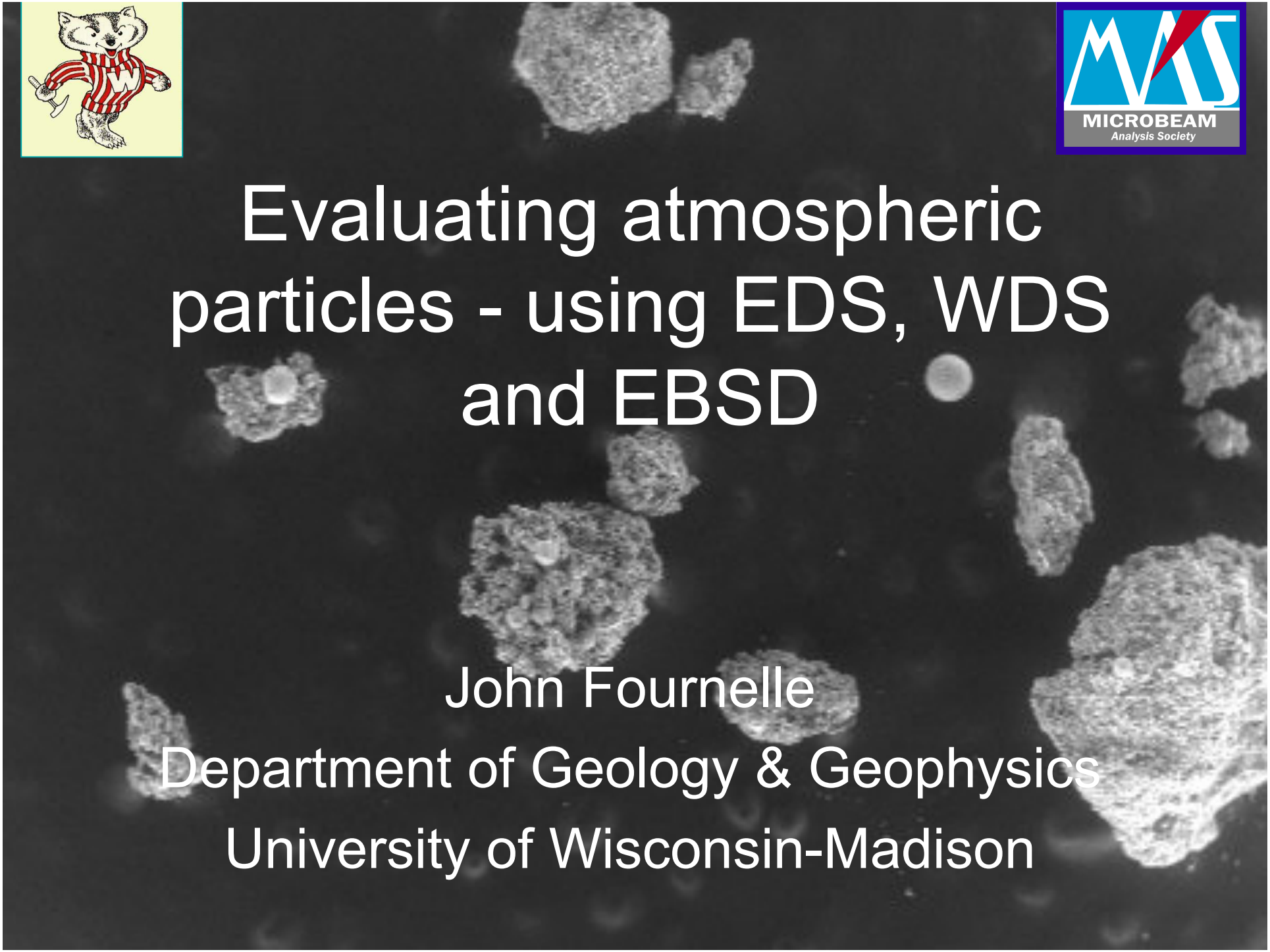
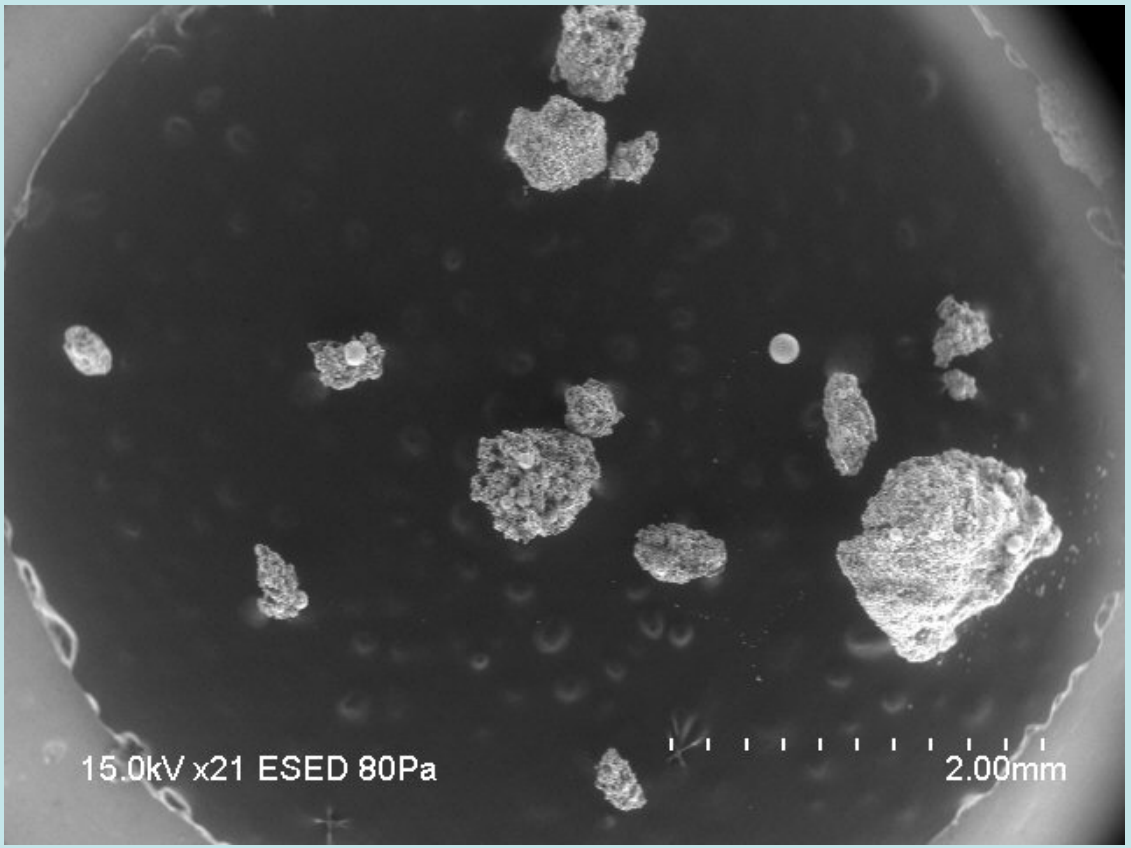


Evaluating atmospheric particles - using EDS, WDS and EBSD

John Fournelle
Department of Geology & Geophysics
University of Wisconsin-Madison

Background

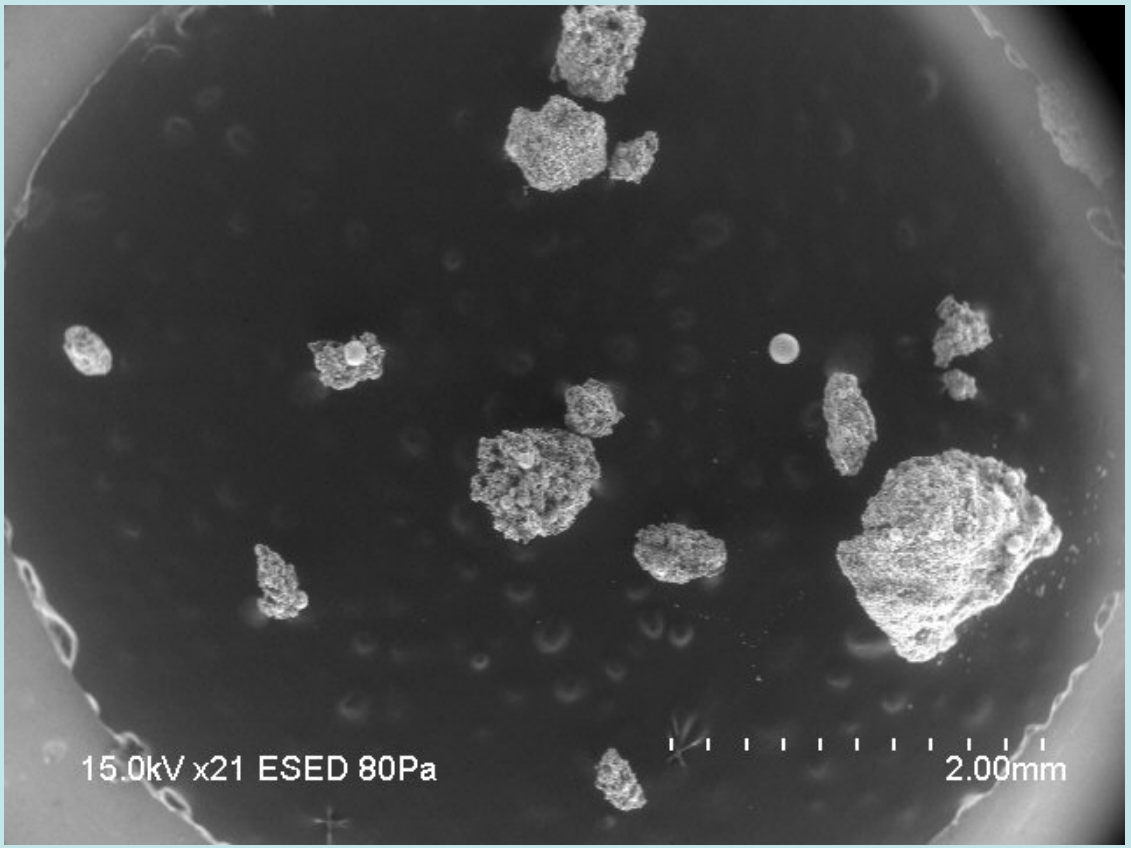
A sample of "small" particles collected in the vicinity of a basic oxygen furnace (BOF) was obtained from Bob Willis (EPA) with Joe Conny's (NIST) assistance.



Disclaimer: While the origin of these samples is the US EPA, interpretations of the data from these samples do not necessarily reflect official EPA policy"

Background

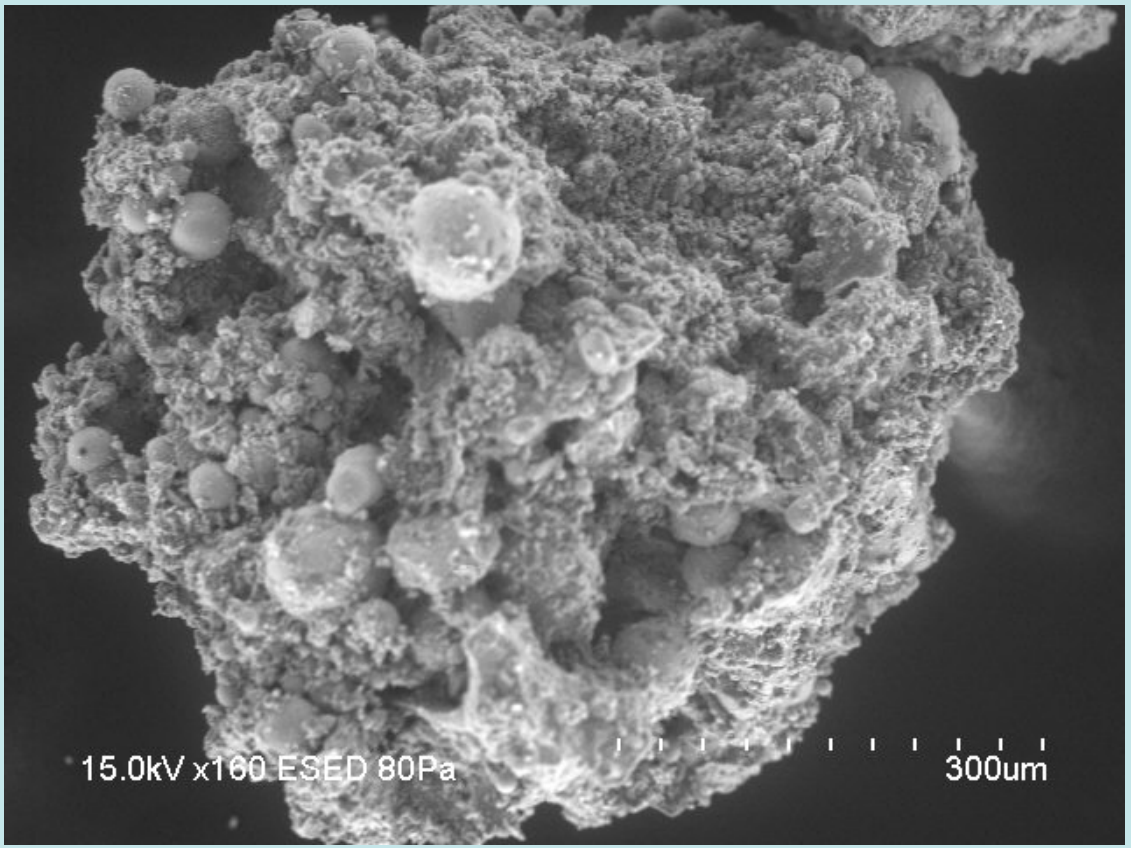
SEM-EDS examination showed 2 general types of spheres: some type of Fe-oxide, and others with more complicated chemistry (Ca, Al, Fe, Mg, P, O …)



Disclaimer: “While the origin of these samples is the US EPA, interpretations of the data from these samples do not necessarily reflect official EPA policy”

Background

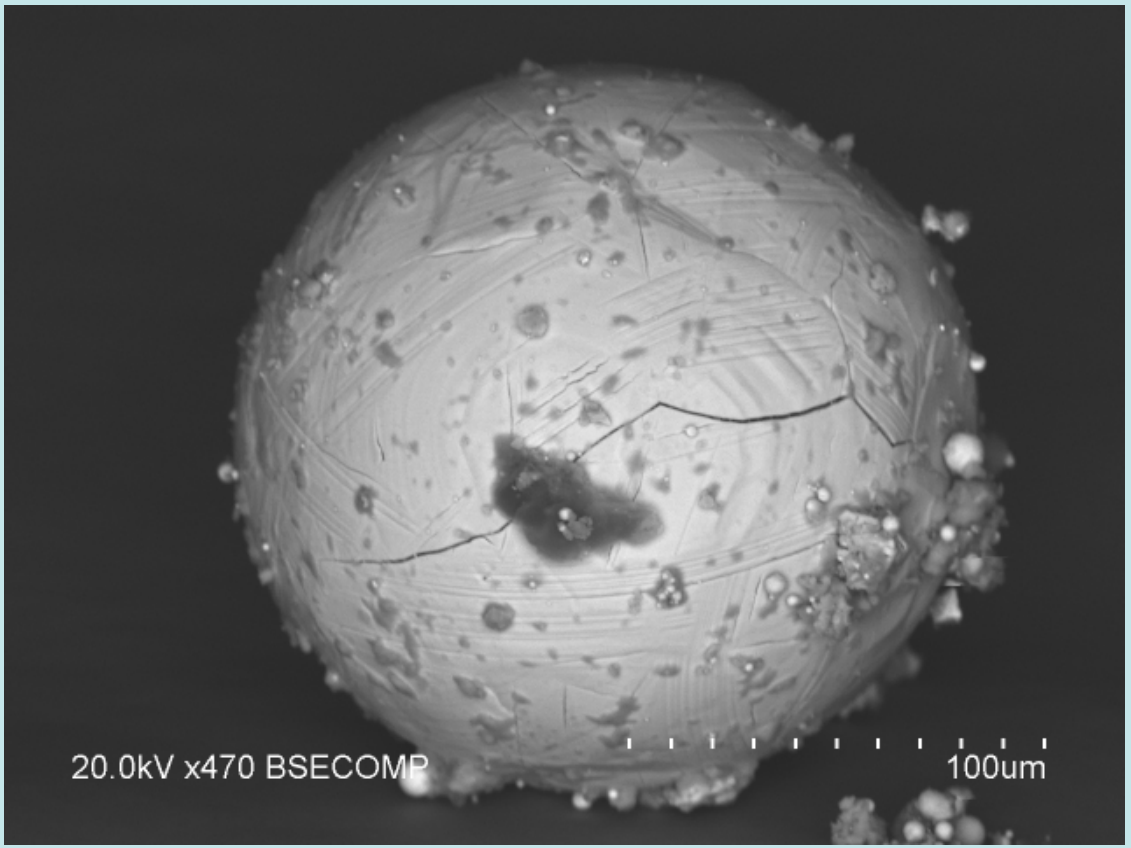
Particles ranged from submicron up to ~ a few hundred microns, with agglomerations even larger



Disclaimer: “While the origin of these samples is the US EPA, interpretations of the data from these samples do not necessarily reflect official EPA policy”

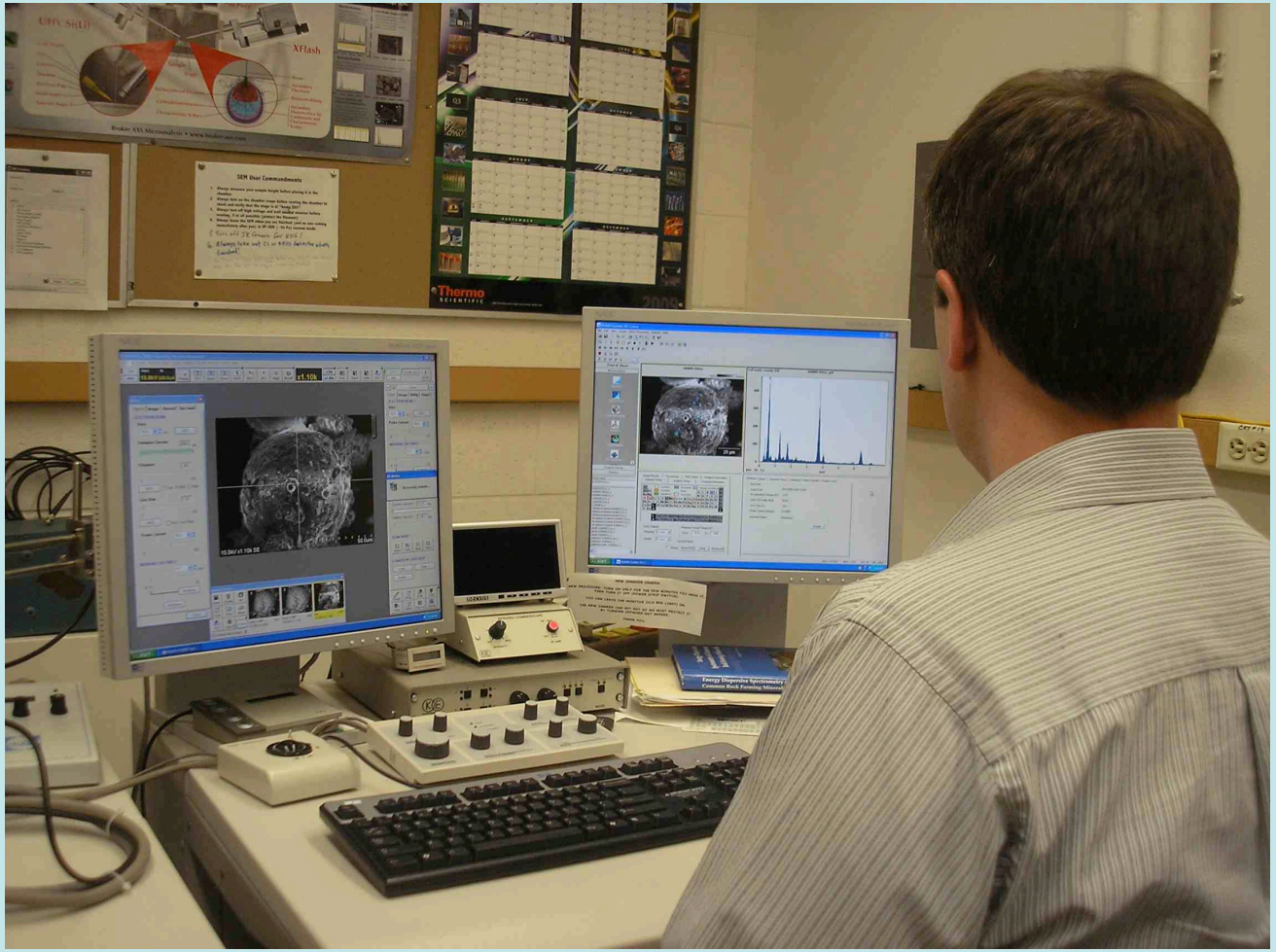
Background

Fe oxide spheres of various sizes



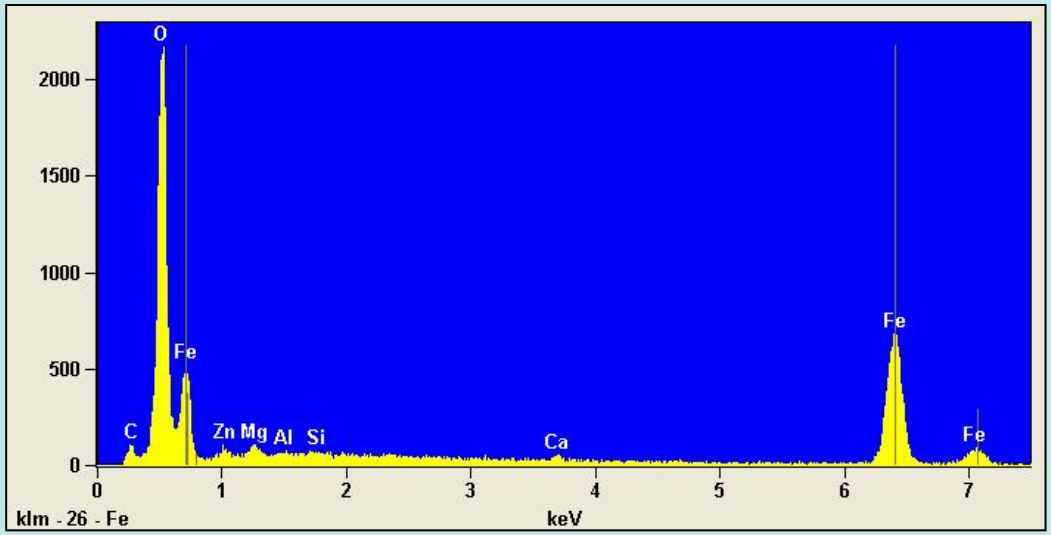
Disclaimer: “While the origin of these samples is the US EPA, interpretations of the data from these samples do not necessarily reflect official EPA policy”

The normal approach typically would be to mount the grains on a stub and examine using EDS in an SEM



However

Magnetite and hematite are virtually impossible to differentiate by EDS, as the differences in Fe and O between phases is small and EDS measurement of Oxygen is not accurate -- particularly on 3D geometries (non-flat surfaces) where variable path lengths lead to more/less absorption of the low energy O Ka.



Nominal compositions:

Mt = Fe_3O_4 = Fe 72 wt% O 28 wt%

Hm = Fe_2O_3 = Fe 70 wt% O 30 wt%

How
to identify
the Fe-oxide
aerosols ?

Two techniques offer potential for distinguishing Fe oxides in atmospheric particles

- WDS - rigorous EPMA quant of flat polished samples
- EBSD - using Kikuchi diffraction patterns

How do you prepare a small particle for WDS? That is, how do you make it polished, flat?

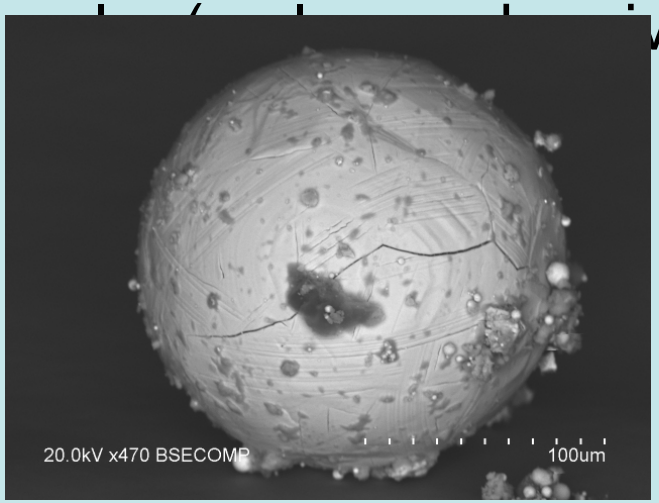
It's not the easiest thing in the world, and "it depends" upon the material and the exact size and the quantity available, but it is not impossible…

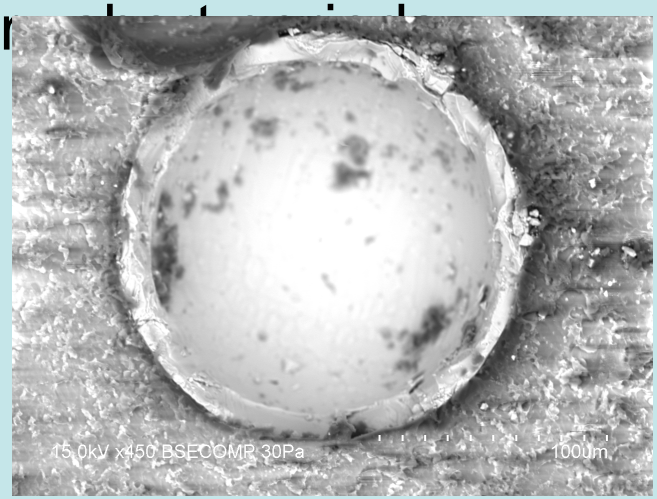
Clearly, techniques like FIB are one approach….but with a little care, you don't necessarily need high technology…

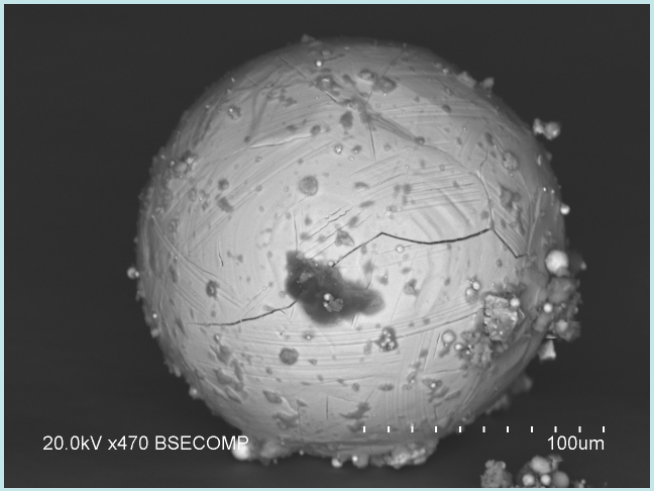
• Carefully position particles on sticky tape (transfer using eyelash glued to popsicle stick or ‘orange’ wood stick) and surround with small (e.g. 1/4” OD) tube

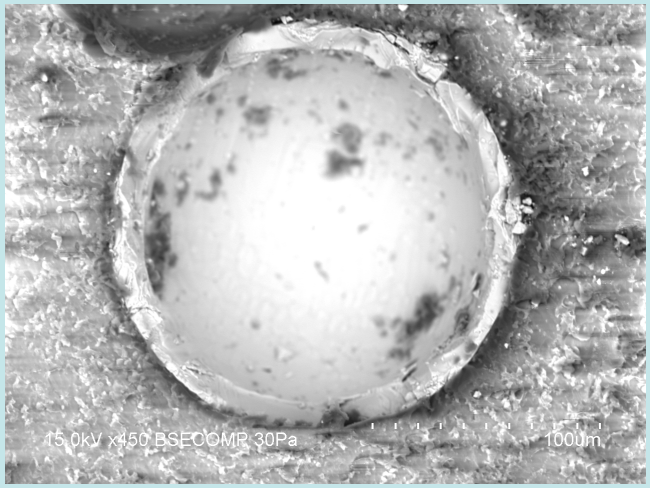
• Cover/embed with low viscosity epoxy (e.g. epothin)

• Very carefully polish with fine diamond embedded

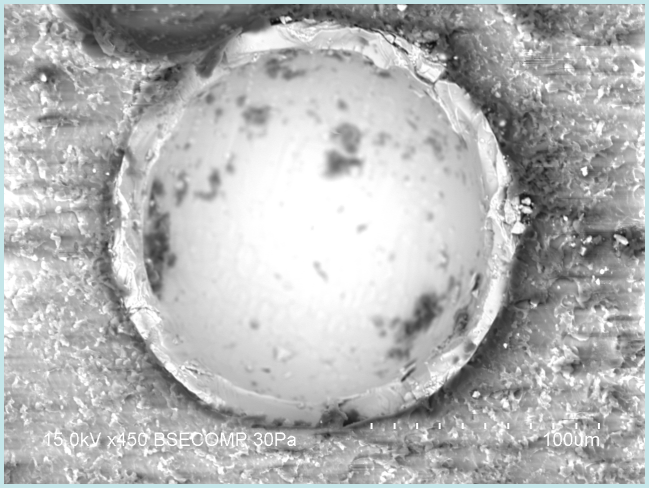








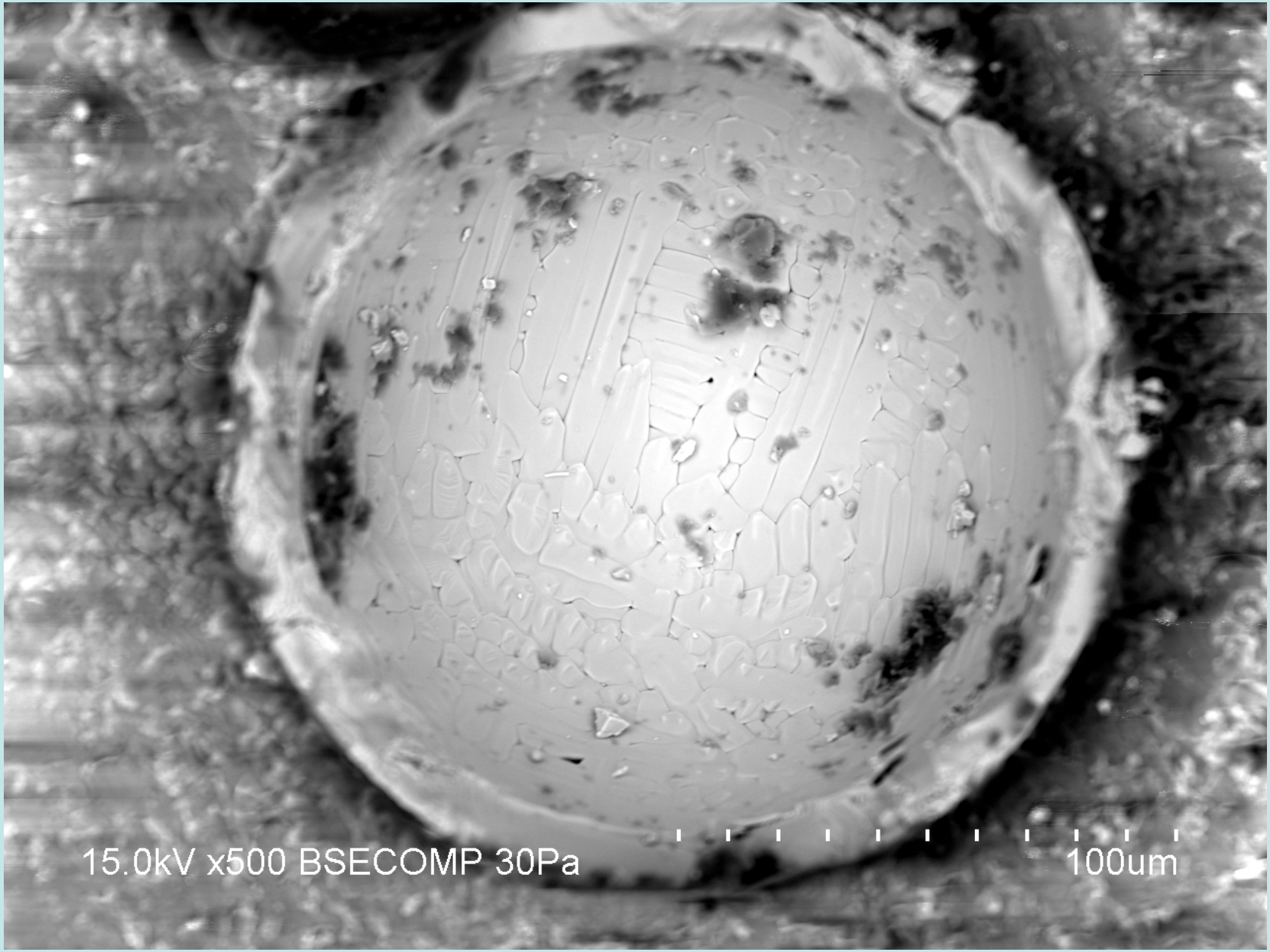
- Small, flat regions ~15 microns wide are created
- Quantitative EPMA requires flat surfaces
- Several regions were analyzed by WDS-EPMA with our SX51 and using Fe_2O_3 and Fe_3O_4 standards



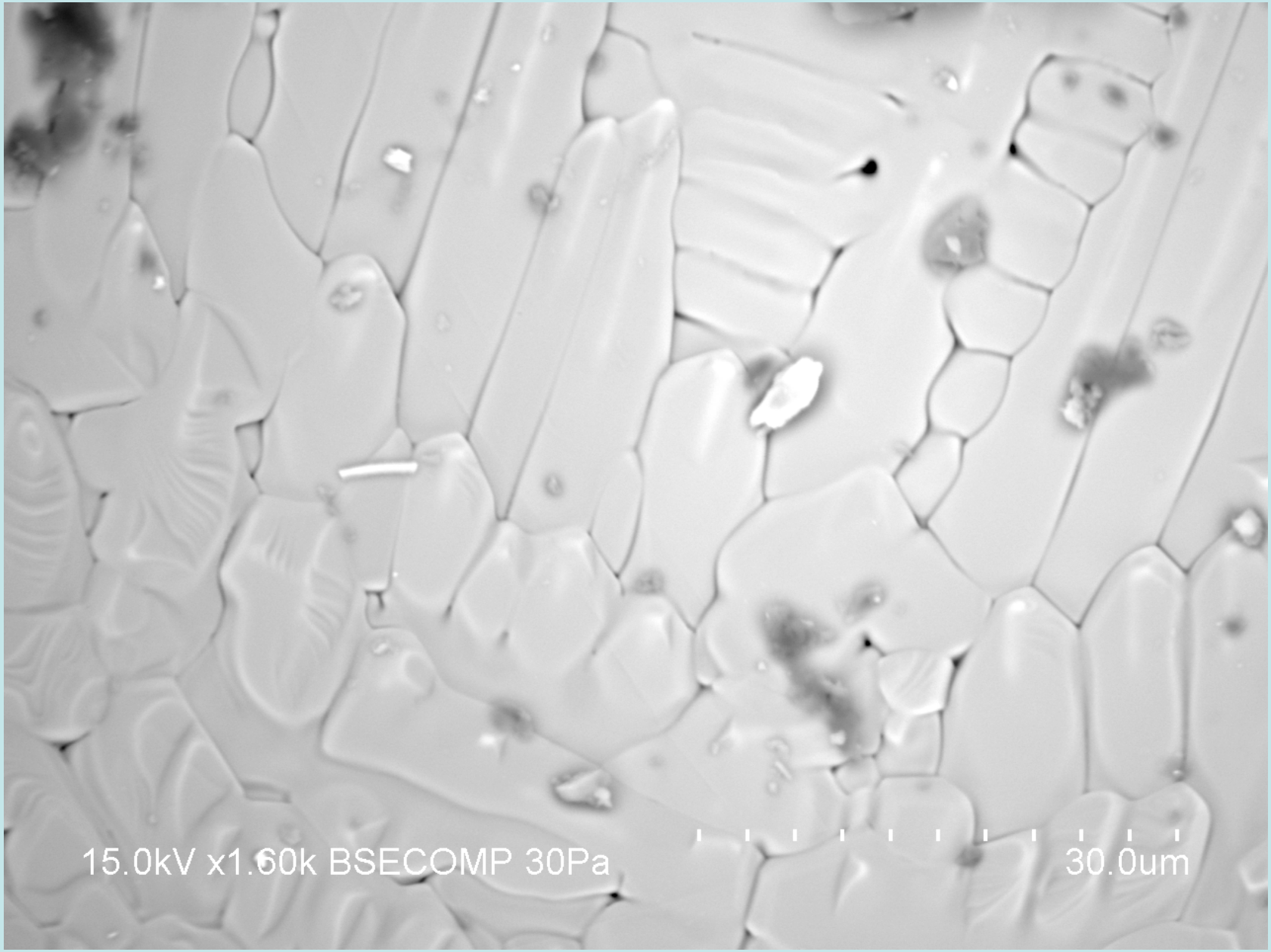
Mt = Fe_3O_4 = Fe 72 wt% O 28 wt%
Hm = Fe_2O_3 = Fe 70 wt% O 30 wt%

- Fe and O and 7 other elements were quantified by WDS-EPMA.
- By explicitly measuring both Fe and O, it is possible to ID the Fe-oxide: for the wall of this sphere, there is 71.2 wt% Fe and 27.9 wt% O, and ~0.3 wt% other elements (Ca, Si, Mn, Al).
- The analytical total is 99.4 wt%.
- Thus, we can say with a high degree of confidence that this sphere is magnetite.

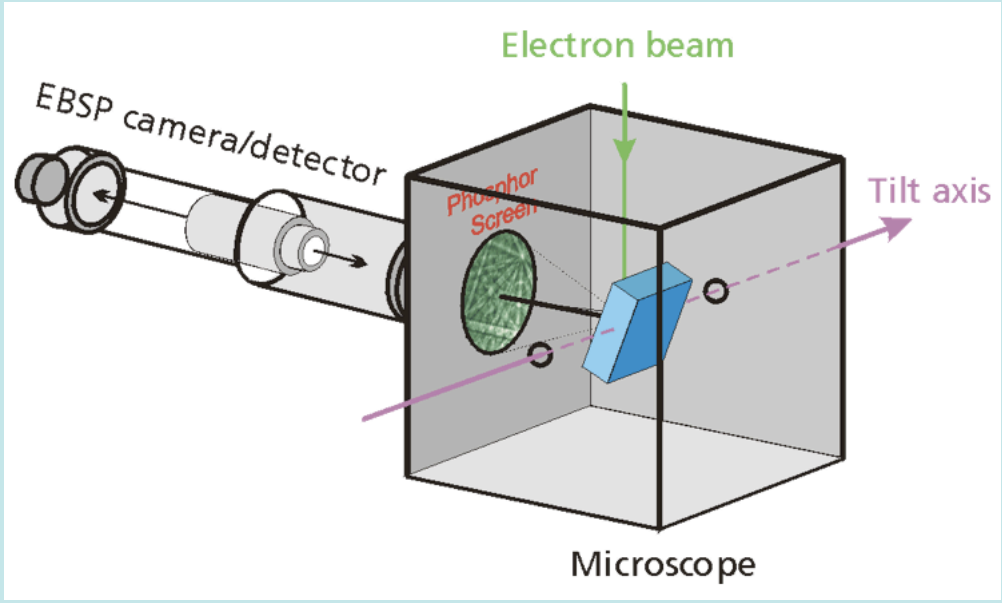
Anyone ever seen something like this?



Anyone ever seen something like this?



EBSD of Fe-oxide particles



Electron backscatter diffraction (EBSD) allows diffraction (”Kikuchi”) patterns to be collected in an SEM, upon a sample surface tilting (70°) sharply away from the electron beam, collected with a special phosphor or cc detector, and then the pattern is compared with a set of possible matching crystal structures (all computerized, of course).

A best fit (MAD < 0.5-1) is calculated if one of the structures can match for any possible orientation direction.

Practical issues

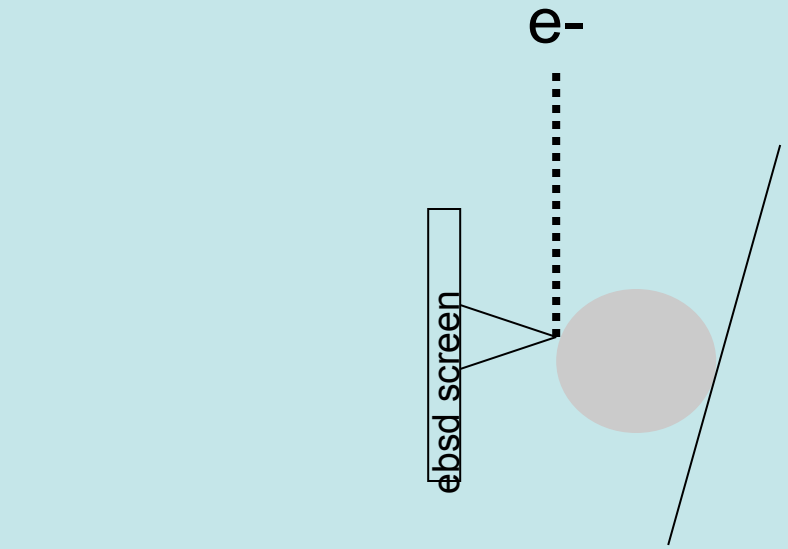
Electron diffraction occurs off the top nanometers of surface … a surface technique.

Bulk materials that are cut/ground/polished prior to examination must have special polishing to remove deformation introduced during sample prep …

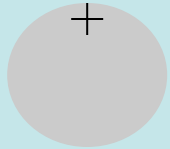
HOWEVER, ‘natural’ particles many times do not require special treatment and can be examined “as is”.

Practical issues

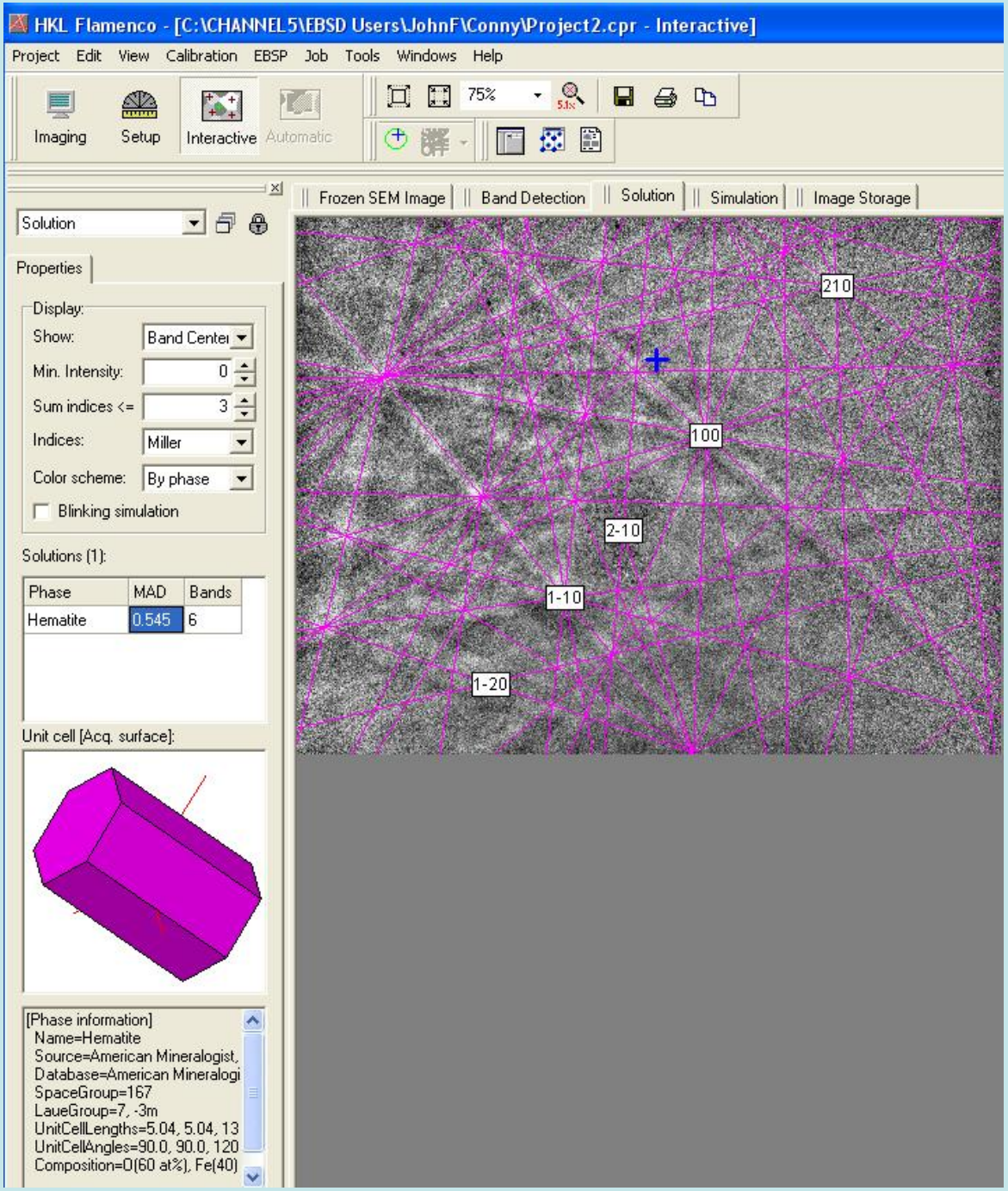
BUT, there may be only a small ‘sweet spot’ where diffraction can yield electrons that hit the EBSD detector screen



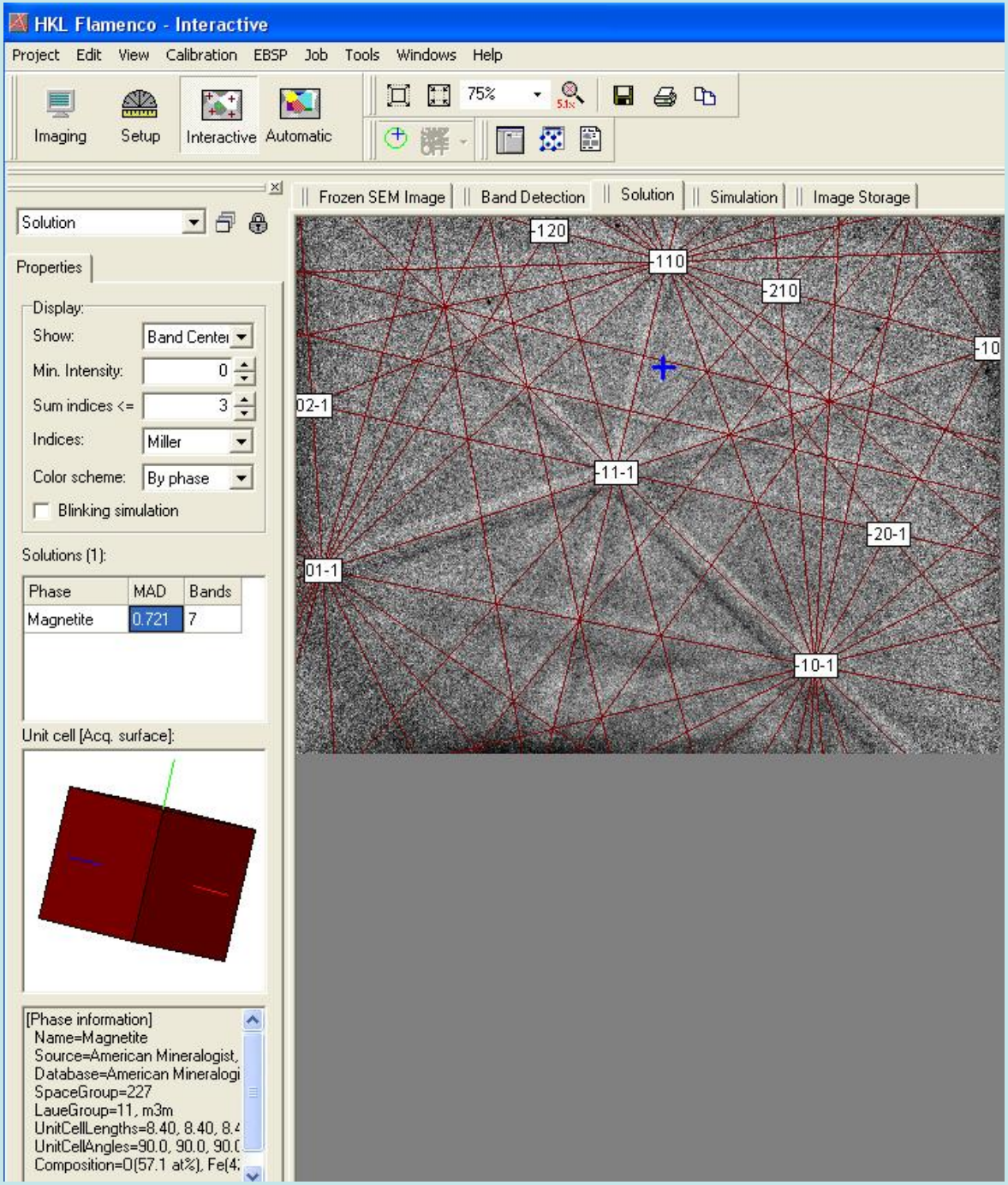
Hypothetical side view



Actual view on SEM screen -- you ‘point and shoot’ at the top edge of the particle, hoping to get some Kikuchi bands

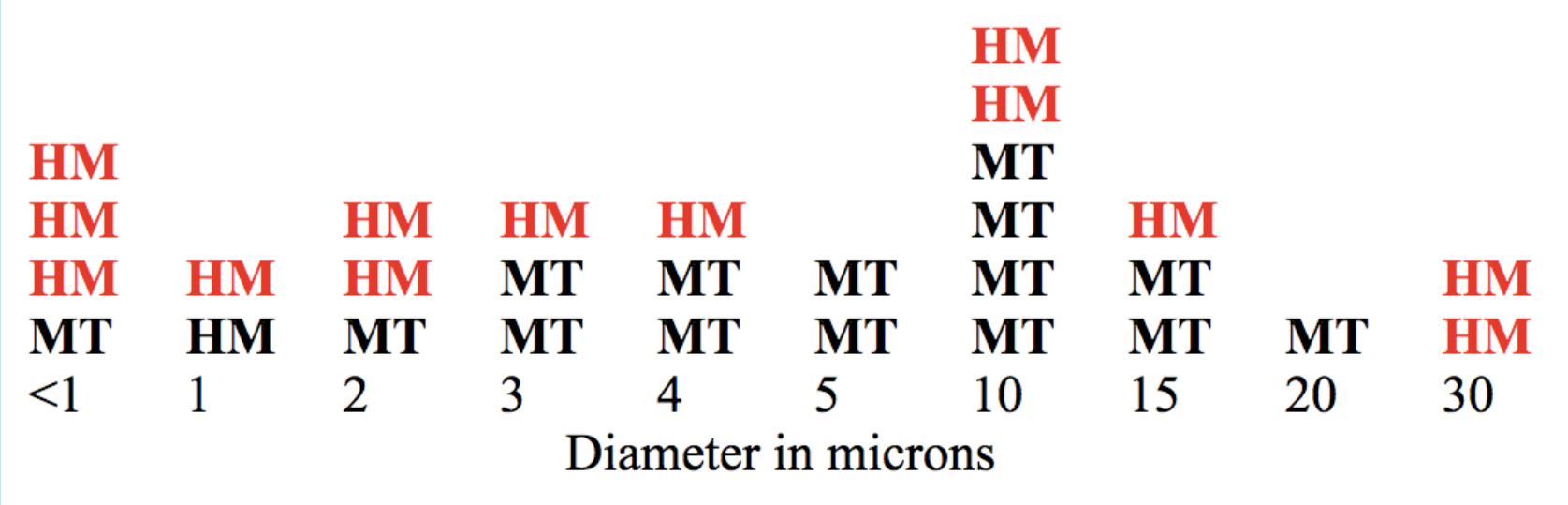


Here 6 bands were used to match a sphere to hematite, with a fit (MAD) of .55



Here 7 bands were used to match a sphere to magnetite, with a fit (MAD) of .72

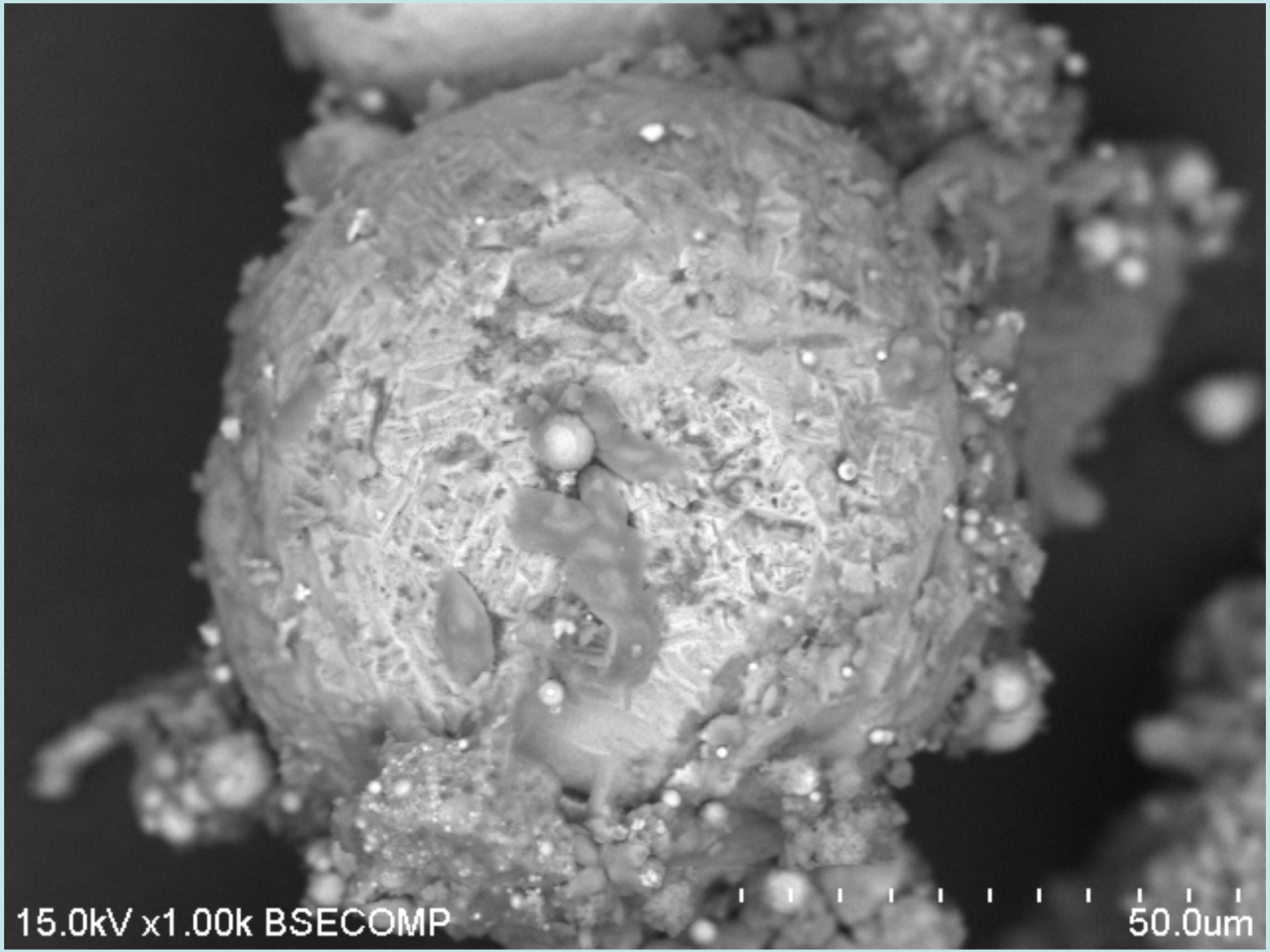
EBSD reconnaissance* of small spheres shows both magnetite and hematite are present…in roughly equal proportions (15 mt, 14 hm)



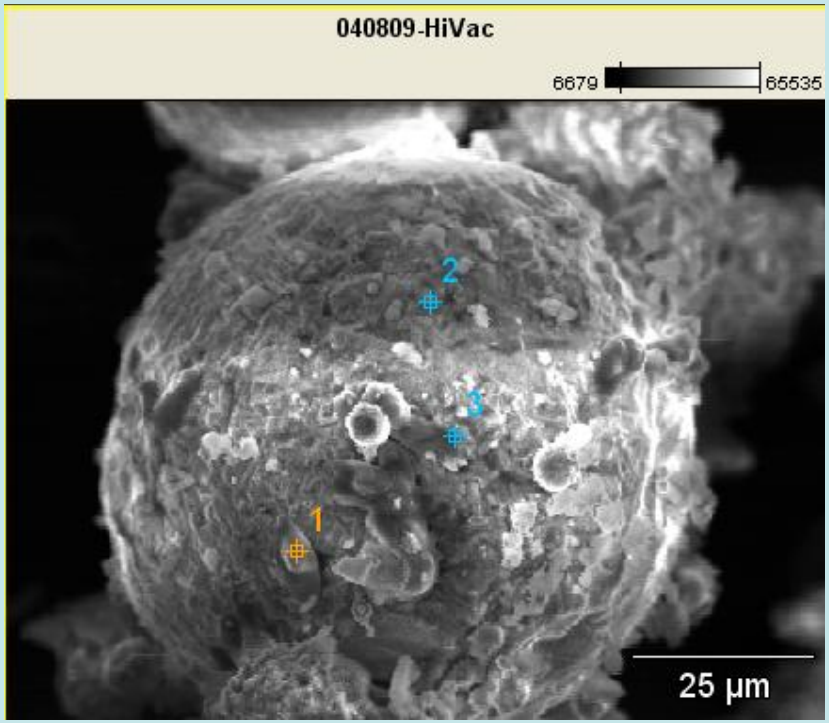
Histogram of Fe-oxide spheres by EBSD

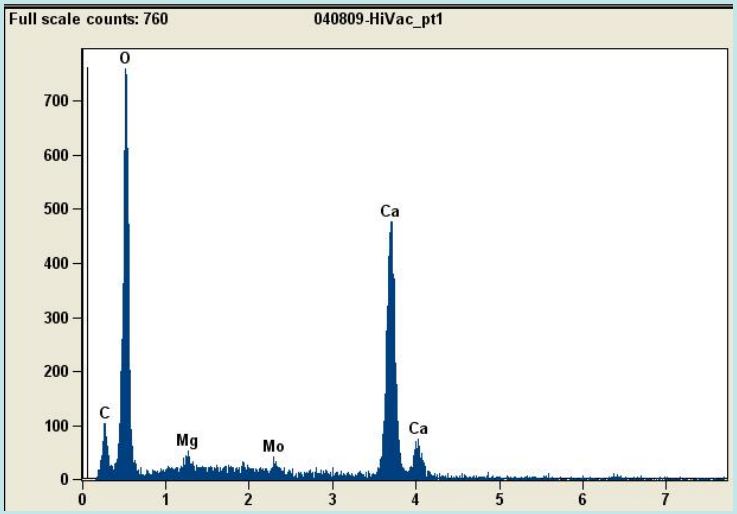
* Approximately 60 spheres were examined over ~60 minutes with ~50% success rate

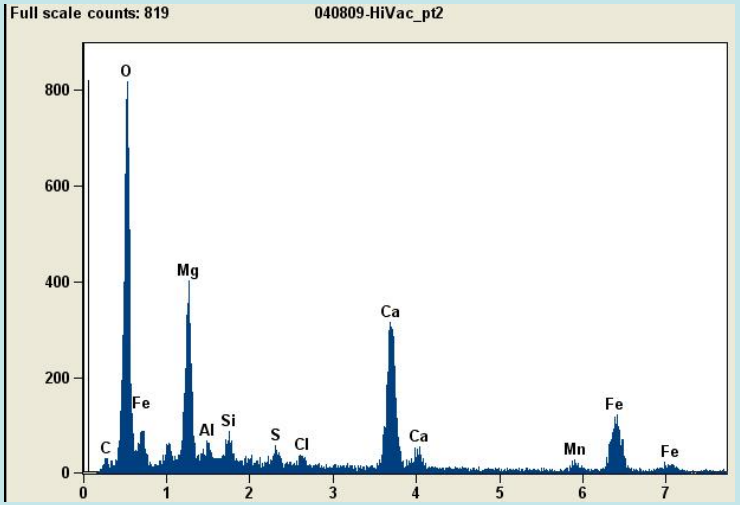
Another particle type was also present…Ca-rich

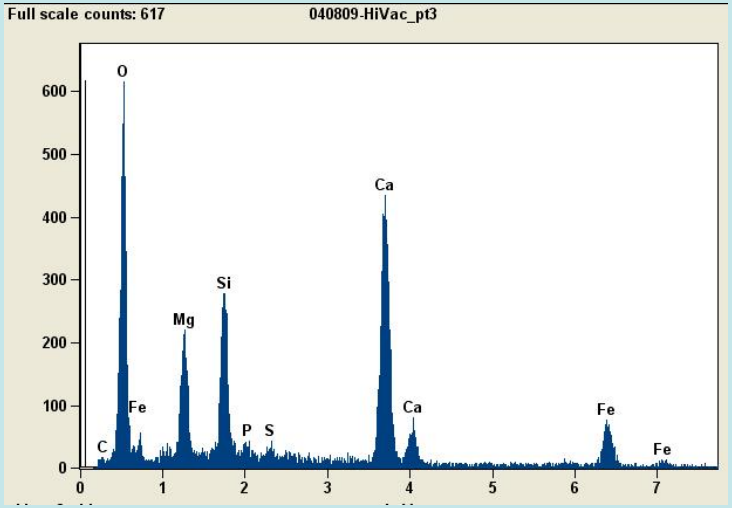


SEM-EDS examination of the outside surface gives a somewhat confusing view of what this particle is

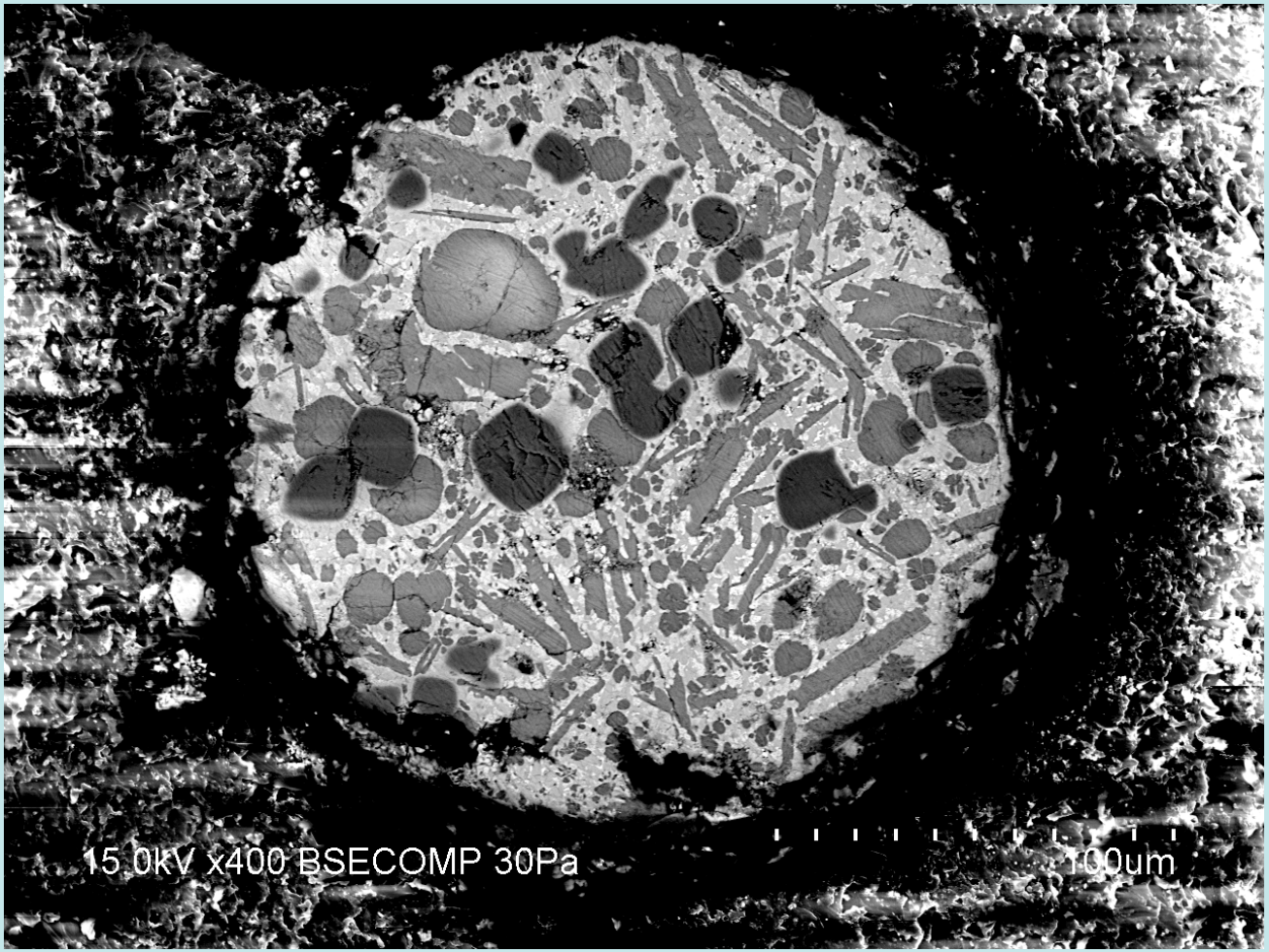






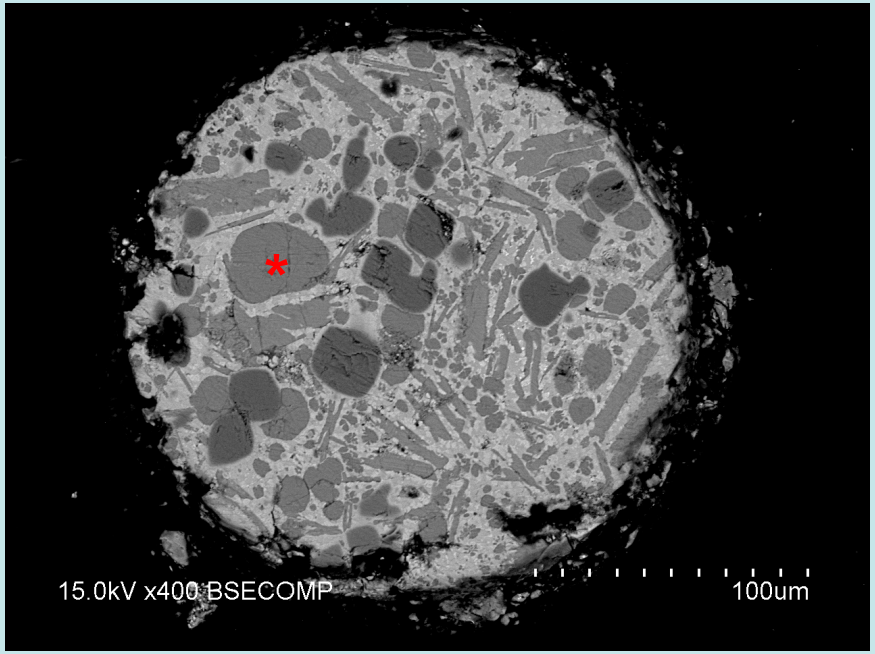


Cross sectioning this particle clarifies its nature



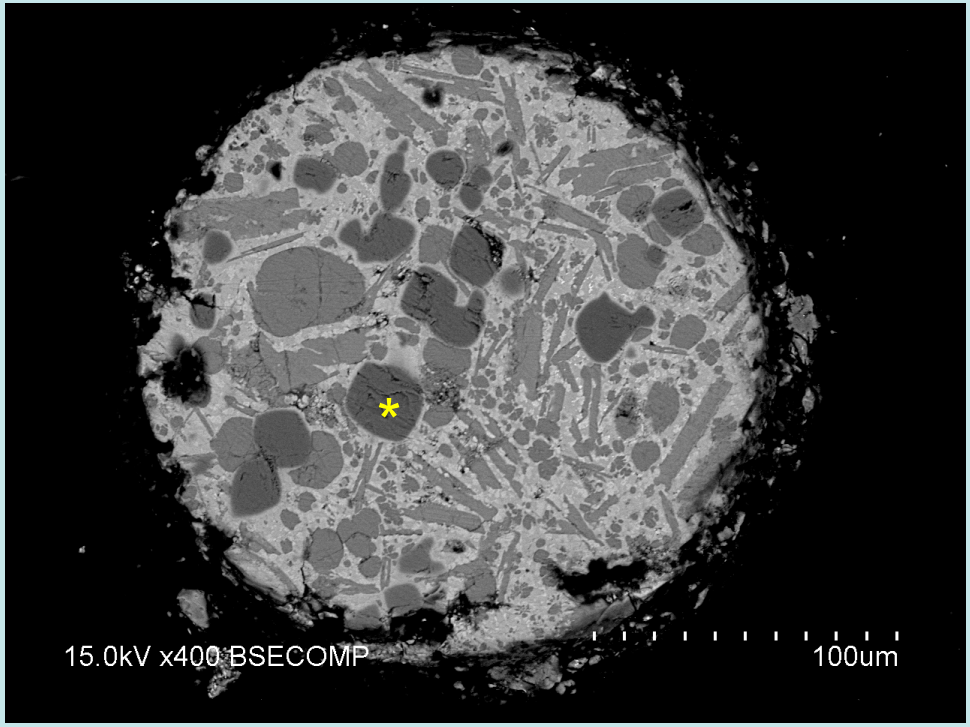
BSE imaging shows at least 4 phases present

The medium grey phase (*) was analyzed both by standardless SEM-EDS and WDS. EDS values for the major SiO_2 and CaO are within 5% of the more accurate WDS-EPMA.



This appears to be a Ca_2SiO_4 phase (~larnite) with some Mg, Fe and P substitution.

	SiO2	TiO2	Al2O3	Fe2O3	Mn2O3	CaO	MgO	P2O5	ExcessO	Total
WDS	30.99	0.22	0.36	1.86	0.42	63.41	0.54	1.89	0.96	100.68
EDS	32.42	0.33	0.33	1.69	0.57	61.62	0.33	2.18	NA	100.00



The dark phase (*) appears to be a Mg-rich spinel with some Mn and Fe, i.e. $(MgMnFe)_3O_4$.

The identity of the light grey matrix phase is not immediately obvious, though seems to have a large Fe+Mn component (~70 wt% Fe_2O_3+Mn_2O_3) plus MgO and CaO.

Conclusions

Small atmospheric Fe-oxides from BOF can be identified as magnetite or hematite by EBSD or WDS-EPMA.

EBSD appears to be the simplest technique, requiring no delicate sample preparation (i.e. mounting and cross sectioning), permitting ID of the raw particles.

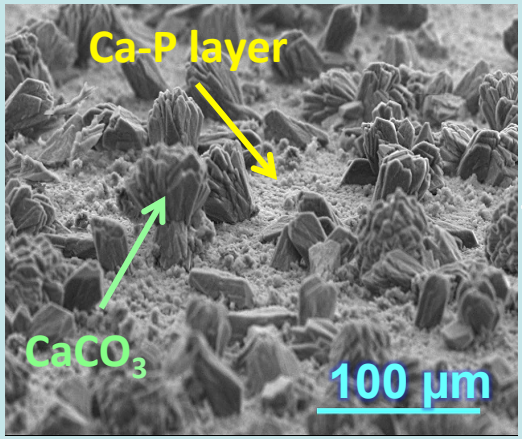
More complex particles from BOF that are rich in CaO and SiO_2 and composed by at least 4 phases cannot be adequately characterized by simple SEM-EDS of the raw particles. Particles must be sectioned and then characterized by EDS or WDS.

Some other particles +
EBSD
that I have known….

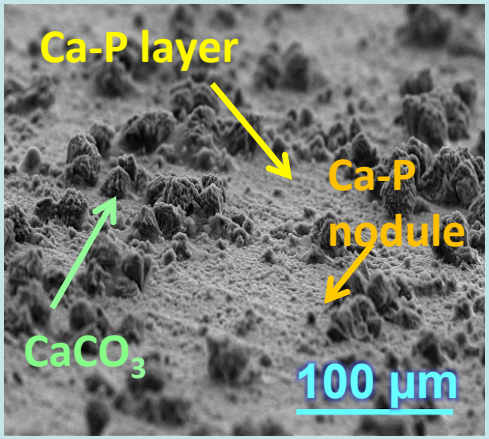
SURFACE TEXTURE EFFECTS ON PRECIPITATES FORMED

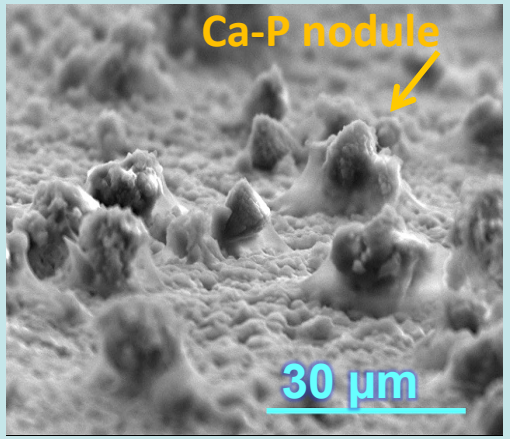
Using Stem Cells (Initial seeding density: 30,000 cells/cm^2, 13 days)

psWs control - hMSC cells

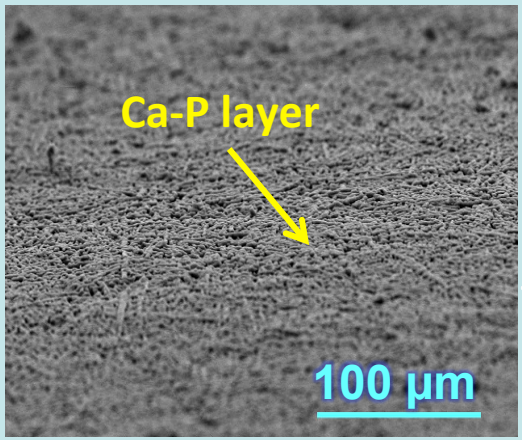


psWs + hMSC cells

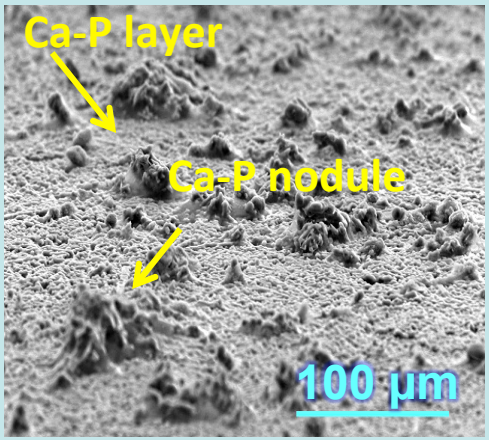


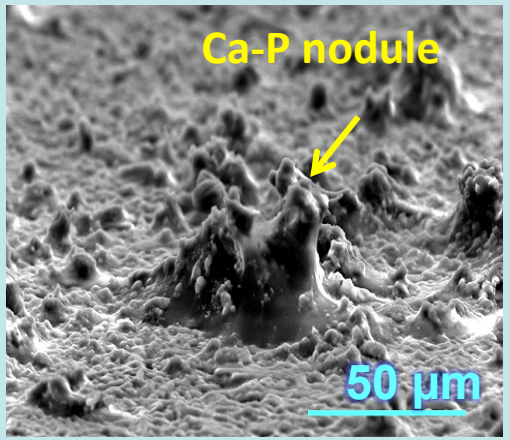


psWr control -hMSC -cells



psWr + hMSC cells

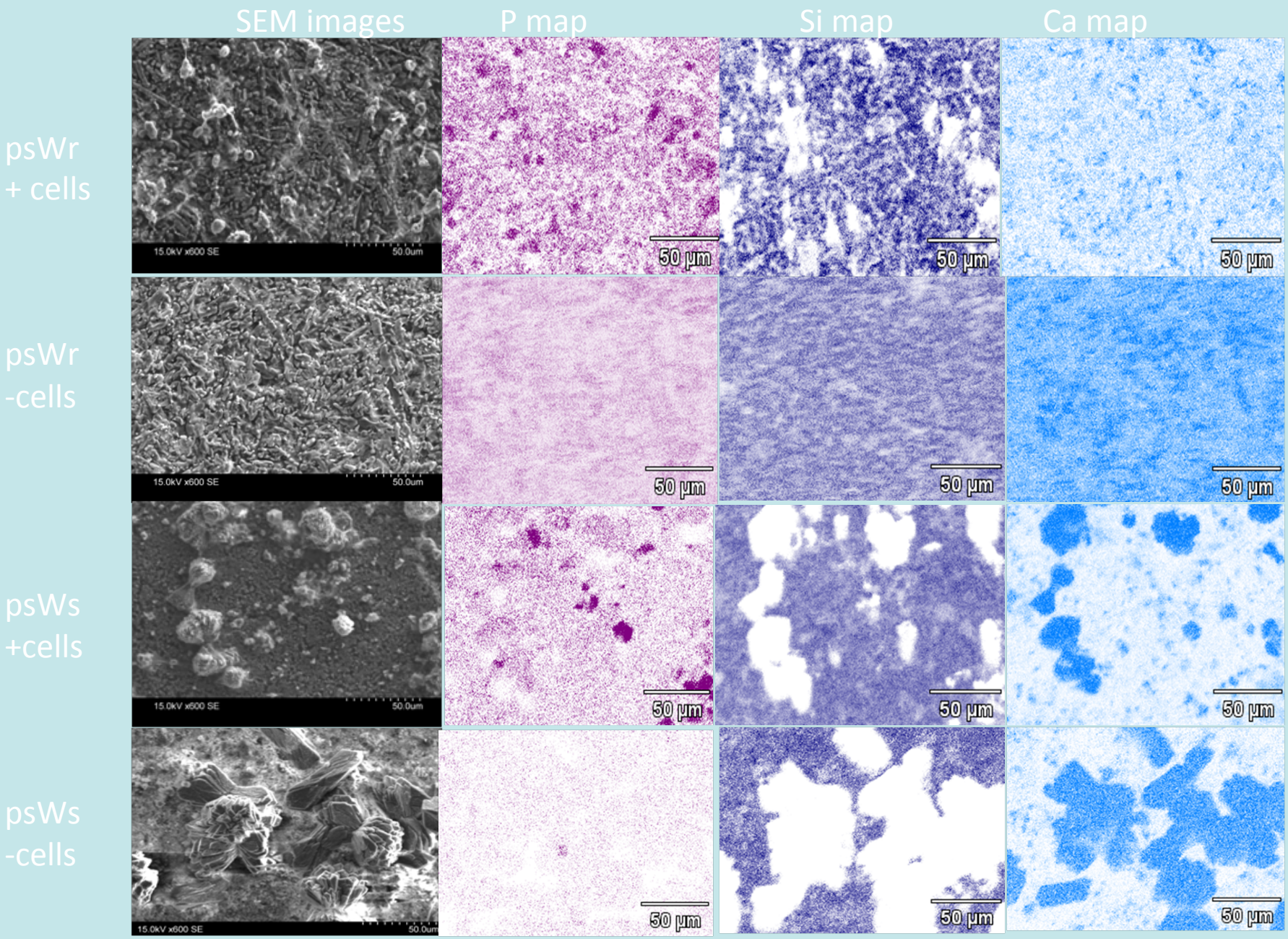




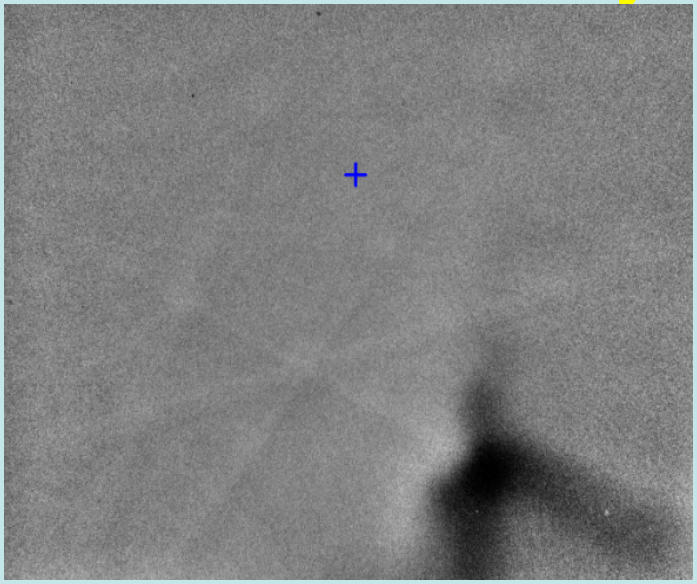
- Ca-P background layer ⇒ chemical processes
- * Calcite crystals on psWs ⇒ chemical processes

Research of Nianli Zhang / Nita Sahai

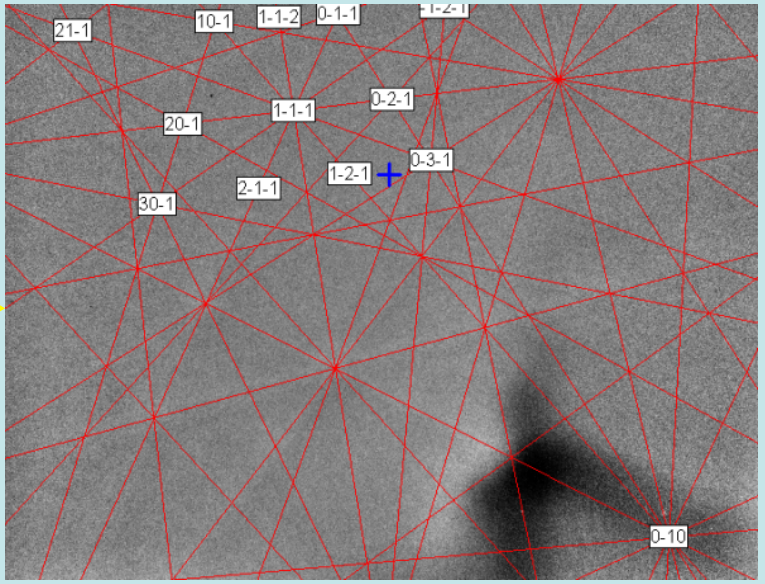
* Ca-P nodules on psWr and psWs ⇒ cell activities

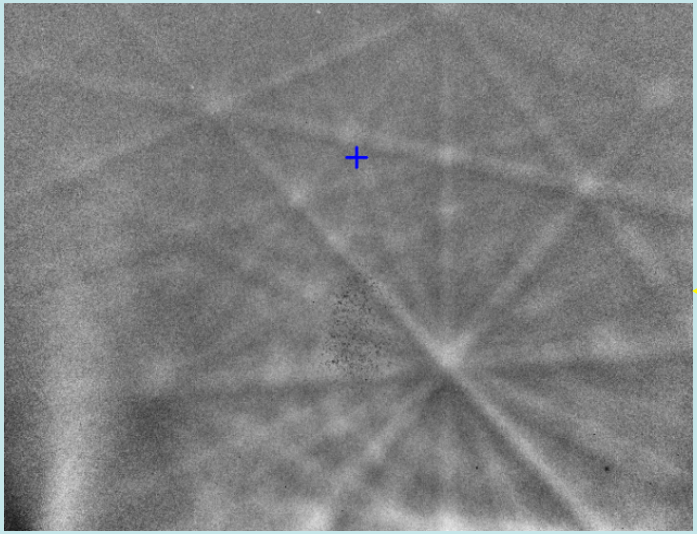

SEM images
P map
Si map
Ca map
psWr
+ cells
psWr
-cells
psWs
+cells
psWs
-cells
15.0kV x600 SE
50.0um
50 µm

Calcite only found on psWs surfaces

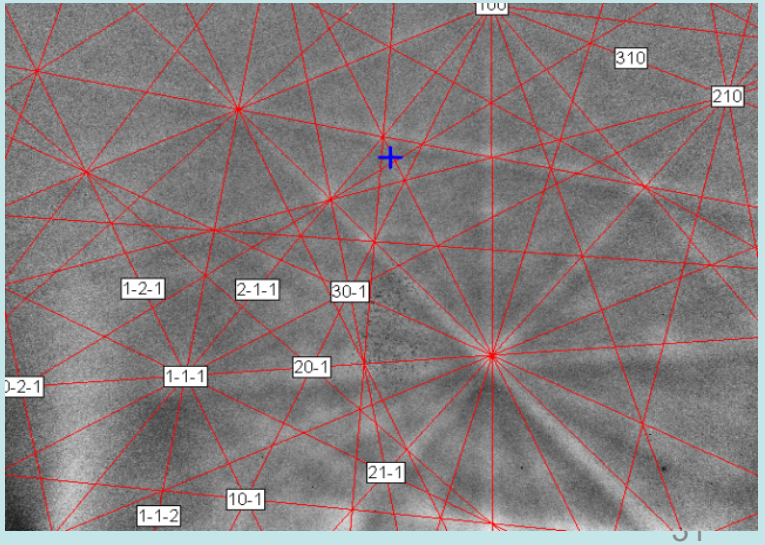


Cacite on psWs + cells

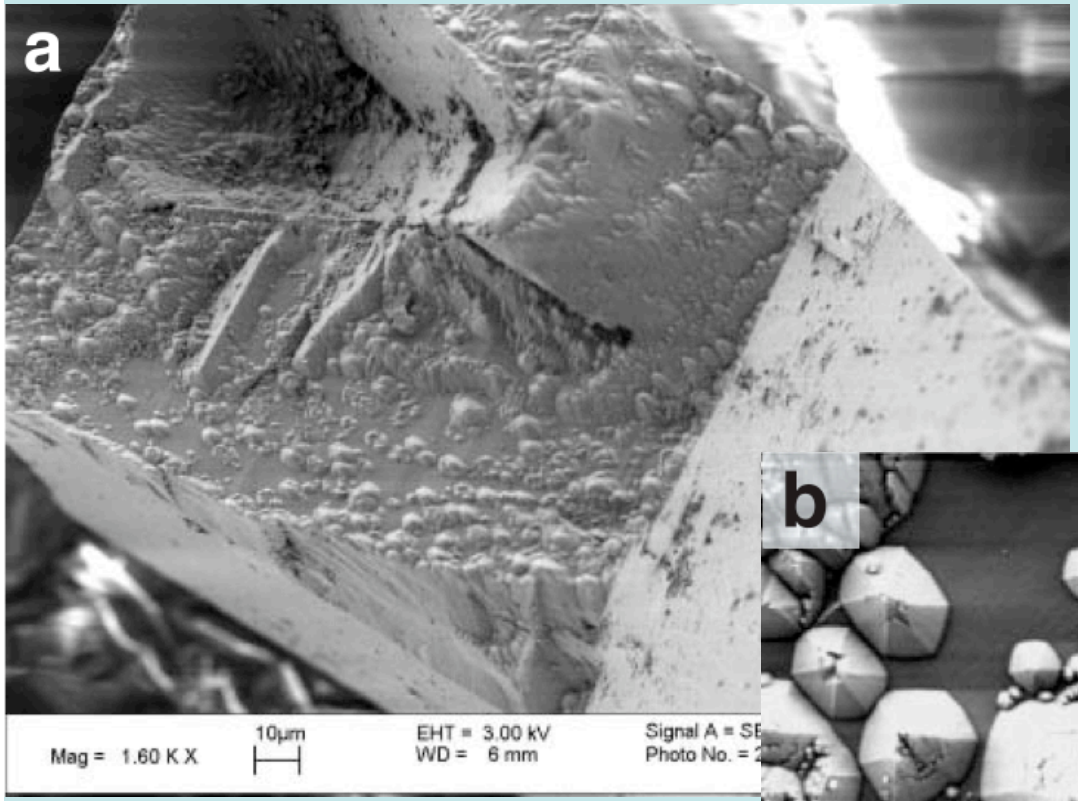




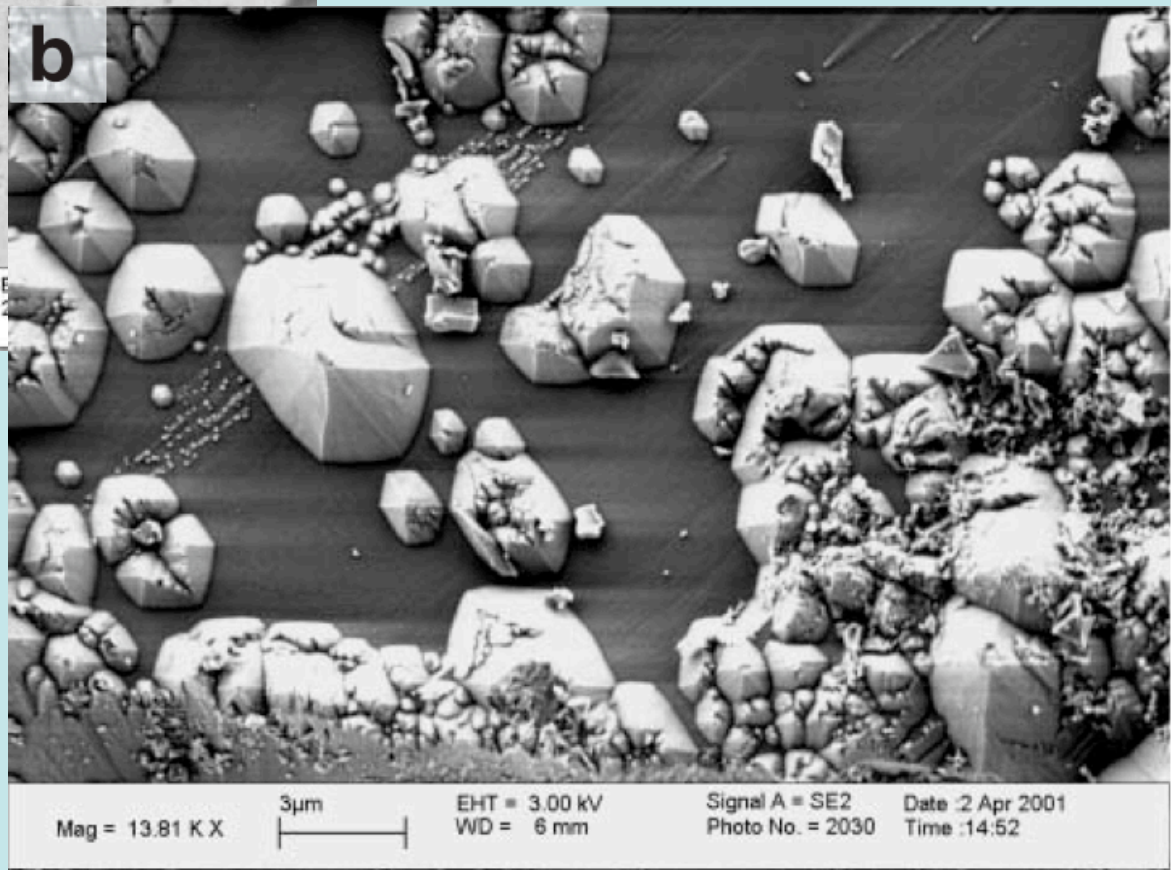
Cacite on psWs - cells



Particles from Mt Pinatubo eruption ash:



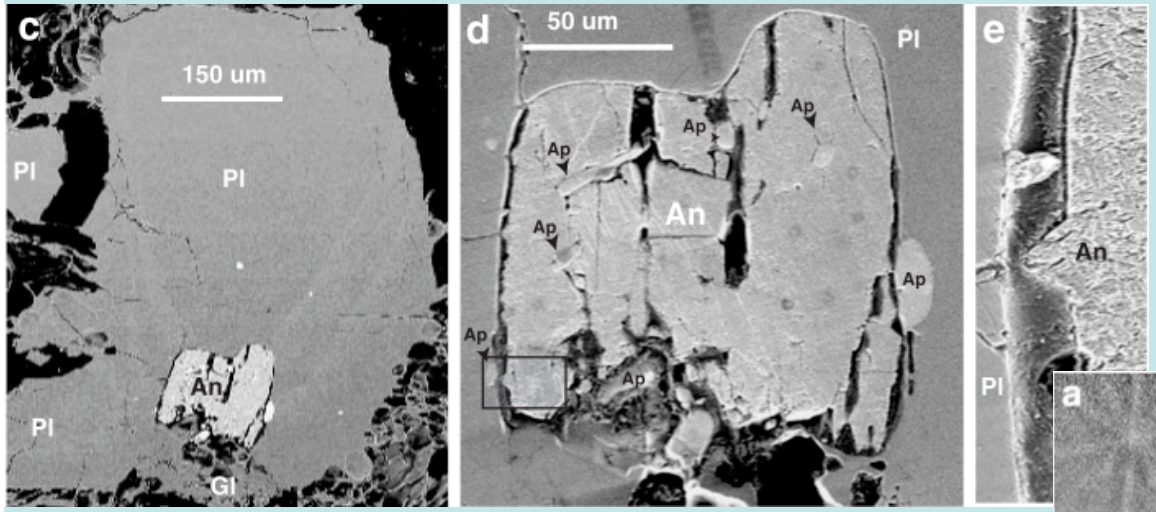
Separated ~100 um anhydrite ($CaSO_4$) crystals



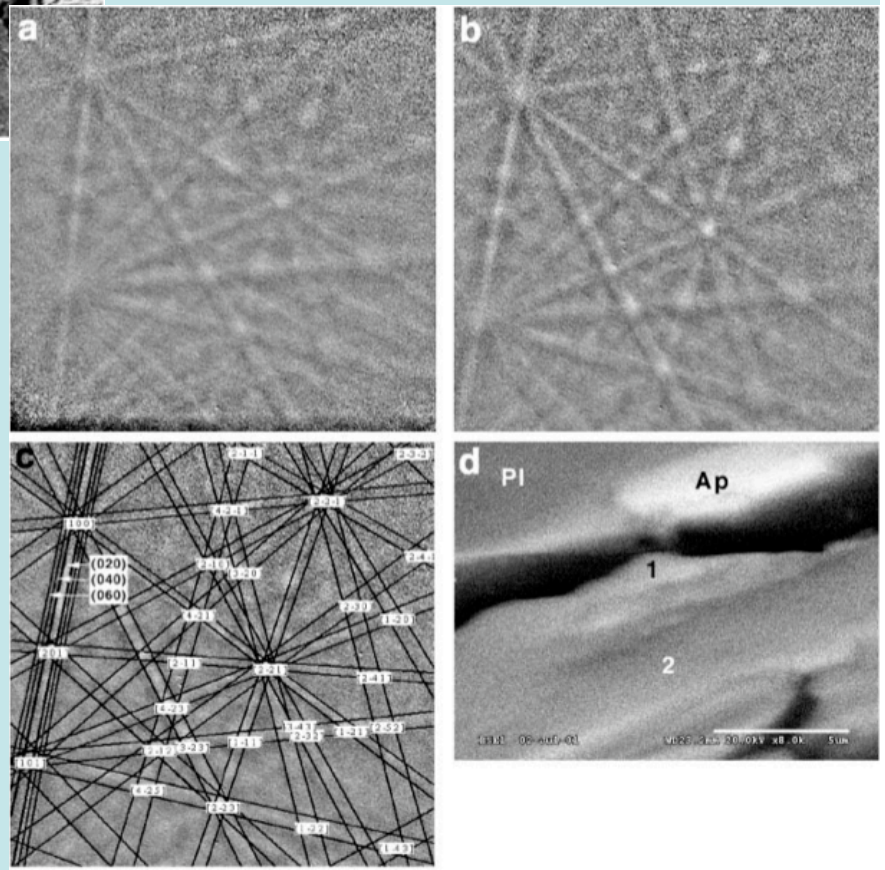
But they have tiny pyramidal particles on some surfaces …

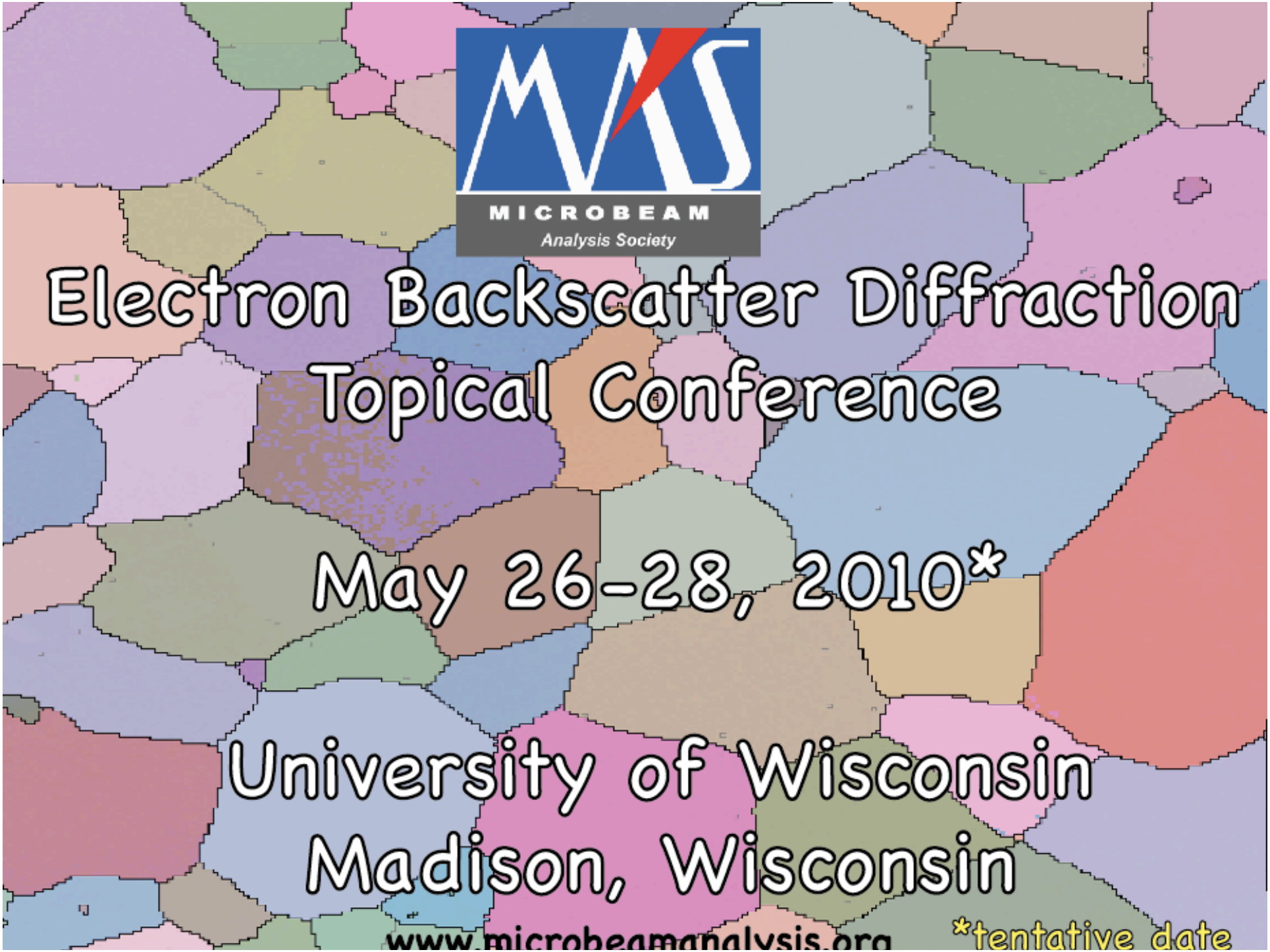
What are they?

EDS: Ca, S, O …but could be any of multiple Ca sulfate phases… gypsum, hemihydrate, anhydrite



…do EBSD on anhydrite crystal trapped in plagioclase (=proof all happened at depth in magma chamber) with trapped pyramid at edge … both anhydrite

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Electron Backscatter Diffraction
Topical Conference
May 26-28, 2010*
University of Wisconsin
Madison, Wisconsin
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*tentative date