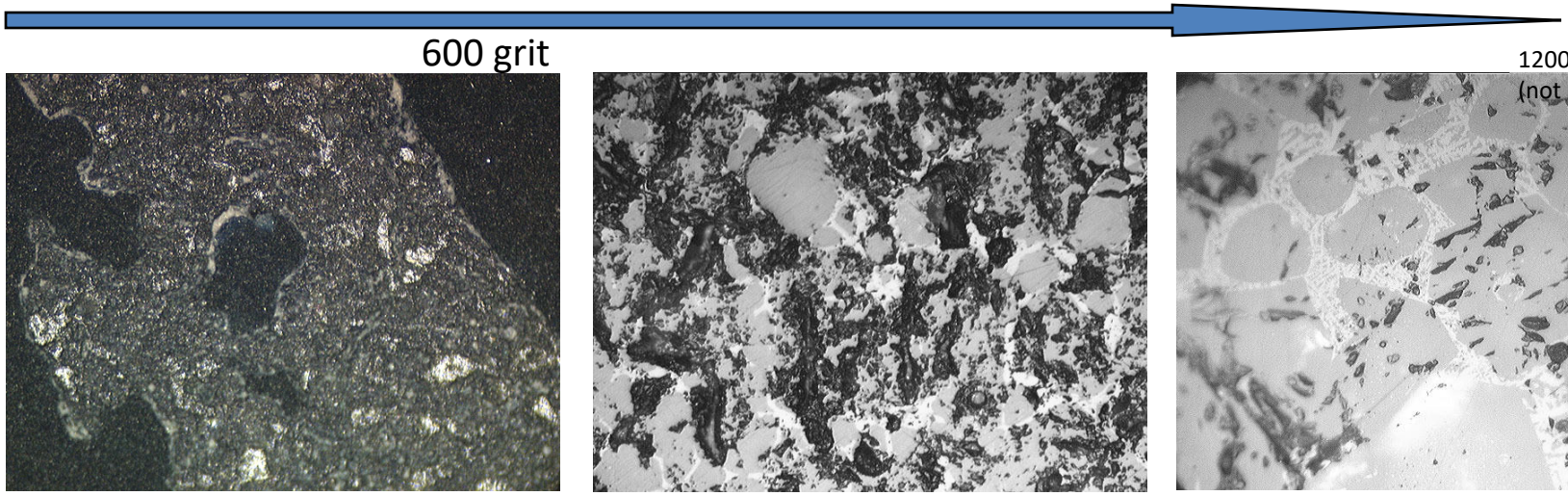
Polishing removes the damage imparted by the sawing and grinding operations.

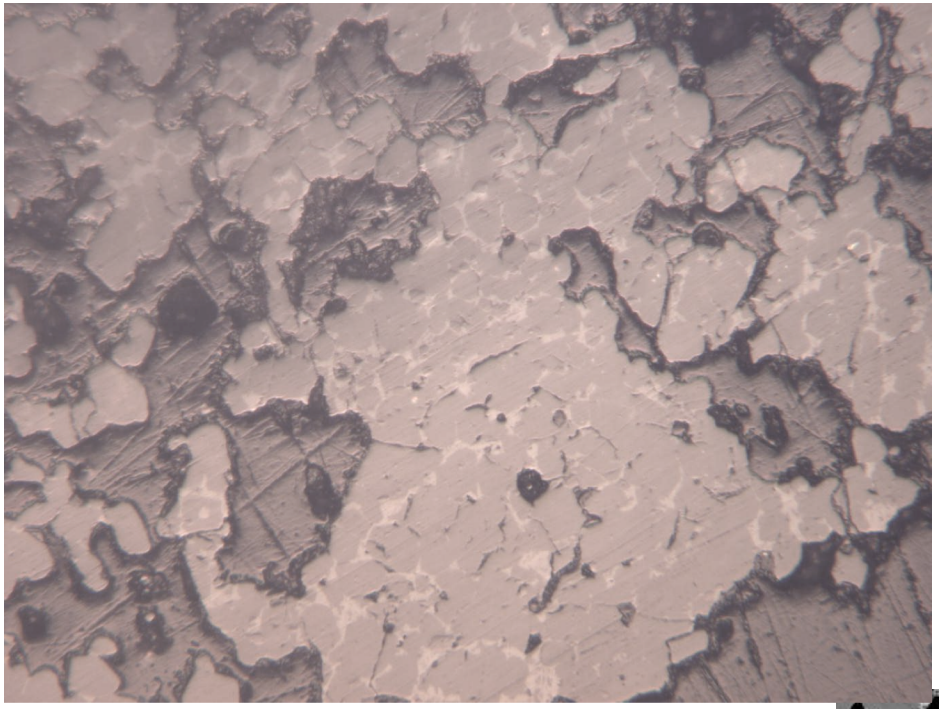
This stage involves use of a sequence of successively finer particle size diamond polishing pastes ranging from 6 μm to 0.25 μm, and a lap wheel covered with a low-relief polishing cloth.

Polish times are about 3 minutes per step using relatively high pressure. Longer polishing times seem to create rounded edges and grain relief.

This may be performed manually or, for greater sample throughput, using a semi-automated polisher.





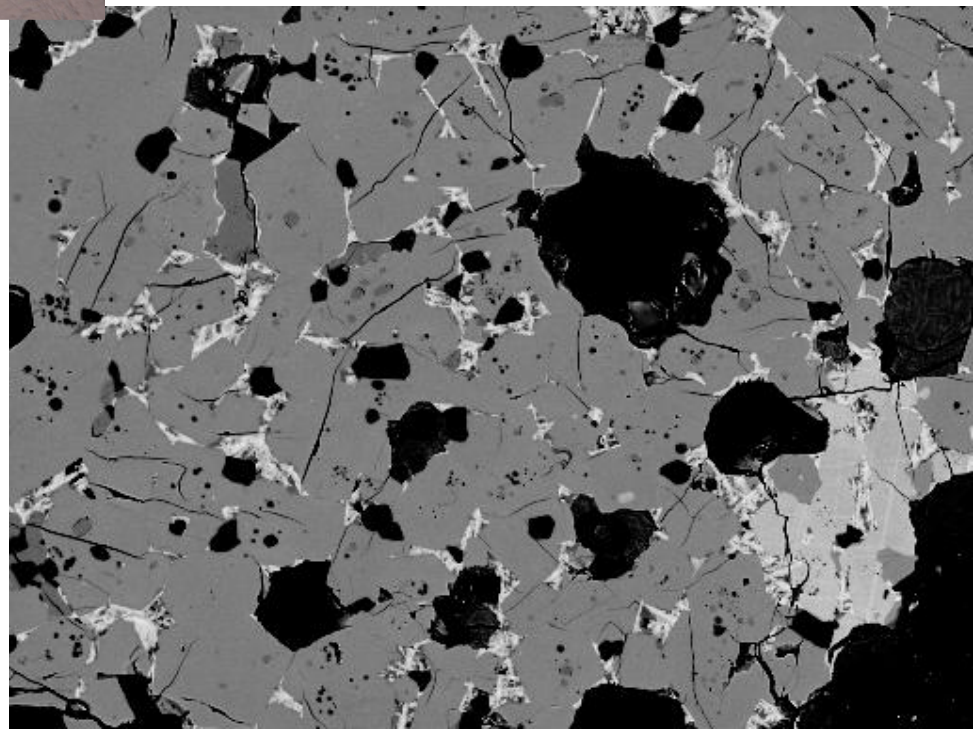


Final Polish Criteria

- Few scratches (on specimen)
- Sharp corners
- Well-defined phases
- Minimal phase surface relief
- No etching
- Filled voids
- No polishing media residue

Over-polishing or using polishing cloths designed to impart grain boundary relief can lead to rounded edges,

This will adversely affect the BE and X-ray imaging and, subsequently, the image processing and analysis

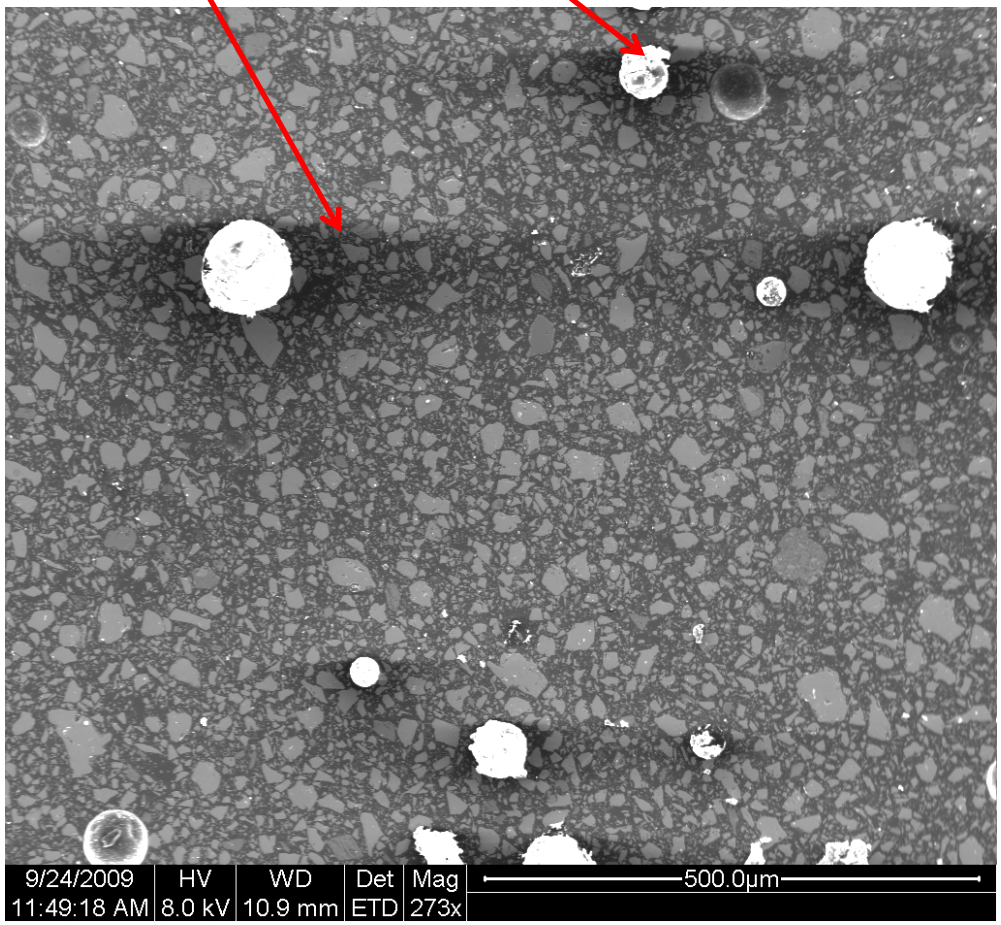


A Clean Surface is Necessary

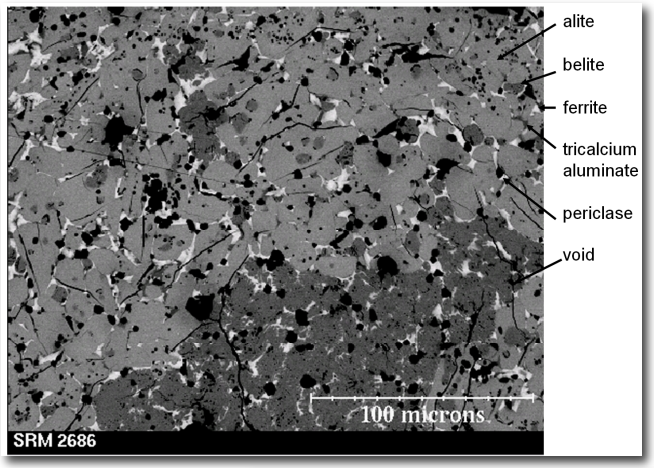
- Try to minimize entrapped air voids (they trap powder that will charge)
- Sonication using isopropyl may be useful
- Wiping the polished surface on a fresh polishing cloth saturated with isopropyl will remove stubborn polishing residue
- Compressed gas to evaporate alcohol and remove surface dust
- Acetone final rinse for a few seconds seems to leave a cleaner surface that is better able to hold the carbon coating

Charging is not always evident in BE imaging but can be seen in SE imaging.

Charging artifacts – bright ungrounded particles and dark surfaces that have repelled the electron beam

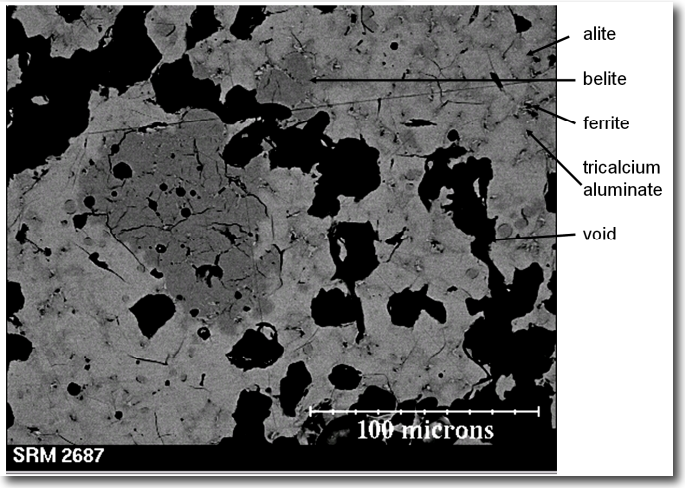


SEM Imaging



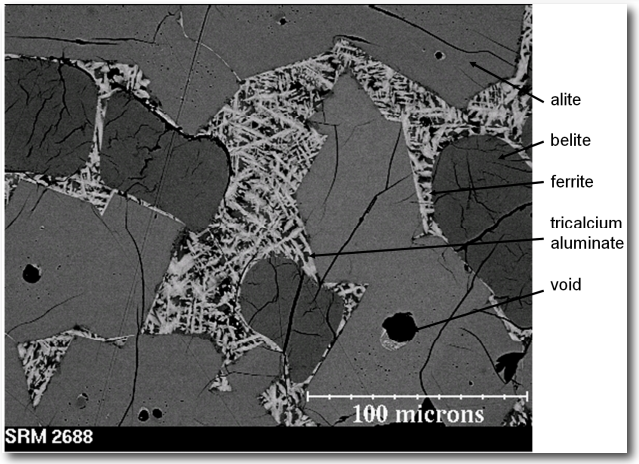
Polished sections using backscattered electron and X-ray imaging provide an image set like that of the early-day reflected light microscopy, with the advantage of being able to perform qualitative and quantitative chemical measurement and produce an image set amenable to image processing and analysis

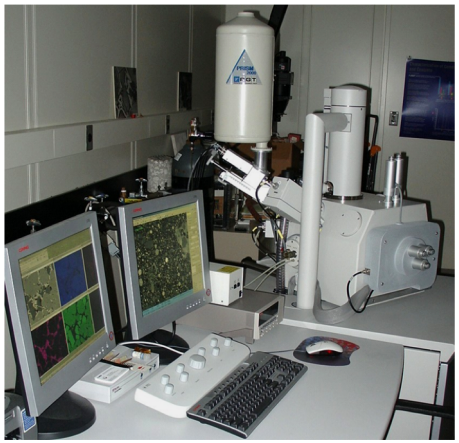
Backscattered electrons (BE) are sensitive to phase chemistry, referred to as the compositional image, with brightness proportional to average atomic number



The backscattered electron coefficient, η, provides an estimate of relative brightness and is useful along with phase occurrence within the microstructure, shape and chemistry for identification.

< The three NIST SRM clinkers are from Type I cements, yet exhibit substantial differences in texture and composition

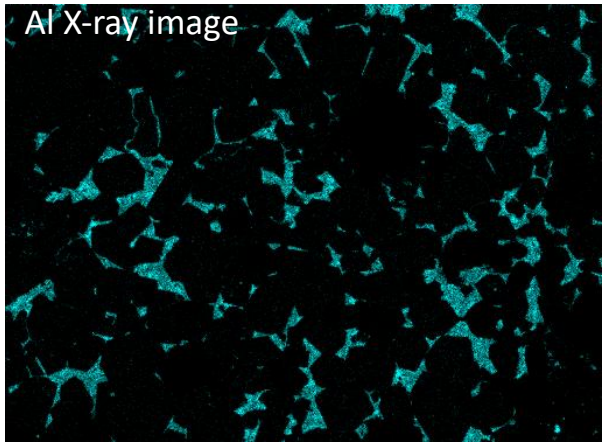


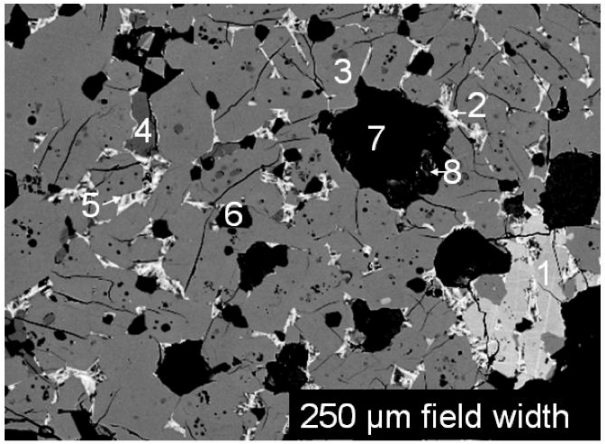


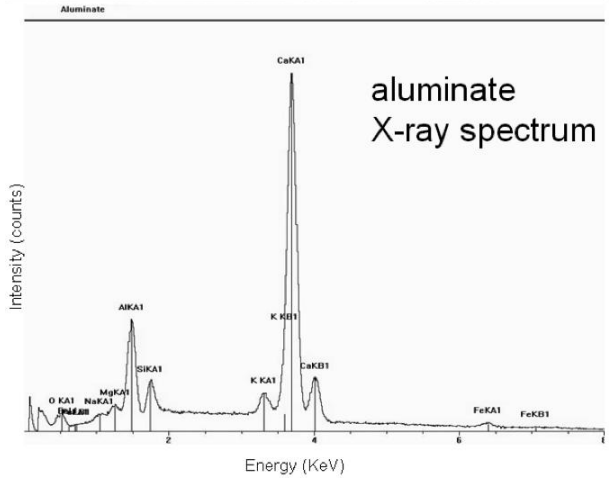
Phase	*Composition*	*Notation*	*Density* (Mg/m^3)	$\overline{Z}$	η
Ferrite	$Ca_2(Al,Fe)_2O_5$	C4AF	3.77	16.65	0.1860
free lime	CaO	C	3.32	16.58	0.1882
alite	Ca_3SiO_5	C3S	3.13 to 3.22	15.06	0.1716
belite	Ca_2SiO_4	C2S	3.28 to 3.31	14.56	0.1662
arcanite	K_2SO_4	$K\overline{S}$	2.67	14.41	0.1652
aluminate-cub.	$Ca_3Al_2O_6$	C3A	3.04	14.34	0.1639
aluminate-ort.	$NaCaAl_3O_9$	C3A	2.56	13.87	0.1588
aphthitalite	$(Na,K)_2SO_4$	$KN\overline{S}$	2.7	13.69	0.1577
syngenite	$K_2Ca(SO_4)_2H_2O$	$CK\overline{S}2H$	2.6	13.60	0.1556
anhydrite	$CaSO_4$	$C\overline{S}$	2.98	13.41	0.1535
bassanite	$2CaSO_4\square H_2O$	$C\overline{S}H$	2.7	13.03	0.1489
gypsum	$Ca(SO_4)\square 2H_2O$	$2C\overline{S}H$	2.32	12.12	0.1381
thenardite	Na_2SO_4	$N\overline{S}$	2.66	10.77	0.1249
periclase	MgO	M	3.58	10.41	0.1213

SEM Imaging: X-Ray Microanalysis

- X-rays are generated as a result of the interaction between the high-energy electron beam and the specimen.
- The X-ray spectrum consists of the characteristic lines for each element present, represented by peaks on the spectrum, and a background of white radiation.
- X-ray microanalysis may be used to identify and quantify chemical composition of phases that can be used to generate images of element spatial distribution. The latter capability is particularly useful for image processing as it enables a set of element spatial distribution images to be included in the image processing.
- XR imaging is necessary for distinguishing between phases that have the same BE coefficient yet are compositionally distinct and for identification of phases that are not easily detected in the BE image; periclase and some alkali sulfates will appear dark, like voids.
- Combining the XR and BE images allows a degree of phase discrimination that is not available from any single image.

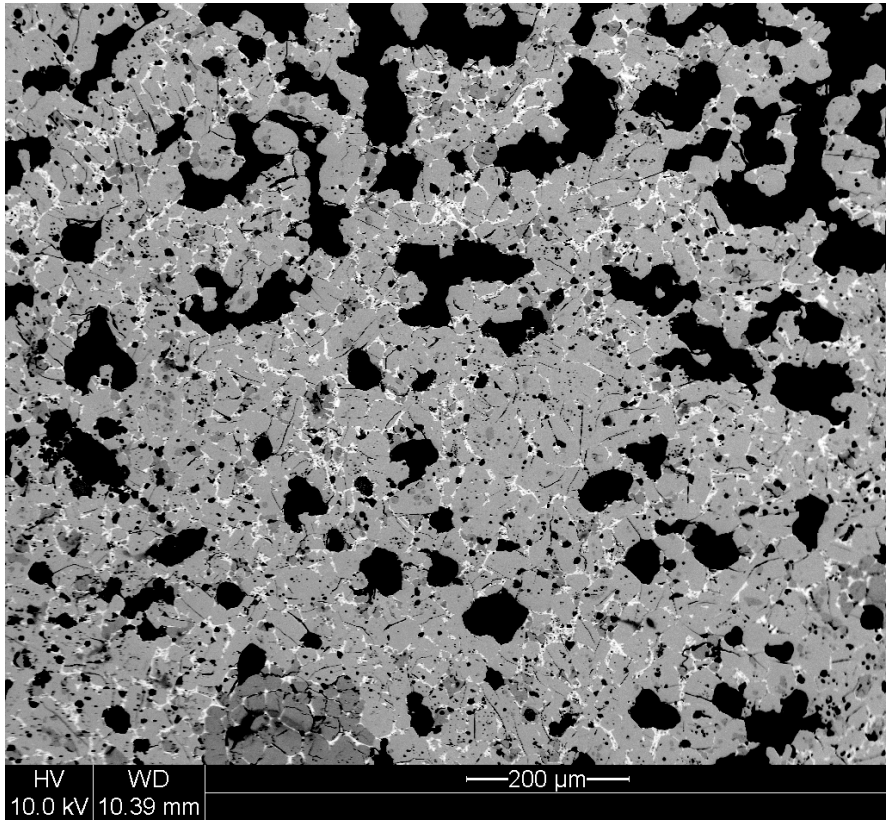


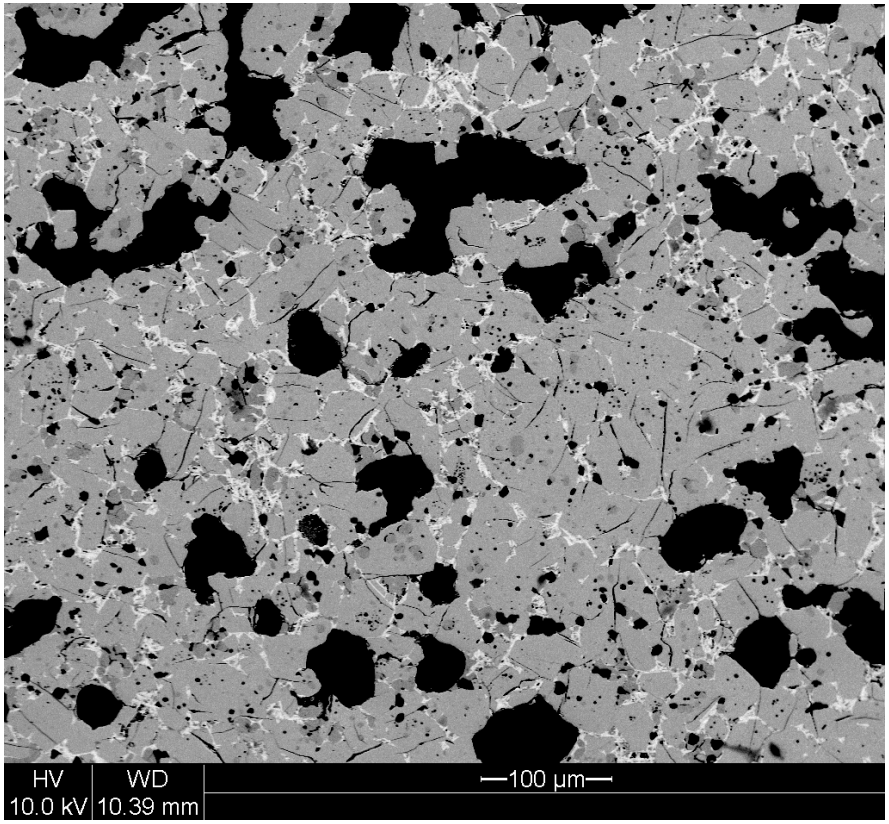




SRM2686a

Phase	$\overline{Z}$	η
ferrite	16.65	0.186
free lime	16.58	0.188
alite	15.06	0.172
belite	14.56	0.166
arcanite	14.41	0.165
aluminate-cubic	14.34	0.164
aluminate-orth.	13.87	0.159
aphthitalite	13.69	0.159
anhydrite	13.42	0.154
bassanite	13.03	0.149
gypsum	12.12	0.138
thenardite	10.77	0.125
periclase	10.41	0.121





SRM 2686a at low magnifications illustrates distribution of phases and porosity. Abundant alite, clustering of belite, a differentiated matrix comprised mostly of ferrite and some fine-grained aluminate, and uniform distribution of periclase is typical for this clinker.

SRM2686a

Phase	$\overline{Z}$	η
ferrite	16.65	0.186
free lime	16.58	0.188
alite	15.06	0.172
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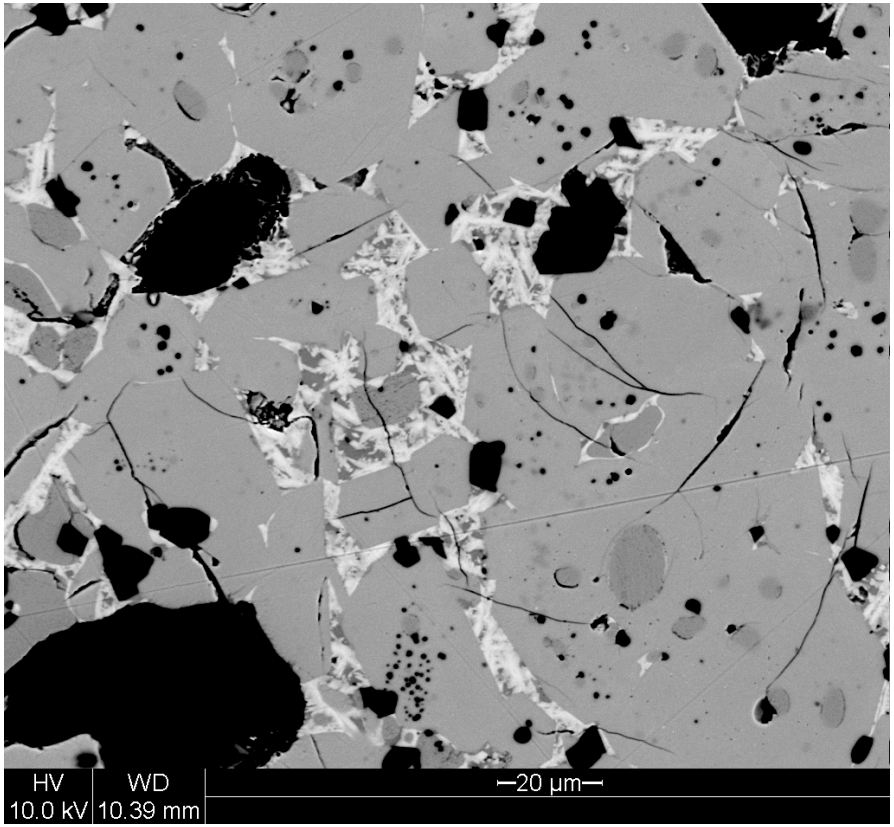

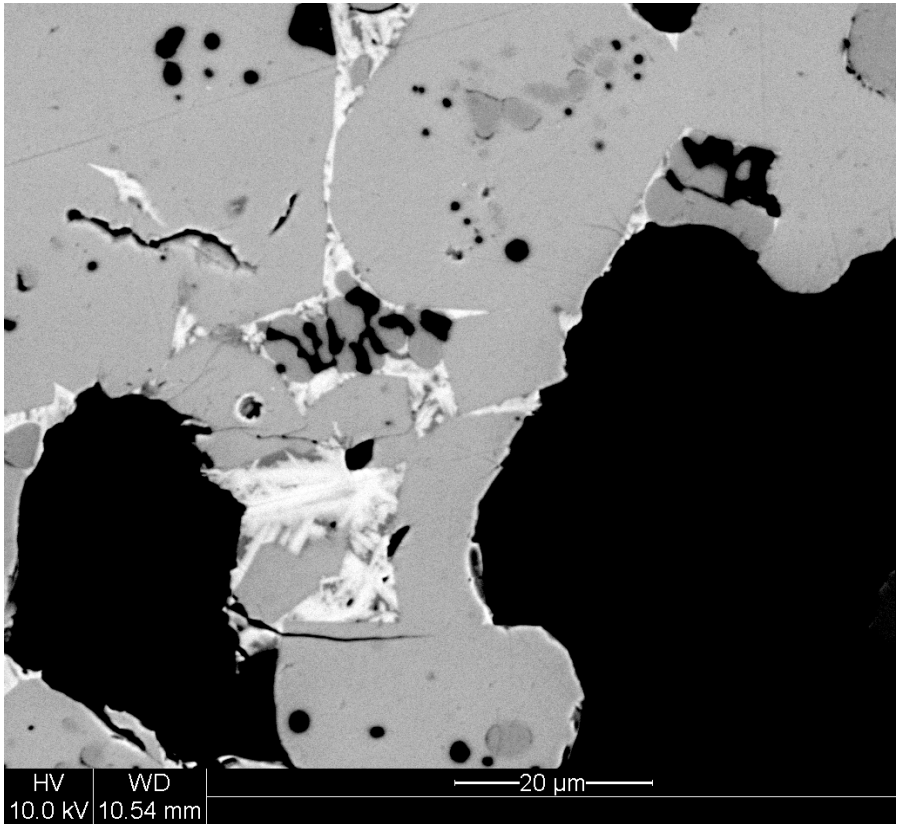

SRM 2686a at higher magnification with belite inclusions in alite crystals, a differentiated matrix dominated by the ferrite phase, and both equant and dendritic (right image) periclase.

SRM2687

Phase	$\overline{Z}$	η
ferrite	16.65	0.186
free lime	16.58	0.188
alite	15.06	0.172
belite	14.56	0.166
arcanite	14.41	0.165
aluminate-cubic	14.34	0.164
aluminate-orth.	13.87	0.159
aphthitalite	13.69	0.159
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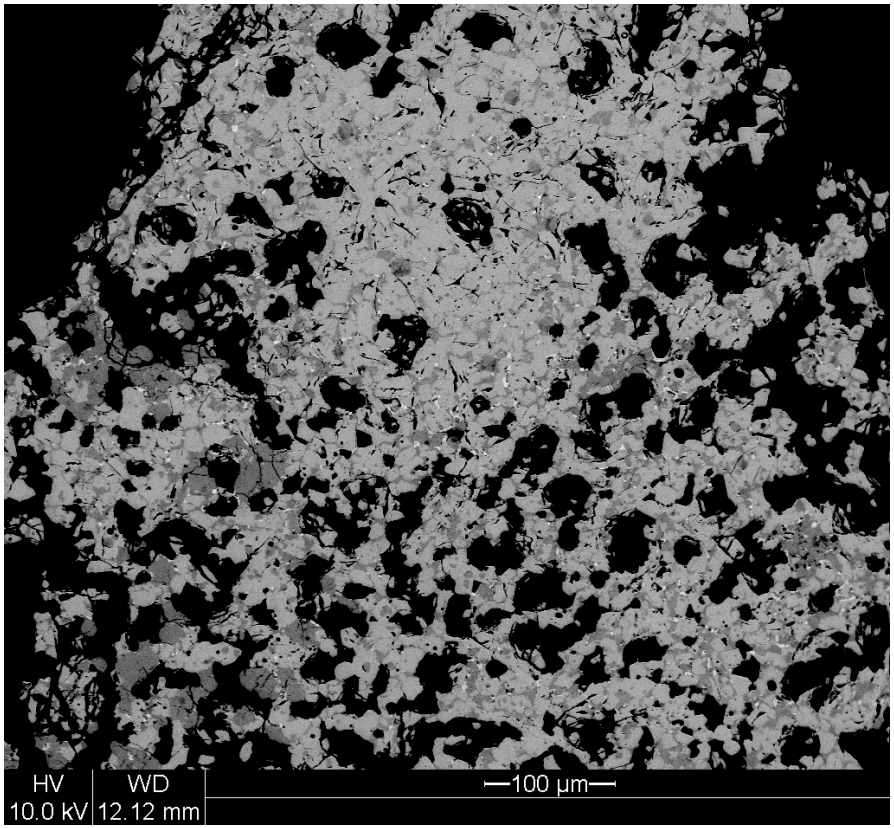

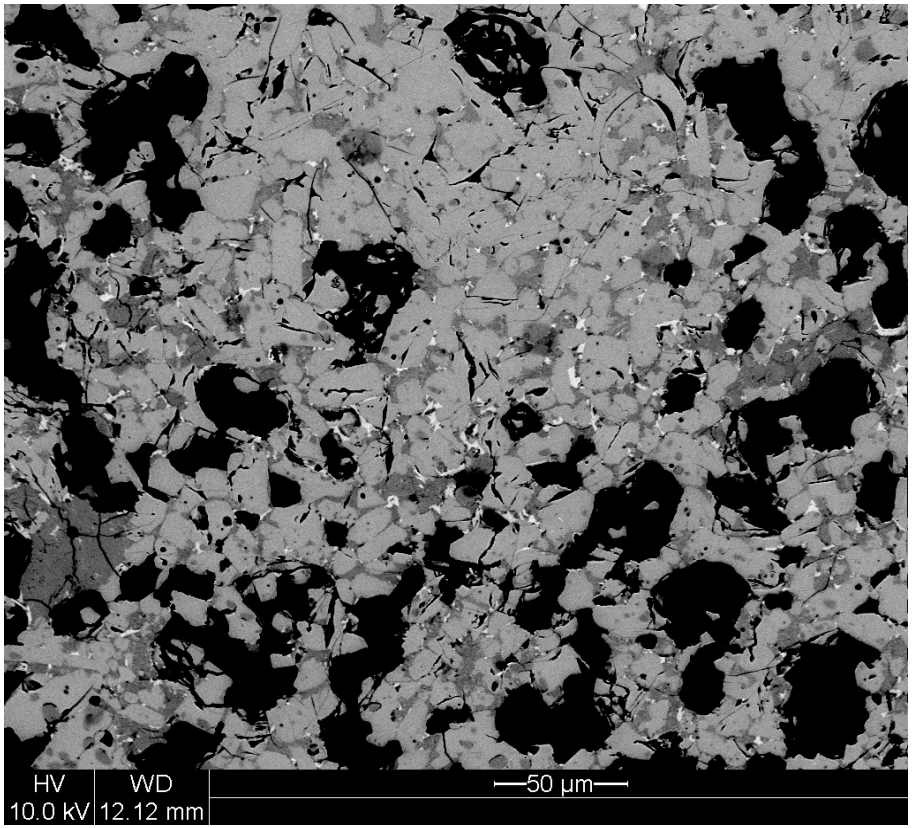

SRM 2687 is a fine-grained clinker with abundant alite, some small nests of belite, variable porosity, and abundant, undifferentiated matrix.

SRM2687

Phase	$\overline{Z}$	η
ferrite	16.65	0.186
free lime	16.58	0.188
alite	15.06	0.172
belite	14.56	0.166
arcanite	14.41	0.165
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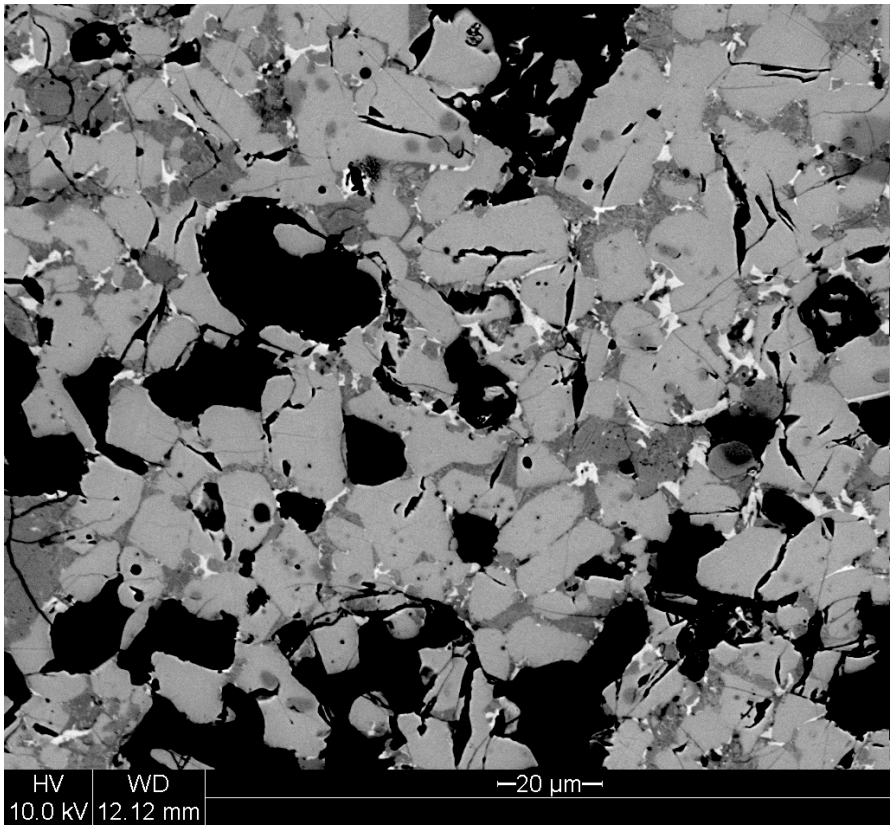

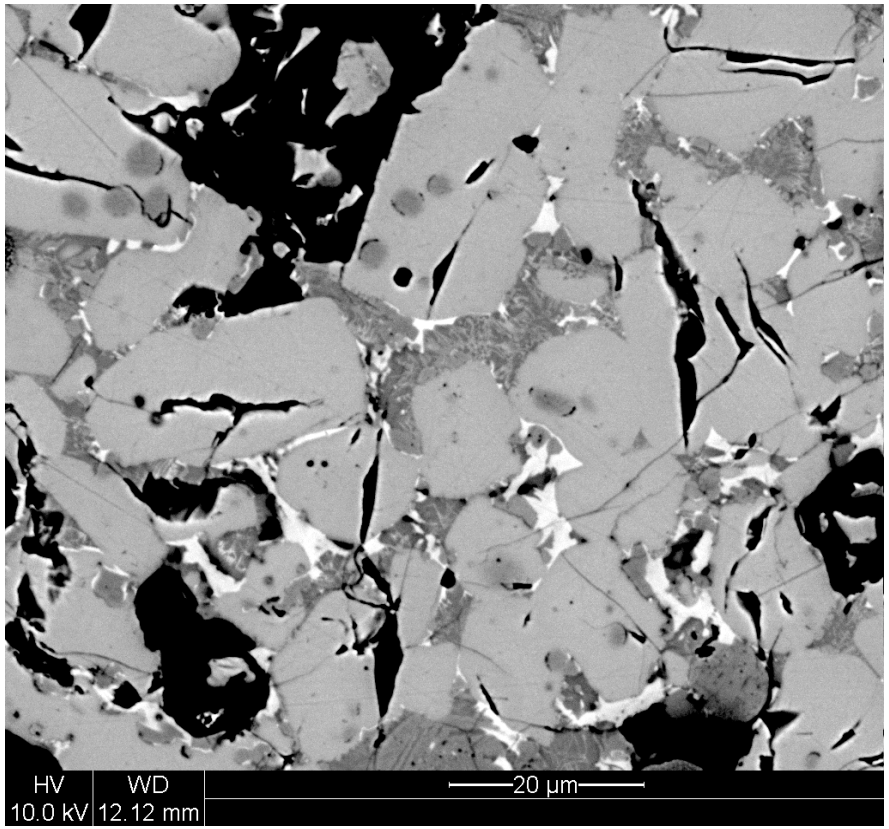

SRM 2687, higher magnification images begin to reveal details of the matrix, which consists of both a medium and fine-grained ferrite

SRM2688

Phase	$\overline{Z}$	η
ferrite	16.65	0.186
free lime	16.58	0.188
alite	15.06	0.172
belite	14.56	0.166
arcanite	14.41	0.165
aluminate-cubic	14.34	0.164
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aphthitalite	13.69	0.159
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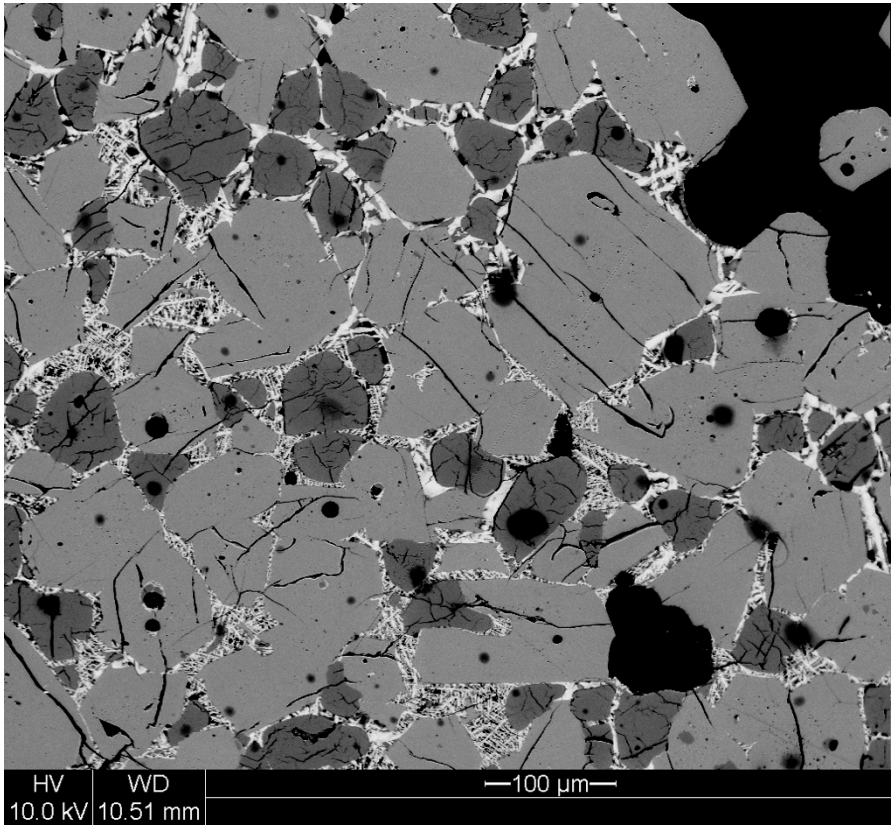
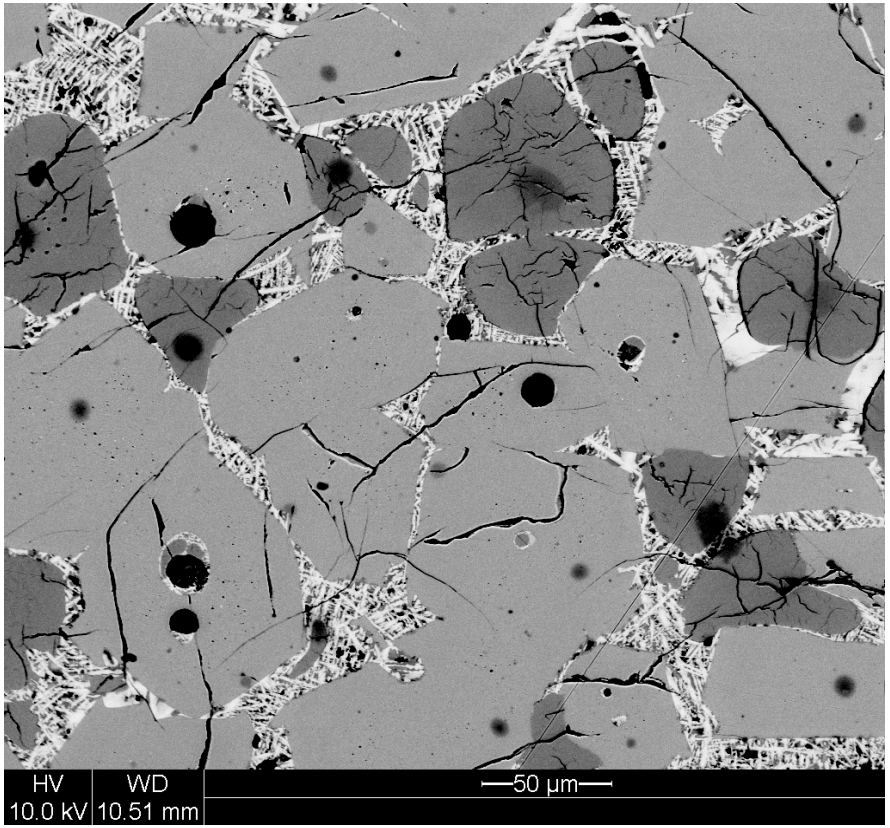
periclase	10.41	0.121

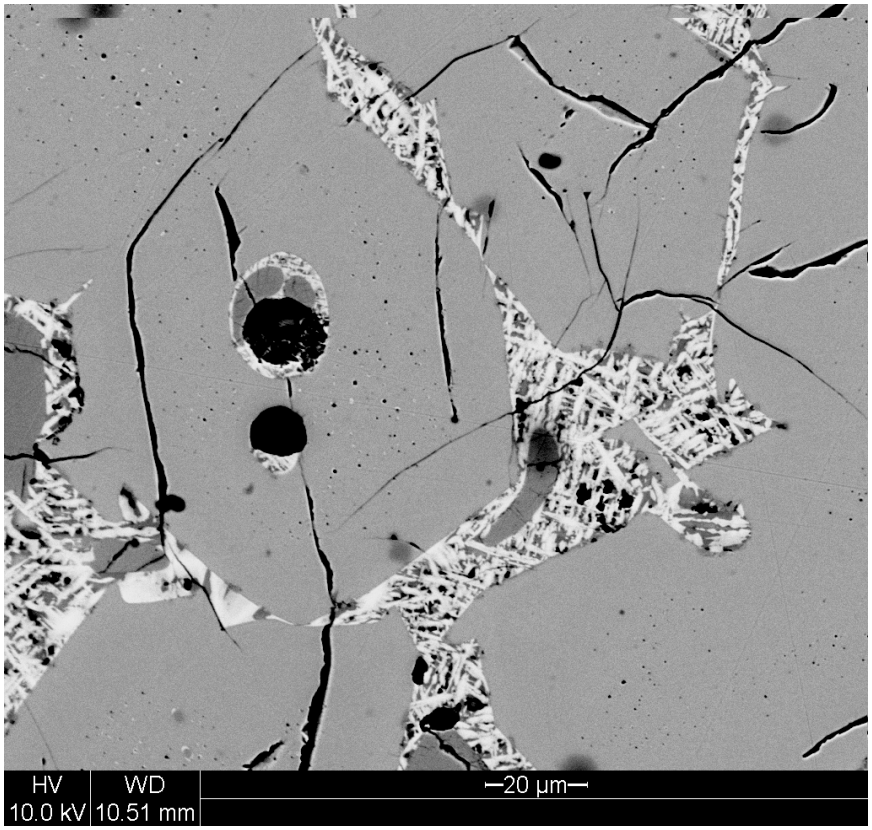


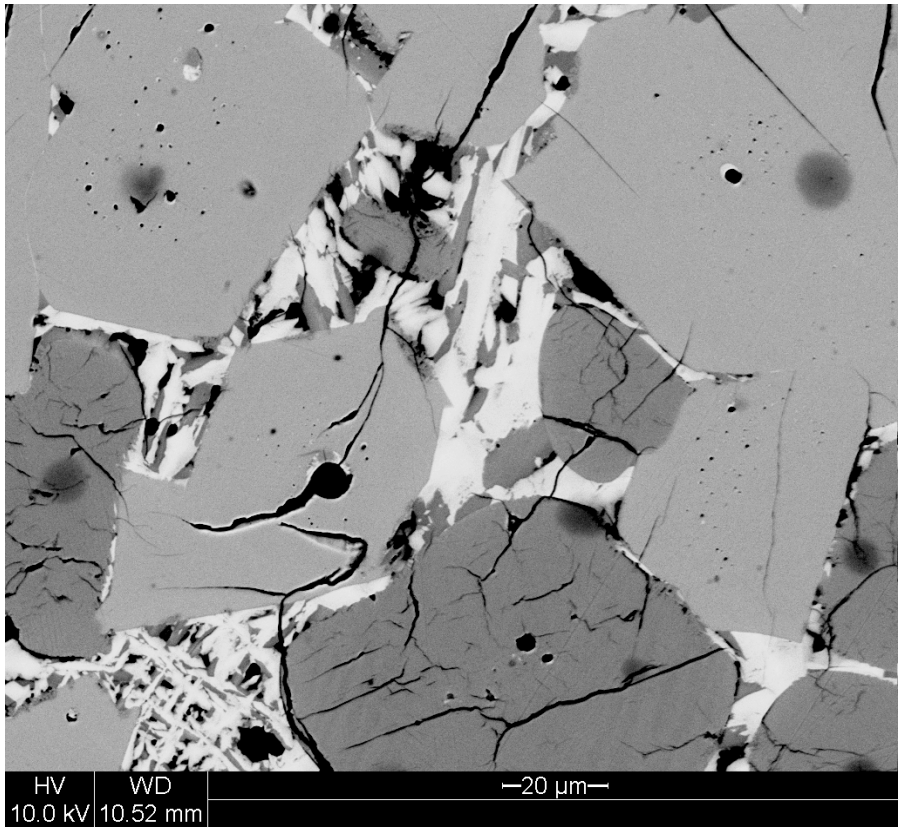


A coarse-grained clinker with uniform phase distribution, no free lime, a medium- to coarse-grained well differentiated matrix, and occasional presence of periclase and alkali sulfates within the matrix and along grain boundaries.

SRM2688

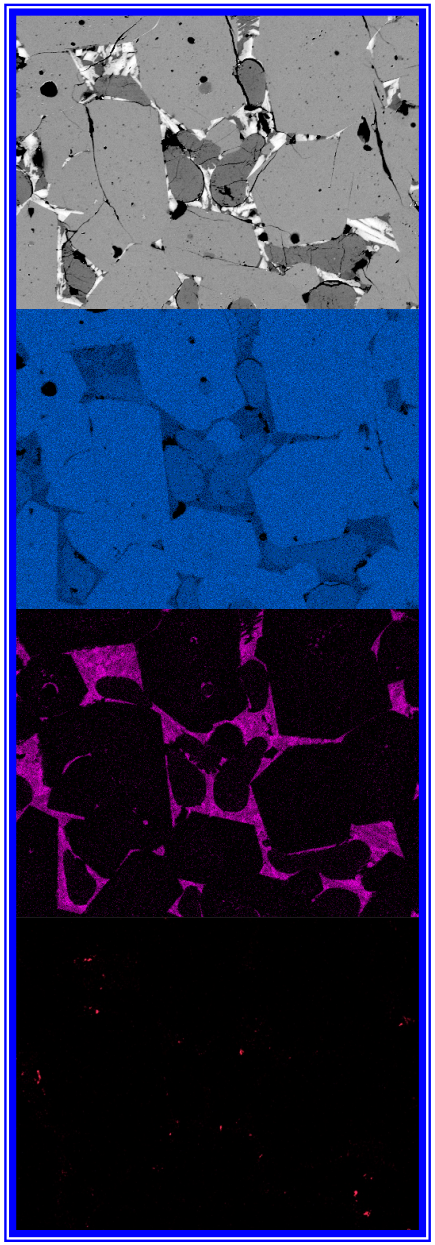
Phase	$\overline{Z}$	η
ferrite	16.65	0.186
free lime	16.58	0.188
alite	15.06	0.172
belite	14.56	0.166
arcanite	14.41	0.165
aluminate-cubic	14.34	0.164
aluminate-orth.	13.87	0.159
aphthitalite	13.69	0.159
anhydrite	13.42	0.154
bassanite	13.03	0.149
gypsum	12.12	0.138
thenardite	10.77	0.125
periclase	10.41	0.121



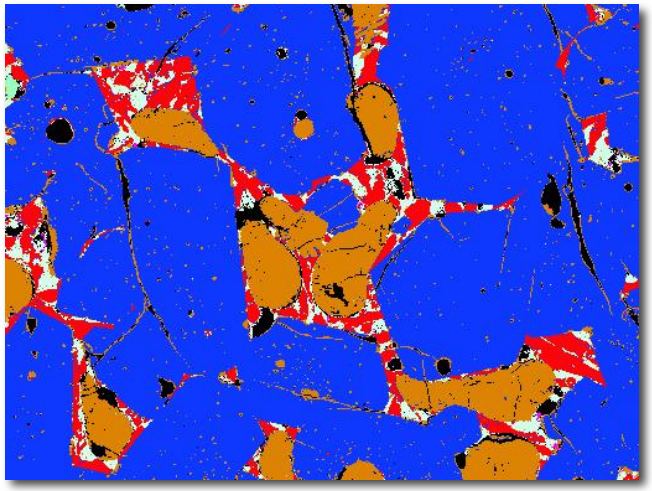


SRM 2688 at higher magnifications showing the belite and ferrite inclusions within alite, and a medium (left) and a coarse-grained (right), well-differentiated matrix.

Quantitative Microscopy Using Image Analysis

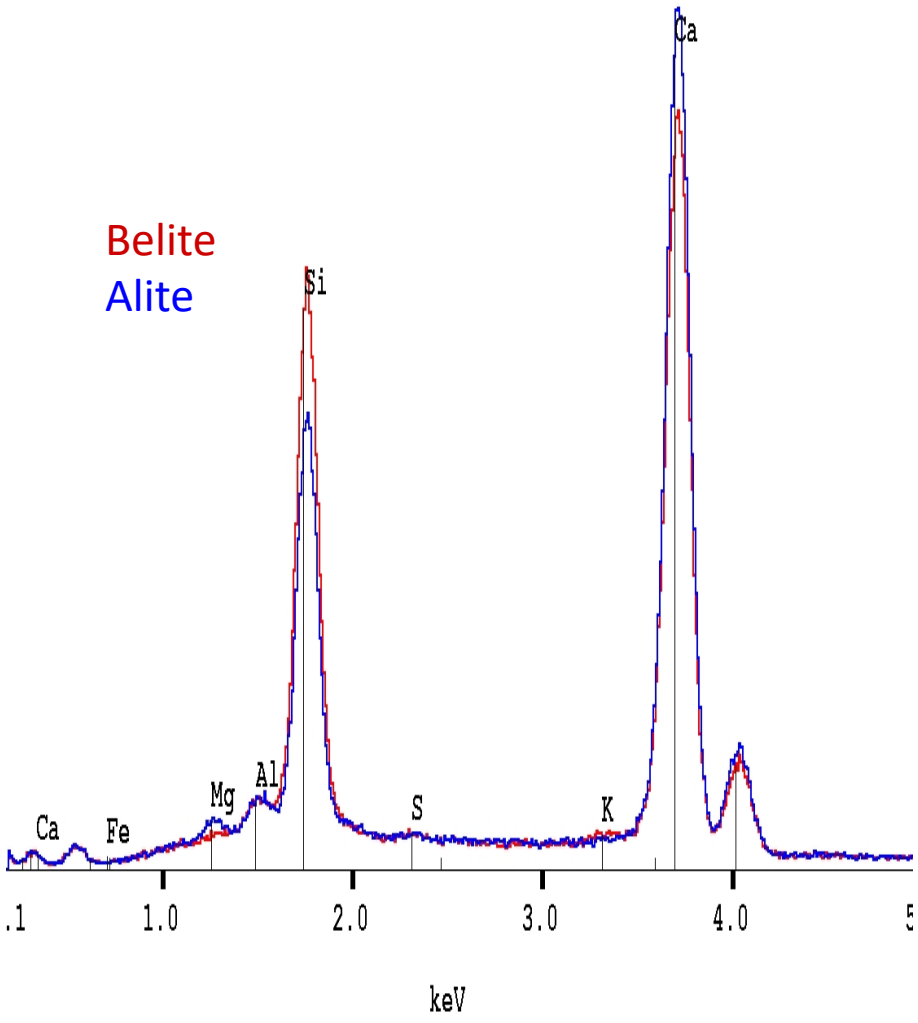


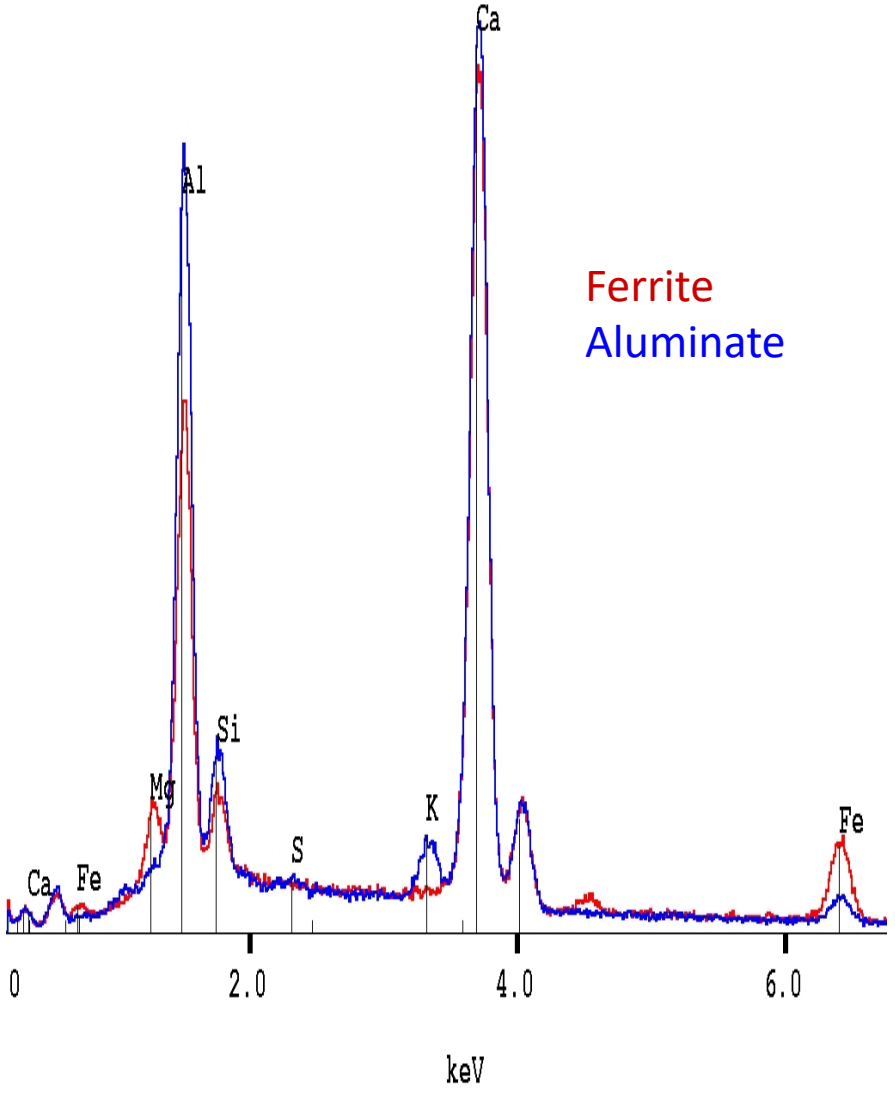
- We want to make the computer “see” and measure features of the material
- We assist through selection of a subset of the data that will provide phase identification
- Image Processing: Manipulating images (combining, subtracting, smoothing) to uniquely identify each phase
- Image Analysis: Quantify phase abundance and surface area



Index	Phase	Pixels	Area Fraction
1	Alite	142372	72.41
2	Belite	26800	13.63
3	Aluminate	7113	3.62
4	Ferrite	12977	6.60
5	Periclase	171	0.01
6	Arcanite	196	0.01
7	Void	6979	3.55

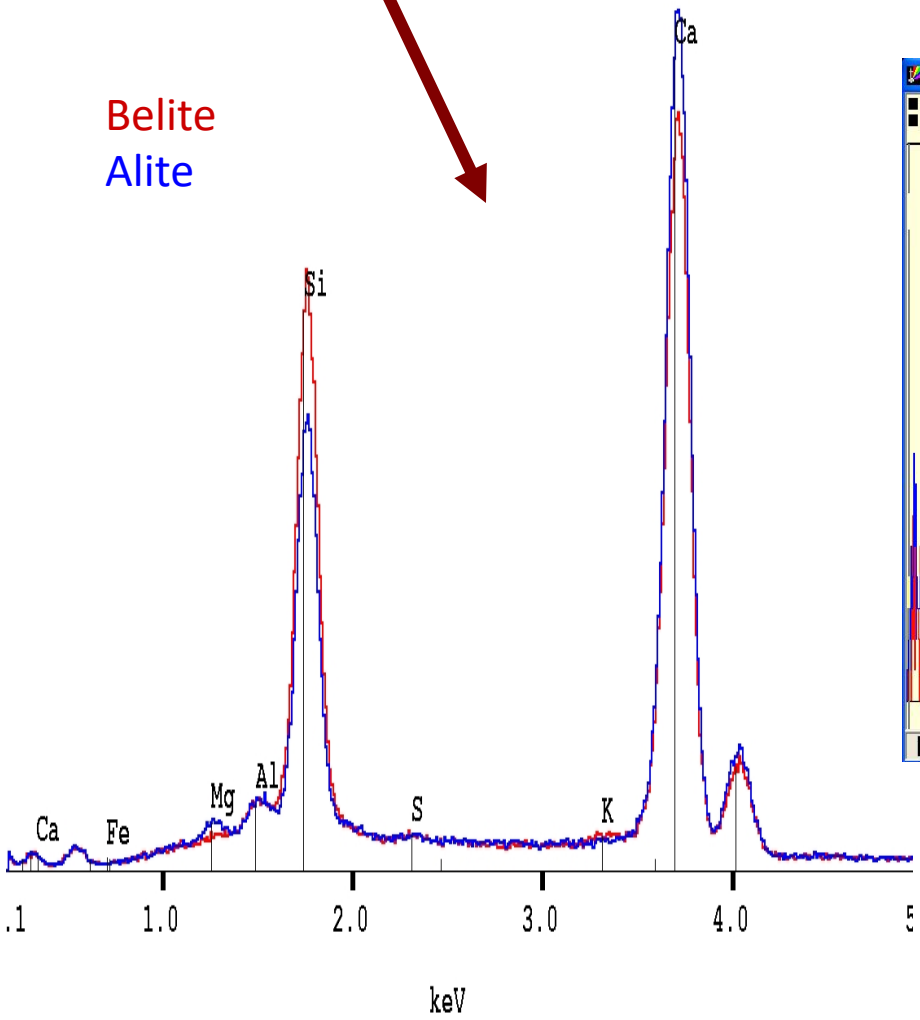
Spot EDS analysis



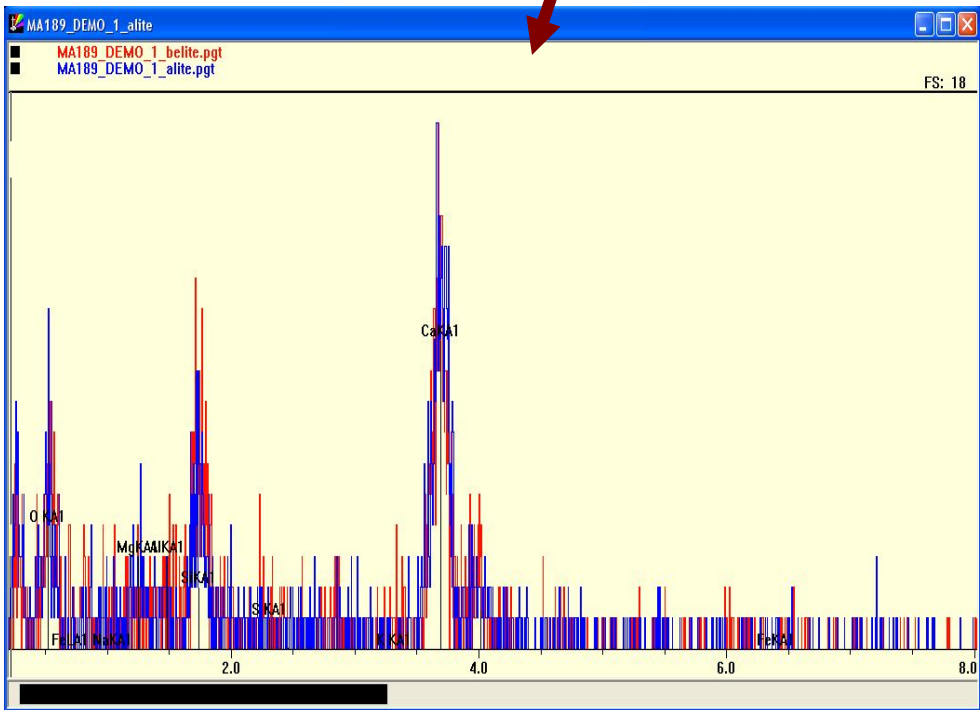


The BE signal provides a high-resolution, high contrast image of the microstructure but needs the addition of some chemical data. The silicates and the matrix phases are chemically distinct, which will be used in conjunction with the BE image for phase segmentation

Spot EDS analysis vs. X-Ray imaging



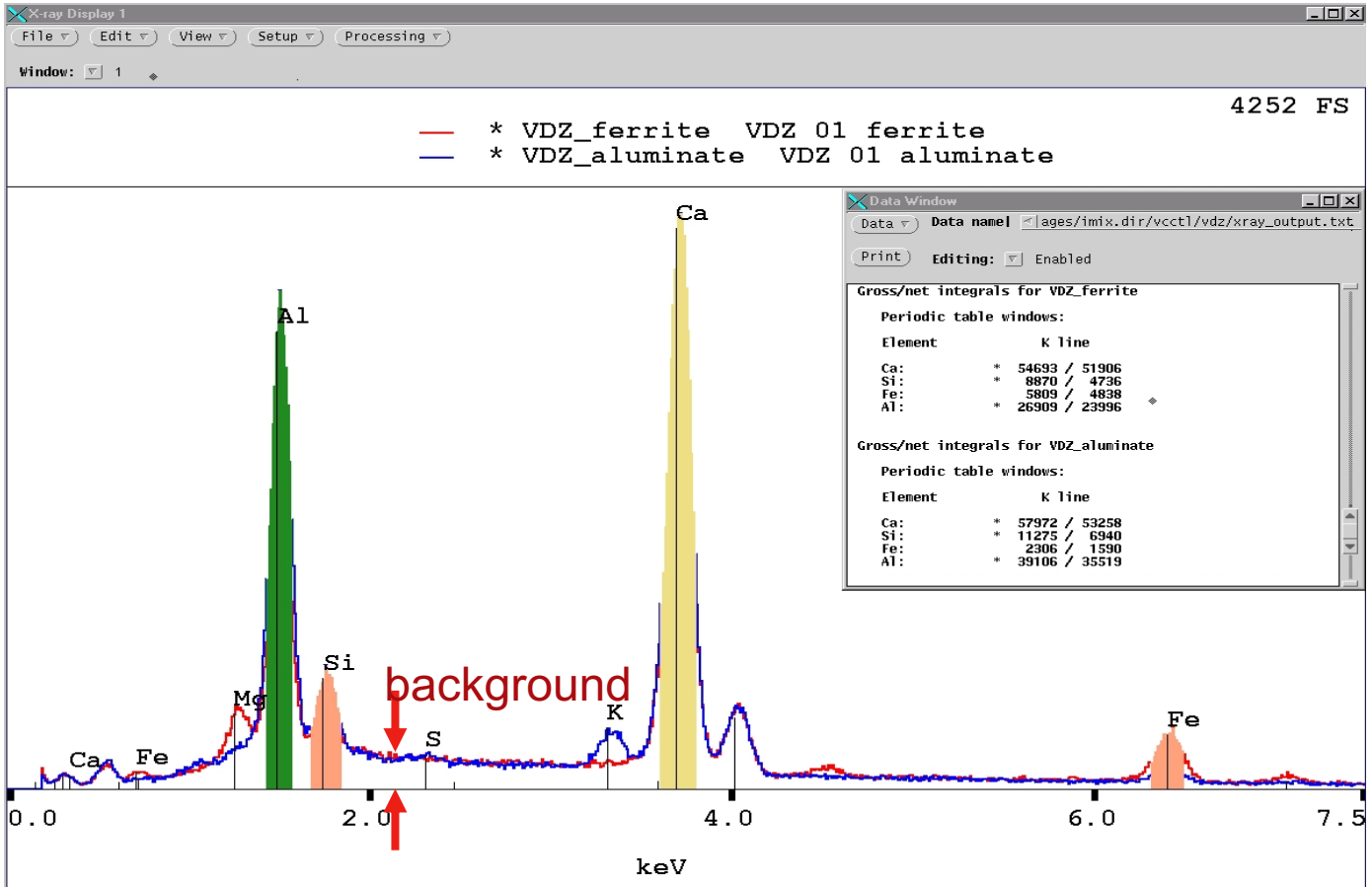
Clear distinction between phases is possible with the longer counting times used for quantitative X-ray microanalysis



***However**, dwell time is too short to allow clear distinction*
We need to optimize collection to enhance the distinction

- *lower kV to enhance low energy X-rays*
- *high probe currents to maximize count rates*
- *slower scan rates to average out noise*
- *sum image frames to improve signal/noise*

X-Ray Imaging Energy Windows



The intensity within a window across characteristic peaks (including background) is used to generate the images. The background can be a significant source of noise for low concentration elements, but we will establish criteria to reduce its influence.

BE and XR images for SRM 2686a

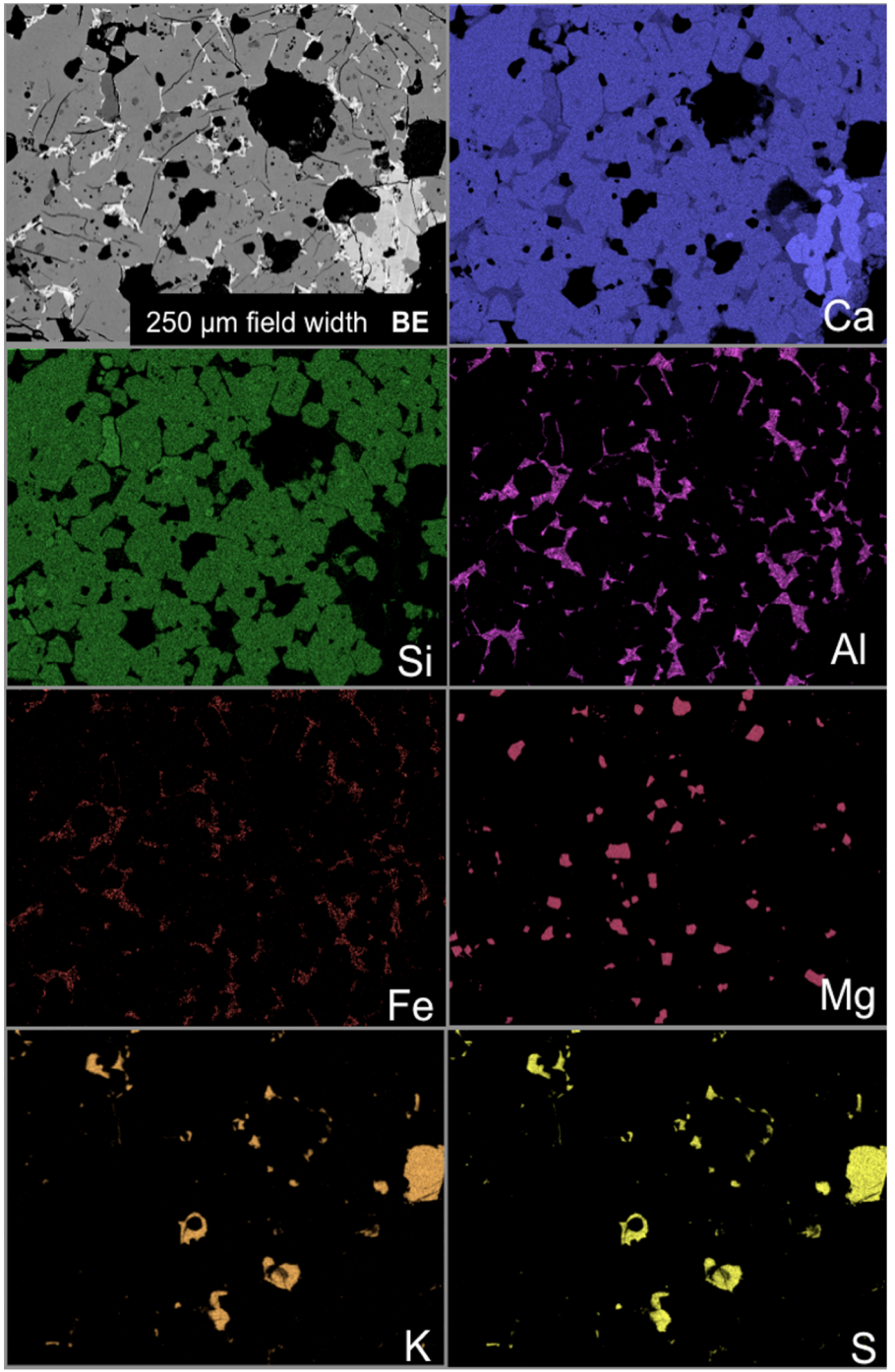
calcium, silicon, aluminum, magnesium, iron, potassium, sodium, and oxygen are the most useful X-ray images

A visual assessment is usually all that is needed to identify significant images

An example: aluminate and belite have distinct chemical compositions, yet exhibit a similar backscattered electron coefficient, therefore have a similar gray level.

However, belite contains appreciable silica while aluminate contains aluminum, so use of one or the other of the X-ray images will serve to distinguish these phases.

Similarly, the calcium sulfate addition (for cement) and the alkali sulfates are usually difficult to see given the high brightness and contrast of the BE image. The X-ray images Ca, S, K, and Na may be used to aid in their distinction

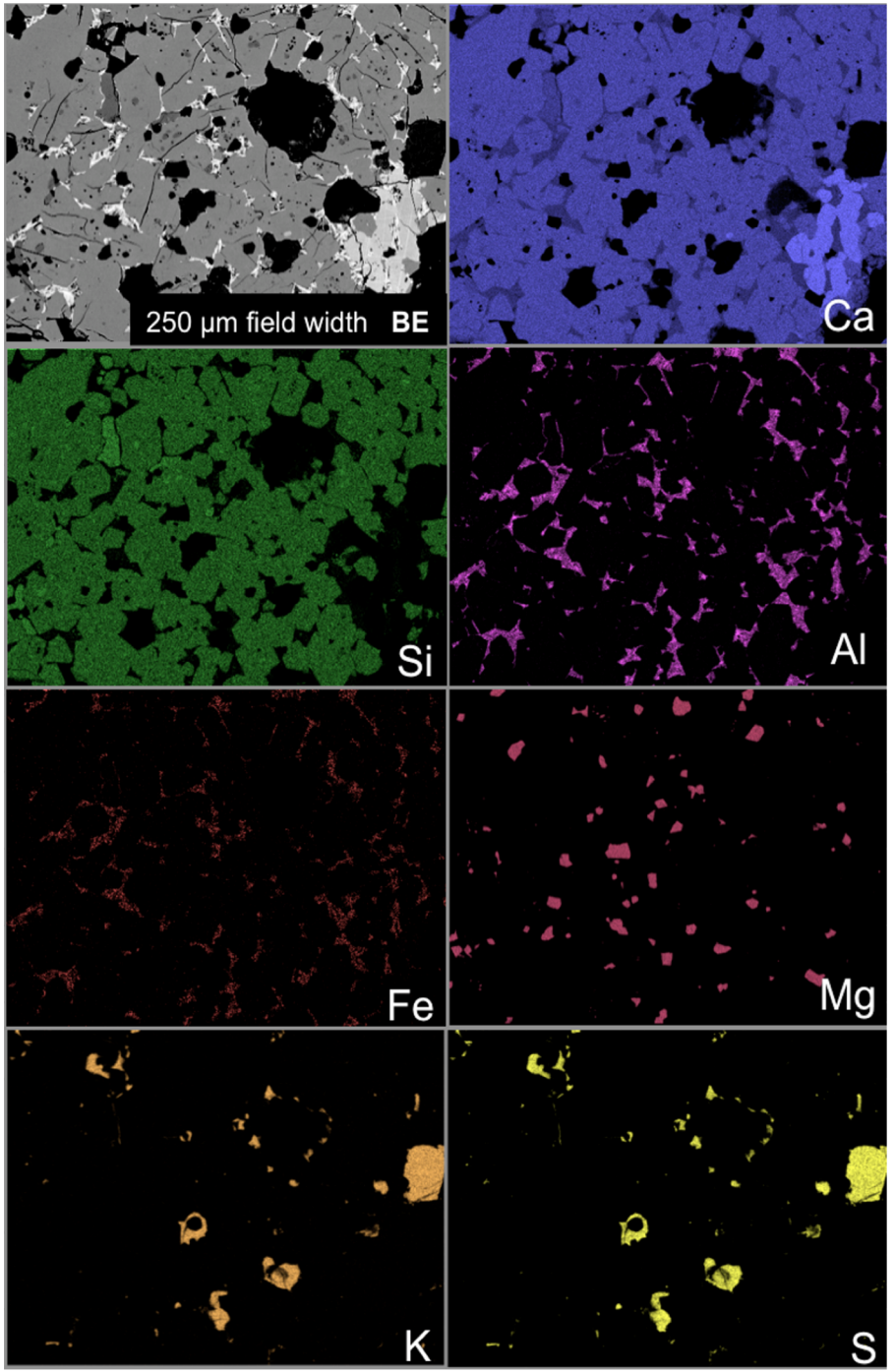


BE and XR images for SRM 2686a

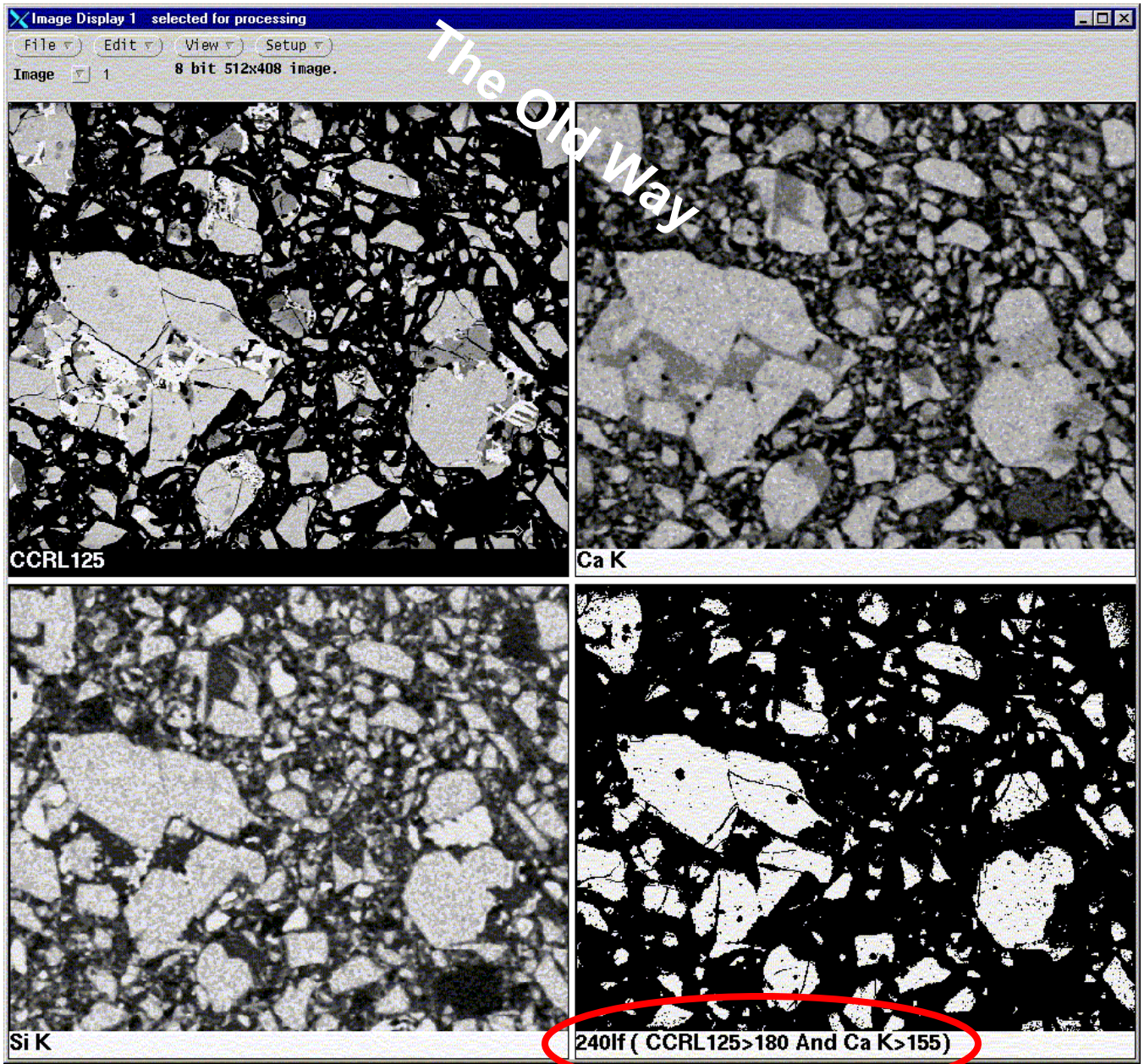
General Rules for Phase Distinction

free lime - bright BEI, strong Ca, rounded
ferrite – bright BEI, matrix, high iron, prismatic
aluminate – intermediate BEI, matrix, high Al
belite – intermediate BEI + little Al, rounded
alite – medium-high BEI, hexagonal shape, abundant
periclase – low BE, high Mg, equant to dendritic
alkali sulfate – high S + K (sometimes Na), occurs along grain boundaries
gypsum – low BE, high S, low K, Ca
calcite – low BE, stronger Ca
dolomite – low BE, stronger Ca, Mg
quartz – intermediate BE, high Si
kaolin – Al + Si
slag – angular, uniform grains, Si, Mg, Al

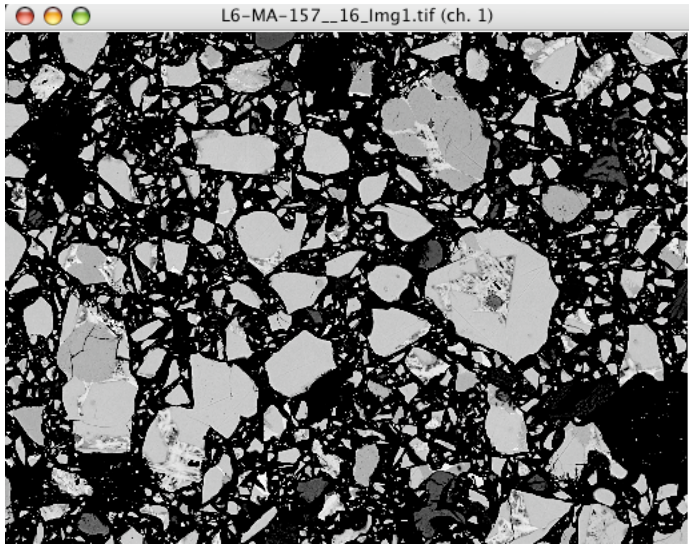
Want to use the fewest number of images to perform the segmentation

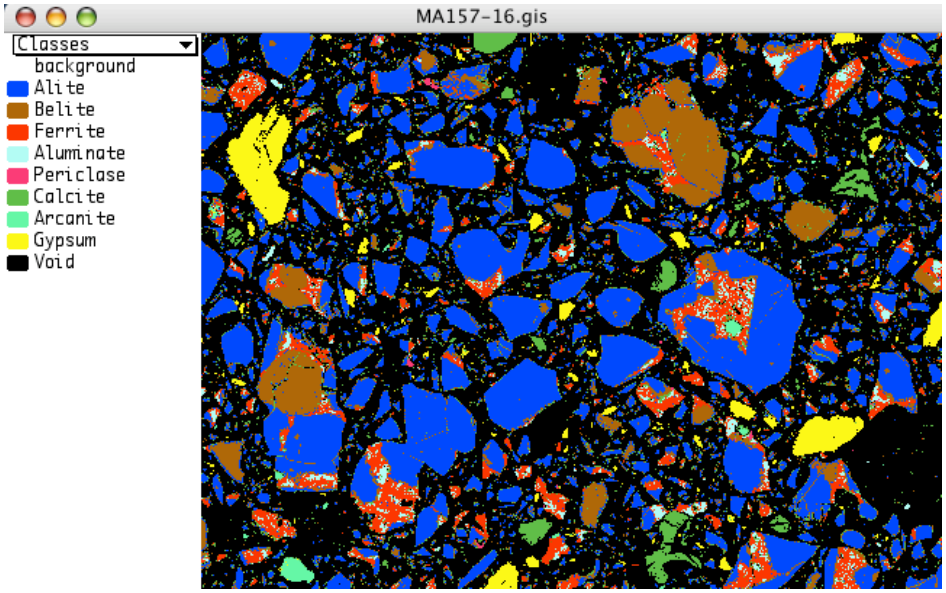


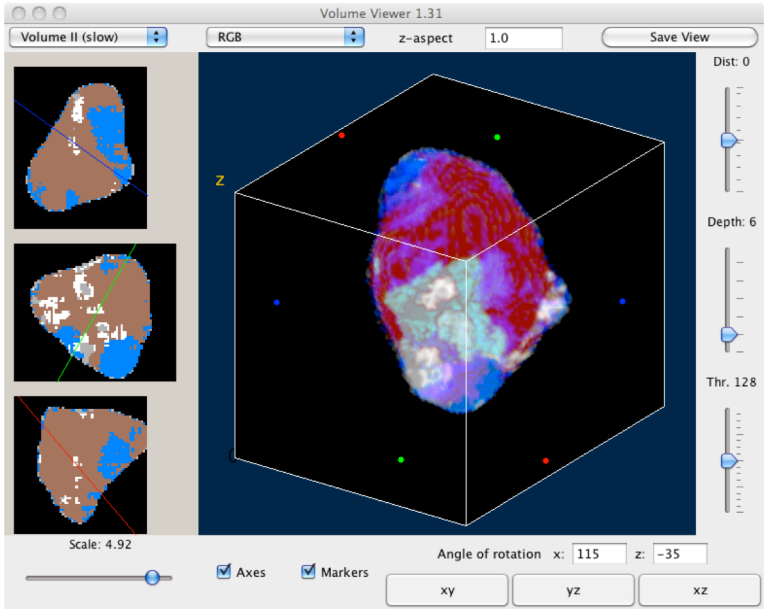
Alite Segmentation Example



Segmented Image







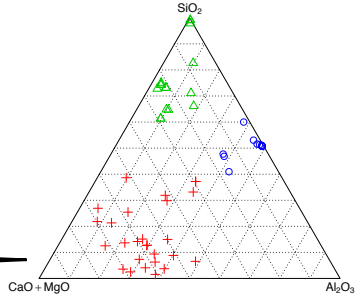
- Segmented image is indexed by phase for each pixel
- ready for analysis of phase area fraction and surface area
- This may be performed by counting pixels for each phase or via spatial correlation functions, which contain information on volume fraction and specific surface for each phase
- input data for hydration model
- generation of virtual 3-d particles after combining phase and surface area with tomographic images of particles

Fly Ash Microscopy: Define mineralogical and textural characterization, along with particle size and shape analysis for performance prediction and improve classification schemes

Constituent Element	2689
Aluminum	12.94 ± 0.21
Barium	(0.08)
Calcium	2.18 ± 0.06
Iron (Total)	9.32 ± 0.06
Potassium	2.20 ± 0.03
Magnesium	0.61 ± 0.05
Manganese	(0.03)
Sodium	0.25 ± 0.03
Phosphorus	0.10 ± 0.01
Silicon	24.06 ± 0.08
Sulfur	-----
Strontium	(0.07)
Titanium	0.75 ± 0.01
LOI 750 °C **	(1.76)
Moisture (110 °C) **	(0.14)

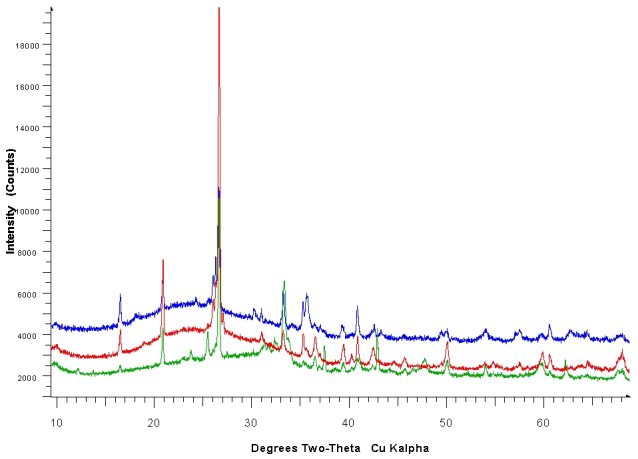
- **Characterize phase type, distribution, and volume,**
- **Identify and quantify mineral and total glass,**
- **Identify, quantify, and classify mineral and glassy phases,**
- **Particle shape and size (X-ray CT and laser diffraction),**
- **Determine the relative reactivity of the fly ash constituents,**
- **Development of new standardized measurement practice,**
- **Provide the basis for improved fly ash classification scheme.**

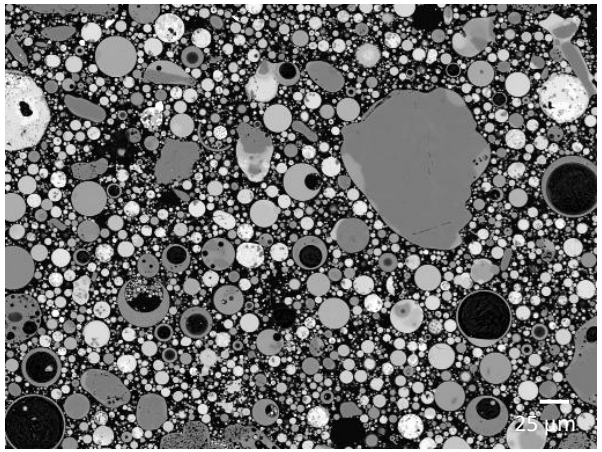
Today: Bulk Chemistry - Class F (ASTM C618)

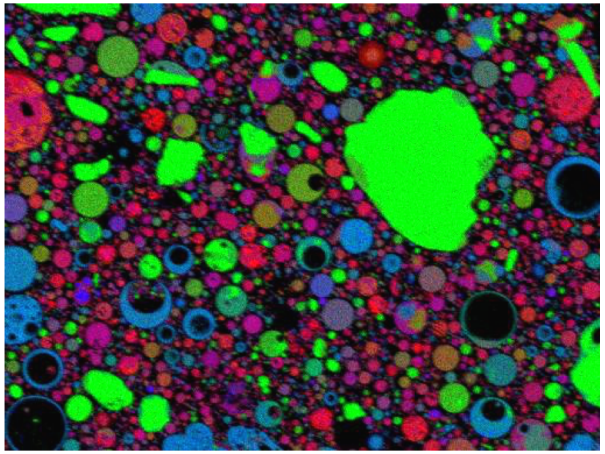


Tomorrow: Bulk Chemistry, Microscopy, X-Ray Powder Diffraction, Particle Size Distribution

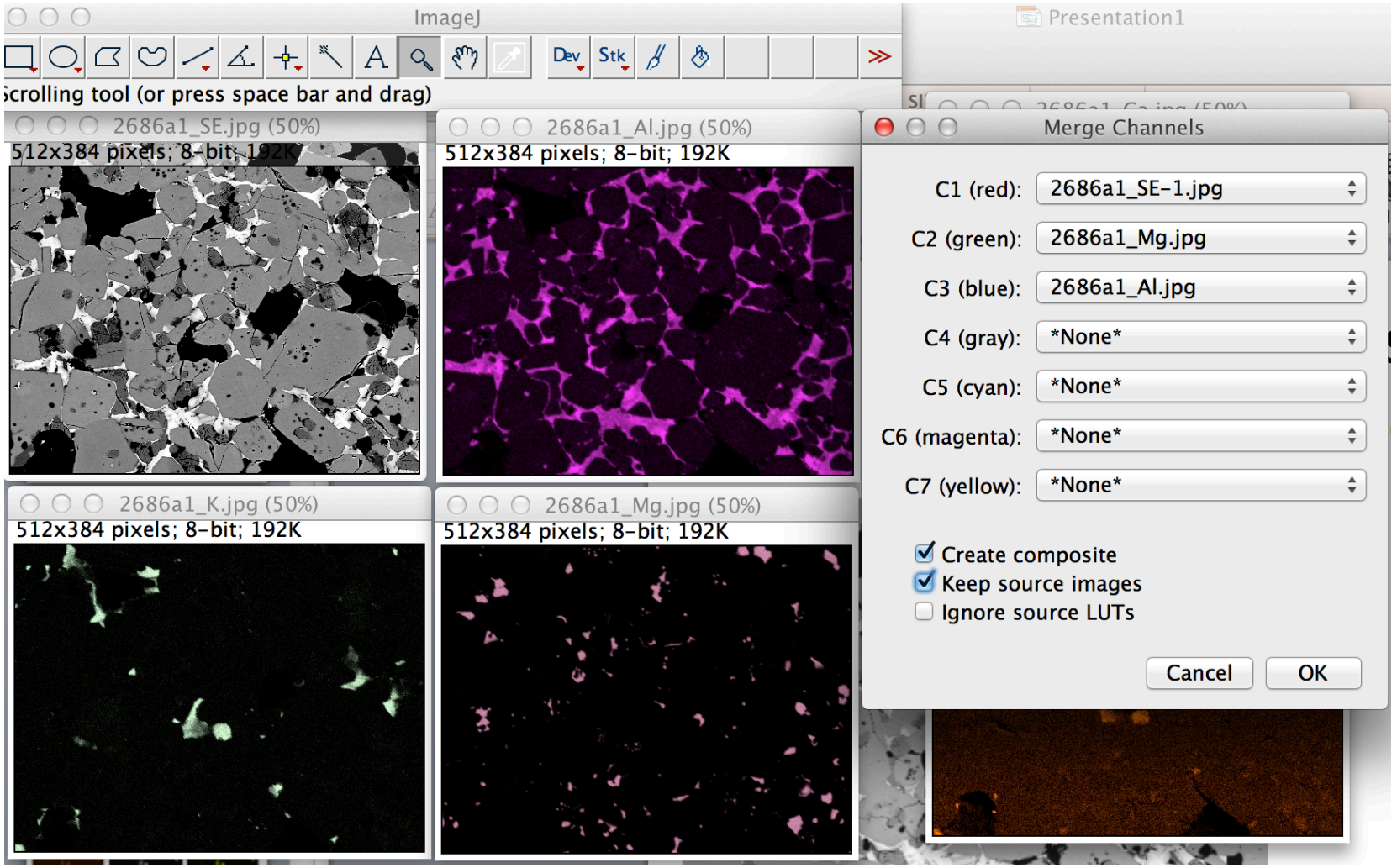
Ca - Si - Al







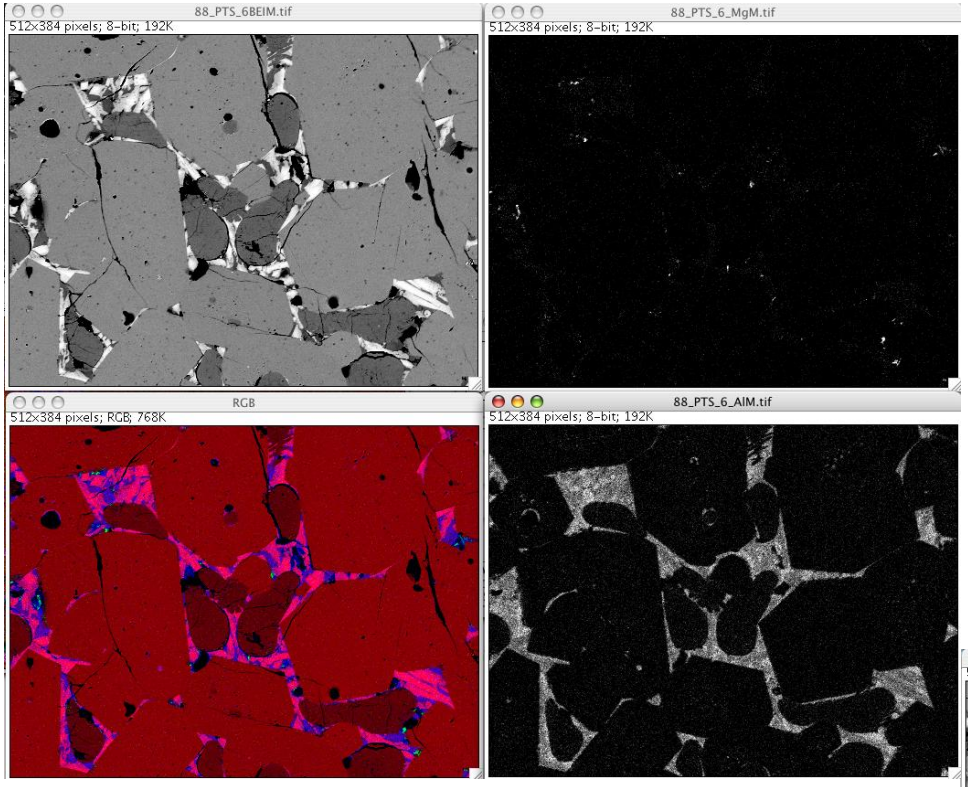
Combine Images – Image->Color-> Merge Channels

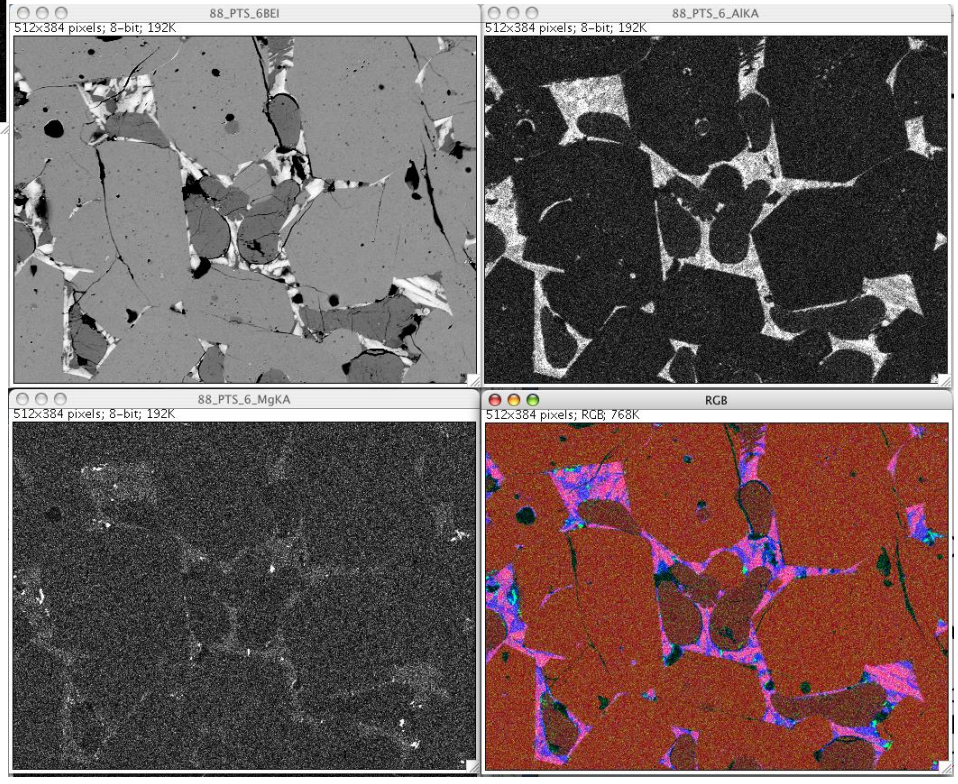


Assign images to color channels, check “Create Composite” and “Keep Source Images”, Select OK

- This works best with 8-bit or 16-bit images and not RGB, as only the first color plane is used
- This example used ImageJ, a public domain imaging code for all platforms: http://imagej.nih.gov/ij

Low-Count Noise Will Affect The Analysis

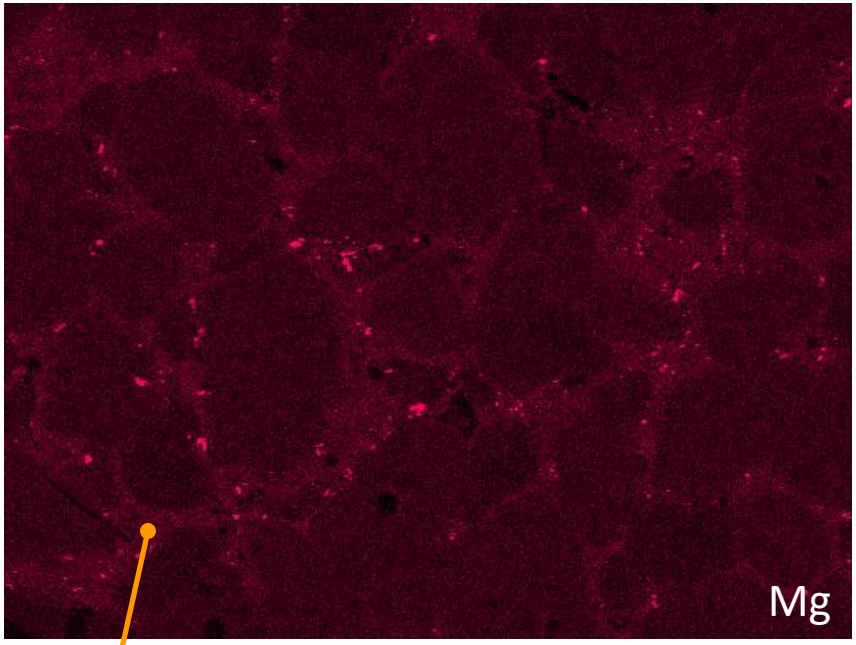


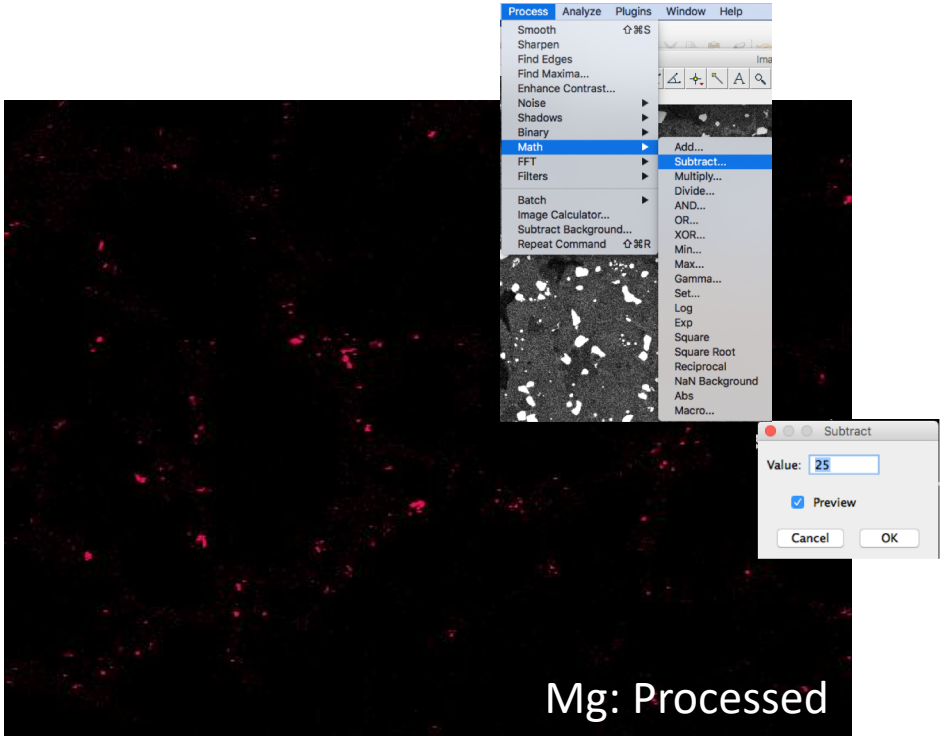


If you see grainy images in a RGB display in ImageJ or Multispec, it can usually be traced to an un-clipped, low-count image such as Mg, K, or Na

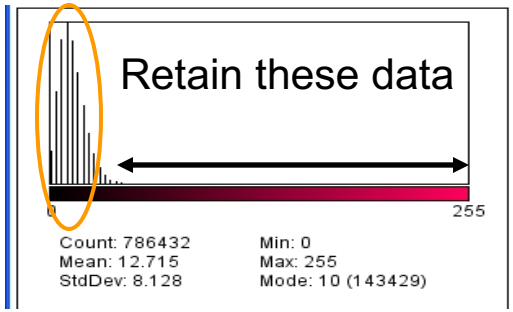
ImageJ provides greater user input in the removal of the noise

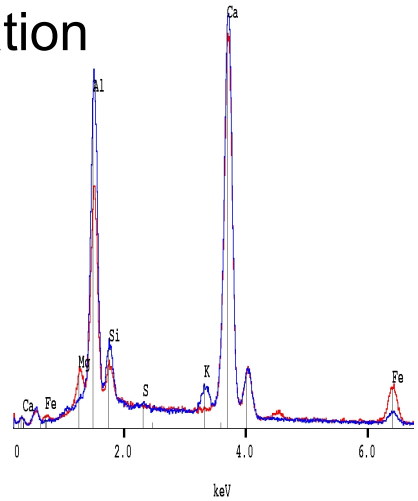
Image Processing: *Process->Math->Subtract*



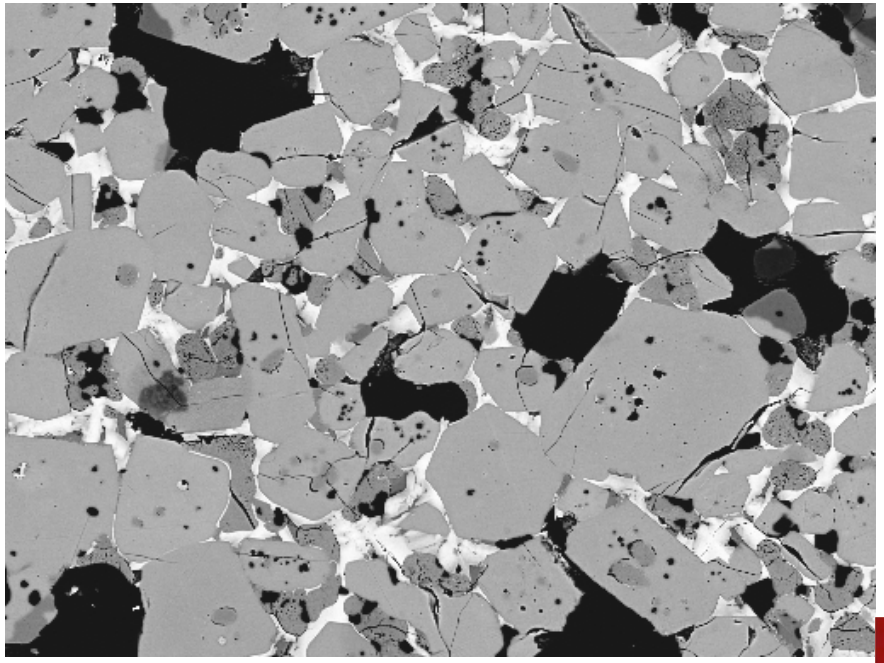


noise and low concentration





- Using the sliders provides a numerical value on the noise level
- You may then subtract that value from the image pixels, or designate that value to be ignored within the Multispec processing



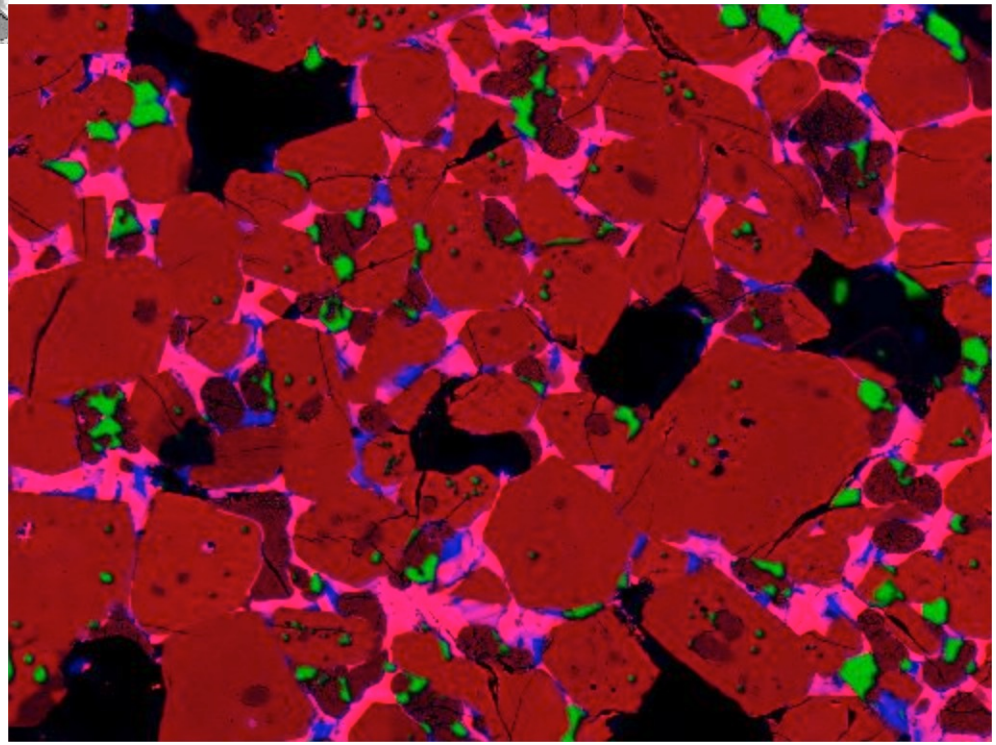
BE – Mg – Al

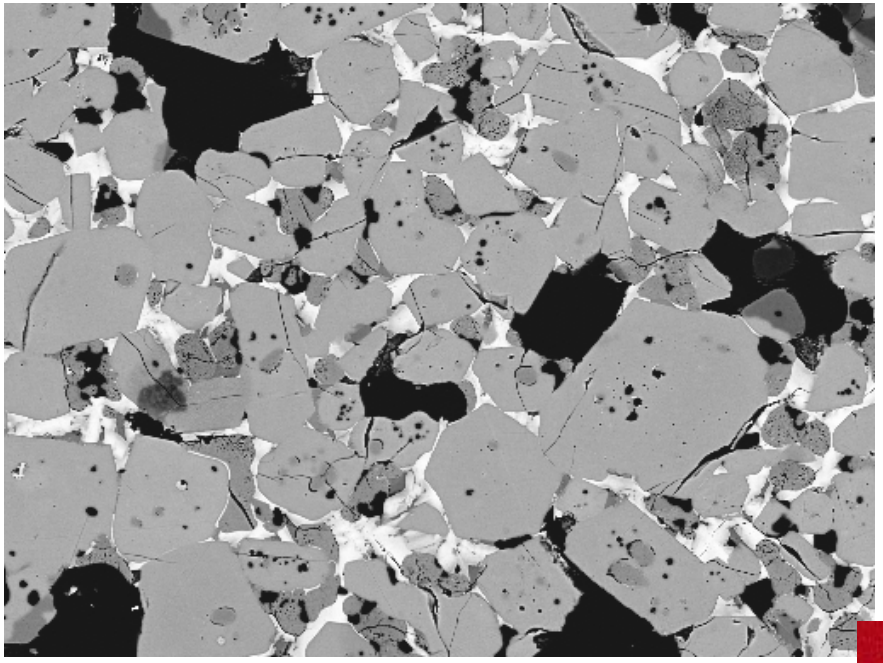
Combining images adds the X-ray image information, facilitating the discrimination of specific phases

In some cases, segmentation of alite, belite, aluminate, ferrite and pores is possible from only the BE image however, the gray contrast between belite and aluminate is not distinct enough.

The addition of the aluminum X-ray image provides that distinction as seen with the blue coloration ->

Periclase, having a low BE coefficient will appear dark, like the voids so the addition of the Mg image data (here in green) will highlight its location within the microstructure

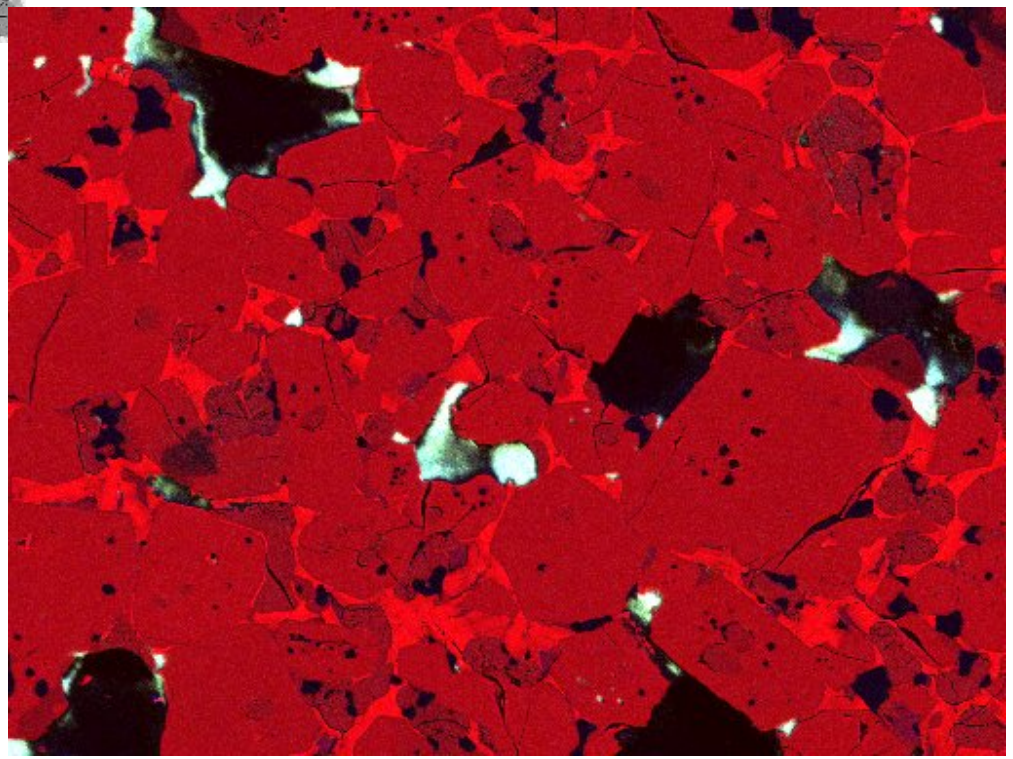




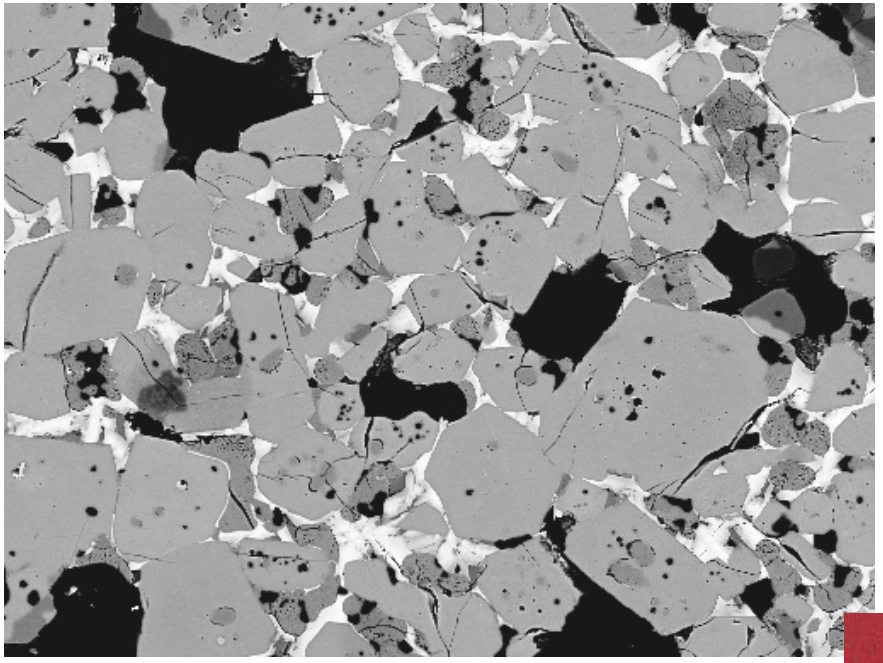
BE – S – Na - K

The addition of K, Na, and S provides distinction of alkali sulfates along pore walls and incorporated between and within silicates

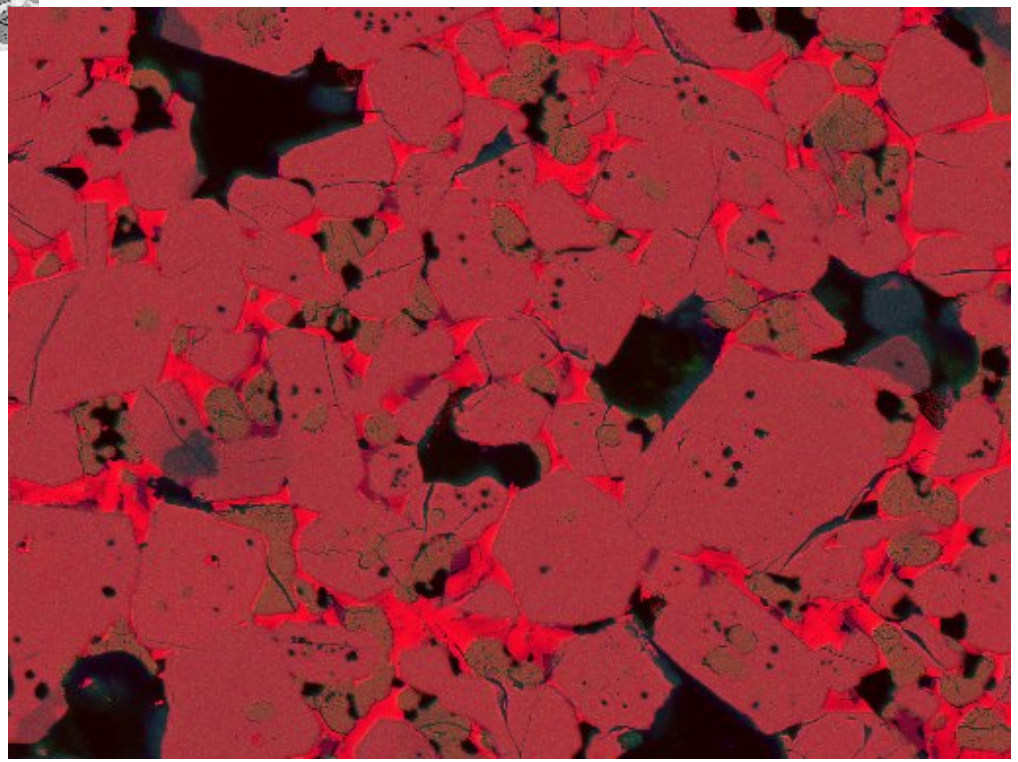
For cements – provides distinction between alkali sulfates and calcium sulfates



- Other combinations may be useful, but the combinations of BE with Mg and Al, and BE with S, Na, and K will highlight most phases.
- In materials with small amounts of Na, or in this case, Na is redundant and is not necessary
- Small amounts of Na may result in a noisier image – as 8 bit images are scaled to 256 levels
- In this case, 16 bit TIF images retain the original X-ray counts rather than scale them to 255 gray levels based upon the highest intensity signal in each image



BE – Si - Ca



- Some combinations are redundant, adding little, or nothing to the segmentation.
- Ca and Si actually make the distinction between alite and belite less clear than in the BE image
- The relatively short dwell time does not provide a distinct difference between the silicates based upon Ca – Si ratios.
- The BE image is vital for segmentation success. Some approaches focus only on the chemical data and are less likely to generate a clean segmentation.