

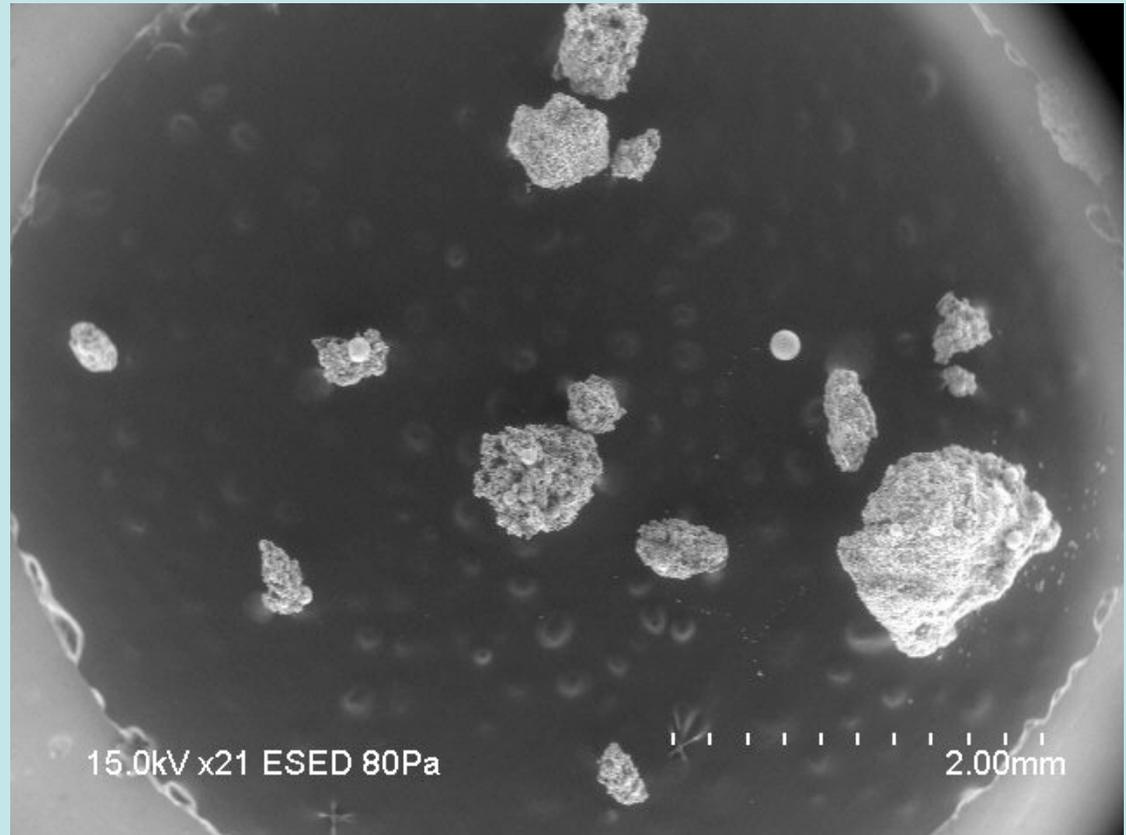
Evaluating atmospheric particles - using EDS, WDS and EBSD

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University of Wisconsin-Madison

Background

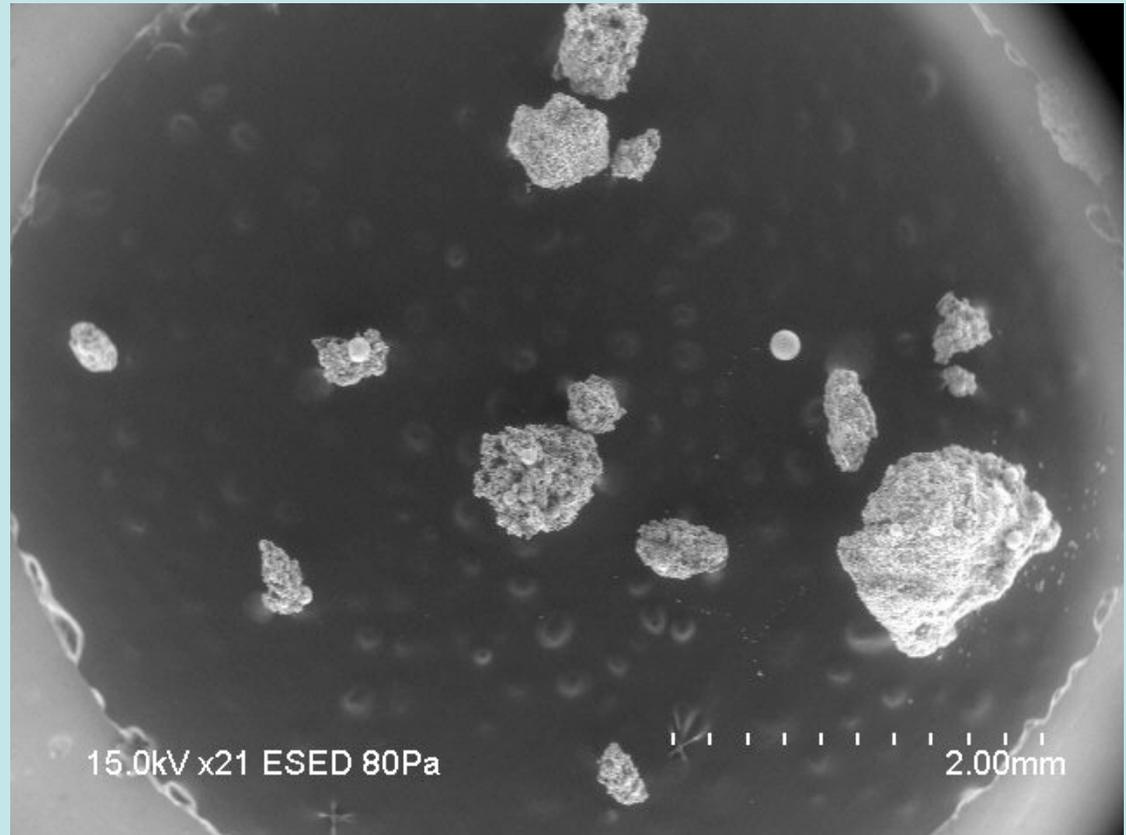
A sample of “small” particles collected in the vicinity of a basic oxygen furnace (BOF) was obtained from Bob Willis (EPA) with Joe Conny’s (NIST) assistance.



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

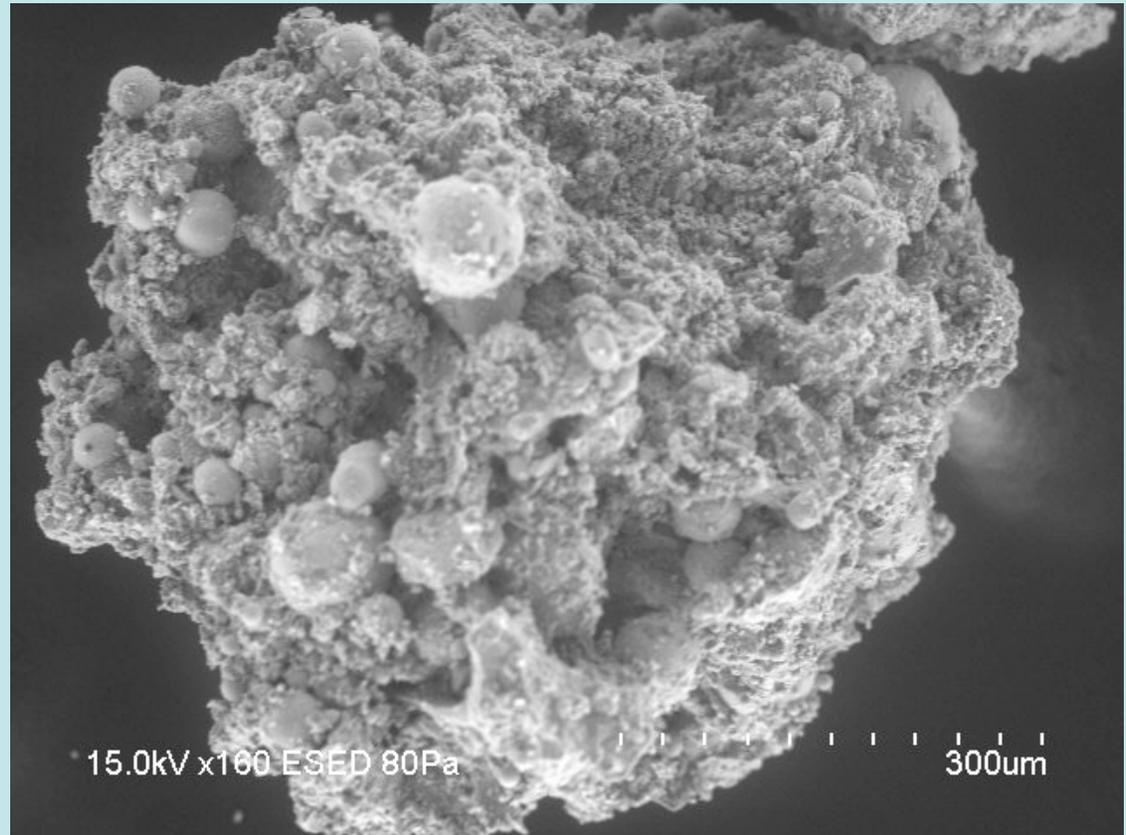
SEM-EDS examination showed 2 general types of spheres: some type of Fe-oxide, and others with more complicated chemistry (Ca, Al, Fe, Mg, P, O ...)



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Background

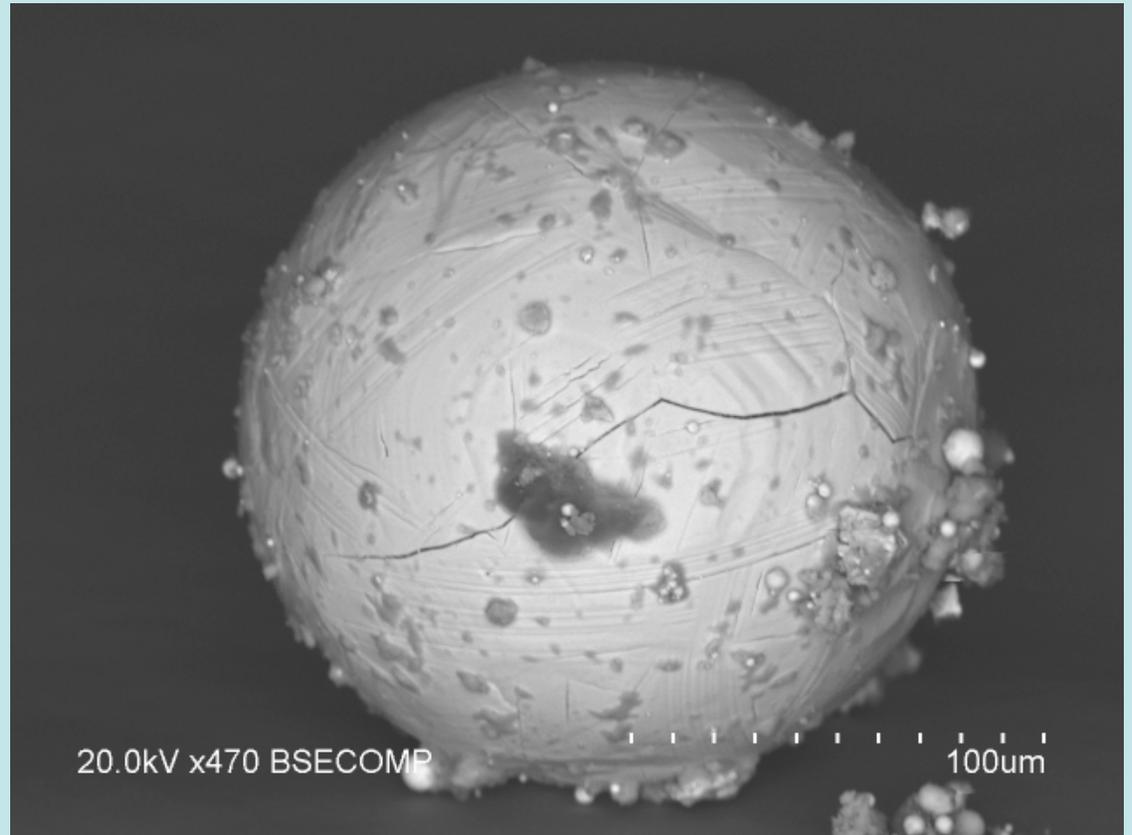
Particles ranged from submicron up to ~ a few hundred microns, with agglomerations even larger



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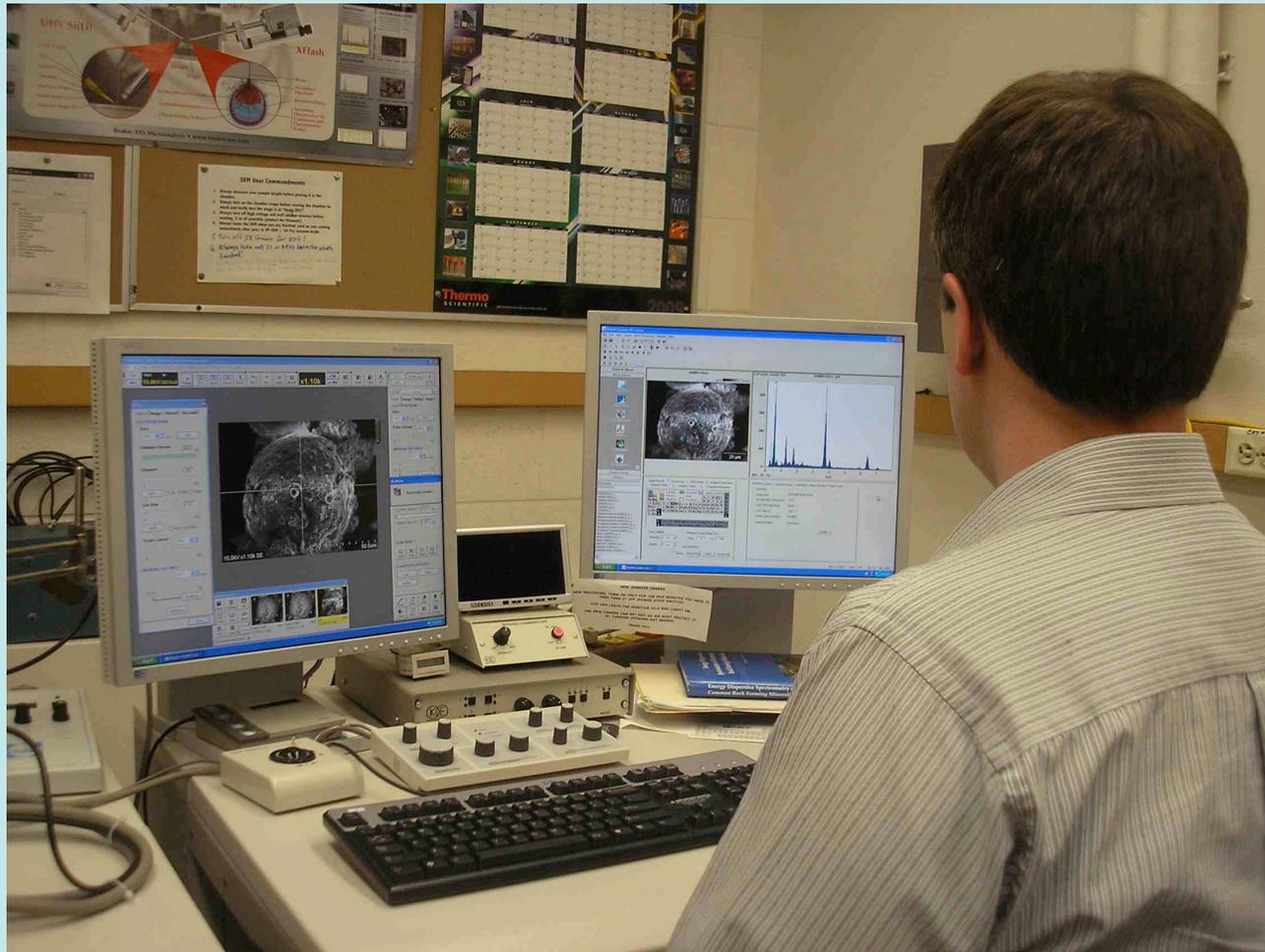
Background

Fe oxide
spheres of
various sizes



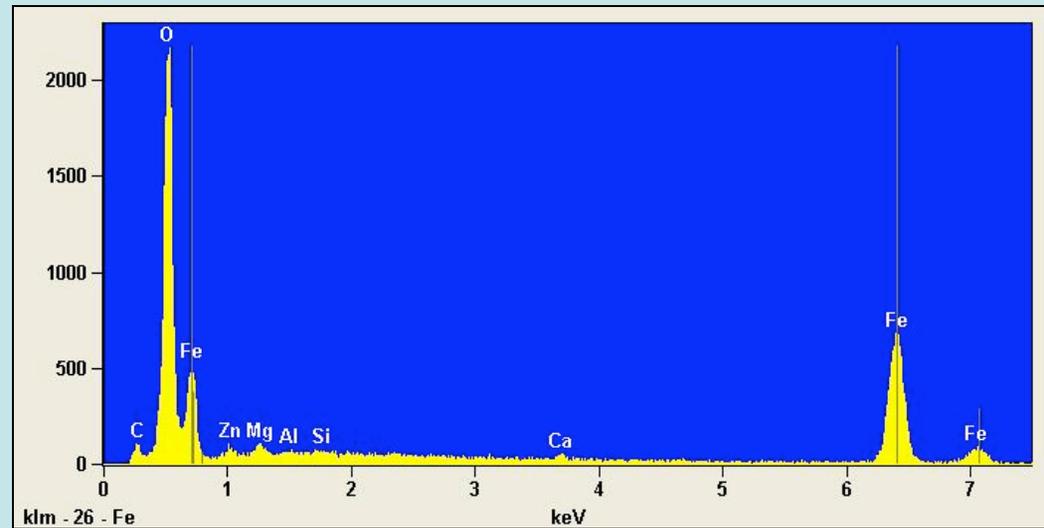
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The normal approach typically would be to mount the grains on a stub and examine using EDS in an SEM



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 K α .



Nominal compositions:

Mt = Fe₃O₄ = Fe 72 wt% O 28 wt%

Hm = Fe₂O₃ = 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

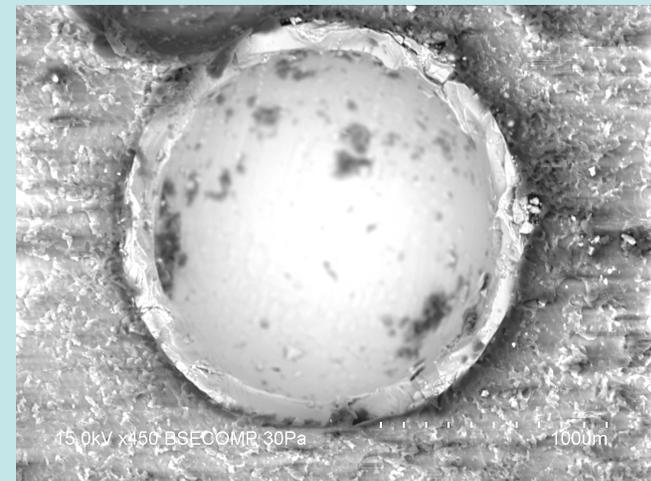
How do you prepare a small particle for WDS? That is, how do you make it polished, flat?

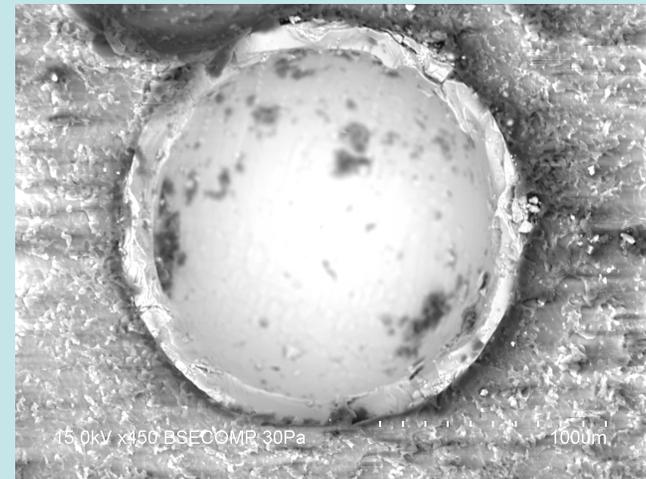
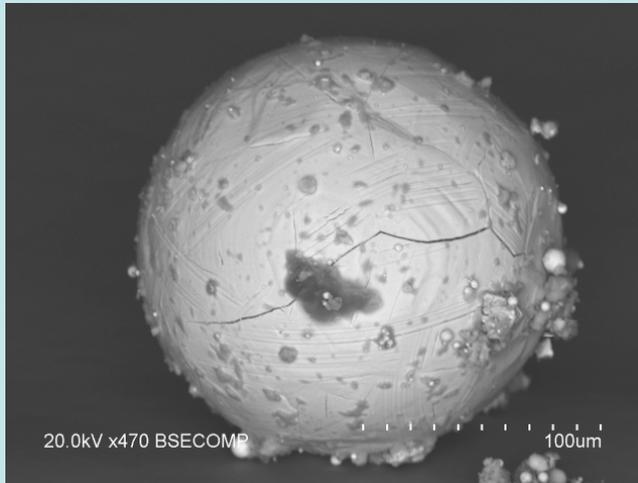
It's not the easiest thing in the world, and "it depends" upon the material and the exact size and the quantity available, but it is not impossible...

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

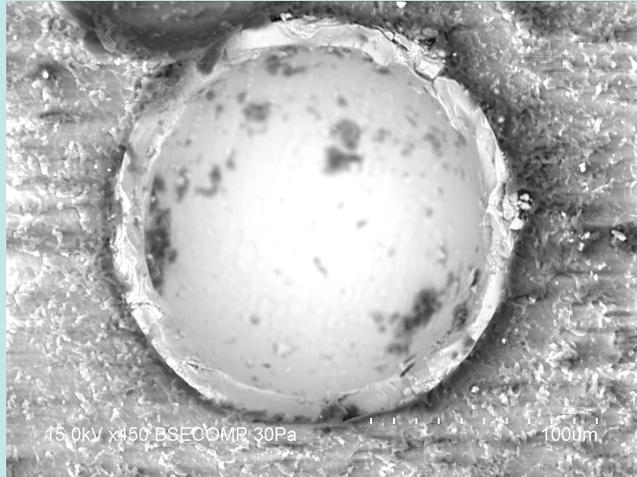


- Carefully position particles on sticky tape (transfer using eyelash glued to popsicle stick or 'orange' wood stick) and surround with small (e.g. 1/4" OD) tube
- Cover/embed with low viscosity epoxy (e.g. epothin)
- Very carefully polish with fine diamond embedded mylar (no loose abrasives) for very short periods





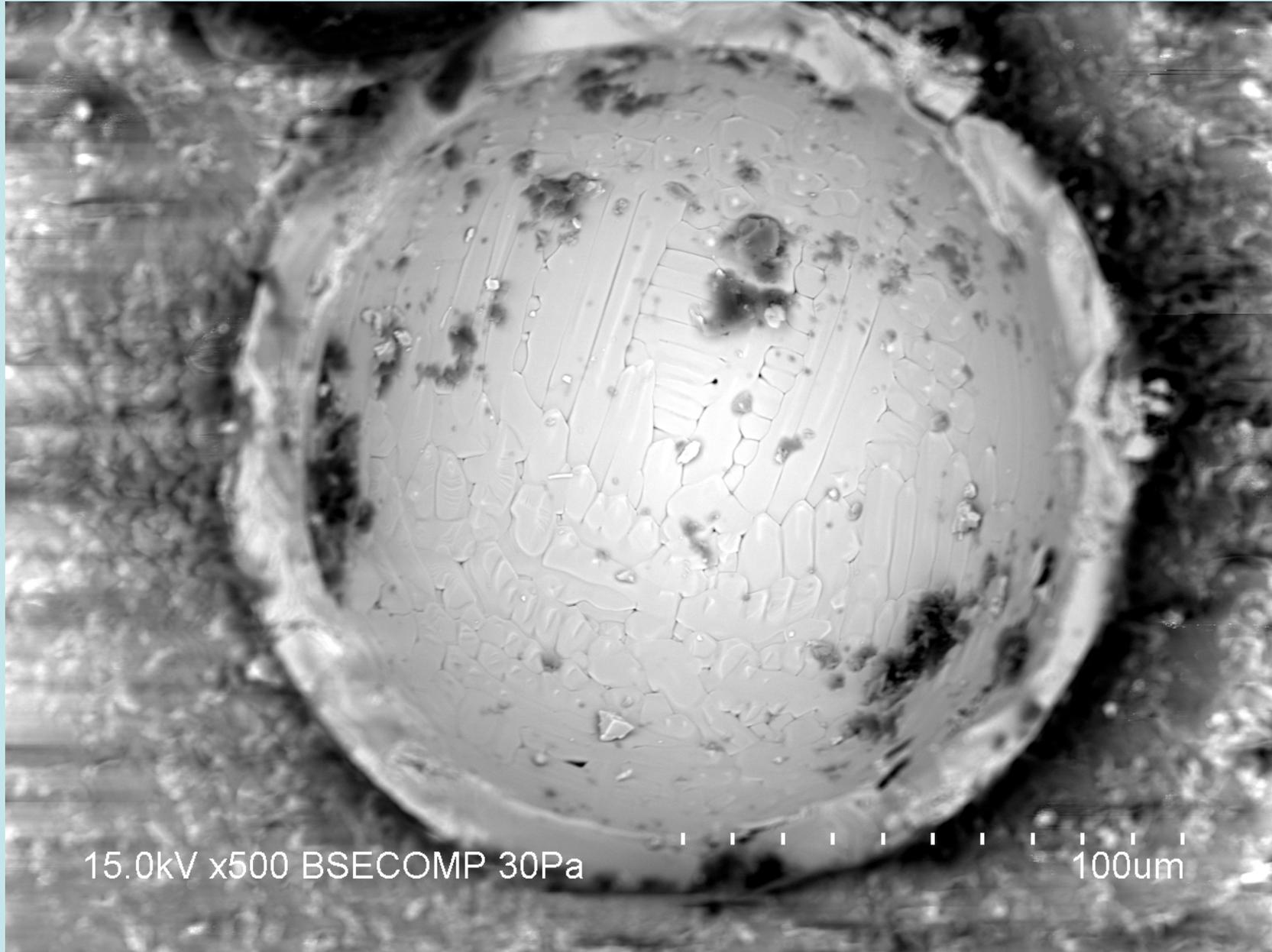
- Small, flat regions ~15 microns wide are created
- Quantitative EPMA requires flat surfaces
- Several regions were analyzed by WDS-EPMA with our SX51 and using Fe₂O₃ and Fe₃O₄ standards



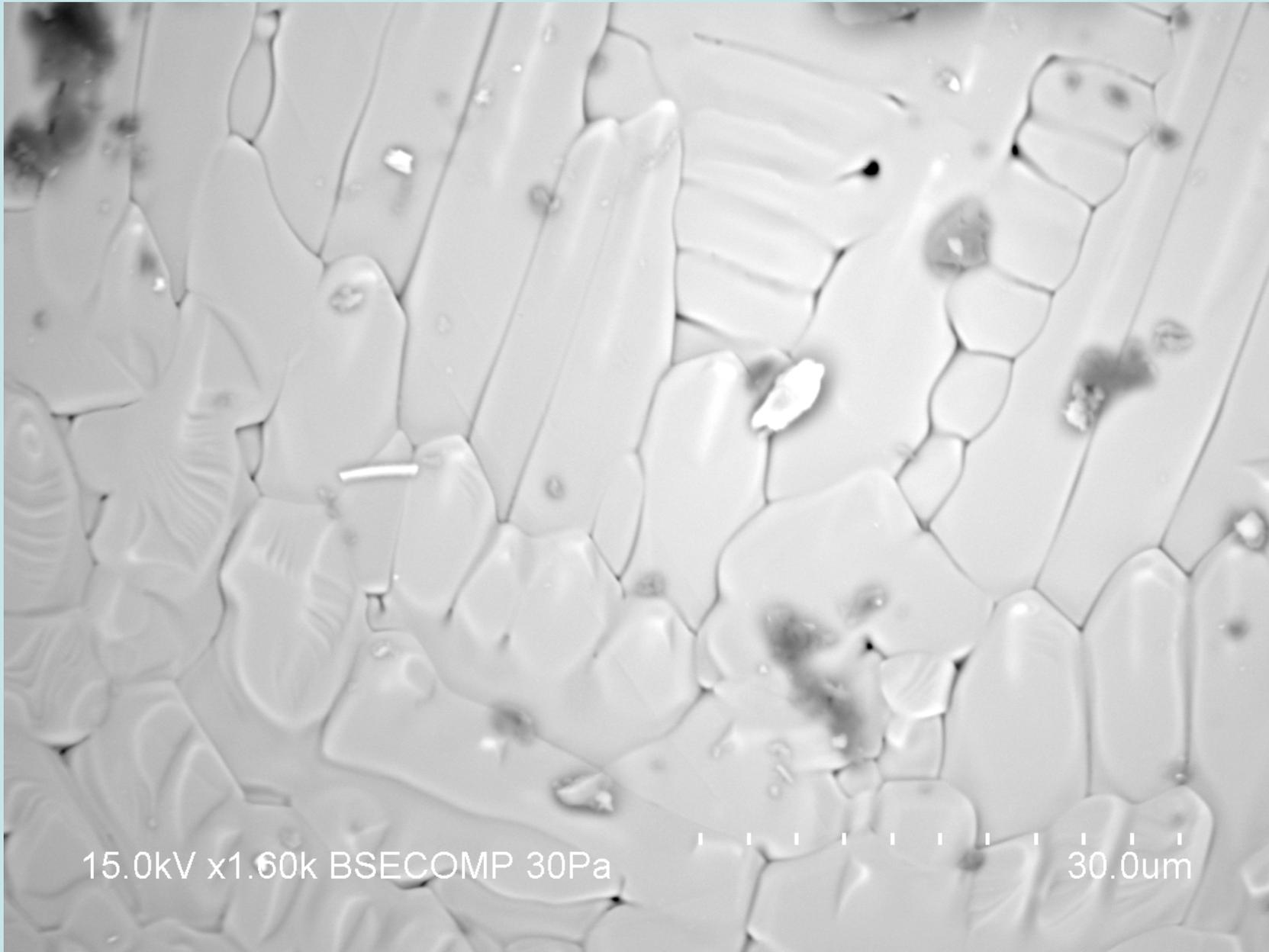
Mt = Fe₃O₄ = Fe 72 wt% O 28 wt%
Hm = Fe₂O₃ = Fe 70 wt% O 30 wt%

- 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?

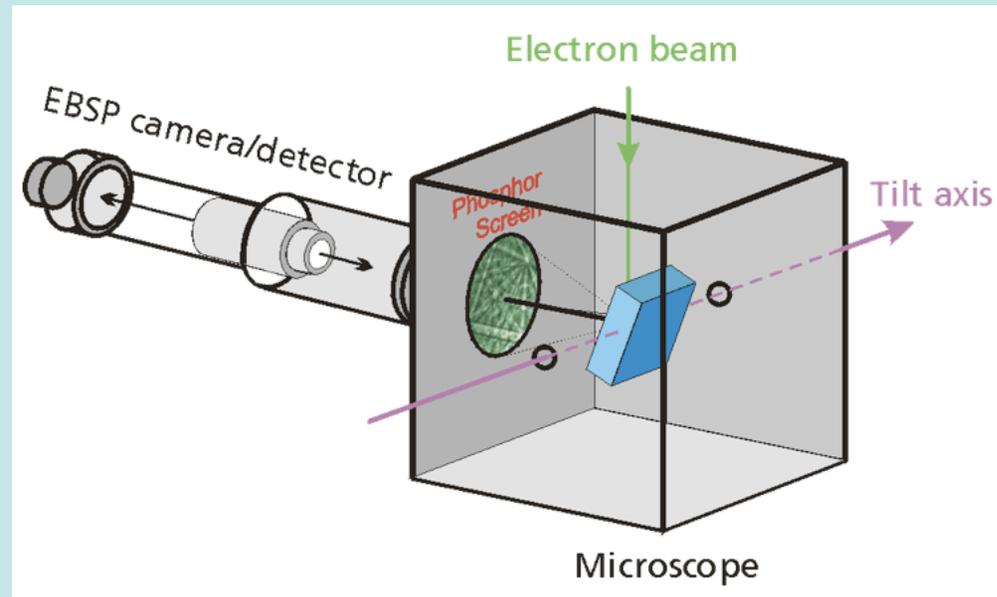


EBSD of Fe-oxide particles

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

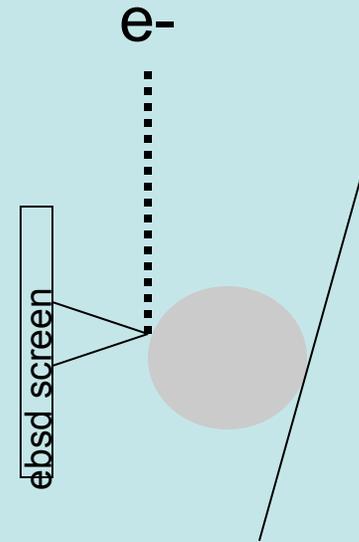
Electron diffraction occurs off the top nanometers of surface ... a surface technique.

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

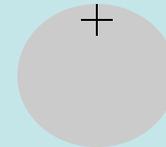
HOWEVER, 'natural' particles many times do not require special treatment and can be examined "as is".

Practical issues

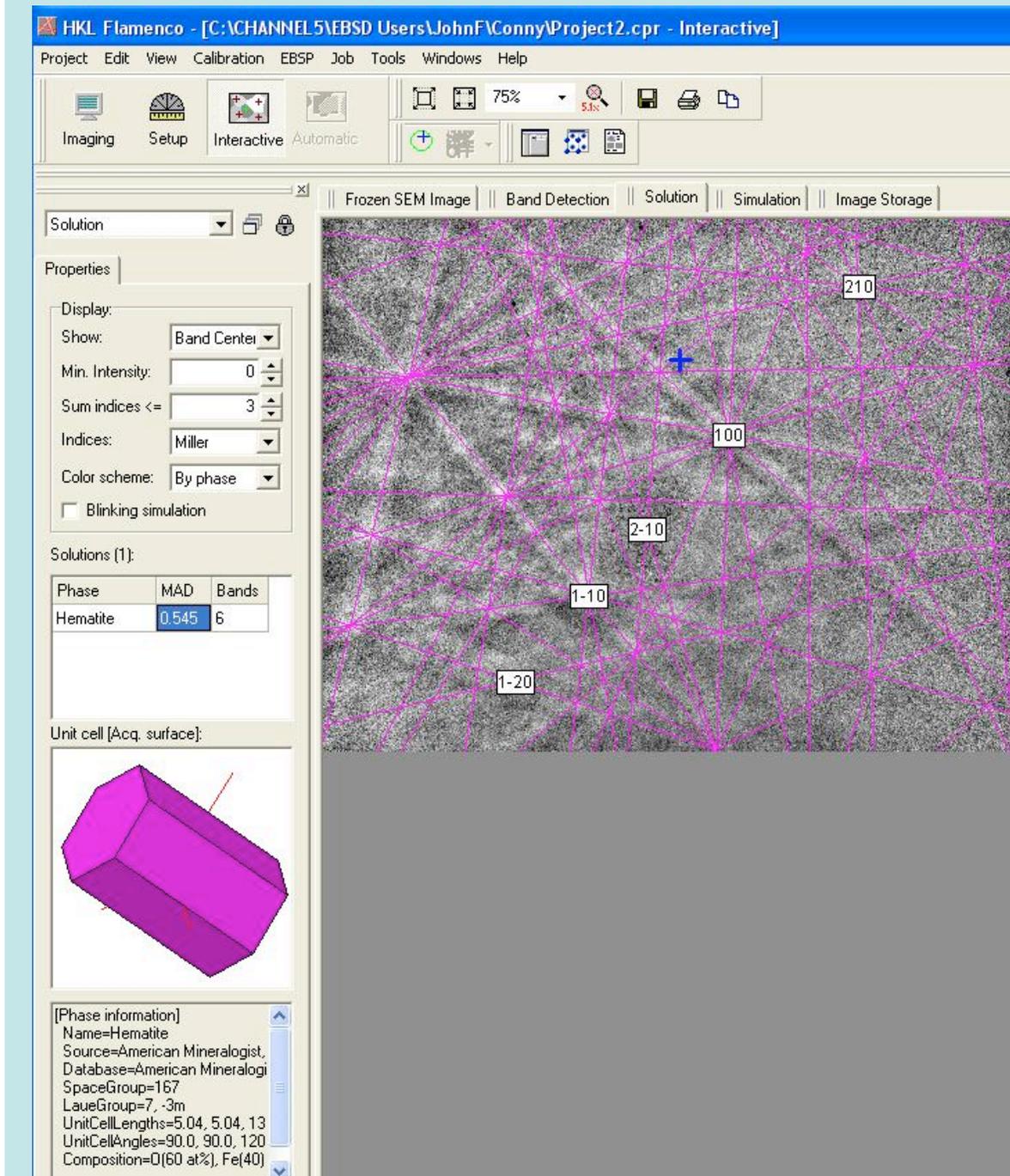
BUT, there may be only a small 'sweet spot' where diffraction can yield electrons that hit the EBSD detector screen



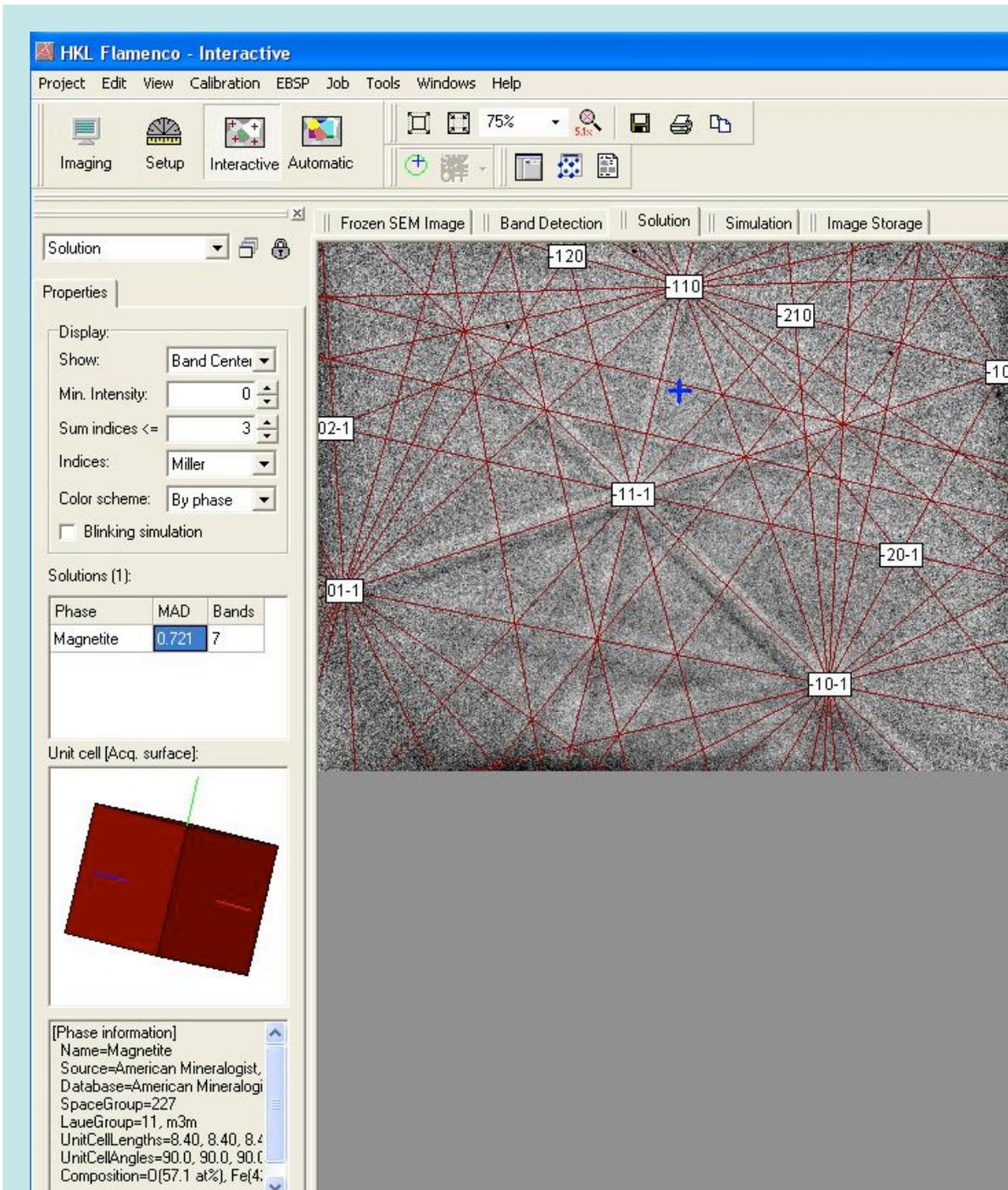
Hypothetical side view



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

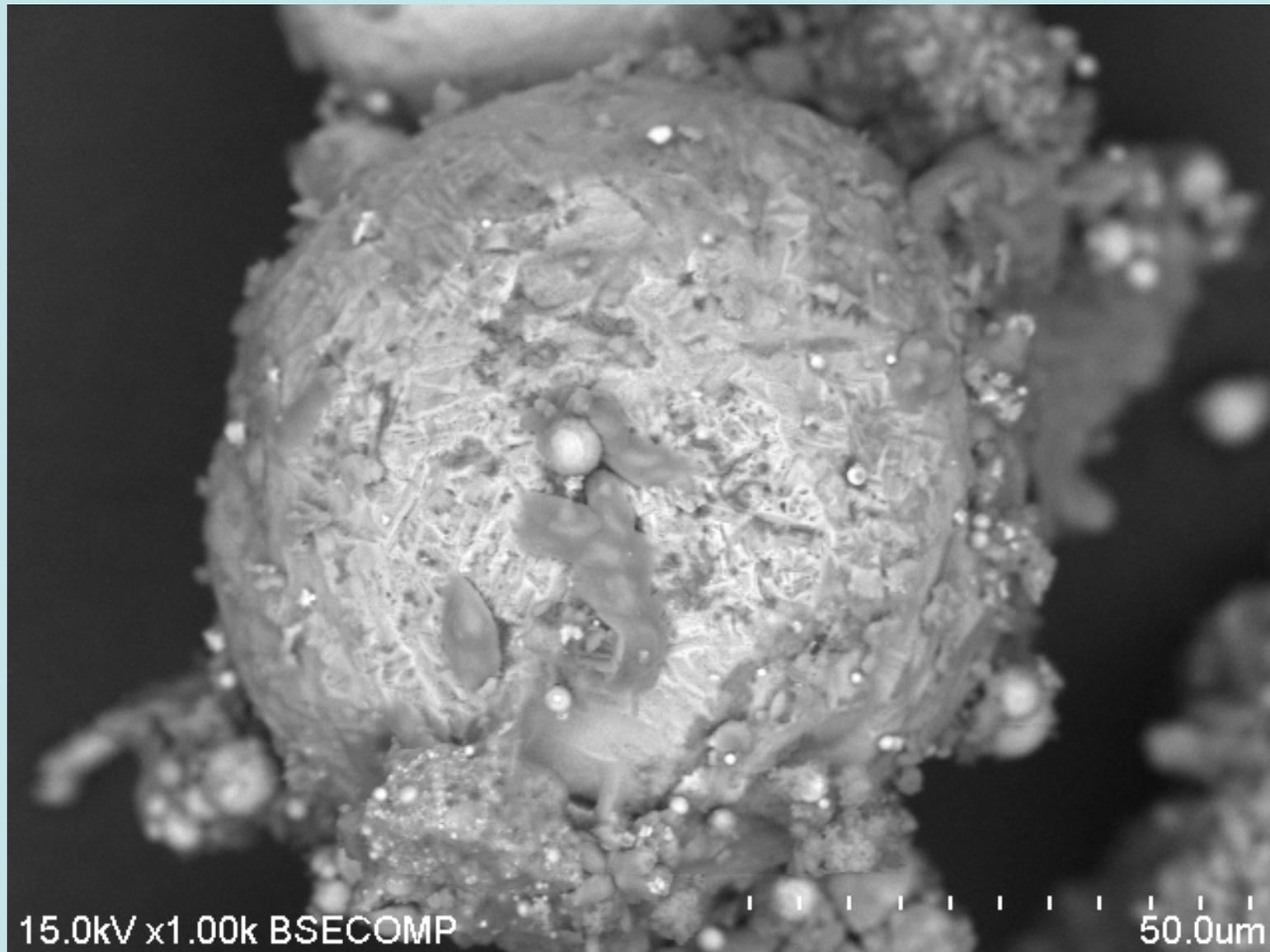
EBSD reconnaissance* of small spheres shows both magnetite and hematite are present...in roughly equal proportions (15 mt, 14 hm)

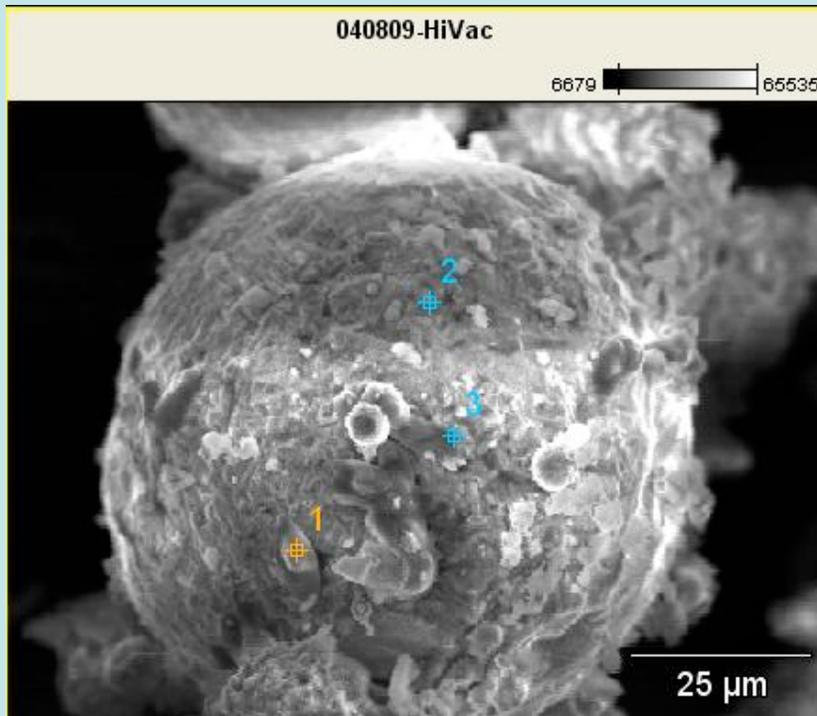
							HM		
							HM		
HM							MT		
HM		HM	HM	HM			MT	HM	
HM	HM	HM	MT	MT	MT	MT	MT	MT	HM
MT	HM	MT	HM						
<1	1	2	3	4	5	10	15	20	30
Diameter in microns									

Histogram of Fe-oxide spheres by EBSD

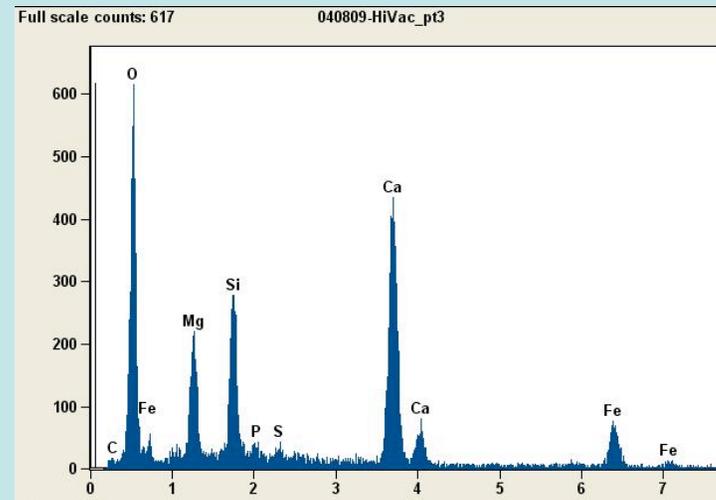
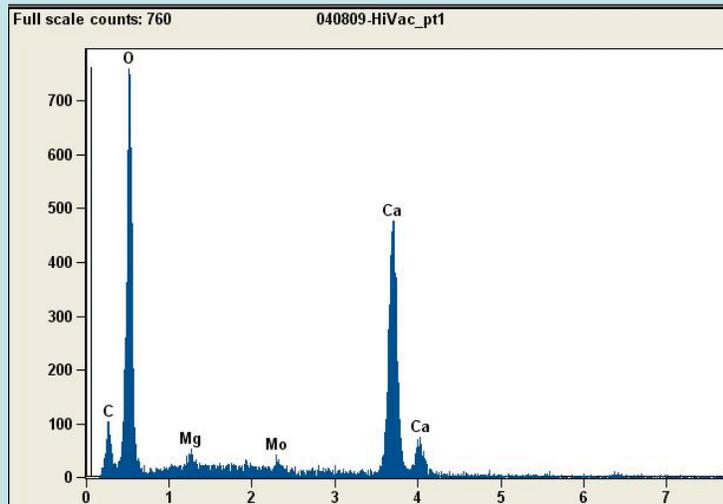
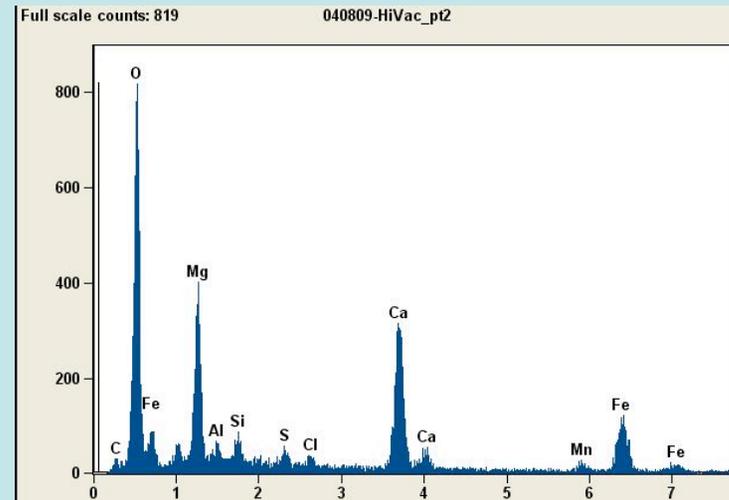
* Approximately 60 spheres were examined over ~60 minutes with ~50% success rate

Another particle type was also present...Ca-rich

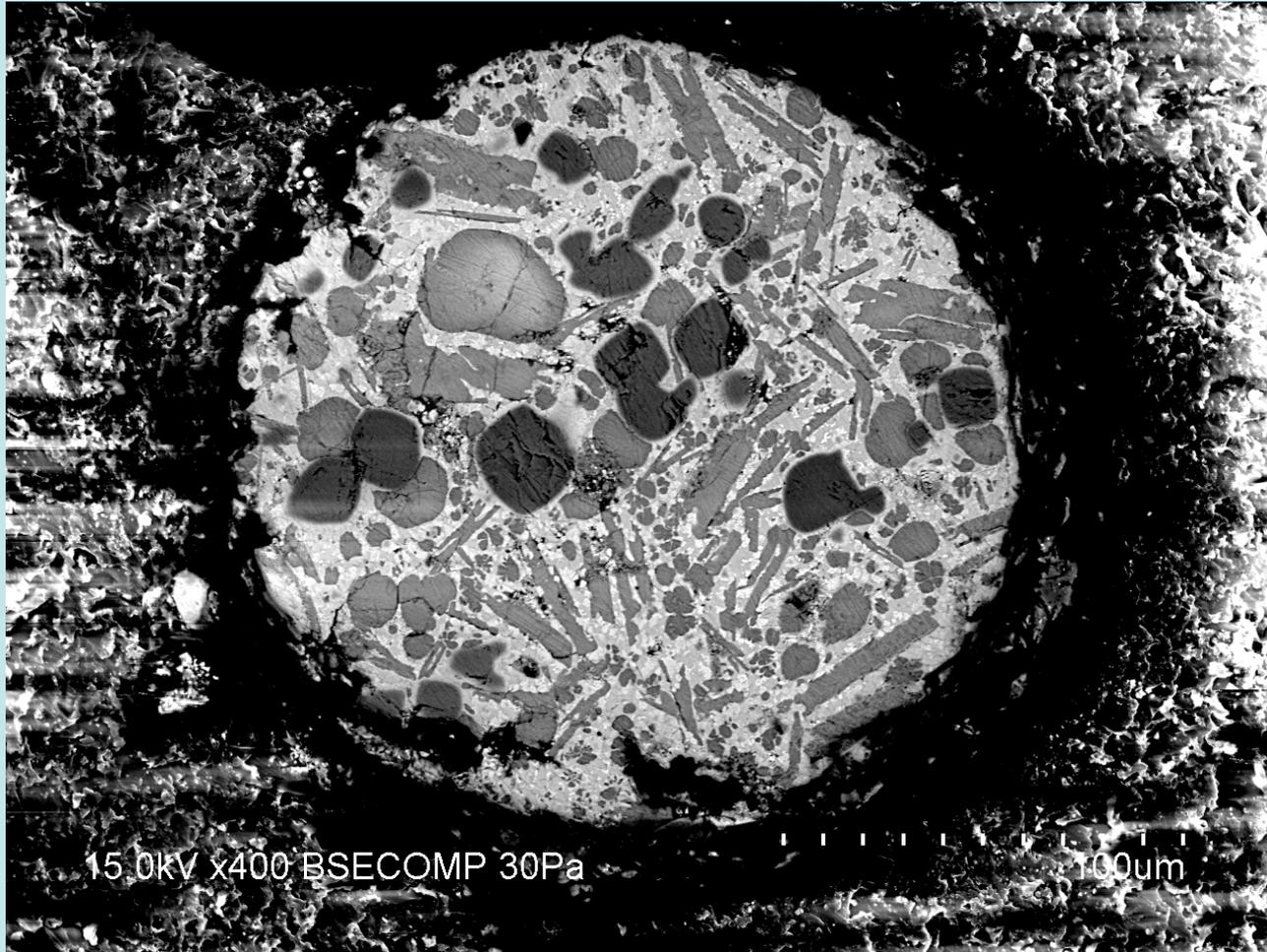




SEM-EDS examination of the outside surface gives a somewhat confusing view of what this particle is

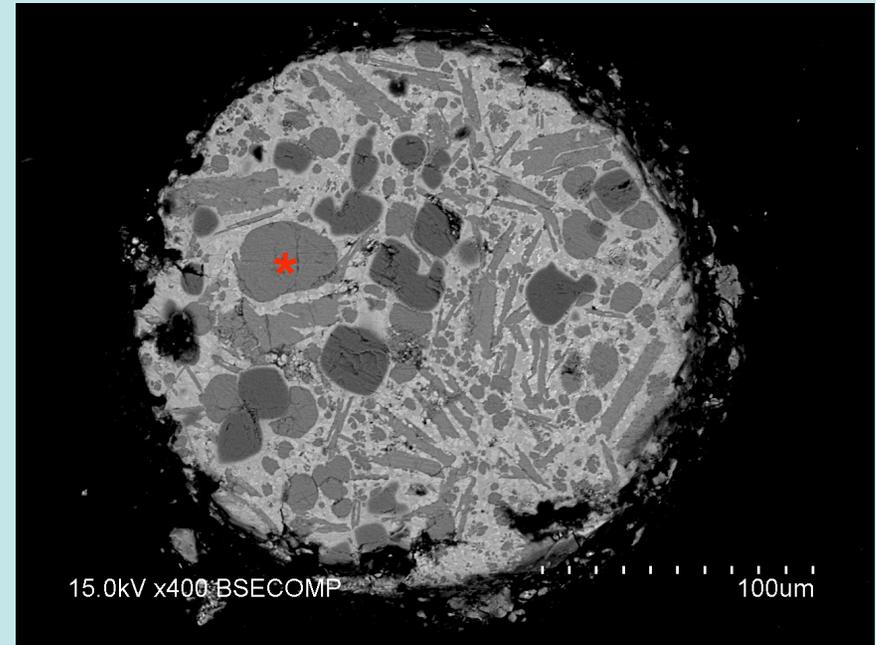


Cross sectioning this particle clarifies its nature



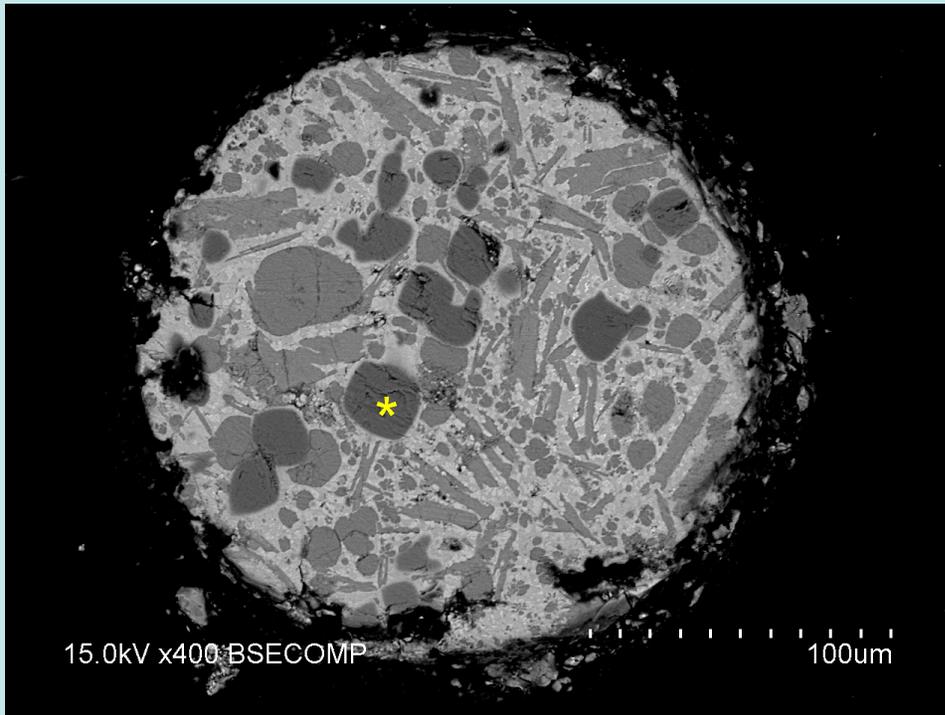
BSE imaging shows at least 4 phases present

The medium grey phase (*) was analyzed both by standardless SEM-EDS and WDS. EDS values for the major SiO₂ and CaO are within 5% of the more accurate WDS-EPMA.



This appears to be a Ca₂SiO₄ phase (~larnite) with some Mg, Fe and P substitution.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	CaO	MgO	P ₂ O ₅	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. $(\text{MgMnFe})_3\text{O}_4$.

The identity of the light grey matrix phase is not immediately obvious, though seems to have a large Fe+Mn component (~ 70 wt% $\text{Fe}_2\text{O}_3 + \text{Mn}_2\text{O}_3$) 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.

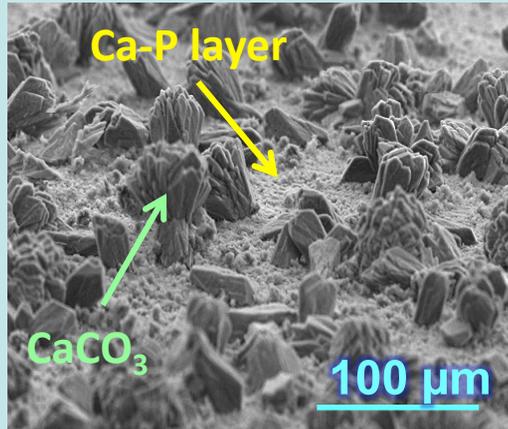
More complex particles from BOF that are rich in CaO and SiO₂ and composed by at least 4 phases cannot be adequately characterized by simple SEM-EDS of the raw particles. Particles must be sectioned and then characterized by EDS or WDS.

Some other particles +
EBSD
that I have known....

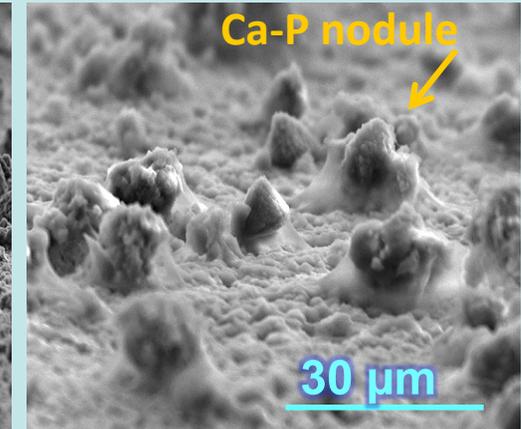
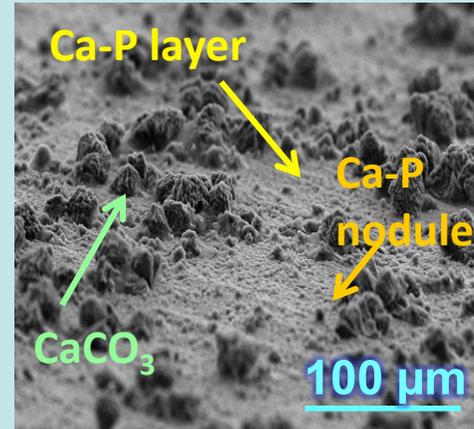
SURFACE TEXTURE EFFECTS ON PRECIPITATES FORMED

Using Stem Cells (Initial seeding density: 30,000 cells/cm², 13 days)

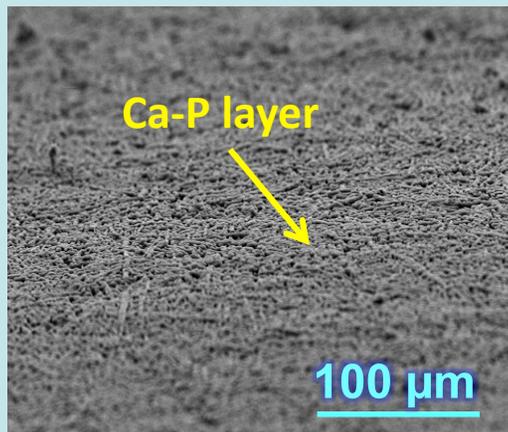
psWs
control
- hMSC
cells



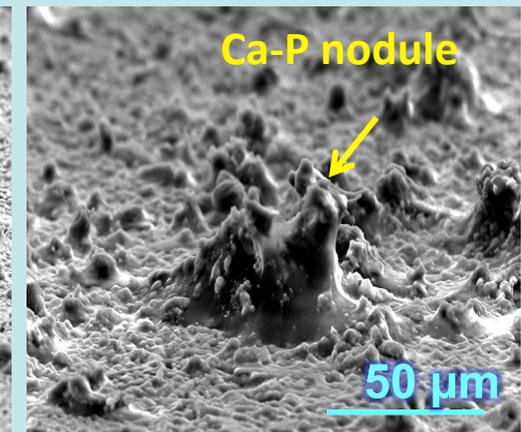
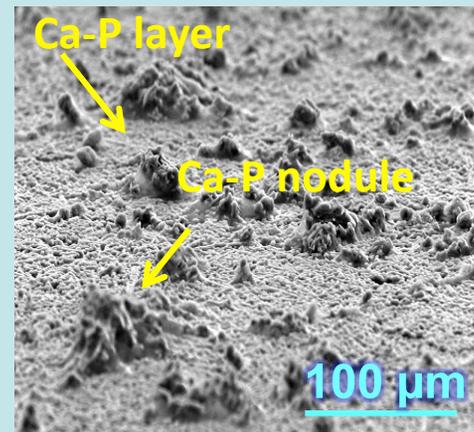
psWs
+ hMSC
cells



psWr
control
- hMSC
- cells



psWr
+ hMSC
cells



Research of
Nianli
Zhang / Nita
Sahai

Ca-P background layer ⇒ chemical processes

* Calcite crystals on psWs ⇒ chemical processes

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

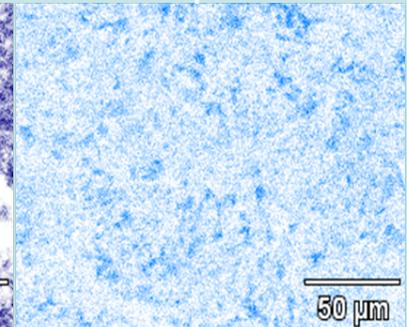
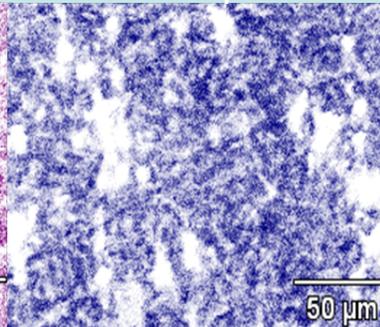
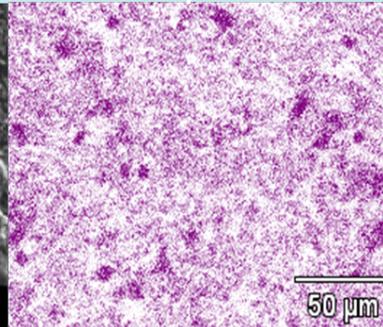
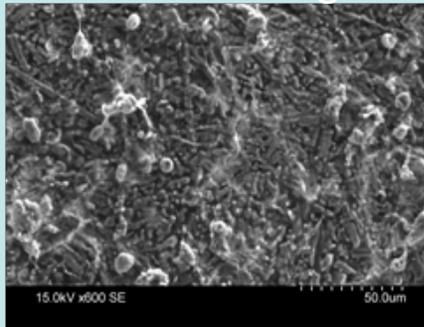
SEM images

P map

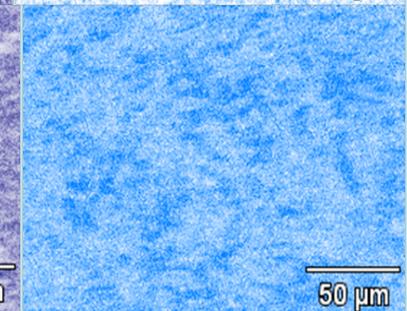
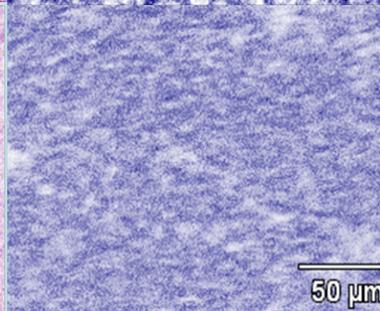
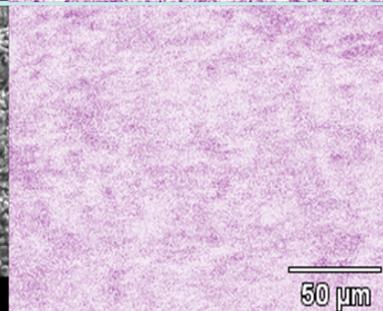
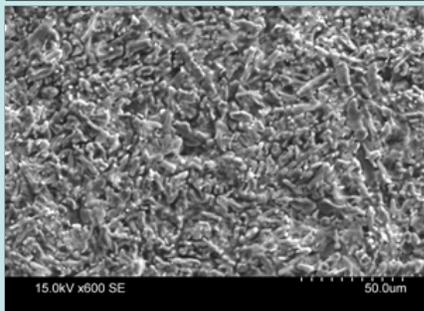
Si map

Ca map

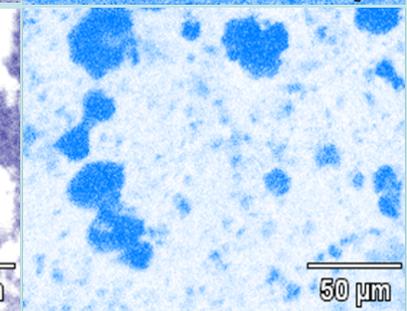
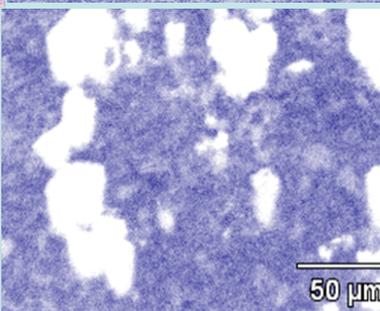
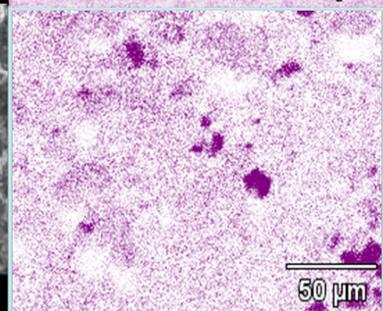
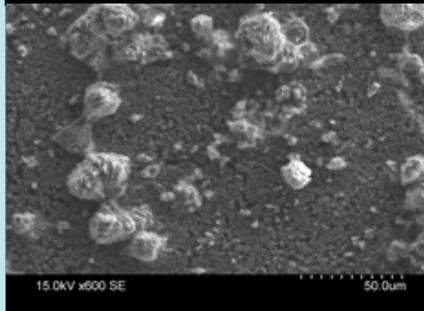
psWr
+ cells



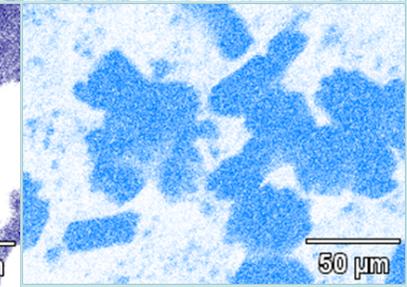
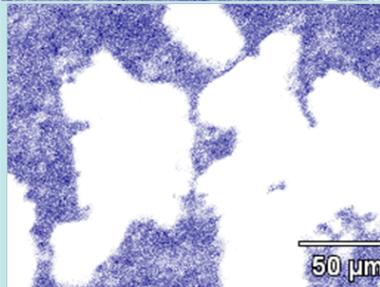
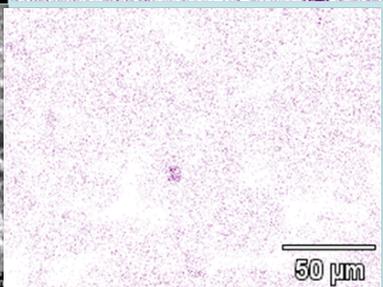
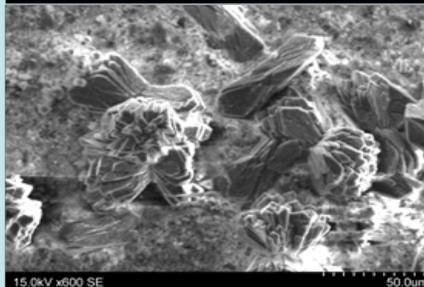
psWr
- cells



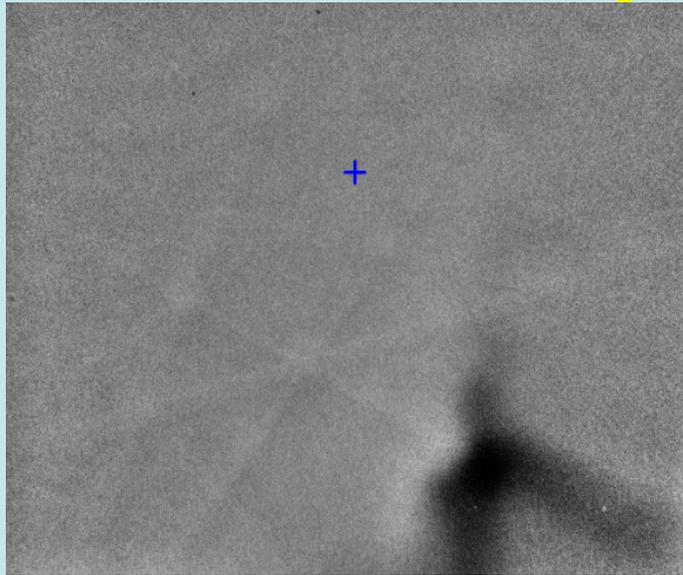
psWs
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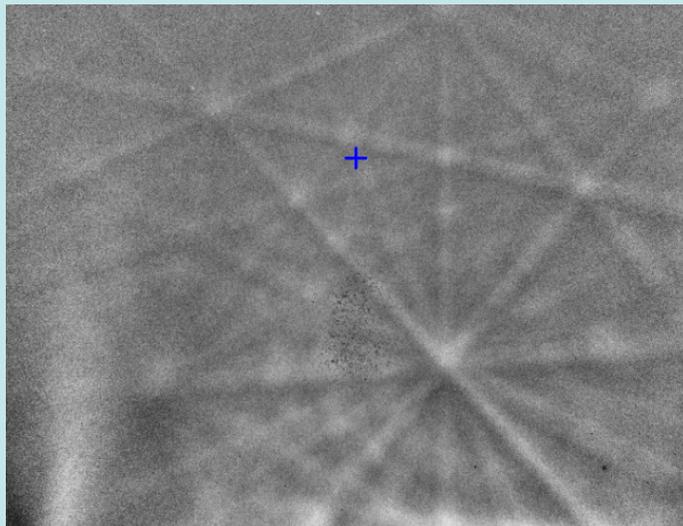
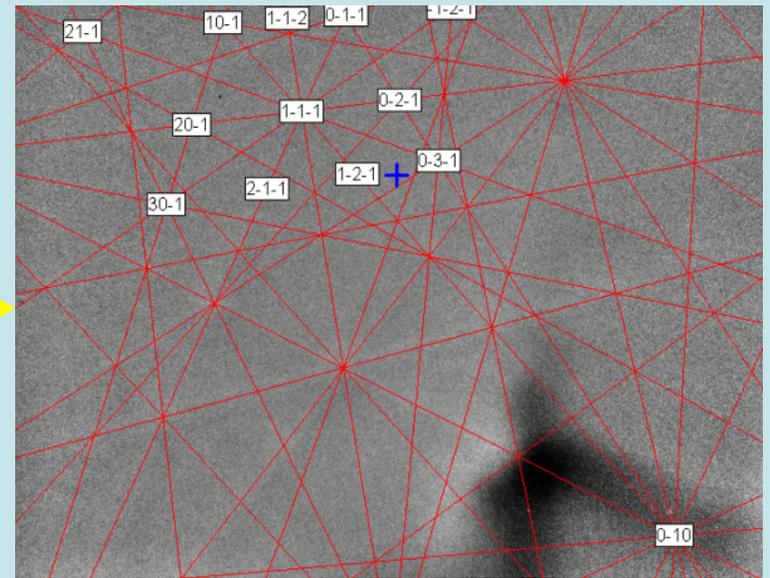
psWs
- cells



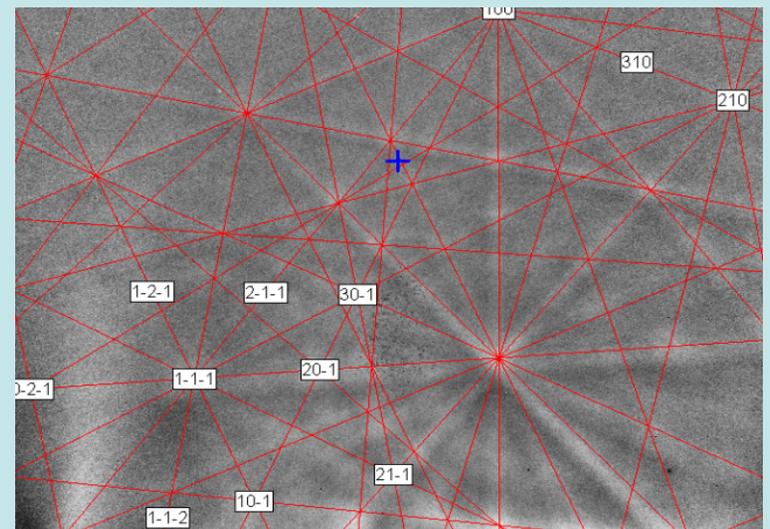
Calcite only found on psWs surfaces



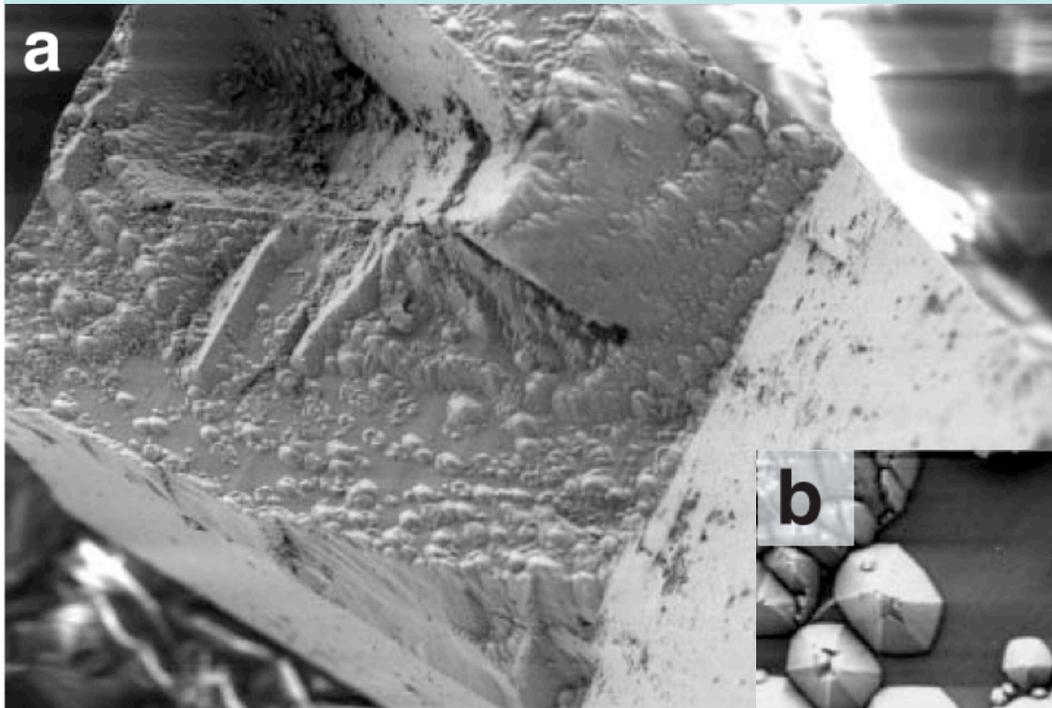
Calcite on
psWs
+ cells



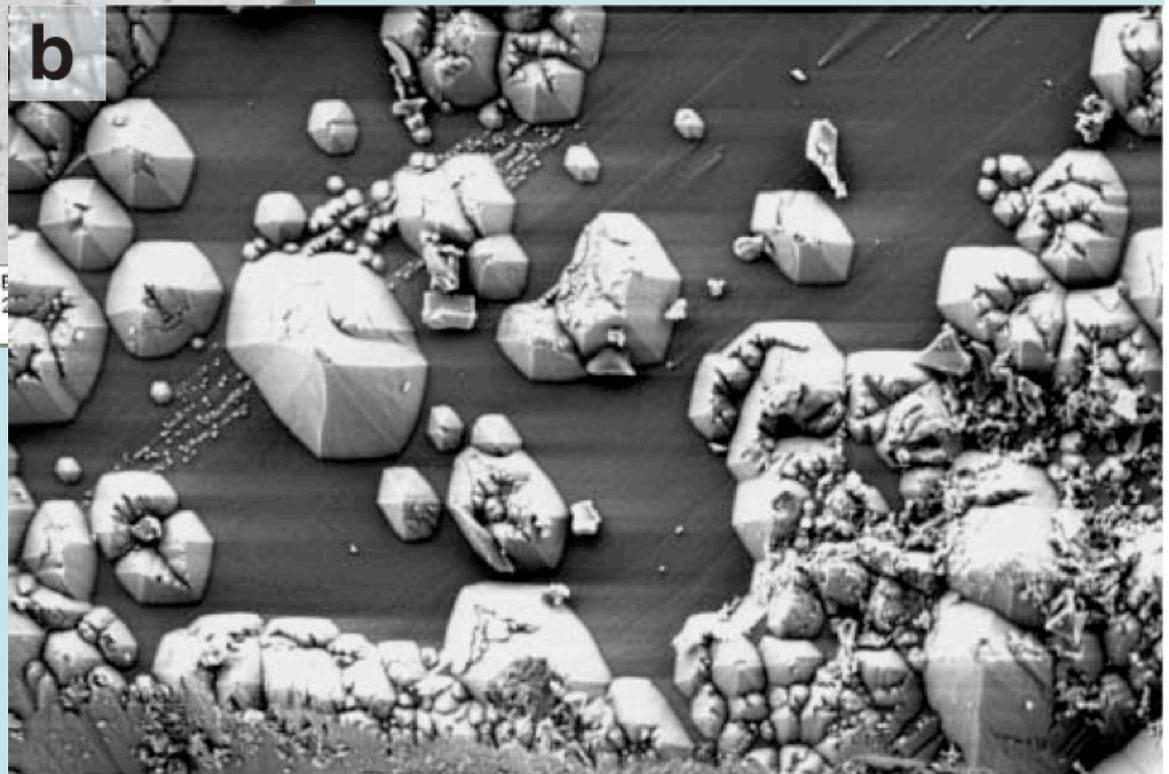
Calcite on
psWs
- cells



Particles from Mt Pinatubo eruption ash:



Separated ~100 μm
anhydrite (CaSO_4)
crystals



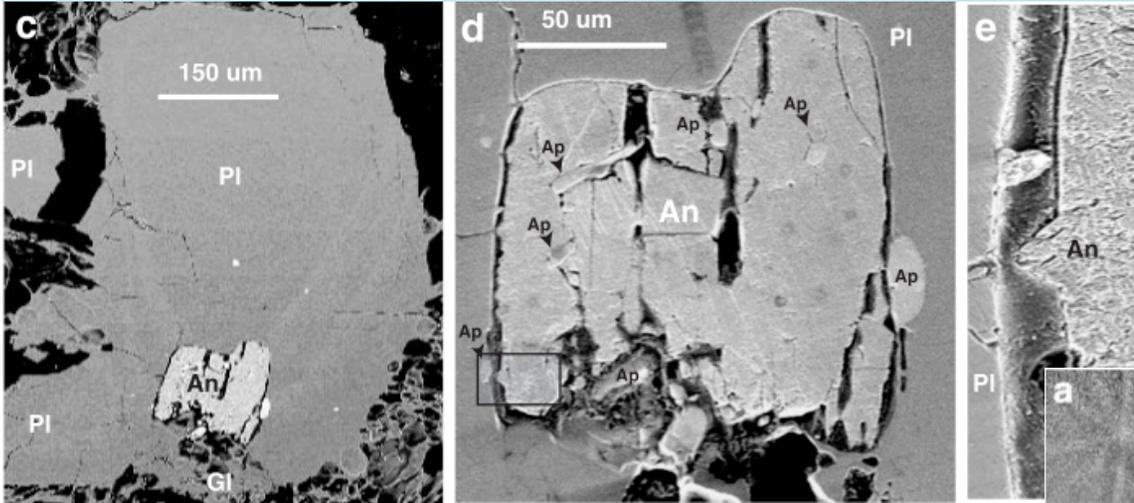
But they have tiny
pyramidal particles
on some surfaces ...

What are they?

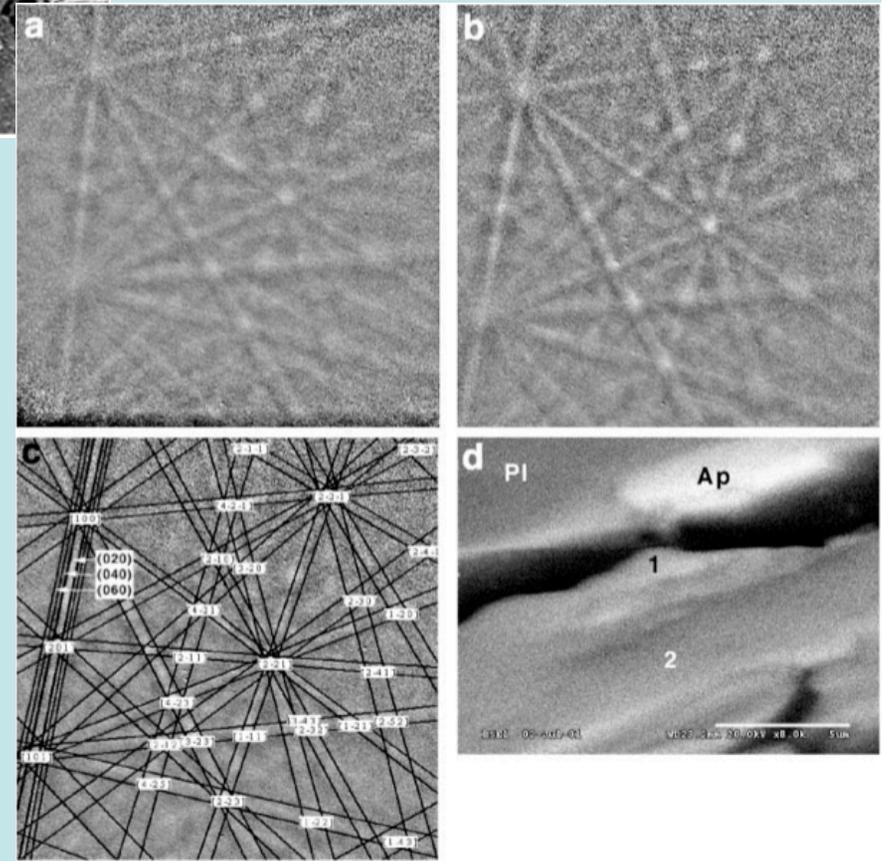
Mag = 1.60 K X 10 μm EHT = 3.00 kV Signal A = SE
WD = 6 mm Photo No. =

Mag = 13.81 K X 3 μm EHT = 3.00 kV Signal A = SE2 Date :2 Apr 2001
WD = 6 mm Photo No. = 2030 Time :14:52

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





Electron Backscatter Diffraction Topical Conference

May 26-28, 2010*

University of Wisconsin
Madison, Wisconsin

www.microbeamanalysis.org

*tentative date