

# Electron Microscopy of LNT Materials: Microstructural Changes with Aging

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# Collaborators

ORNL: Dr. Doug Blom  
Dr. Melanie Moses  
Ms. Dorothy Coffey

NTRC: Dr. Stuart Daw  
Dr. Jim Parks

FRL: Dr. George Graham  
Dr. John Hoard

UCalDavis: Prof. Bruce Gates  
Mr. Vinesh Bhirud

# Facilities/Instruments:

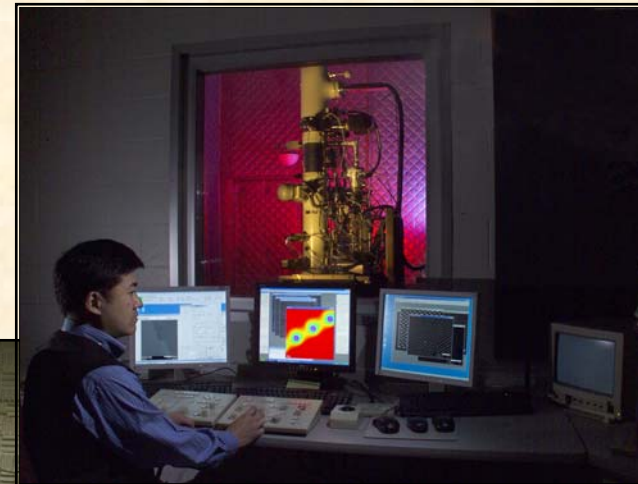


HF-2000 FE-TEM



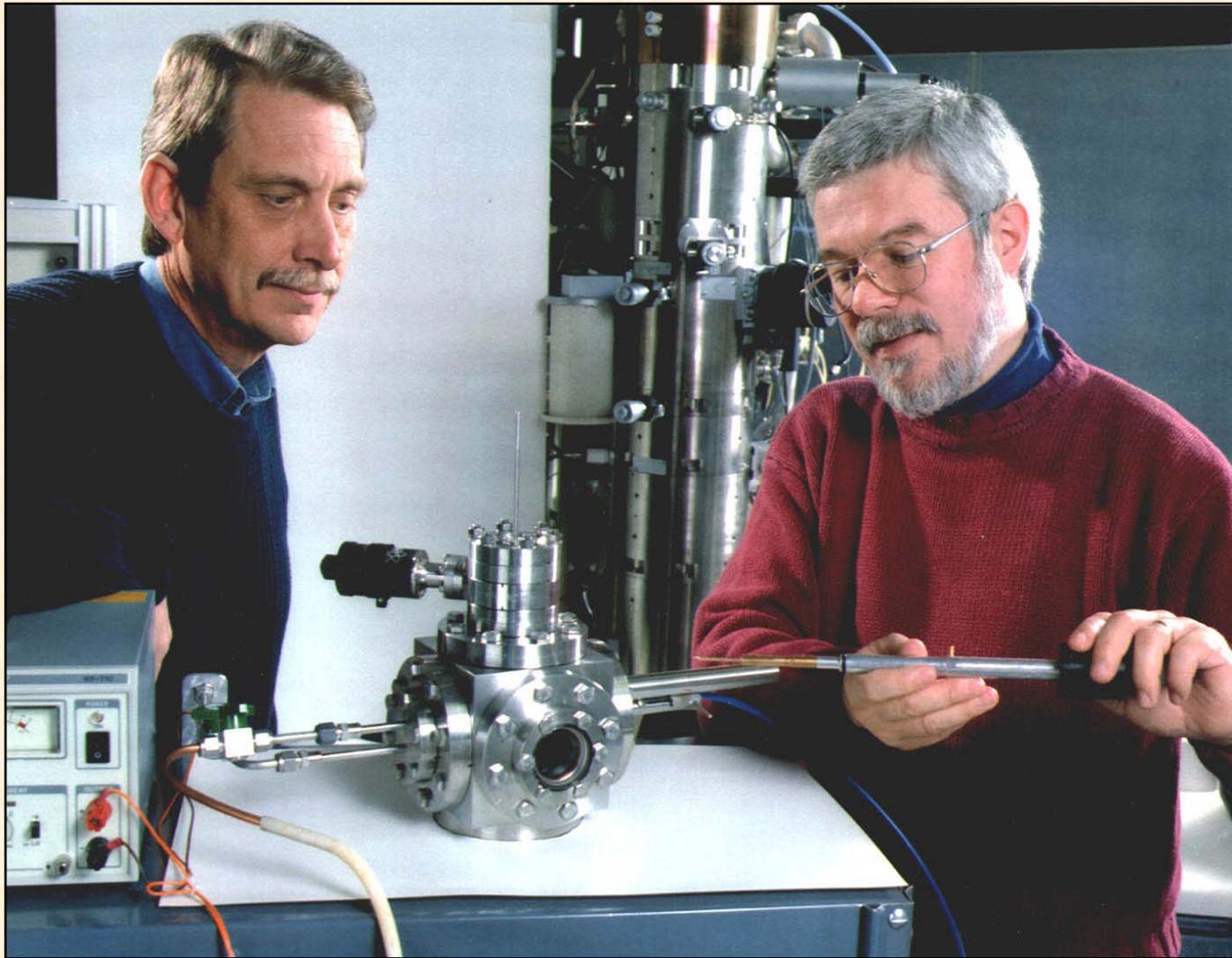
Hitachi  
HD-2000  
D-STEM

JEOL "ACEM"



JEOL 8200  
EMPA





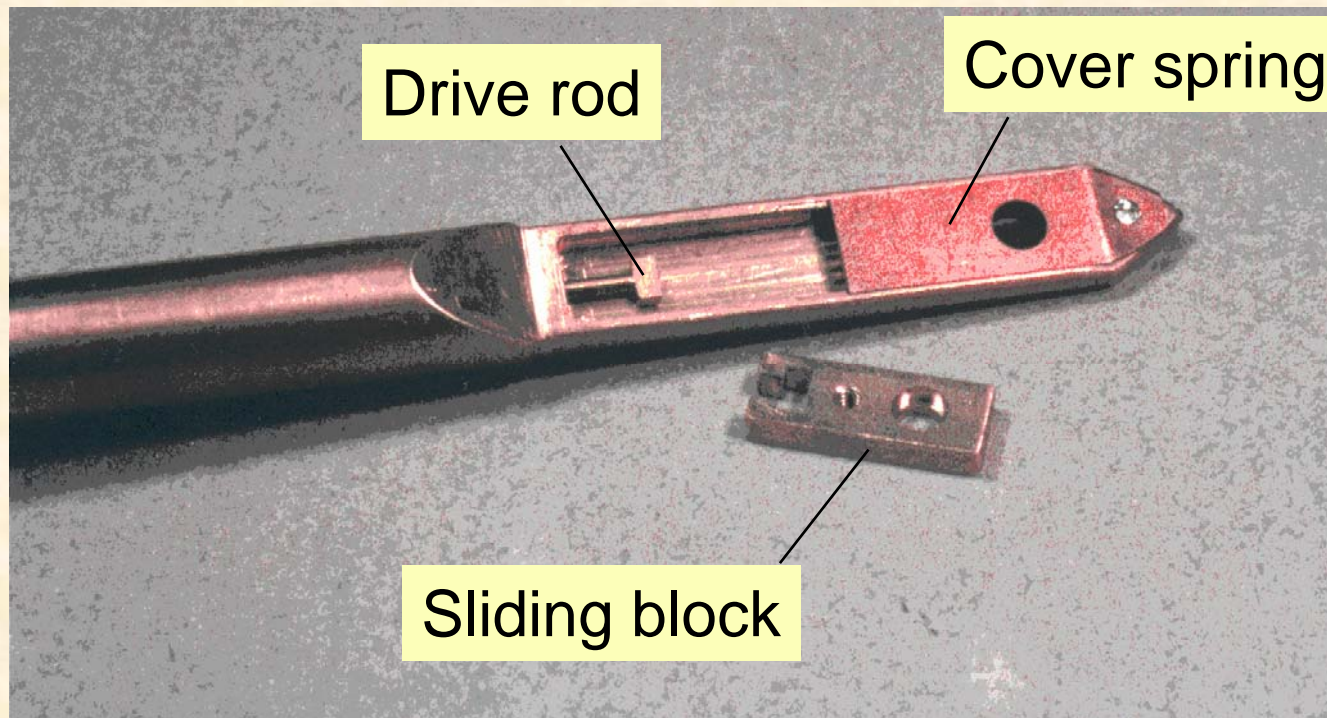
## Ex-situ reactor for TEM characterization of catalyst reactions

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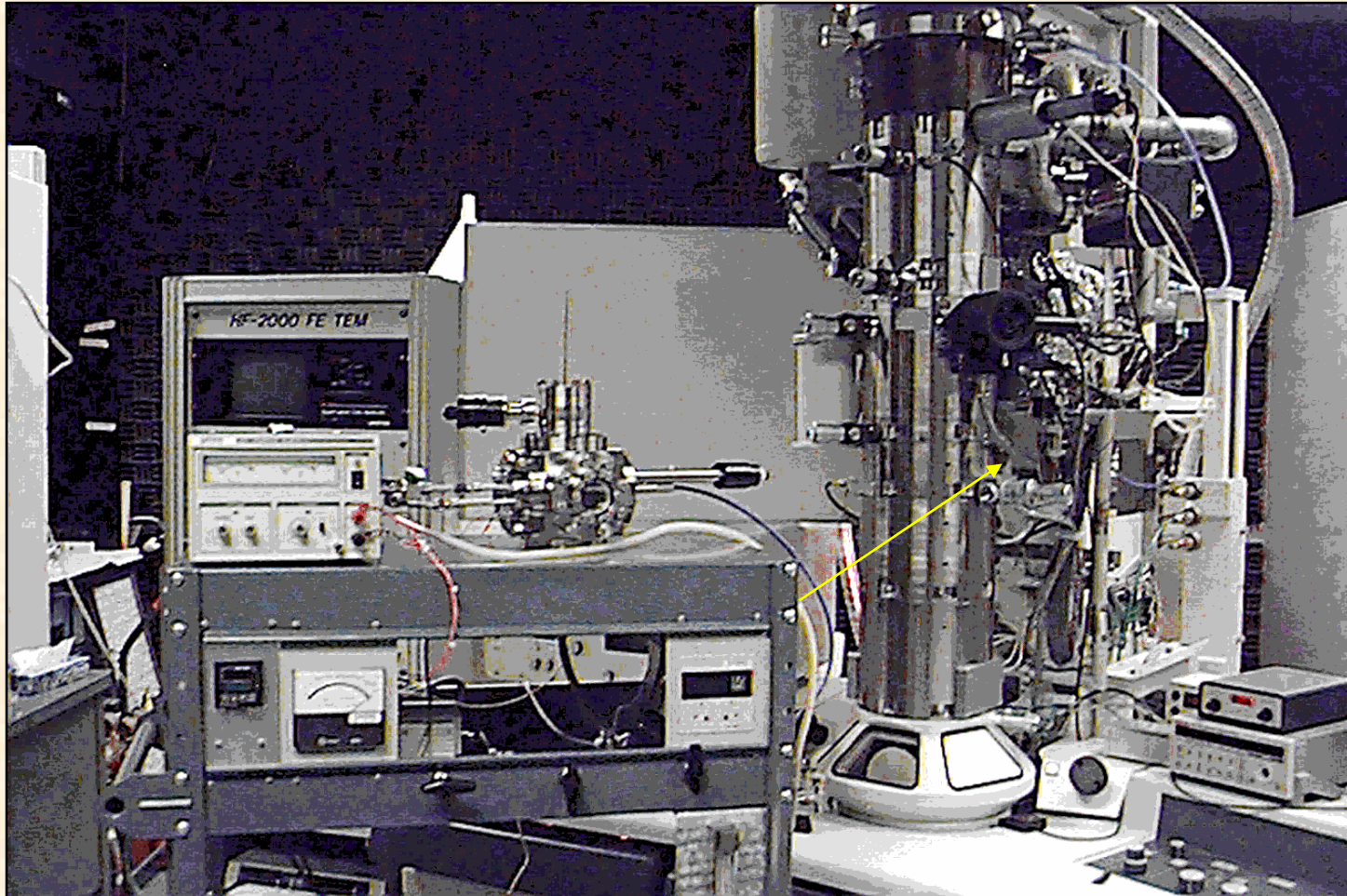




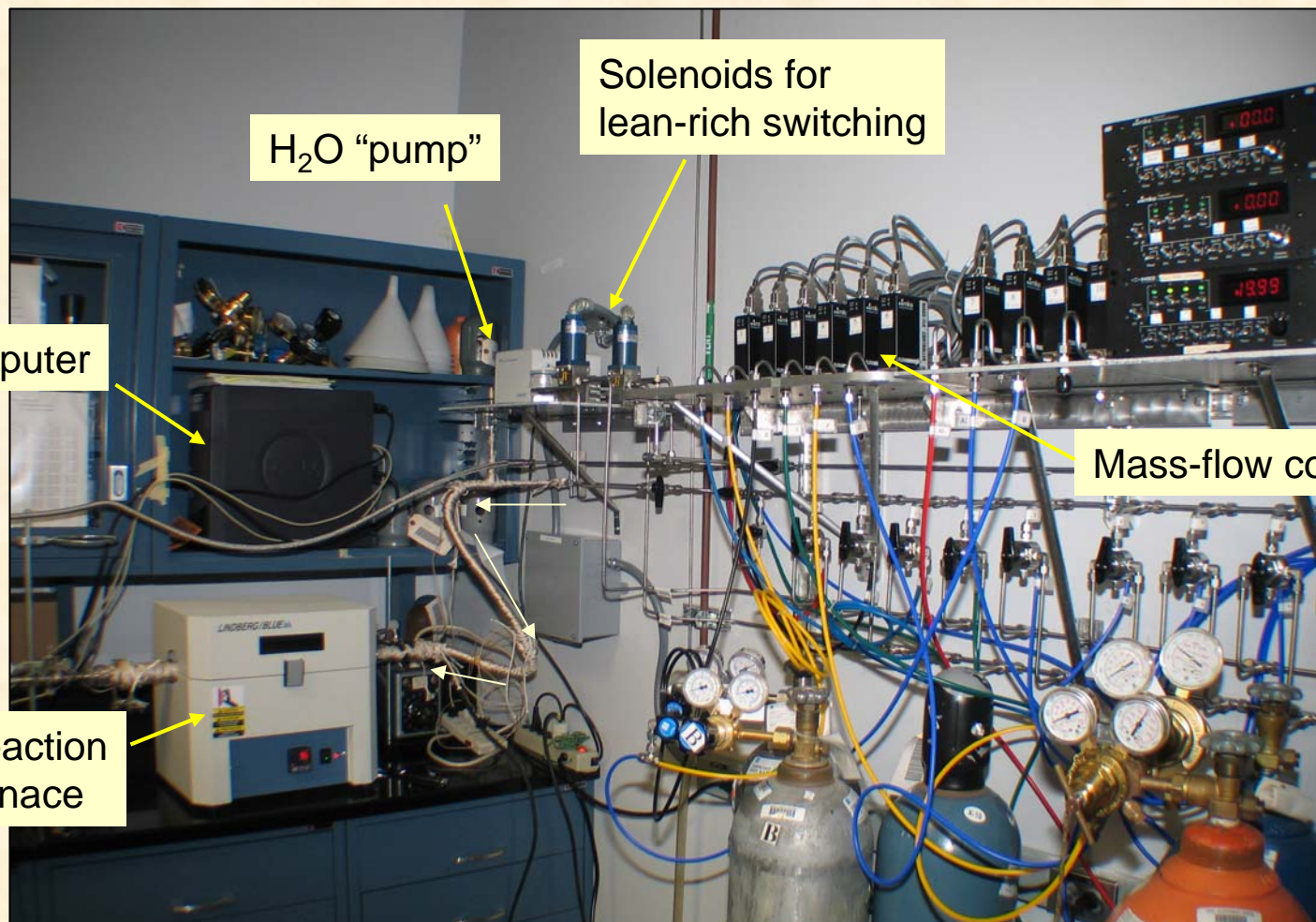
## Tip of the Specimen Rod for the Catalyst Reactor System



# Reactor in Position for Transfer of Specimen Rod to the HRTEM







H<sub>2</sub>O "pump"

Solenoids for lean-rich switching

computer

Mass-flow controllers

Reaction furnace

Ex-situ catalyst reactor, based on tube furnace, for rapid cycling of gases to simulate lean-rich operation.

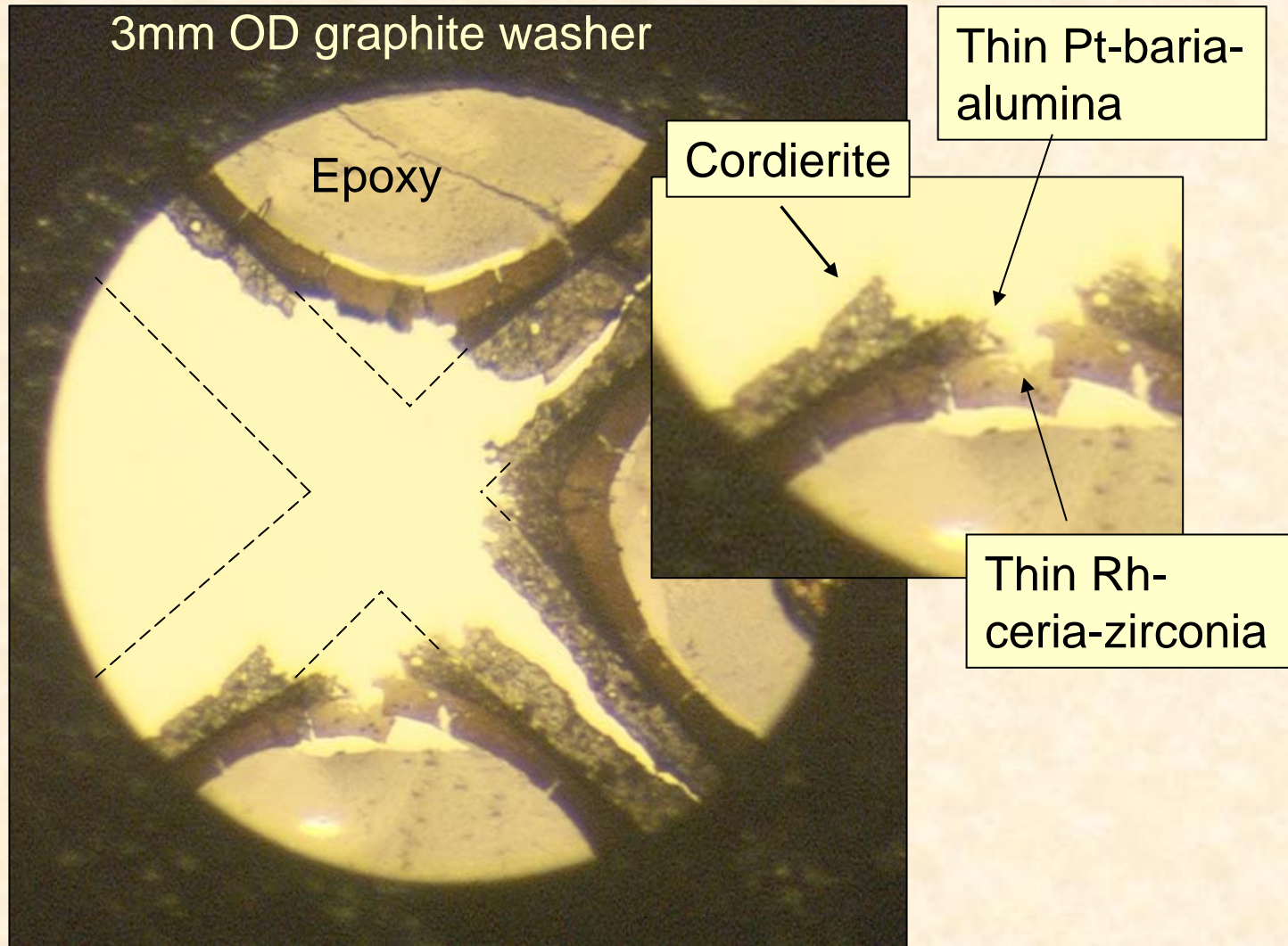


## Samples studied:

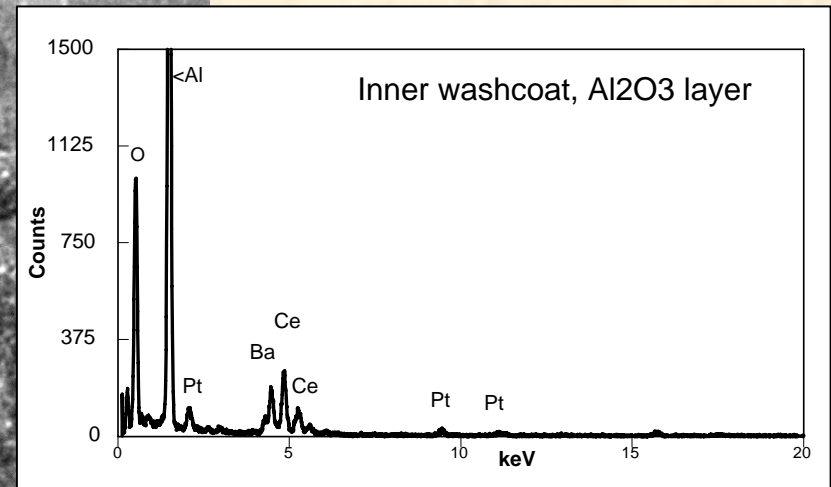
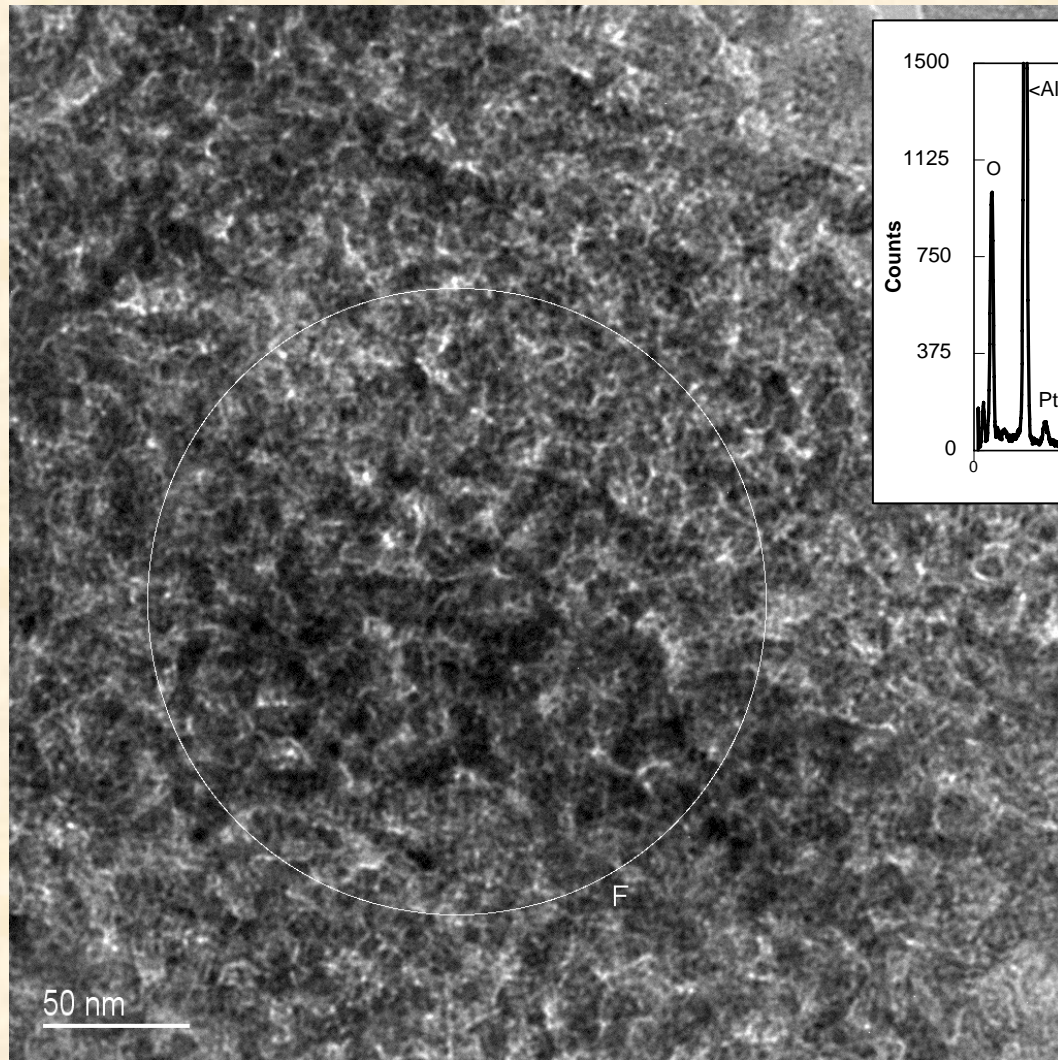
- Supplier NOx traps: Fresh, Dyno Aged
- DISI fleet NOx traps: Fresh, 32K km and 83K km
- Umicore NOx traps: Fresh and de-greened
- Tri-rhenium carbonyl clusters on  $\gamma\text{-Al}_2\text{O}_3$

# Supplier NOx trap

TEM ion-milled  
thin specimen,  
showing double  
washcoat



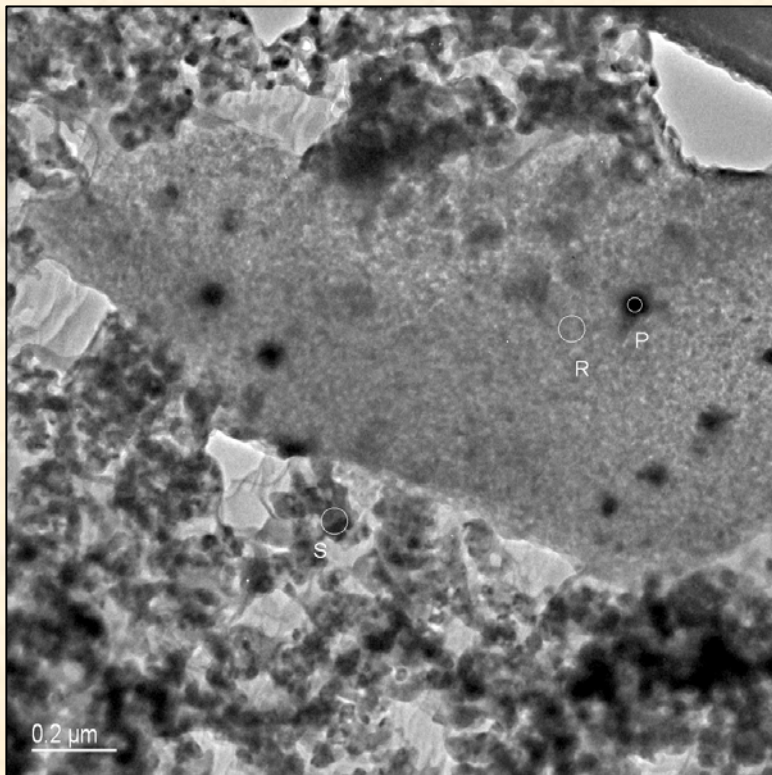
# Supplier NOx trap "Fresh"



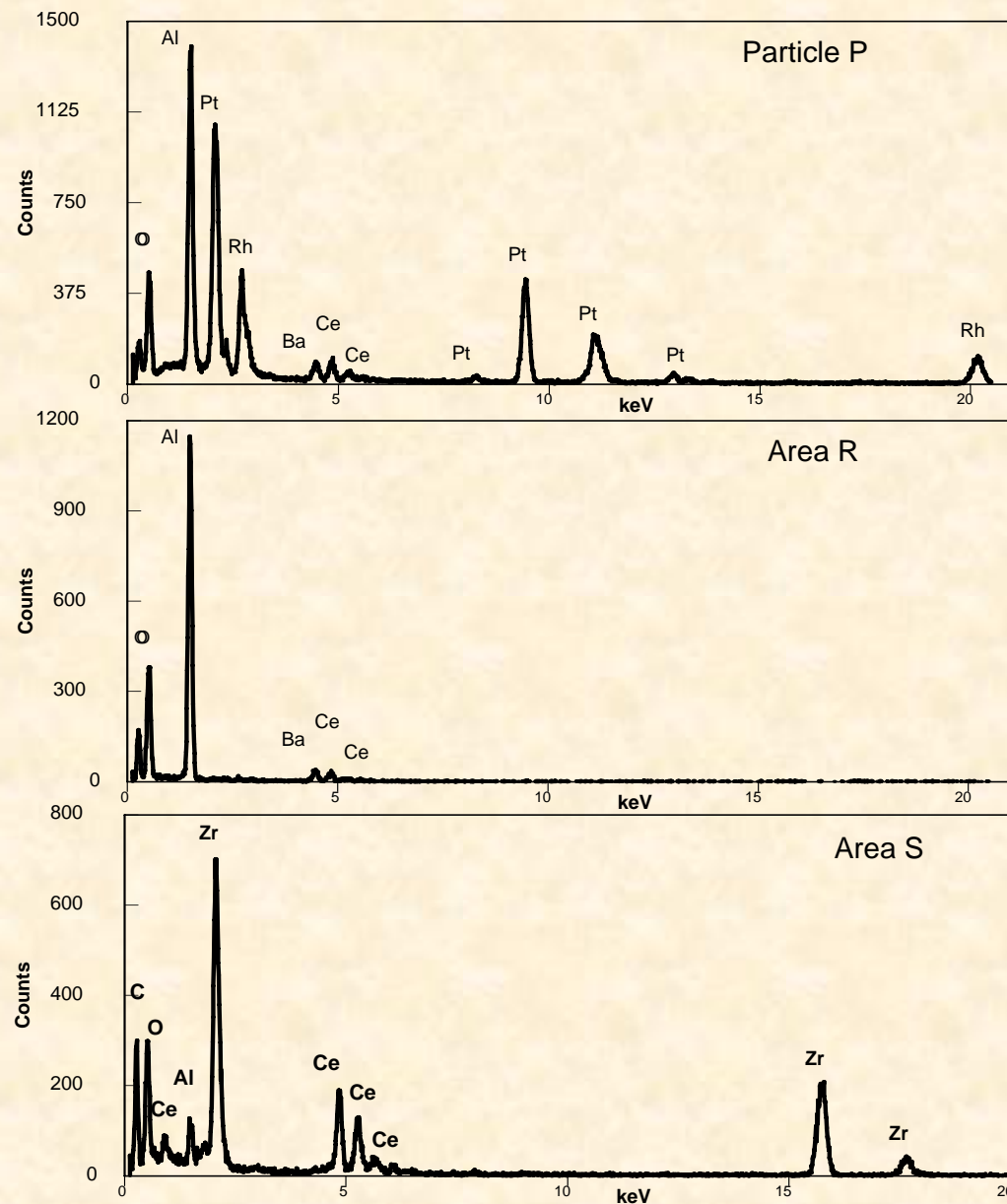
Problem: BF TEM image, Pt detected, but discrete particles not unambiguously located.



# Example of imaging and EDS analysis of catalyst microstructure

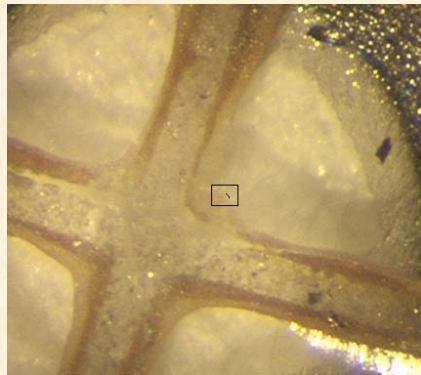


Alumina island with Pt/Rh particles in zirconia-ceria layer, in aged catalyst brick. Pt/Rh particles show large increase in size (40-50nm)

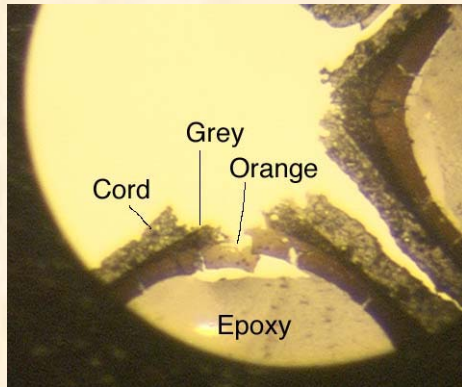


# MICROSTRUCTURAL ANALYSIS OF SUPPLIER SAMPLES

Fresh



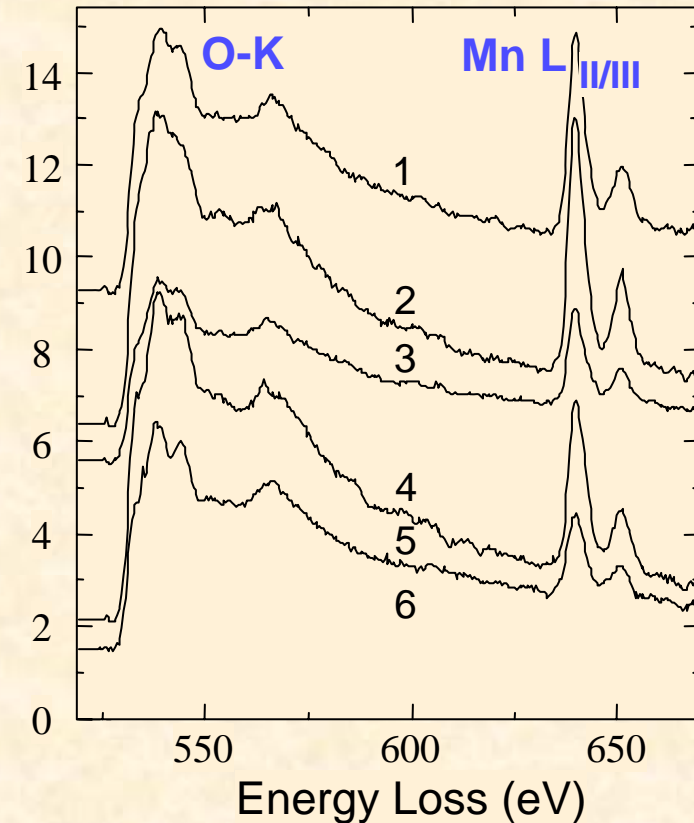
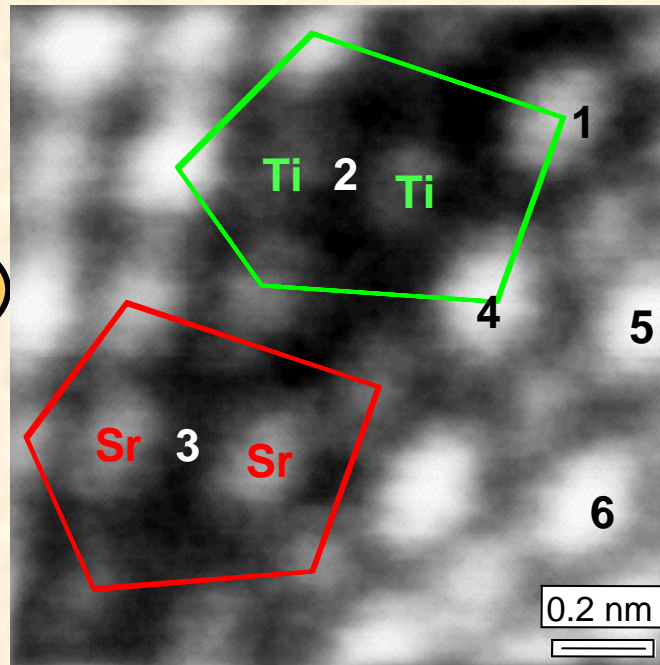
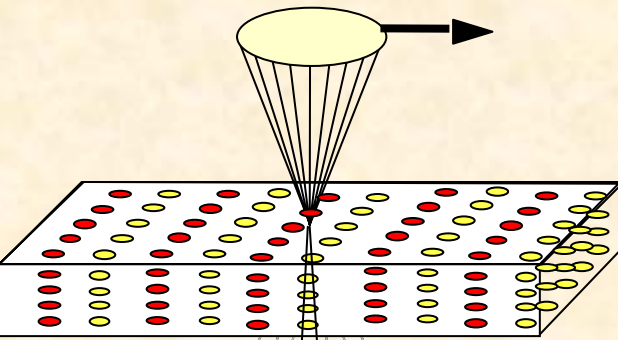
Aged



Fresh	Aged
<b>Inner Layer</b>	
Ba, Al O	Ba, Al, O
PGM – Pt can be observed in EDS, not seen in images	PGM – Pt, Pt-Rh 40-50 nm
<b>Outer Layer</b>	
Ce, Zr, O	Ce, Zr, O, Rh
Alumina Islands	Alumina Islands
BaO grains on Alumina	BaO in Alumina, Pt-Rh alloy in Alumina – 40-50 nm
Hint of Ba in Ceria-Zirconia layer	Ba in Ceria-Zirconia

# Z-Contrast Microscopy

- Atomic and electronic structure



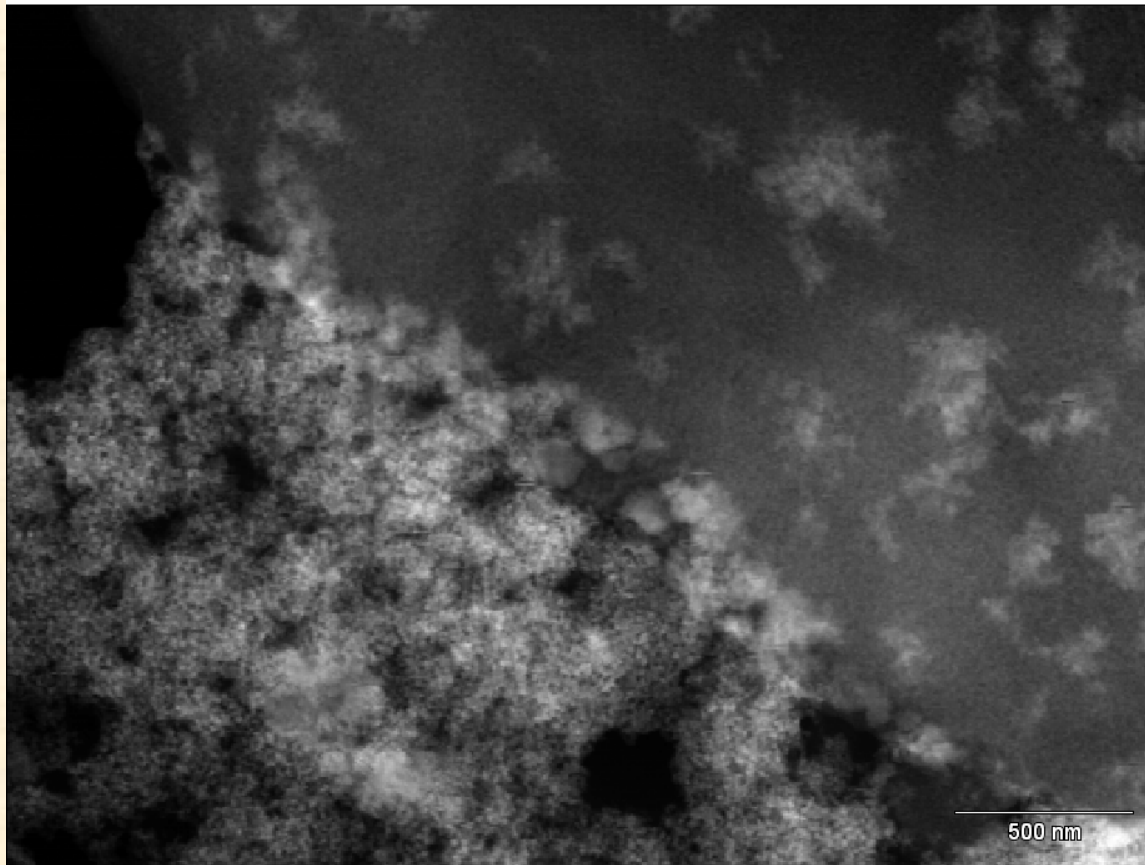
Spectrometer

(courtesy S.J. Pennycook)



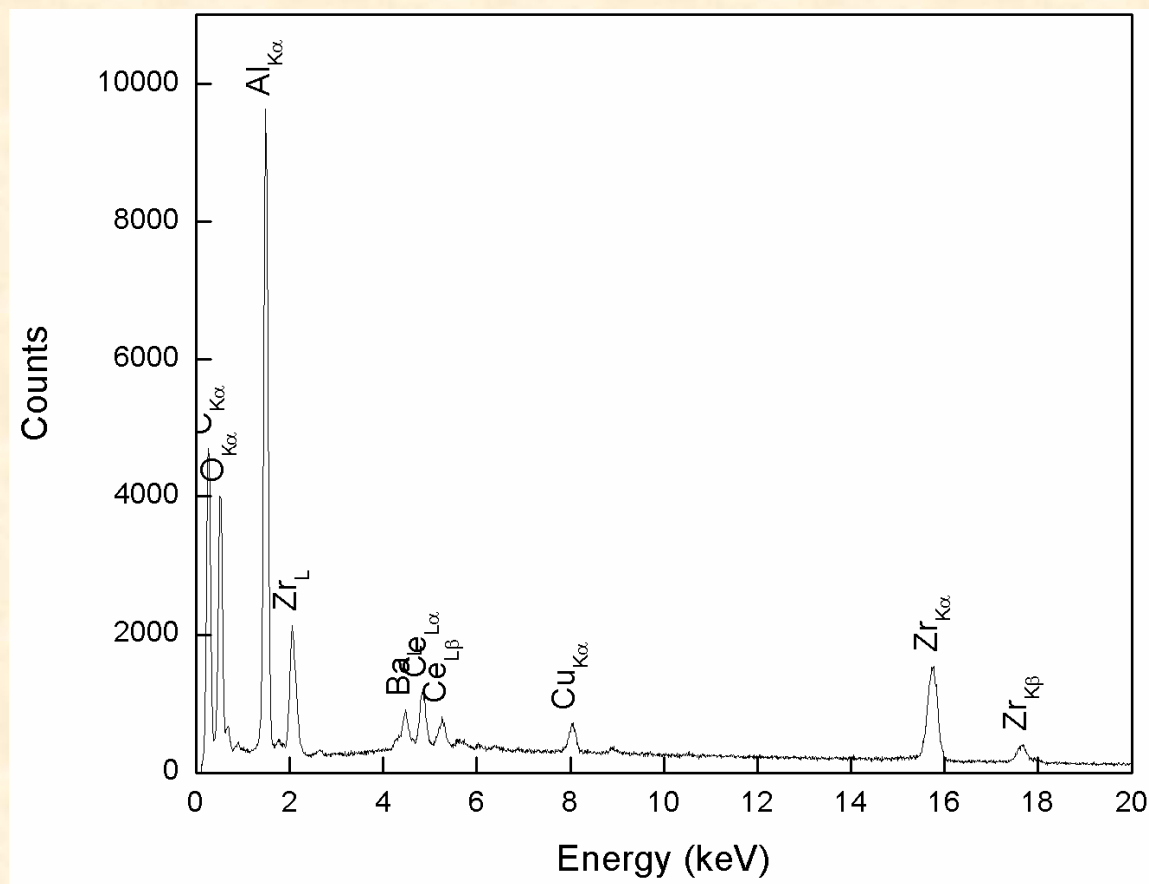
Fresh

DISI LNT



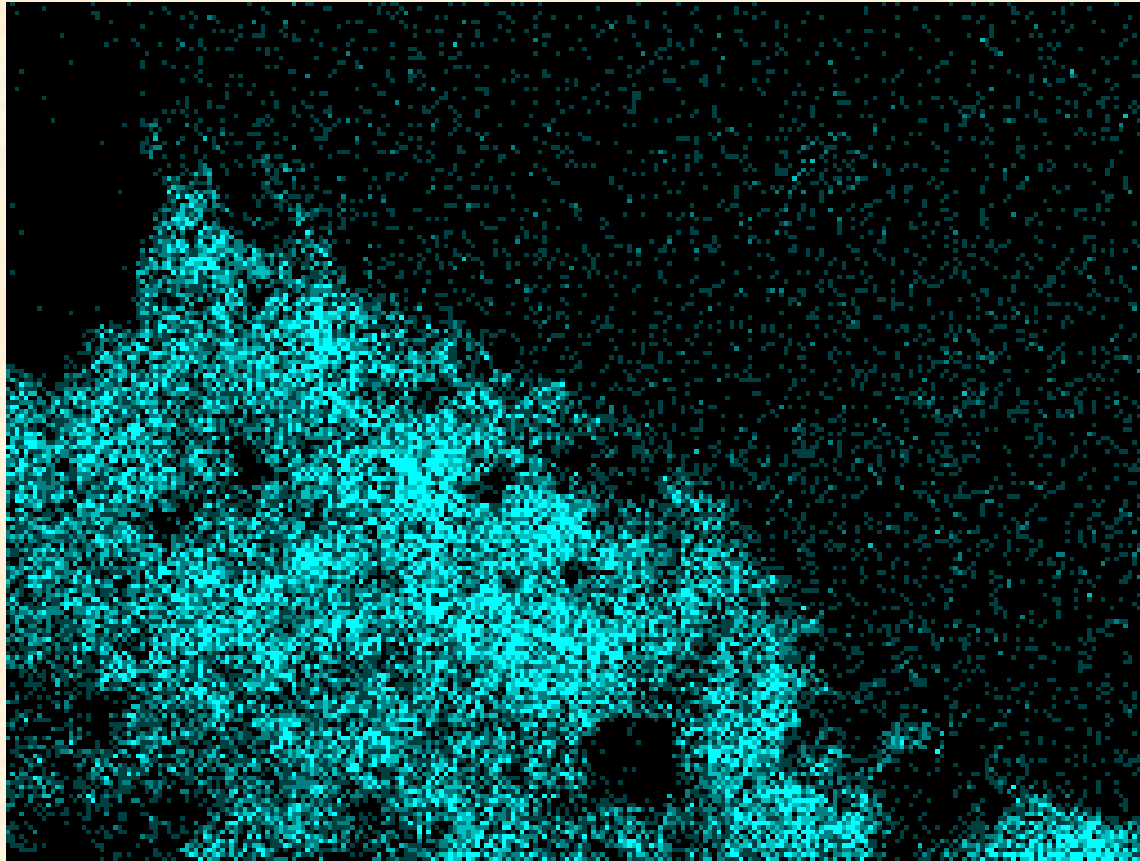
ZC for spectrum image

# Fresh Sum Spectrum



K-lines at ~16keV

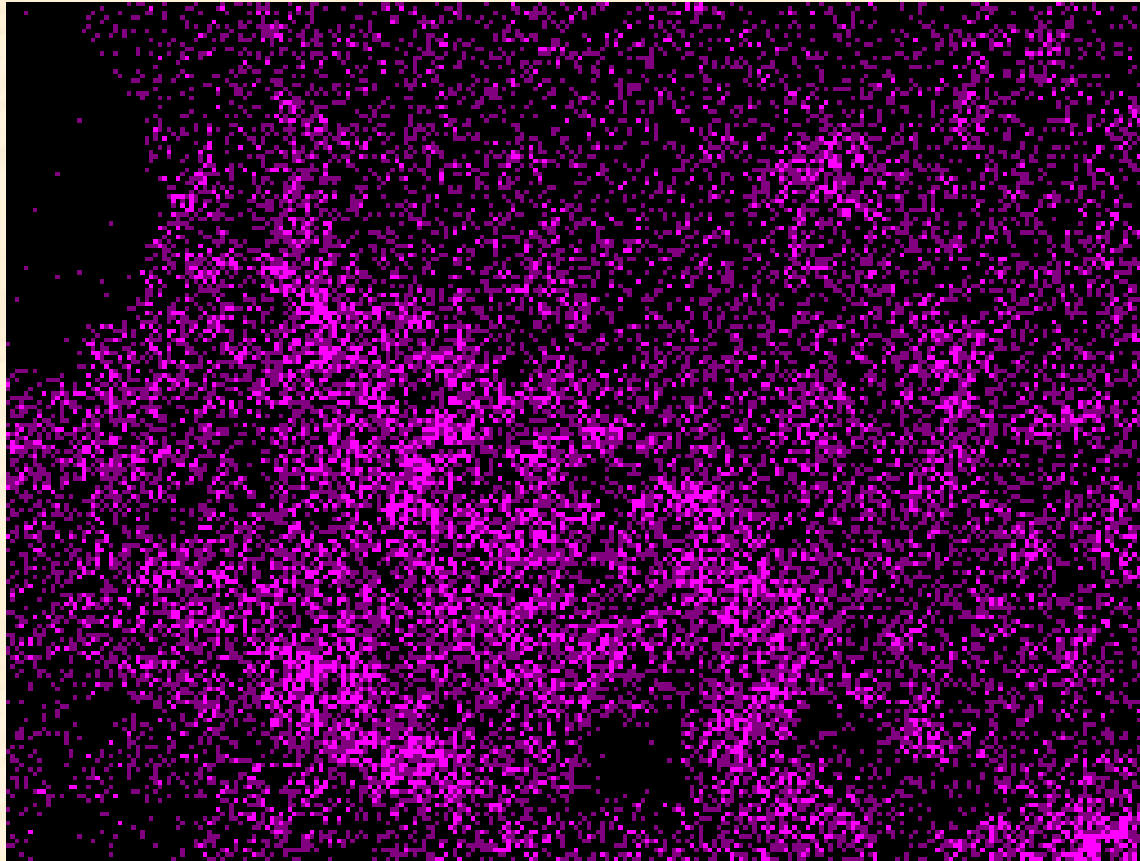
Zr map



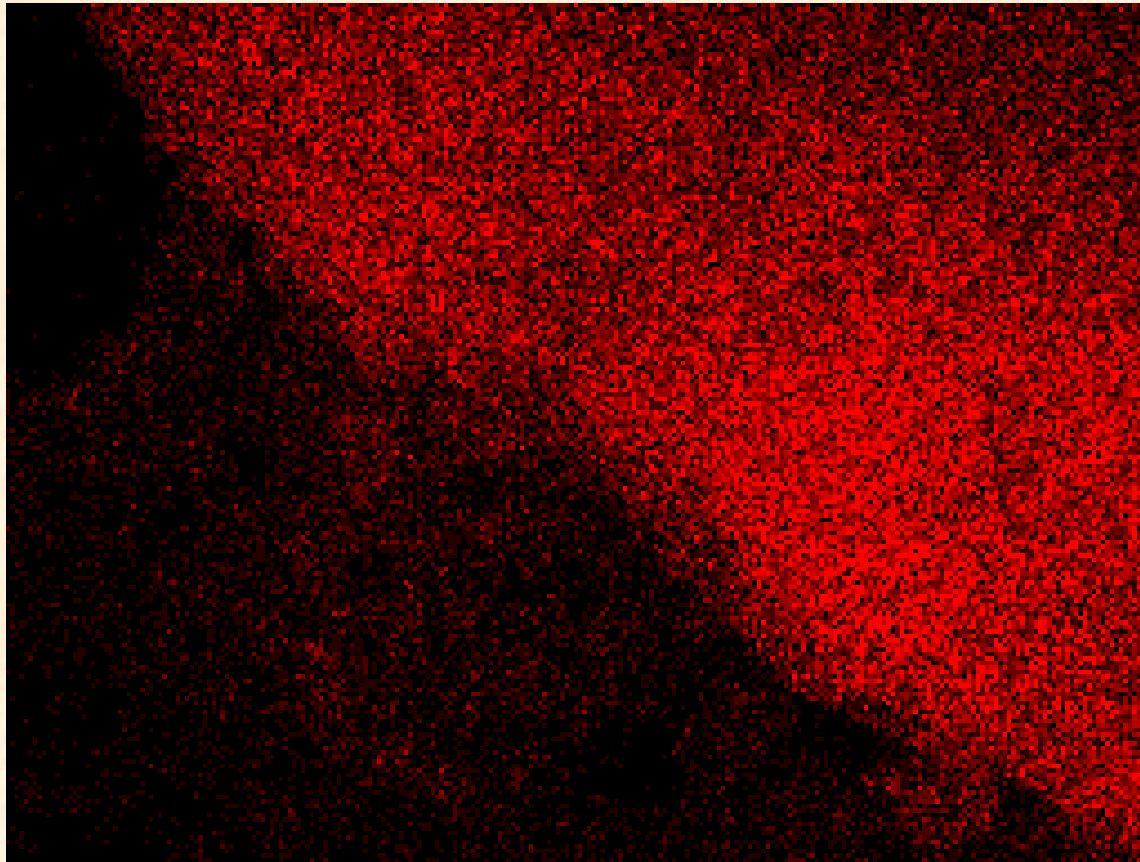


La peak

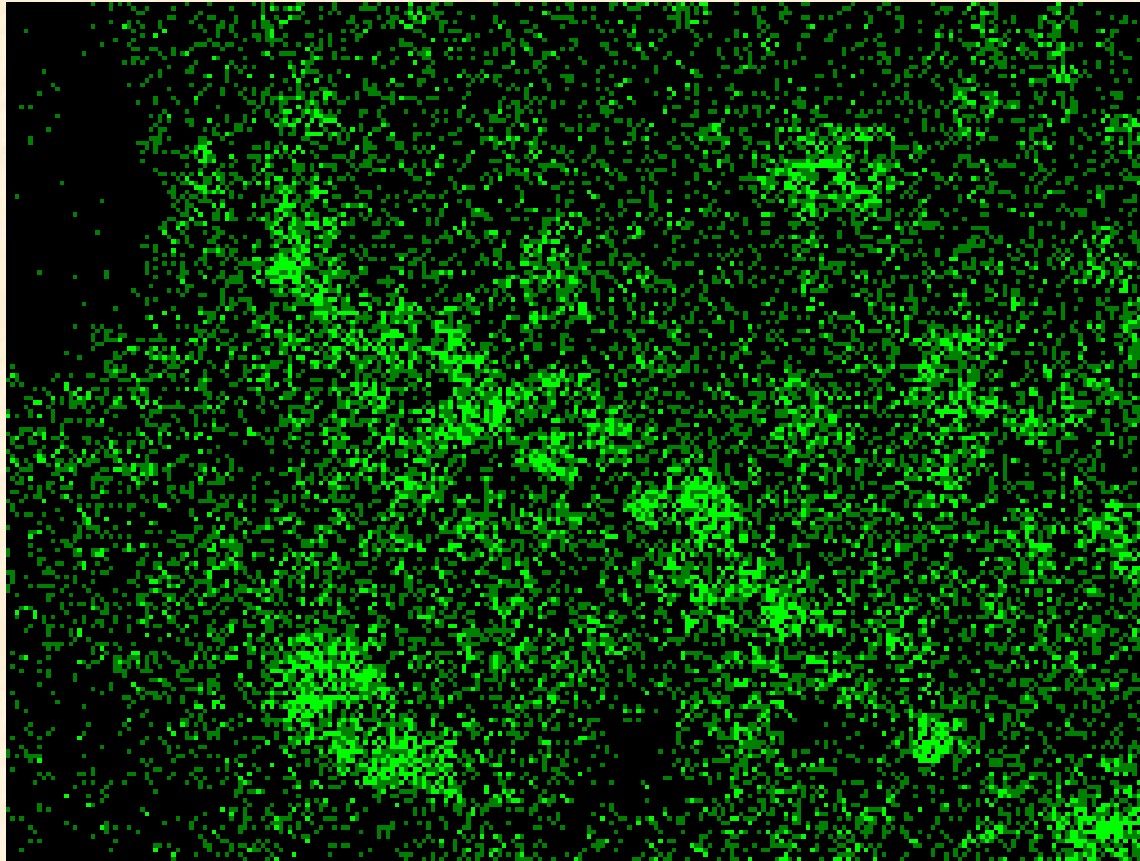
Ce Map



# AI map



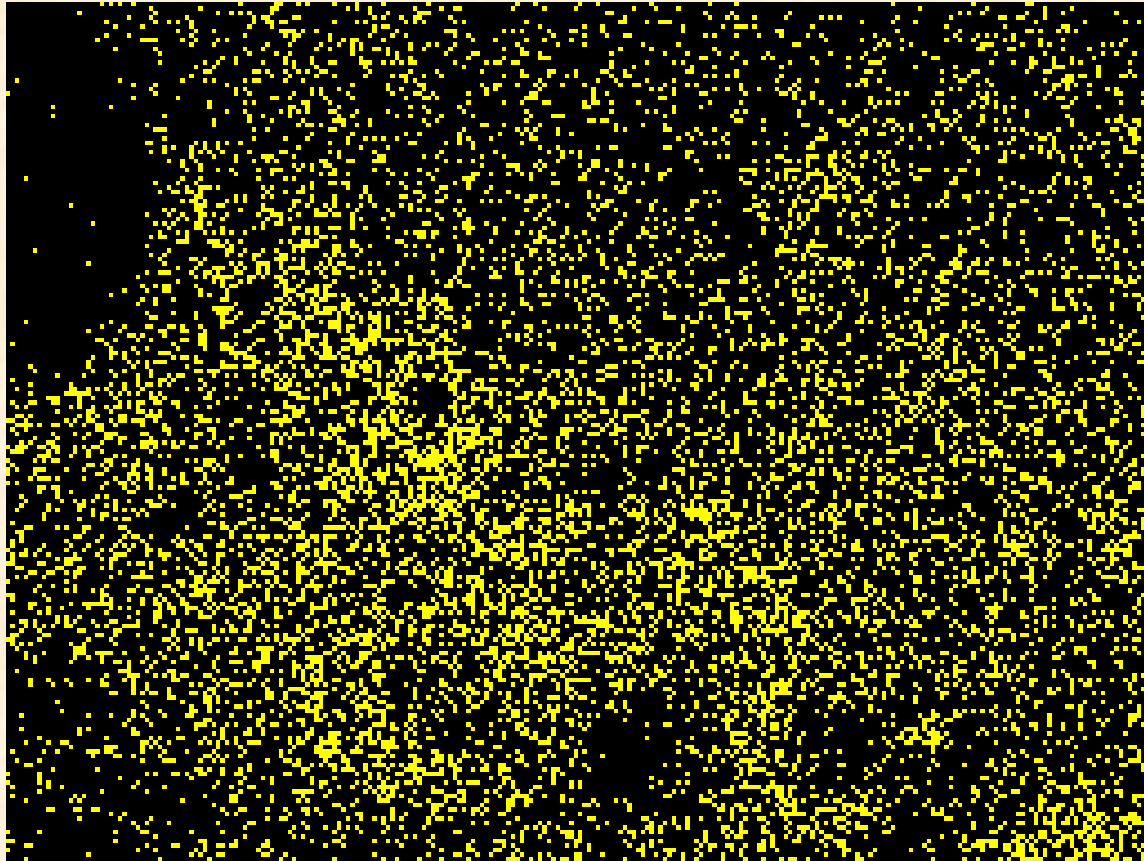
# Ba map



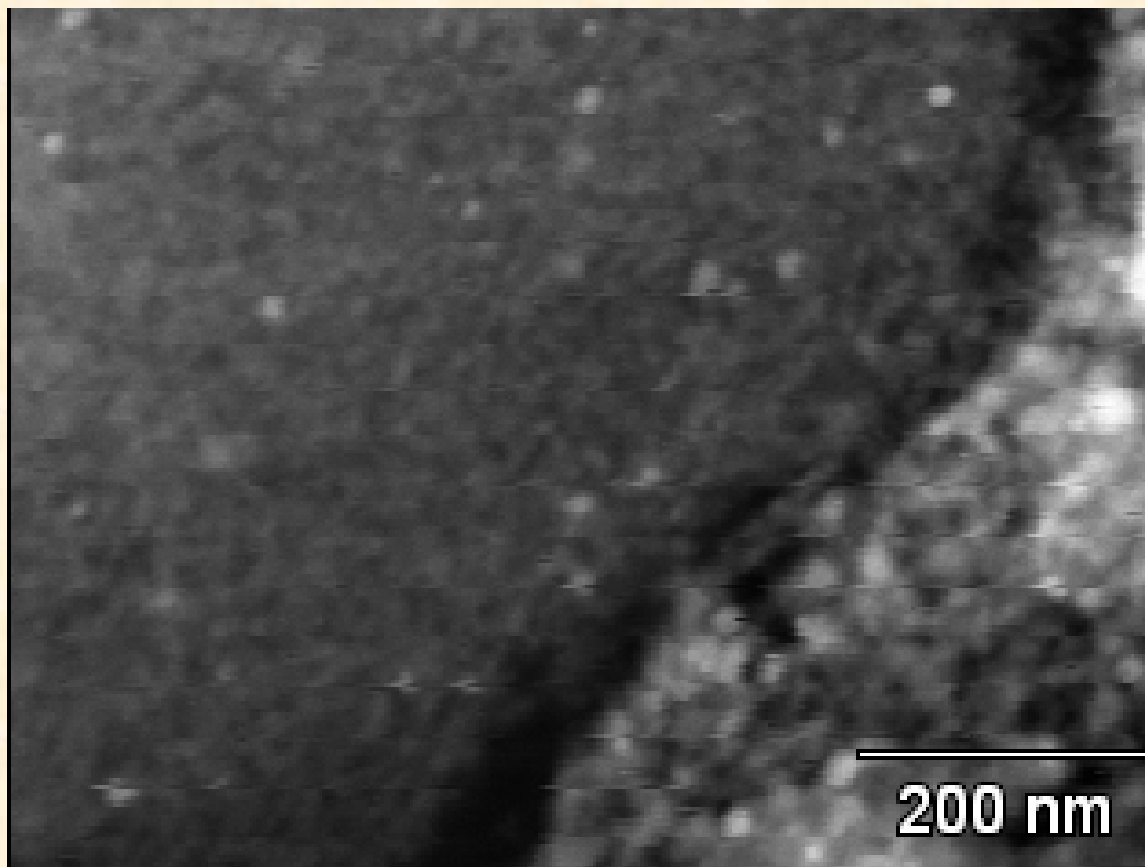


Mostly bkgd?

Pt map

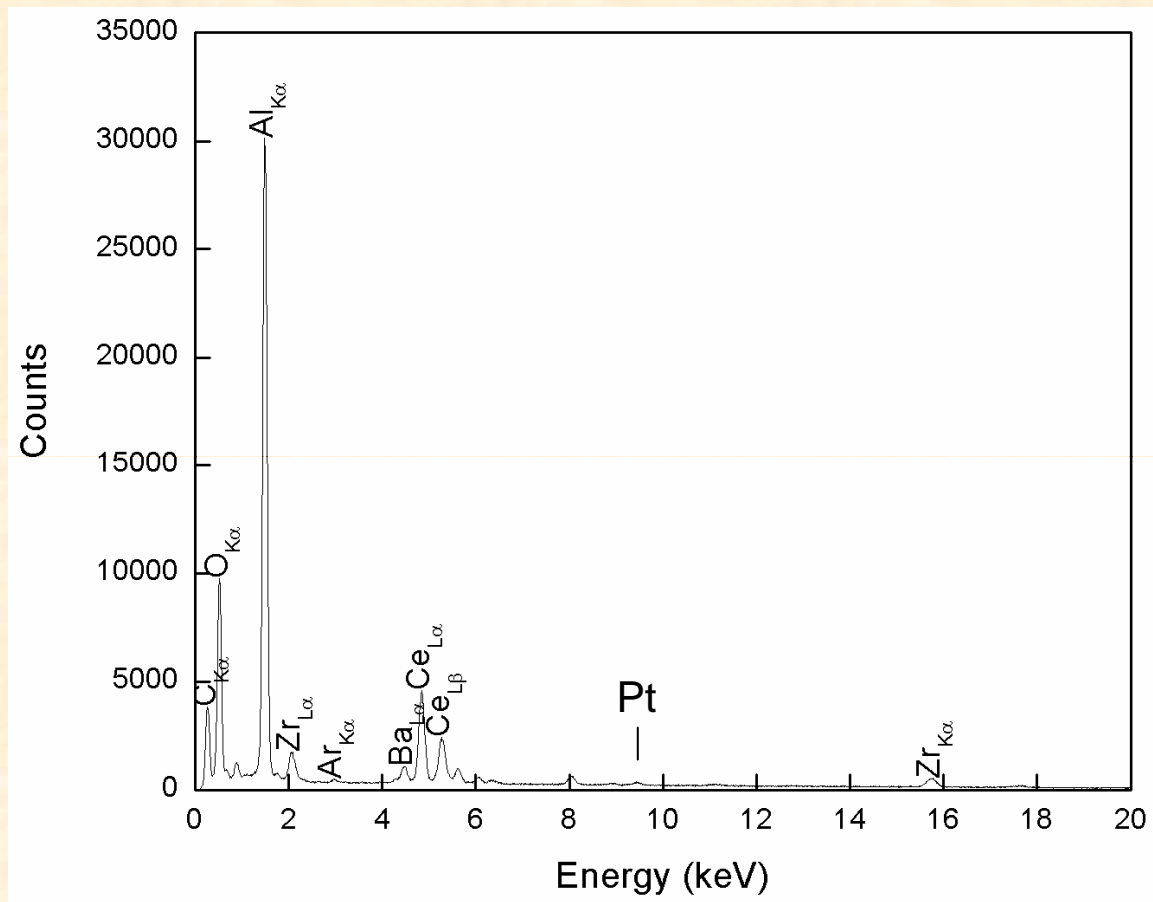


# 30K km sample (vehicle 112)



ZC for spectrum imaging

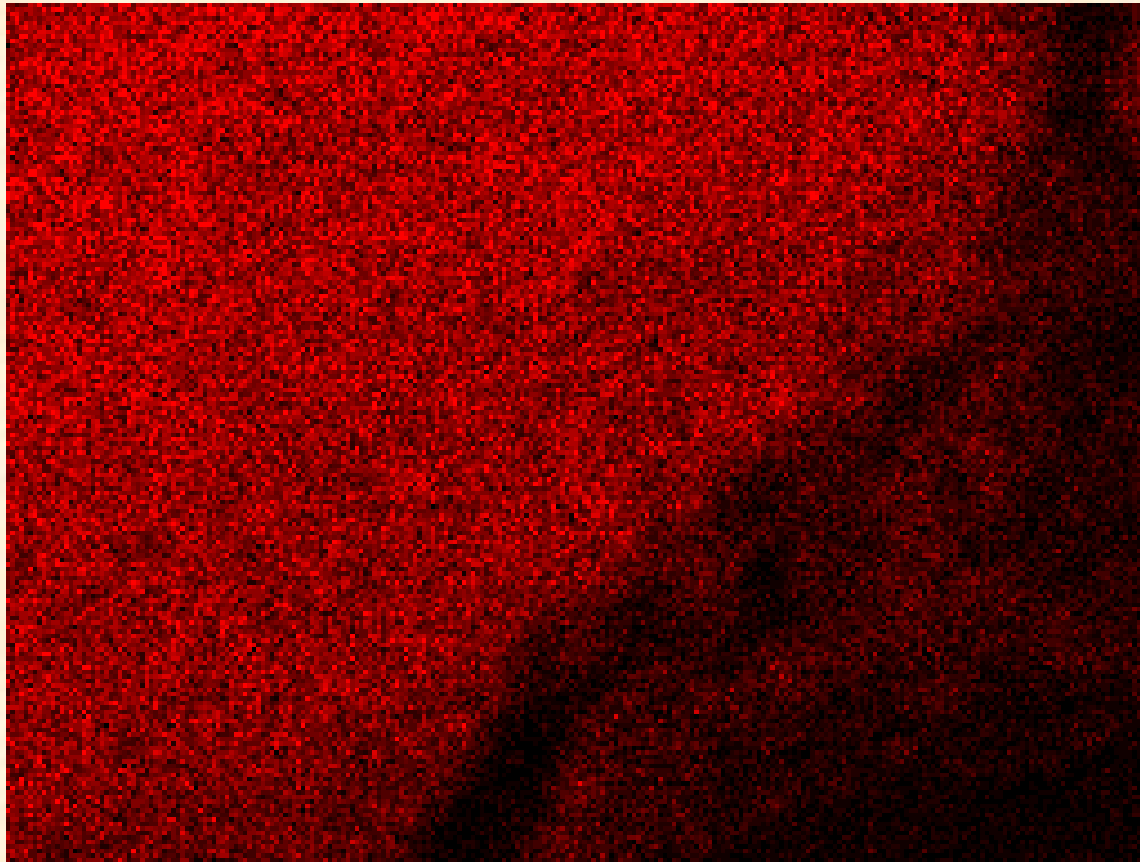
# Sum spectrum



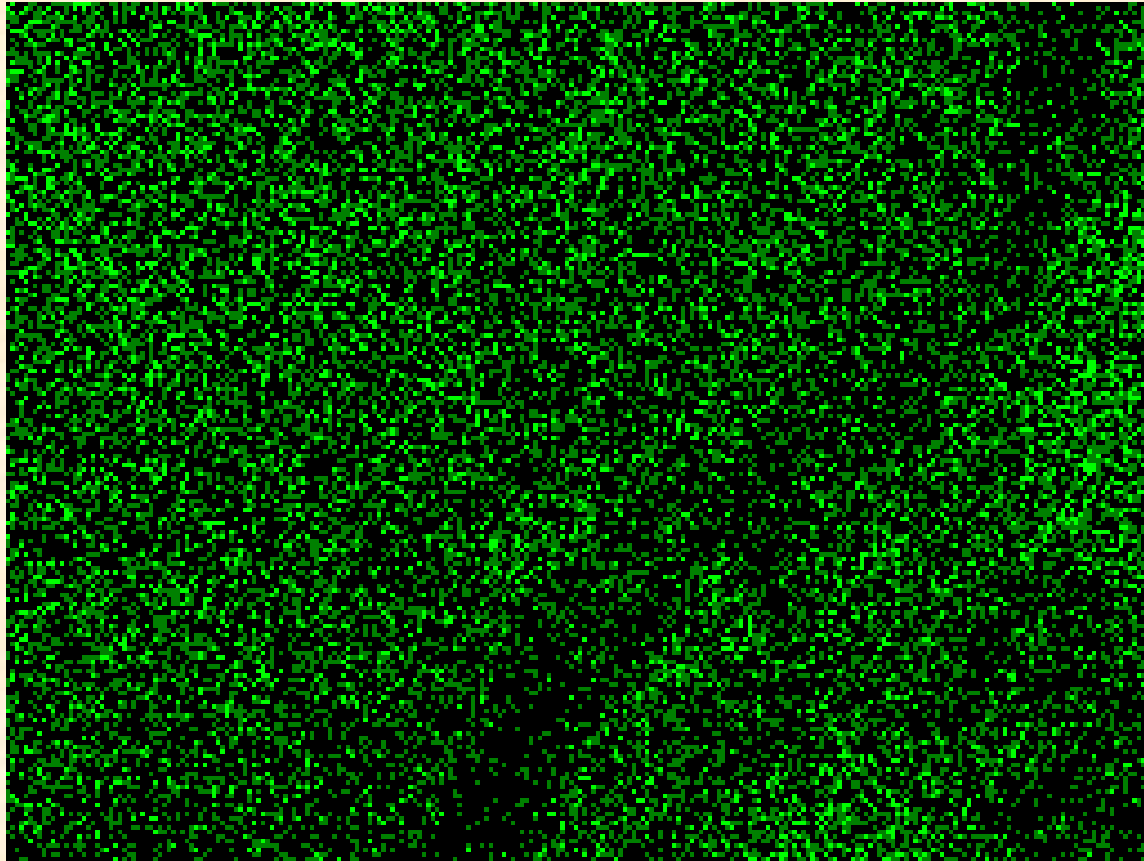


AI Map

From ROI on sum spectrum

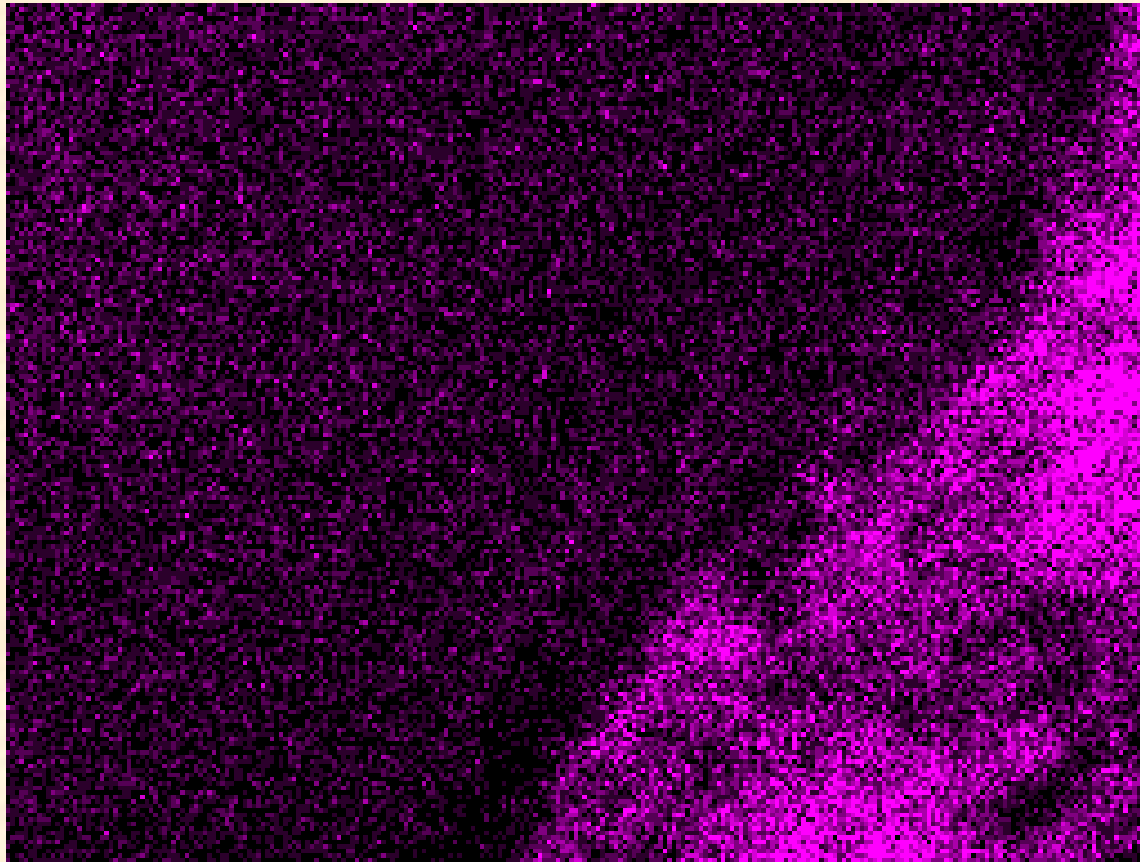


# Ba map



Ce Map

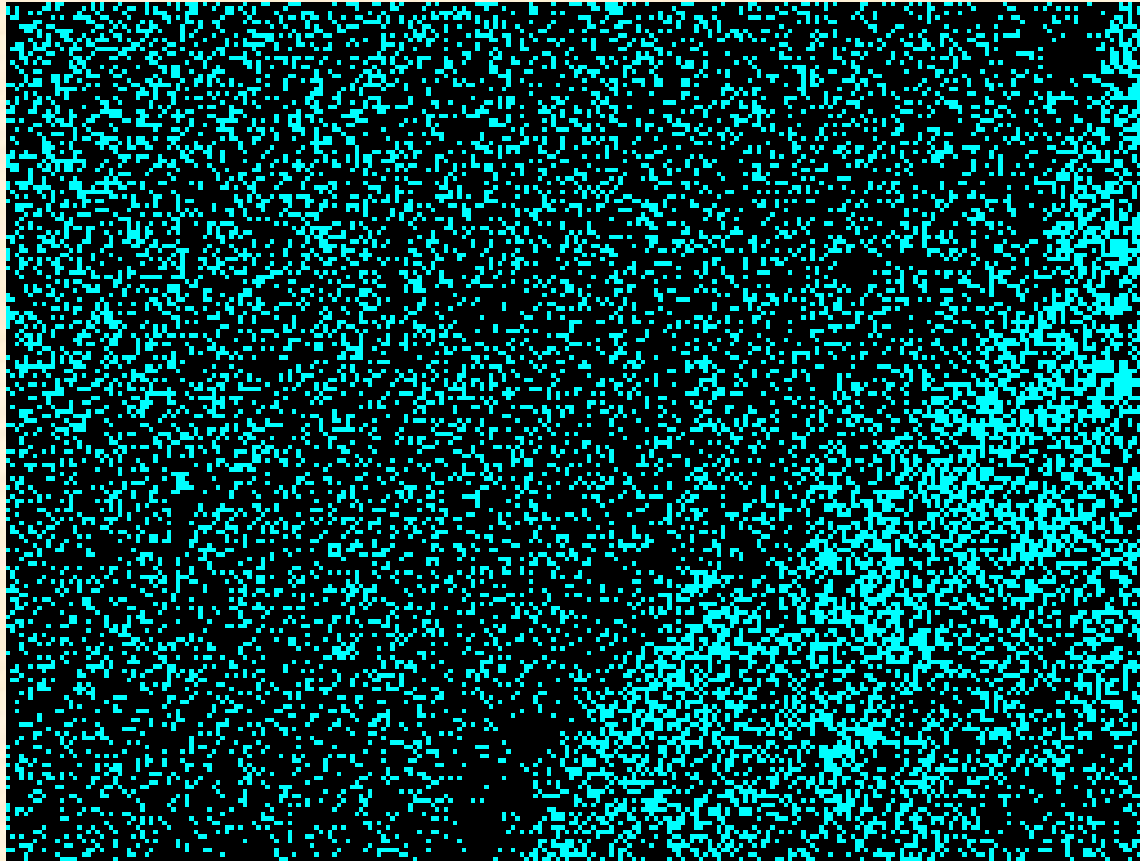
CeLa peak



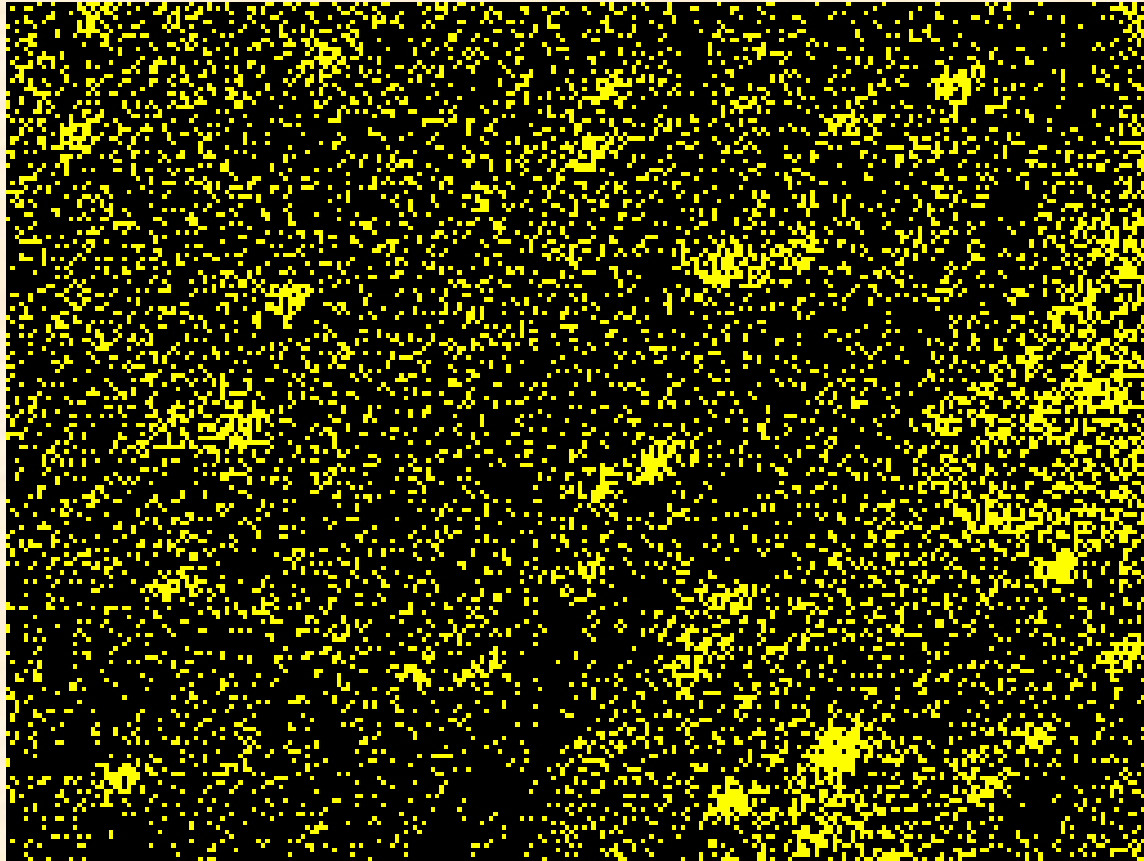


Zr map

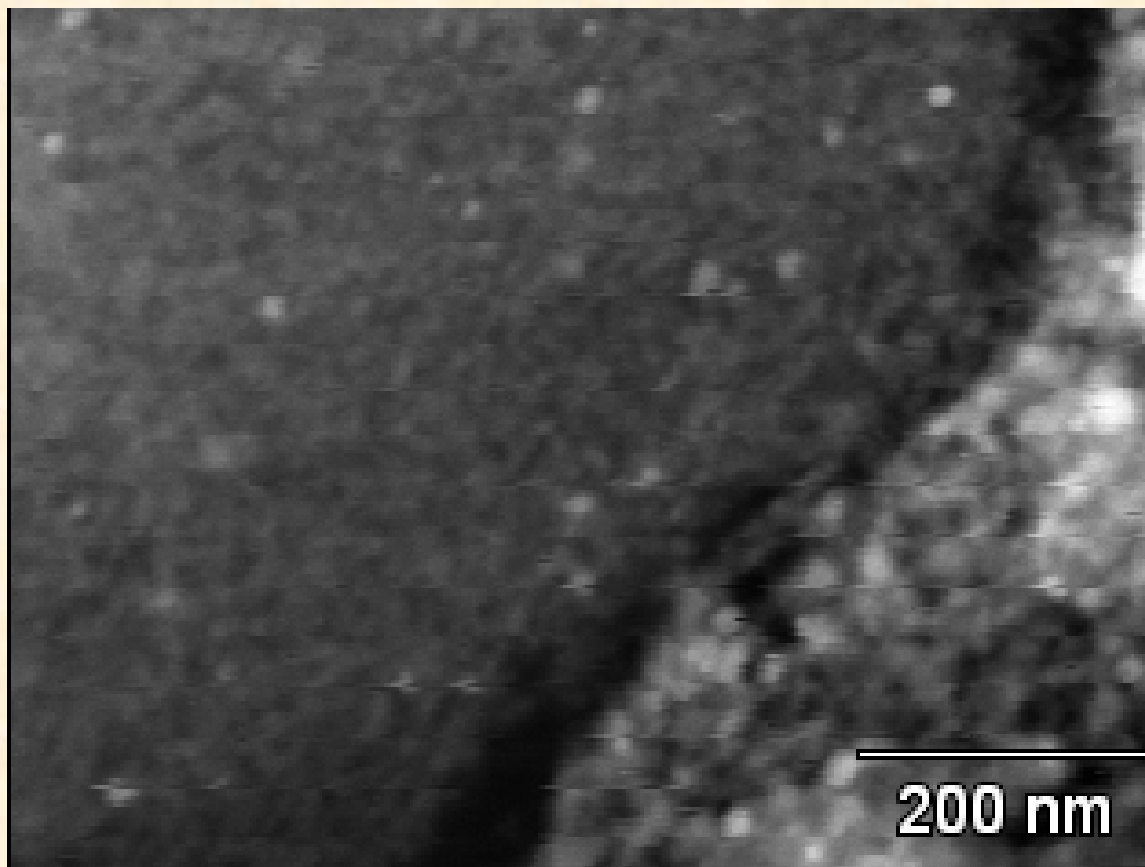
15kV ZrKa



# Pt map



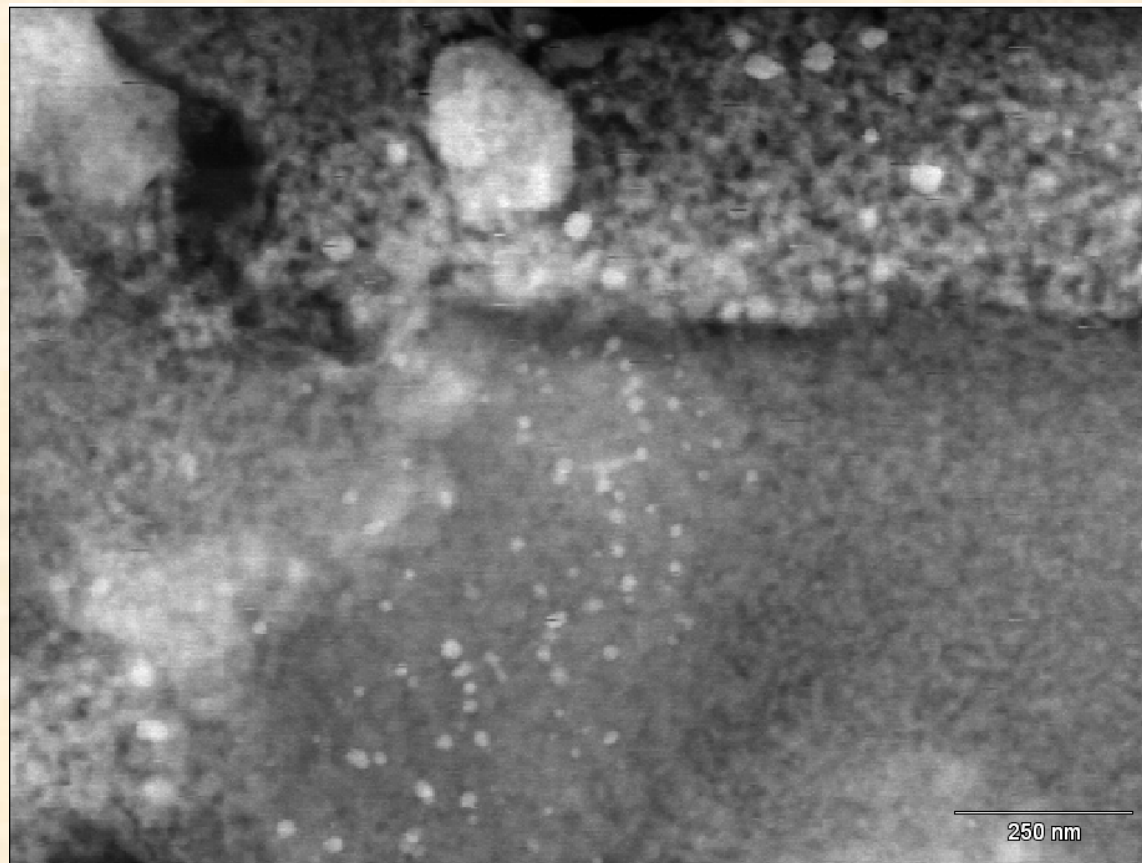
# 30Km sample (vehicle 112)



ZC for spectrum imaging

82K

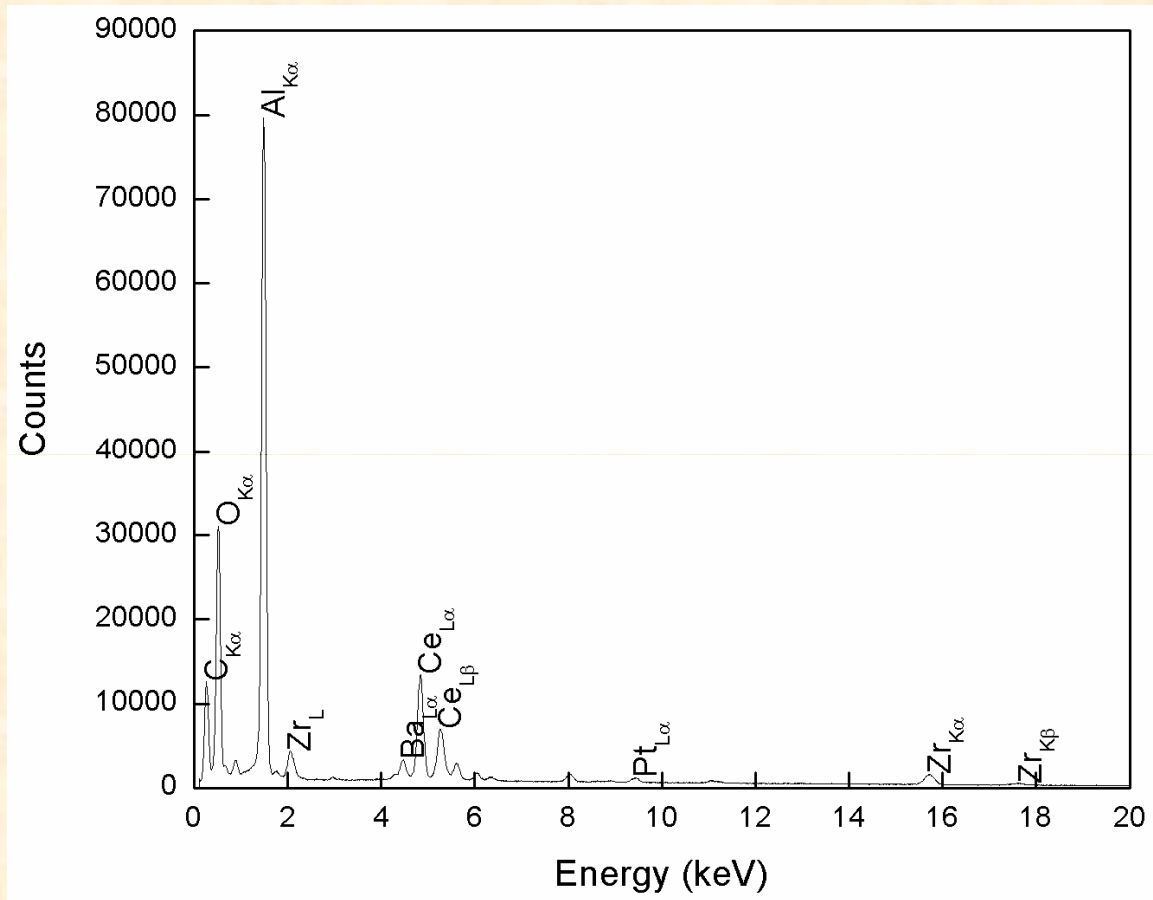
Vehicle 240



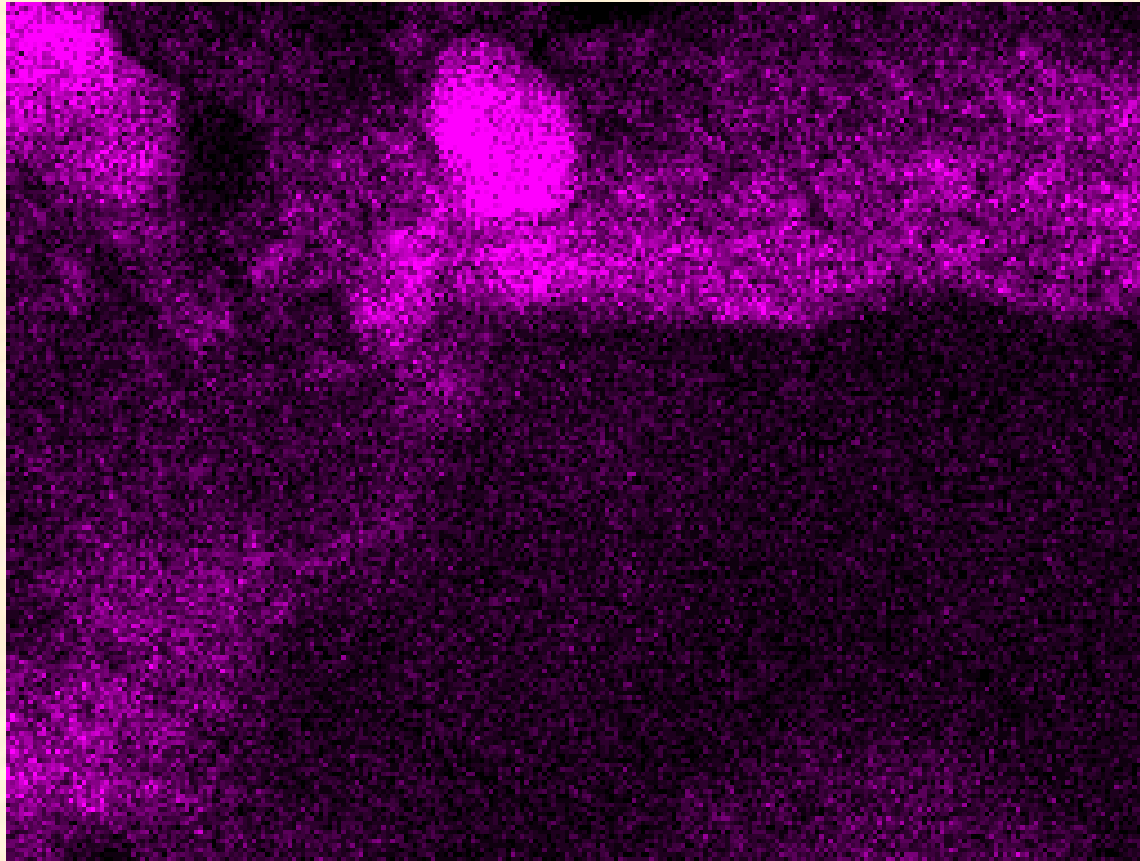
Note bimodal distribution of Pt particles, partitioned betw oxide phases



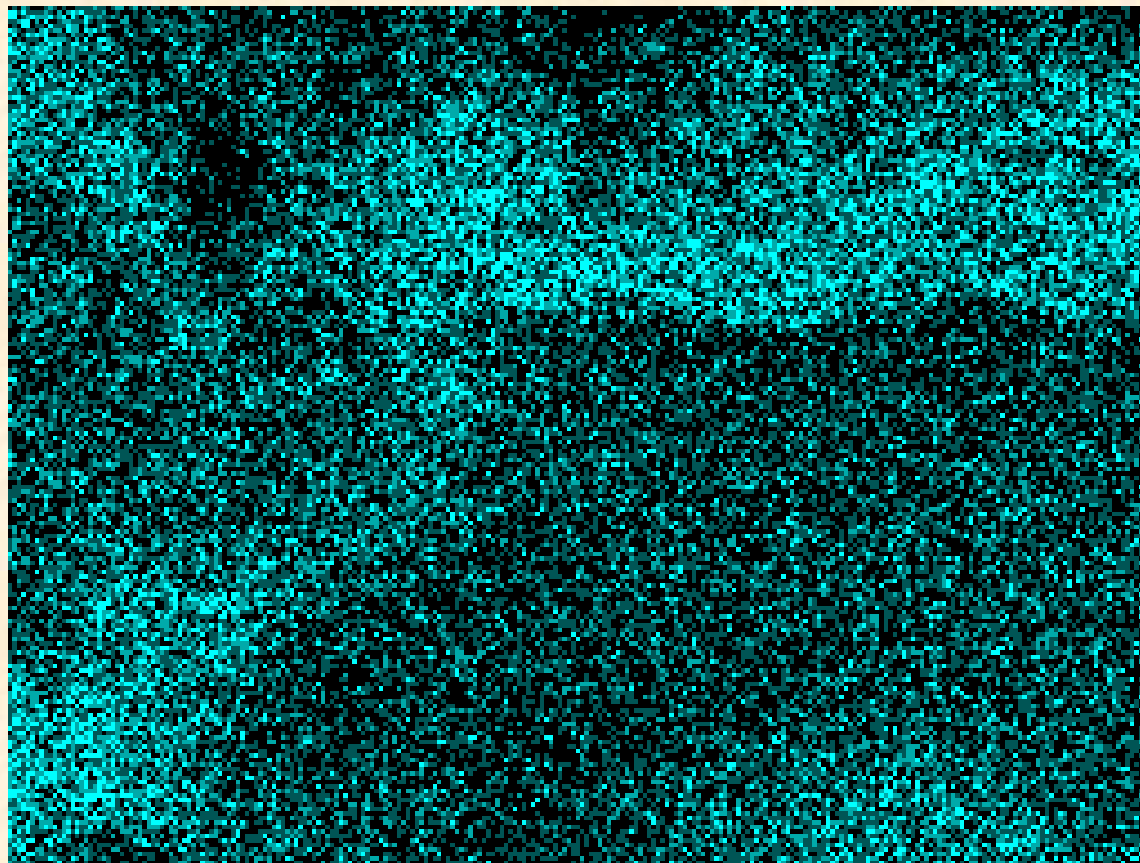
# Sum spectrum



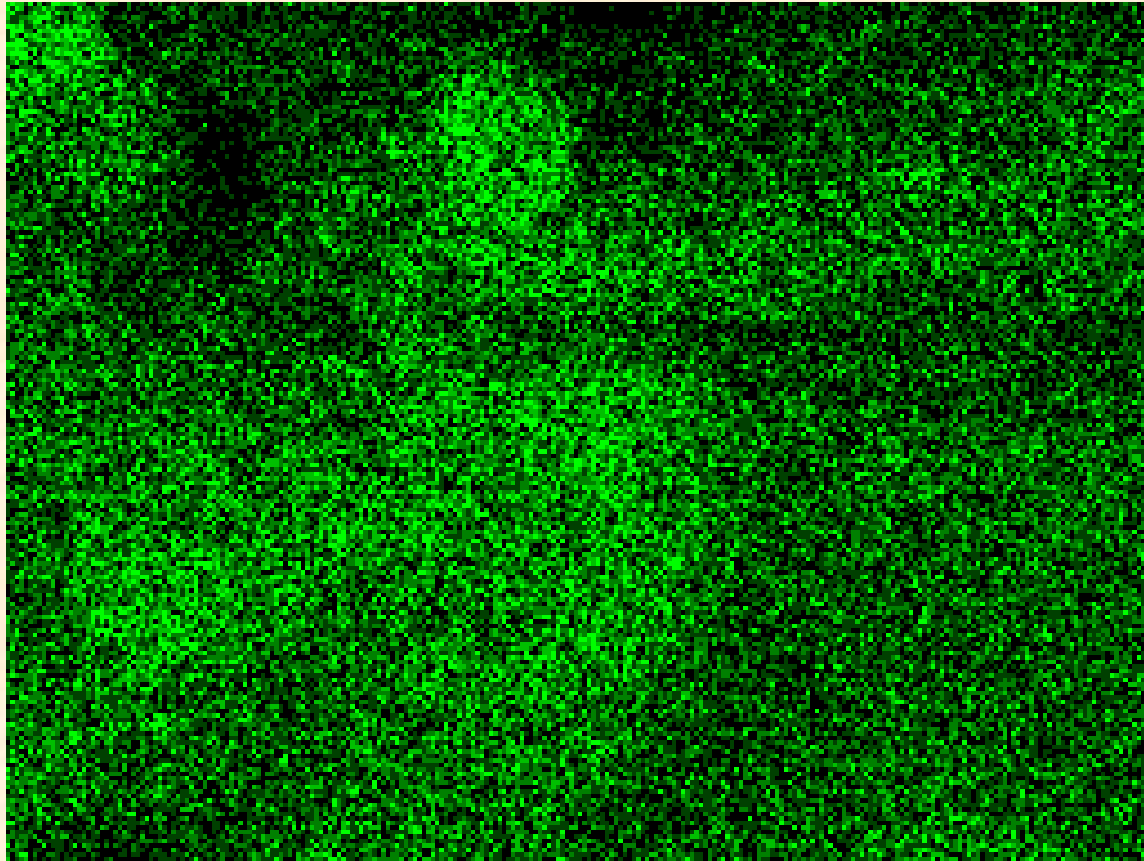
# Ce map



# Zr Map

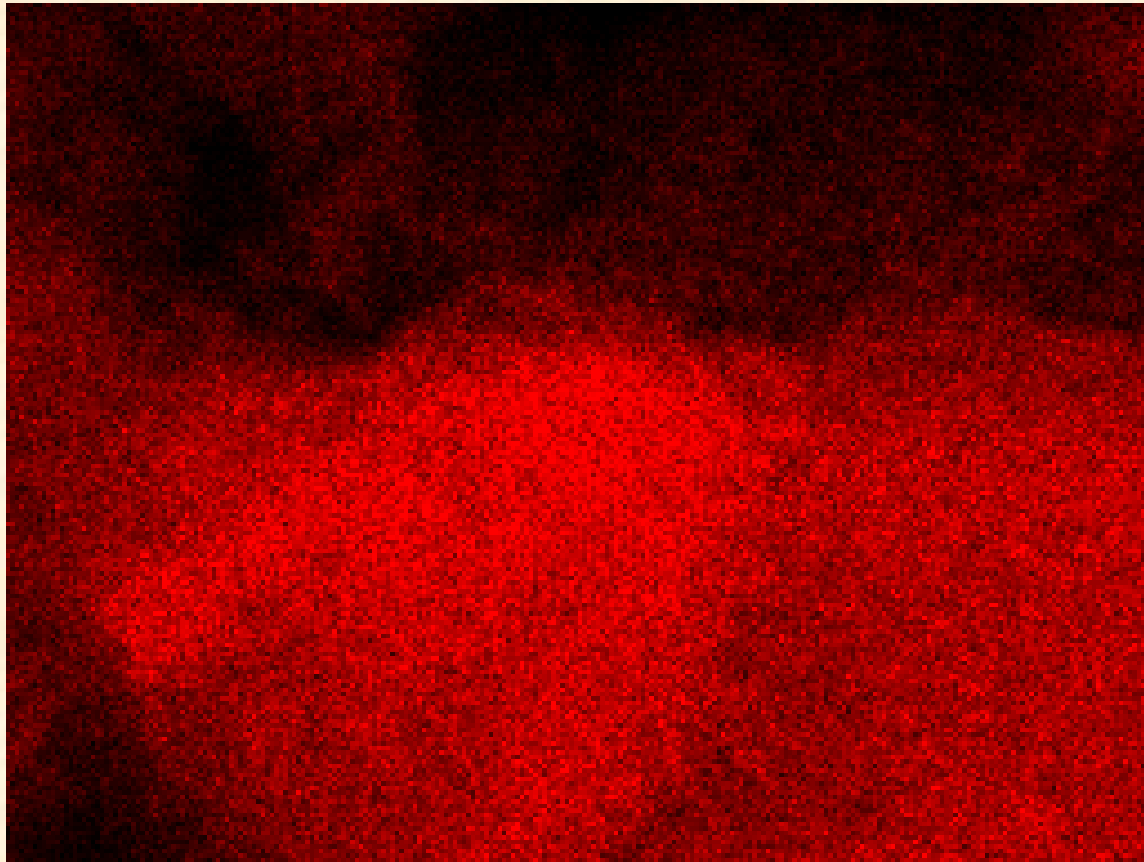


# Ba map





# AI Map

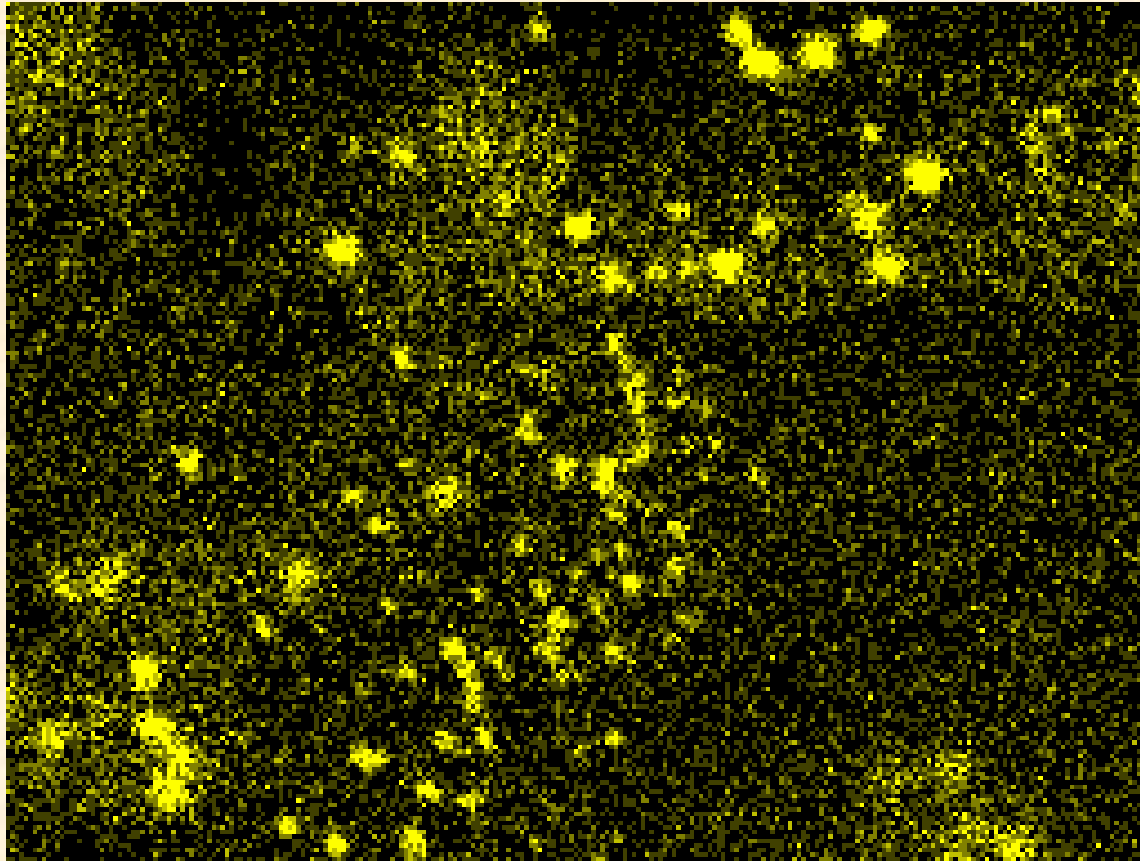


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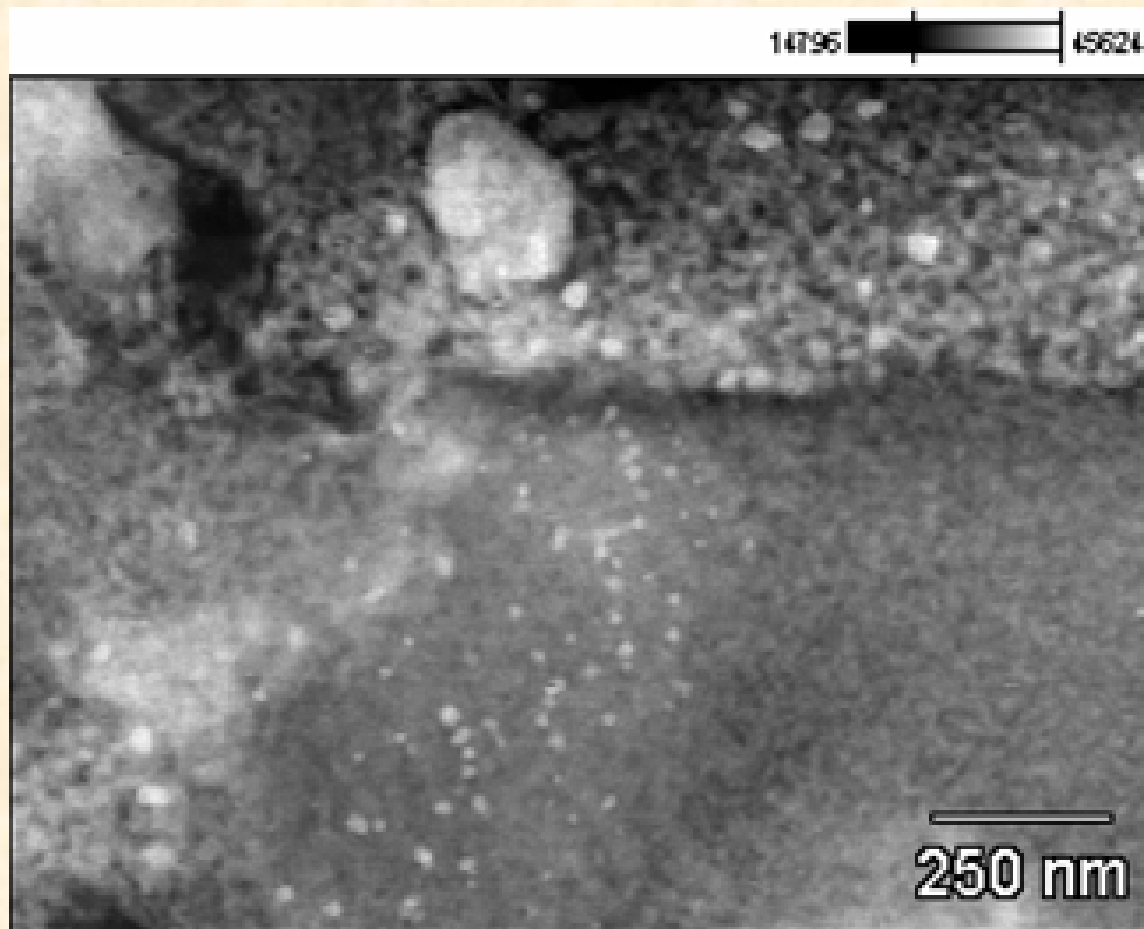


8-hr spectrum image

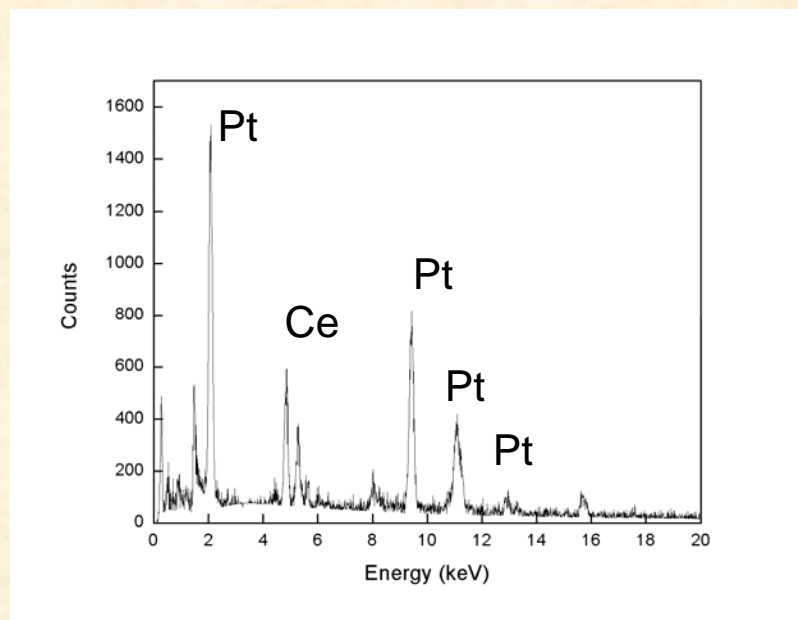
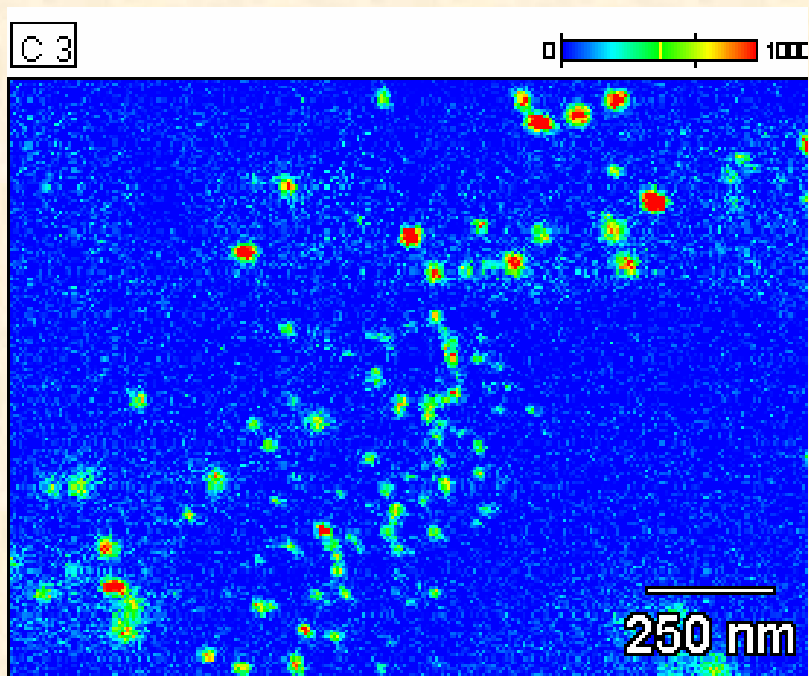
# Pt Map



82K



Principal Component Analysis:  
Basically Pt, with some Ce and Zr



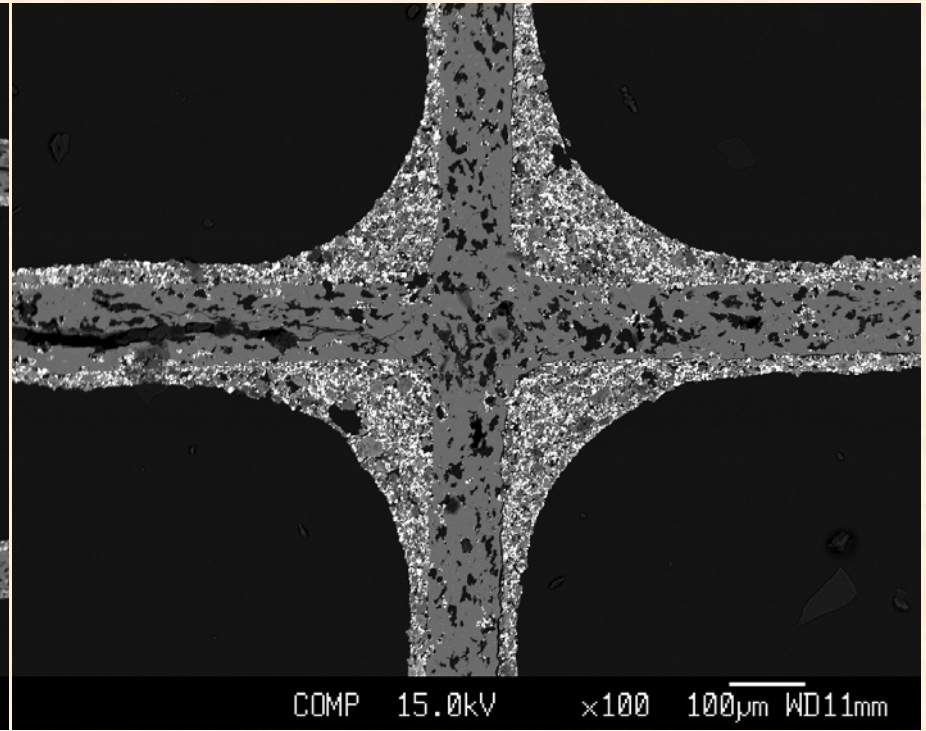
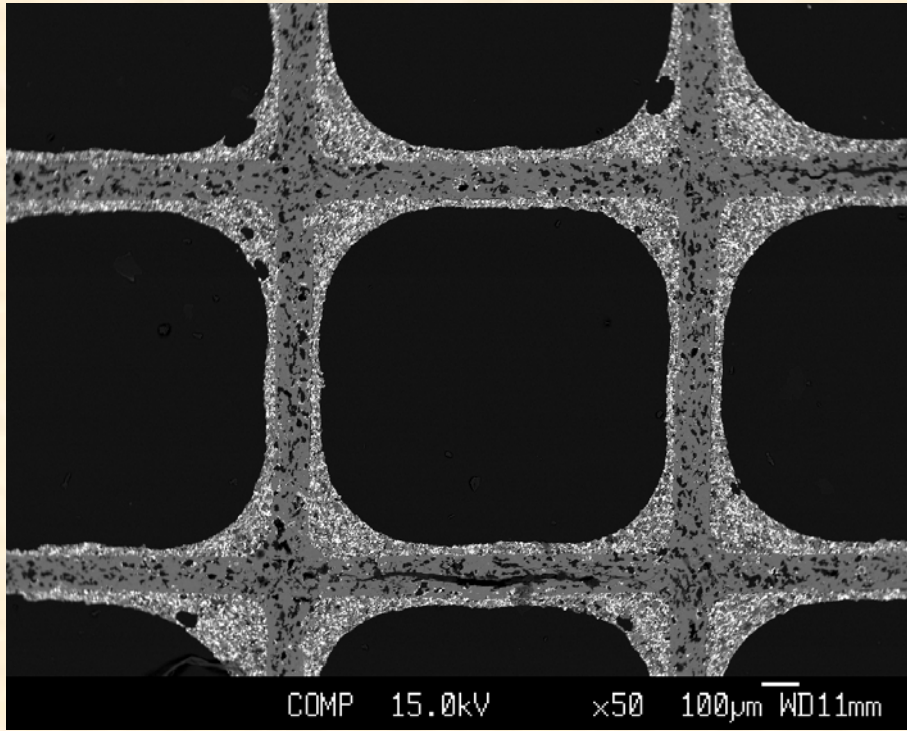


# Microstructural Studies of Supplier NO<sub>x</sub> Traps - Passenger Vehicle (DISI Fleet) Aging

- **The analysis of on vehicle evaluated samples after 32K km and 80K km showed that the bulk of precious metal sintering occurred in the early stages of on vehicle aging**

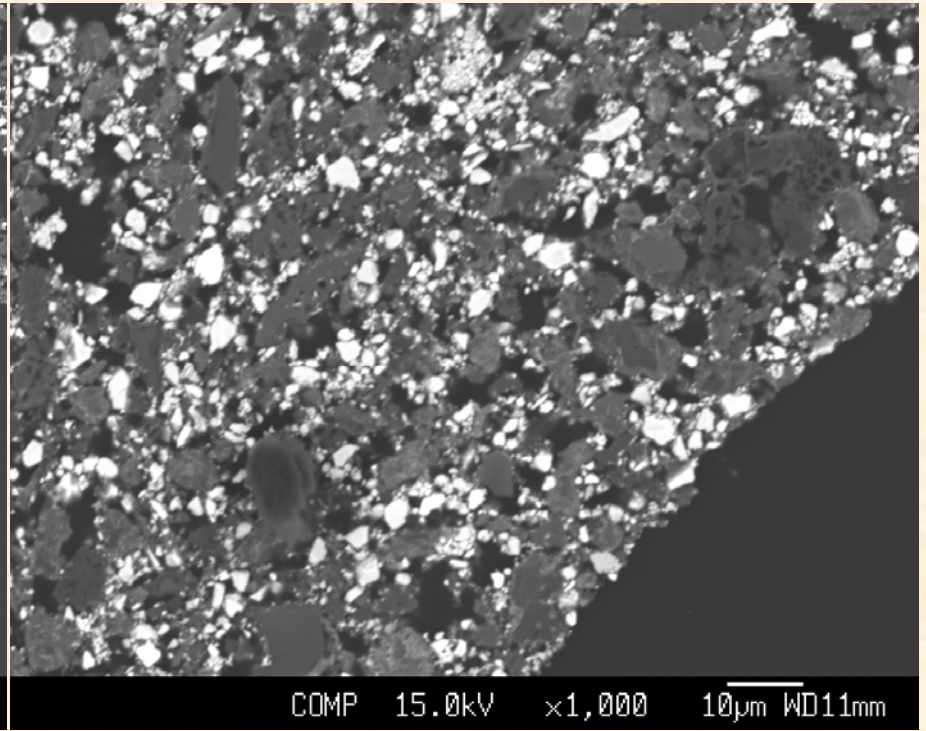
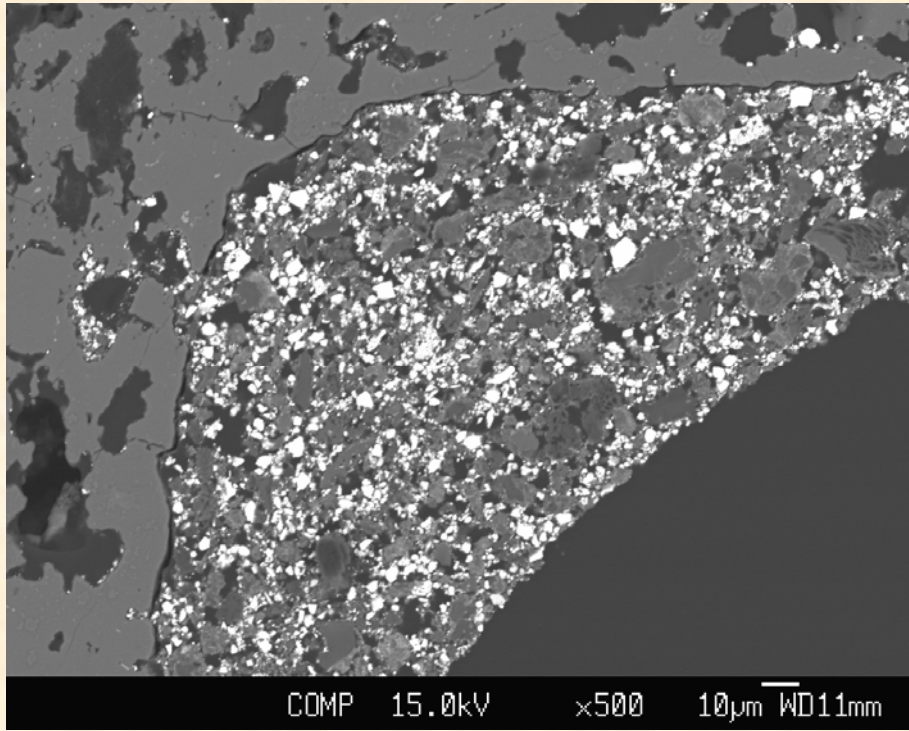
## Umicore LNT Catalysts:

- Fresh
- De-greened



Umicore GDI LNT fresh

BSE microprobe



BSE microprobe

04-3340

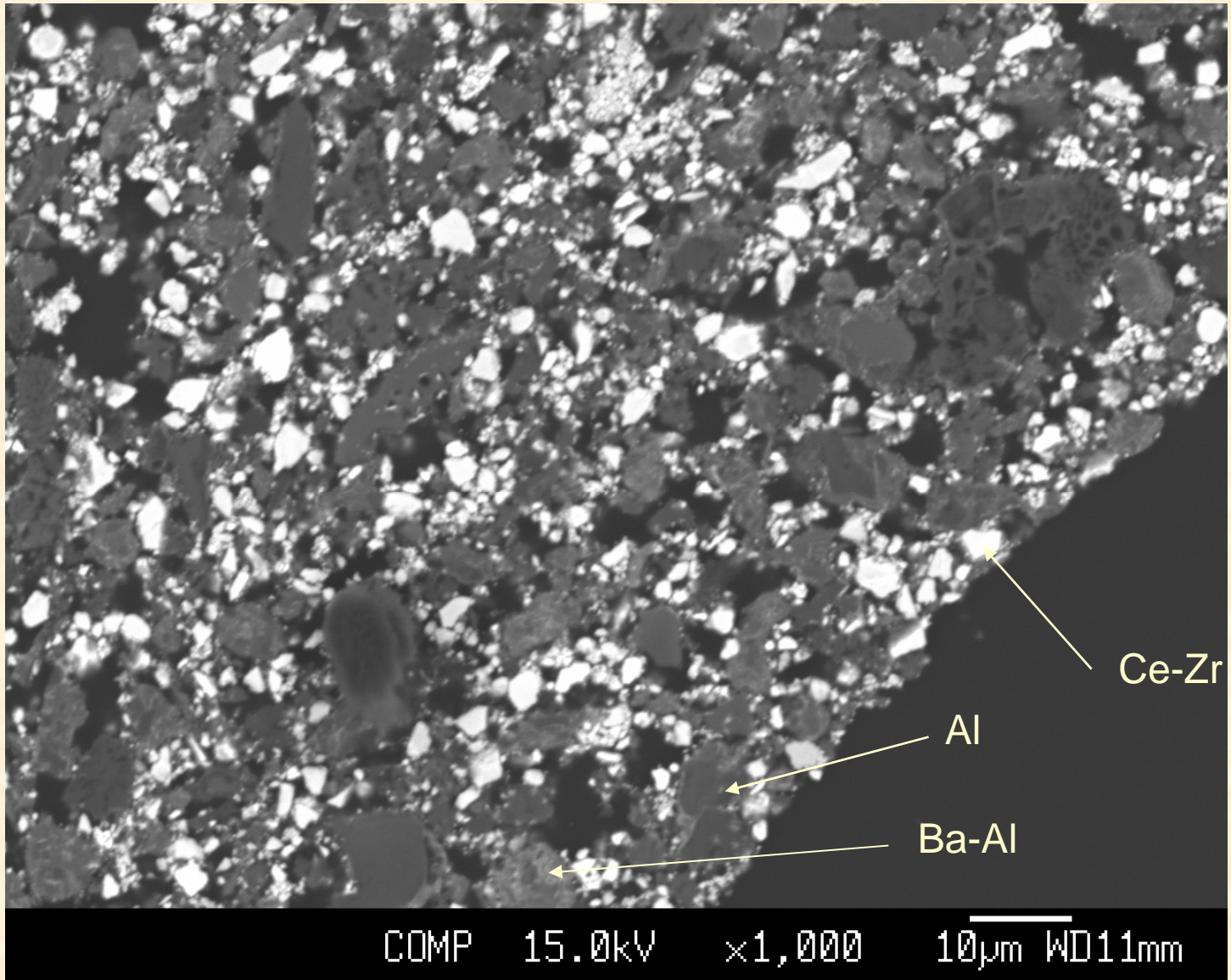
Umicore LNT fresh

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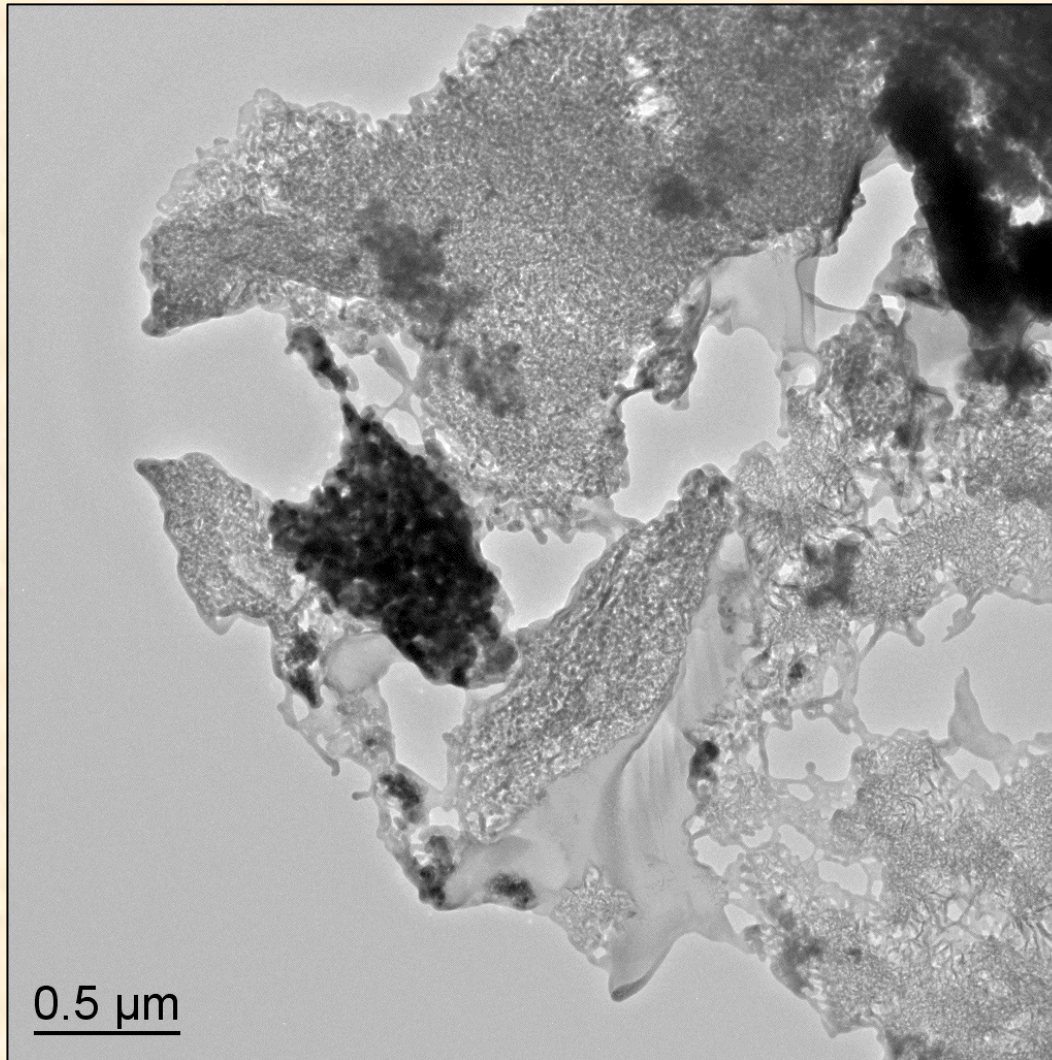




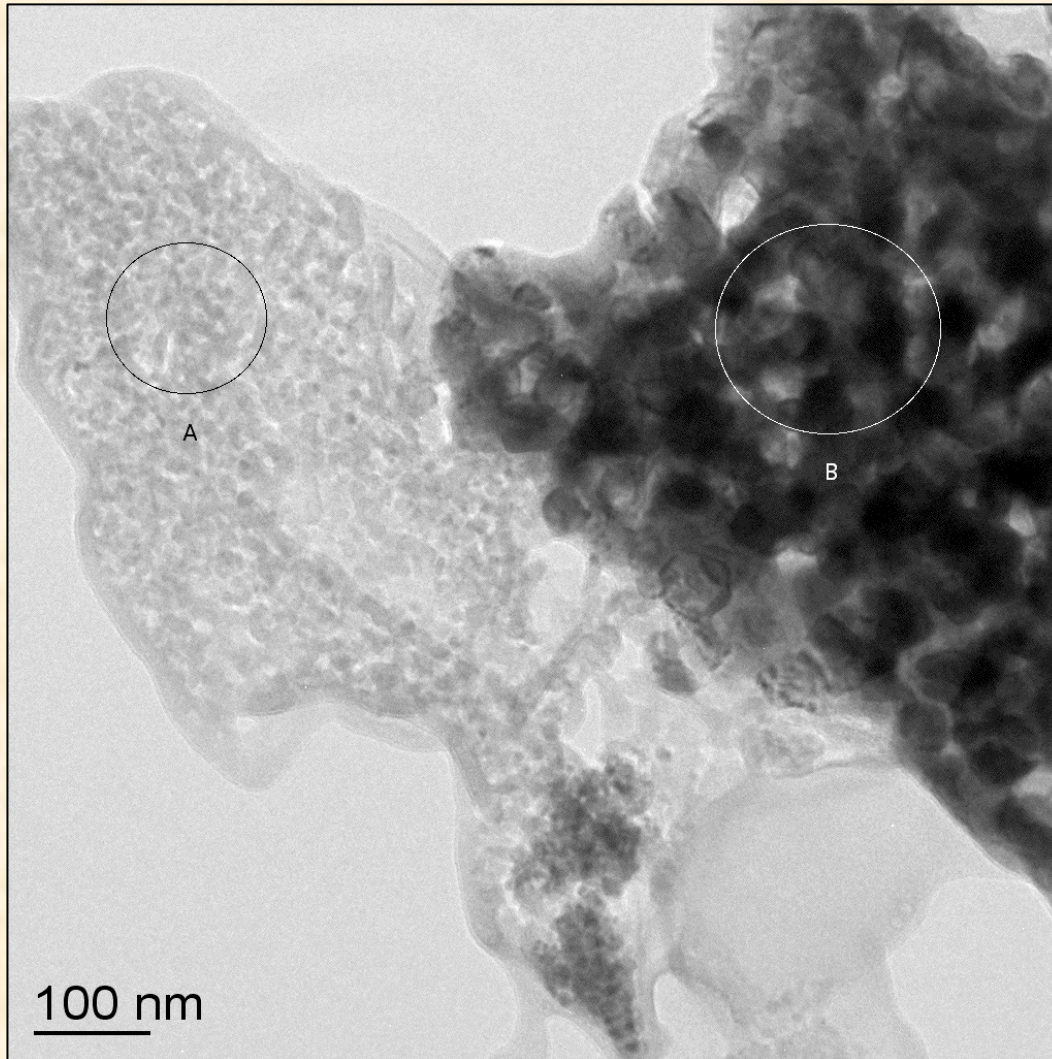
Umicore LNT fresh

large Ba-Al aggregates

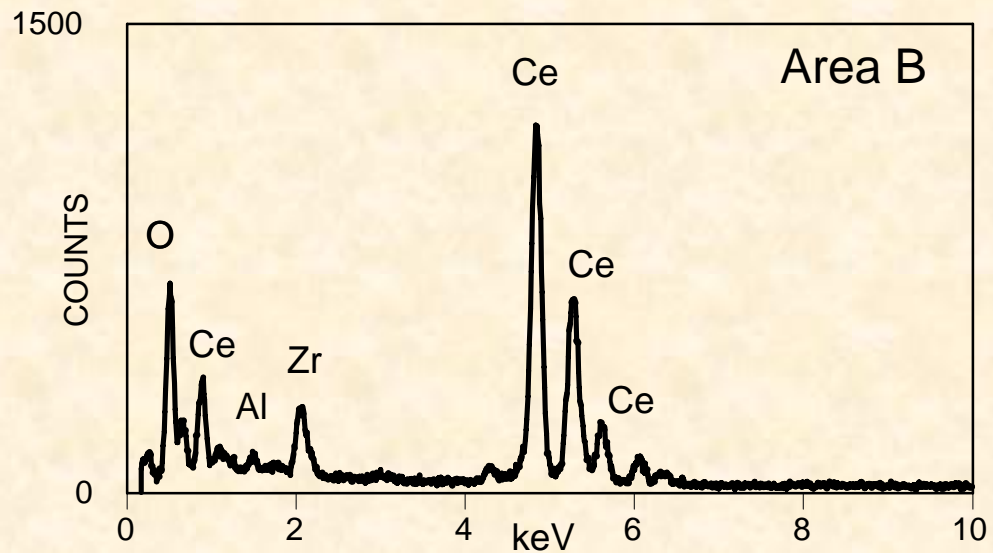
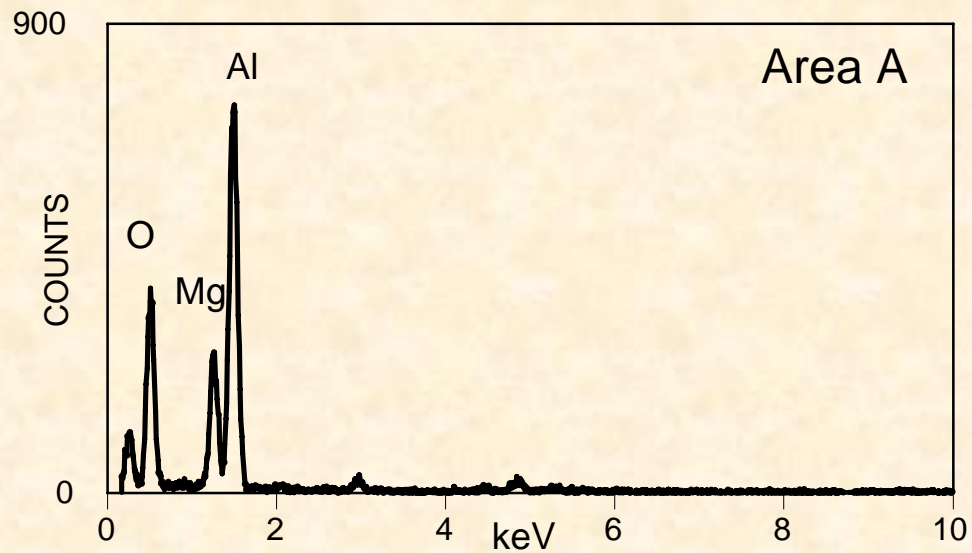




Umicore LNT fresh      Ion-milled thin section



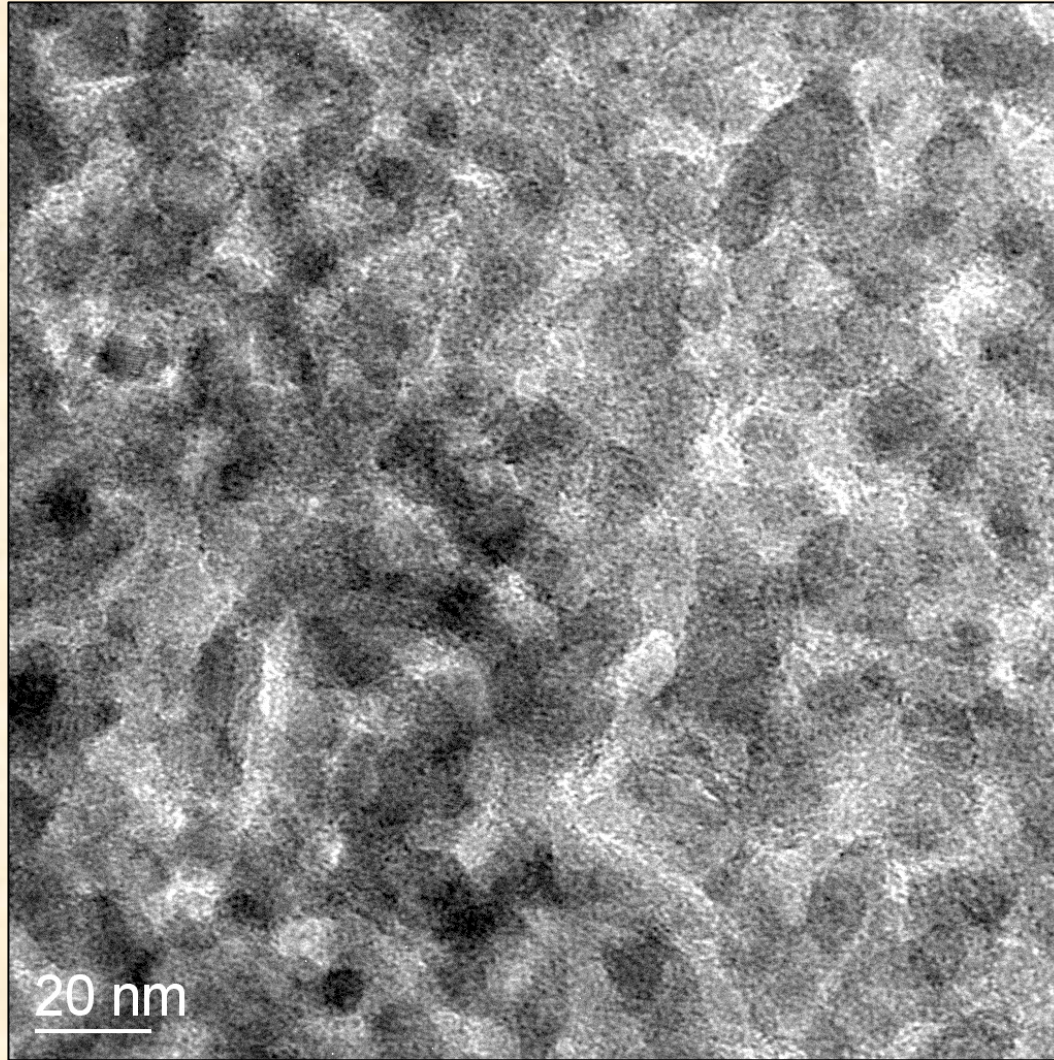
Umicore LNT fresh





Umicore  
LNT Fresh

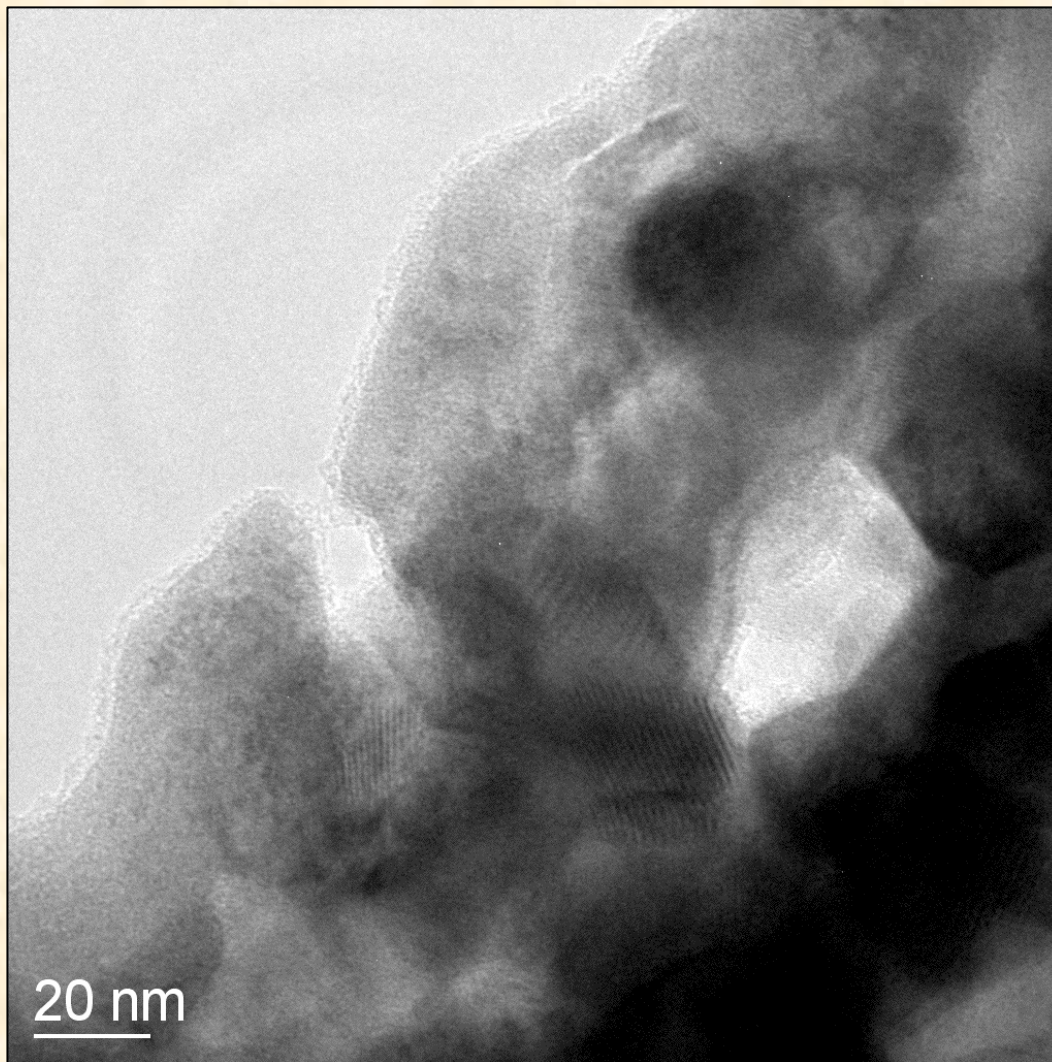
BF TEM



Area A

Alumina-magnesia

Umicore  
LNT Fresh

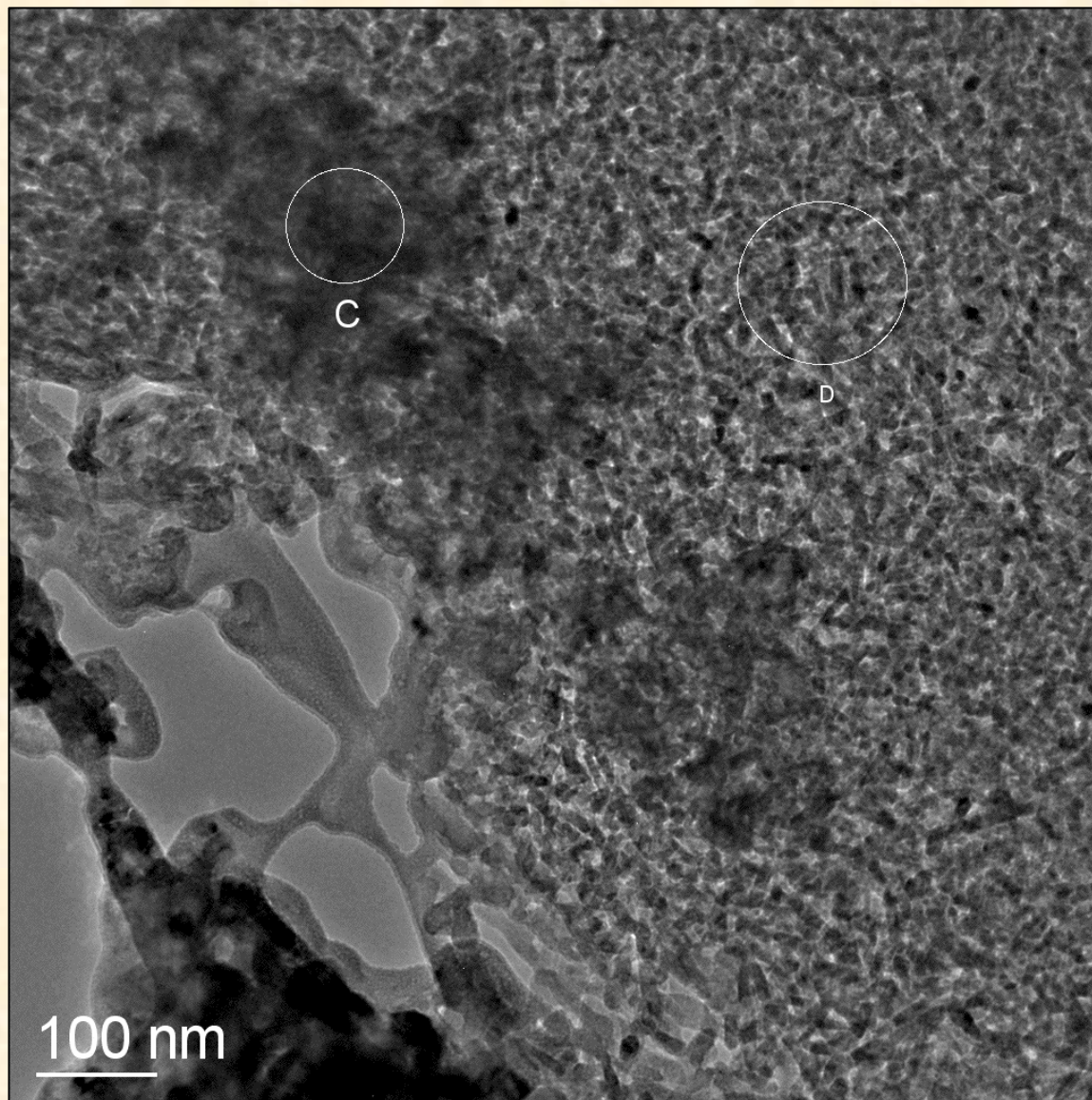


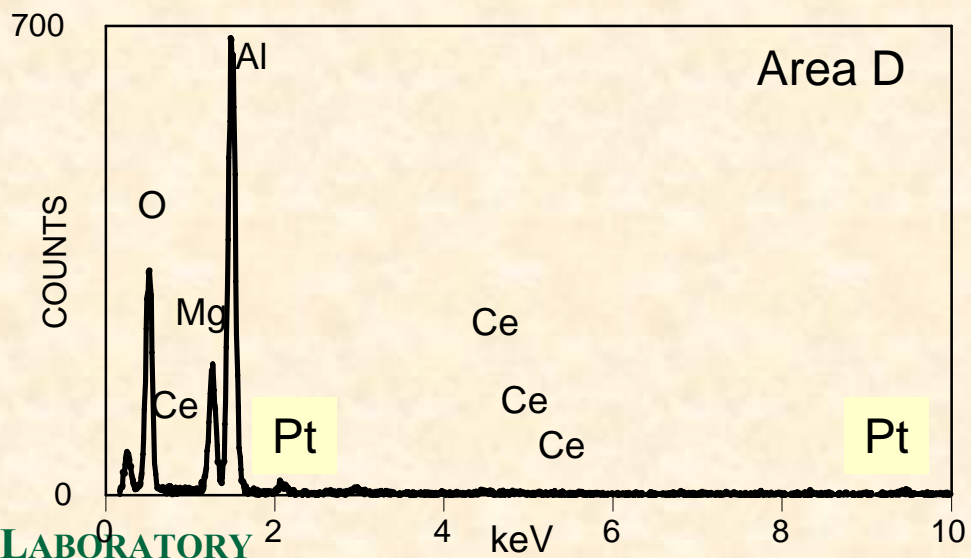
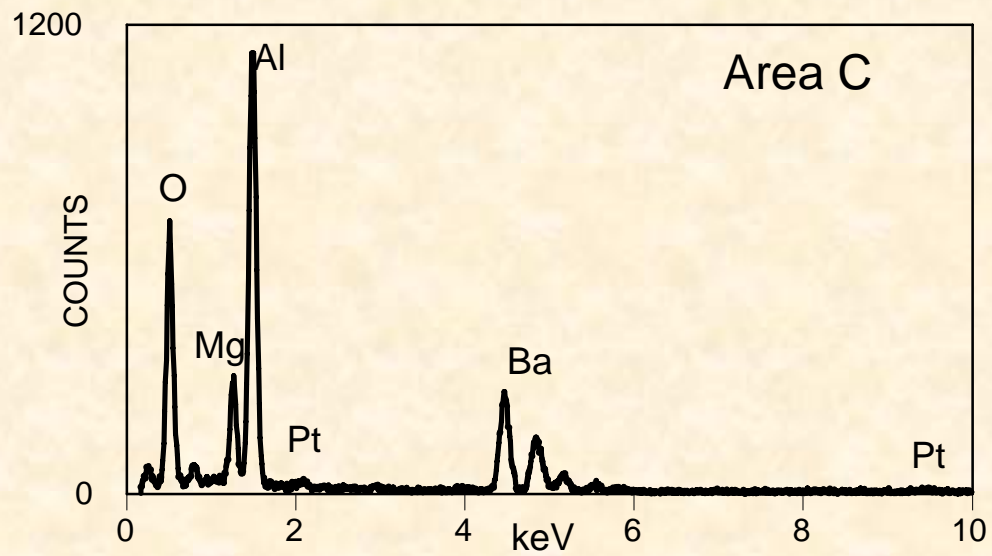
Area B

Ce-Zr (primarily Ce)



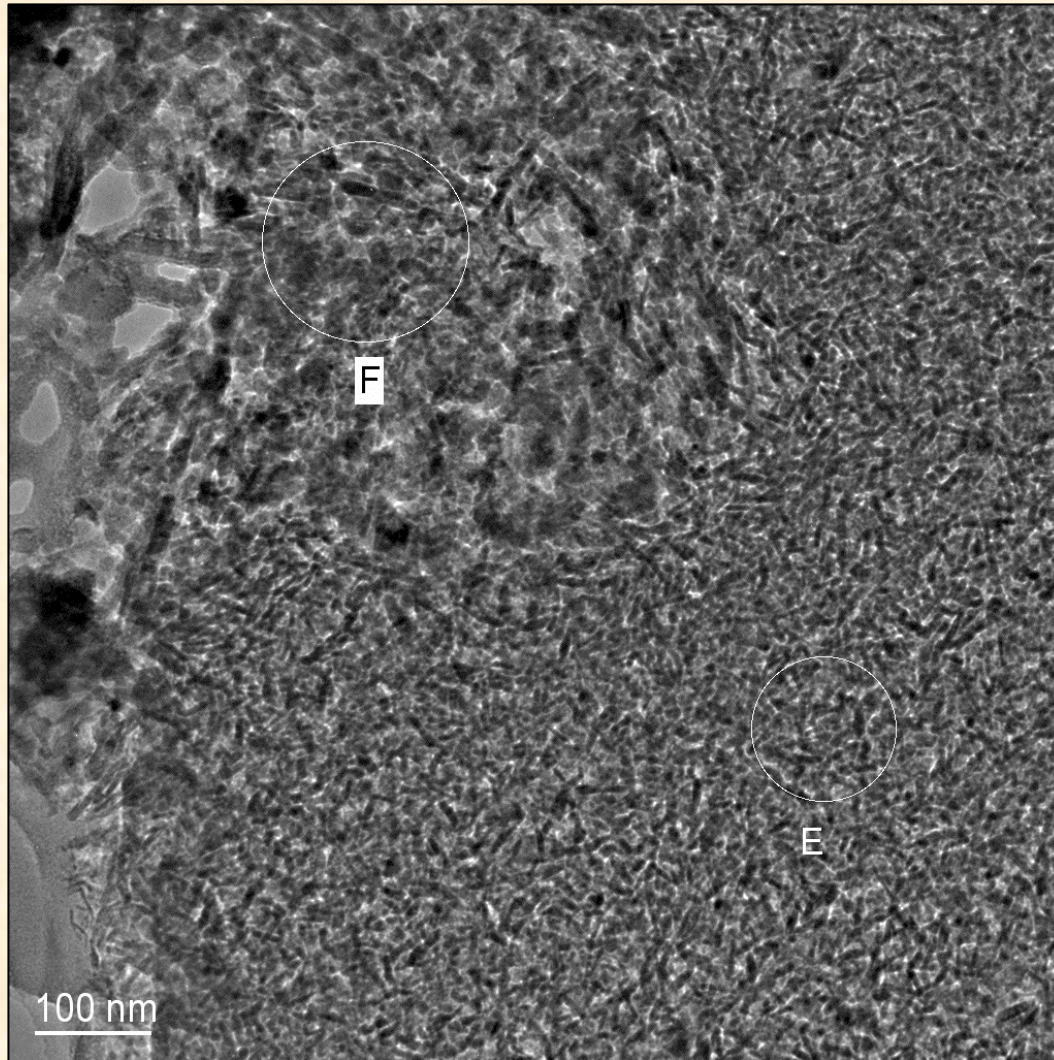
Umicore  
LNT fresh



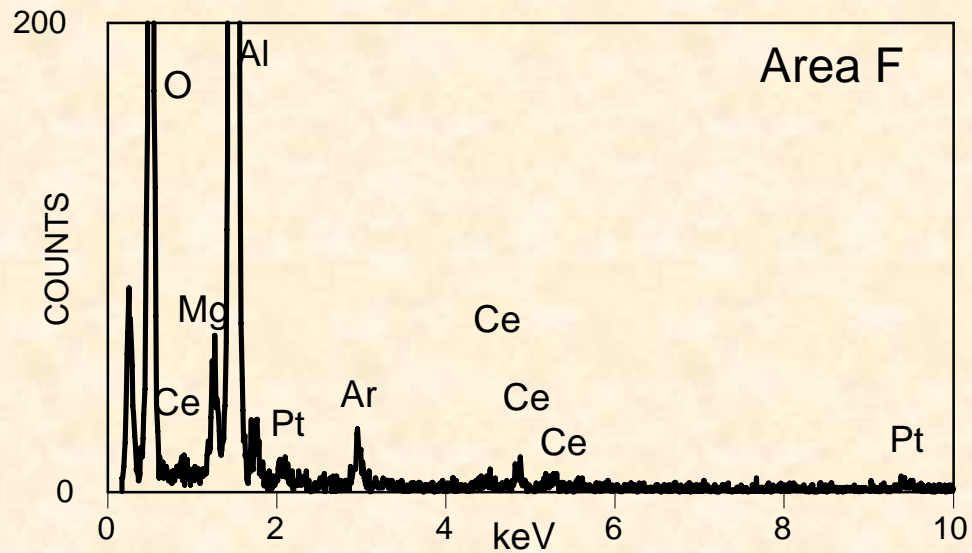
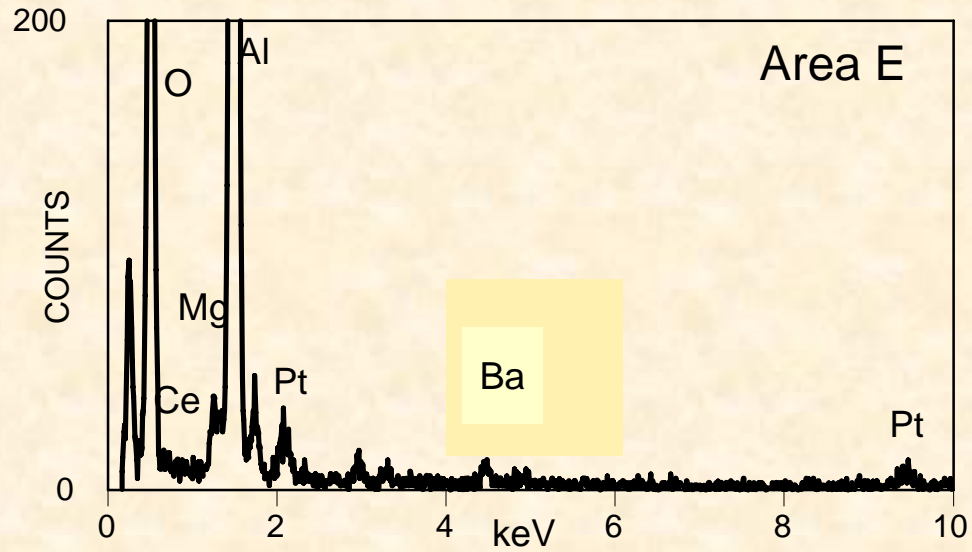




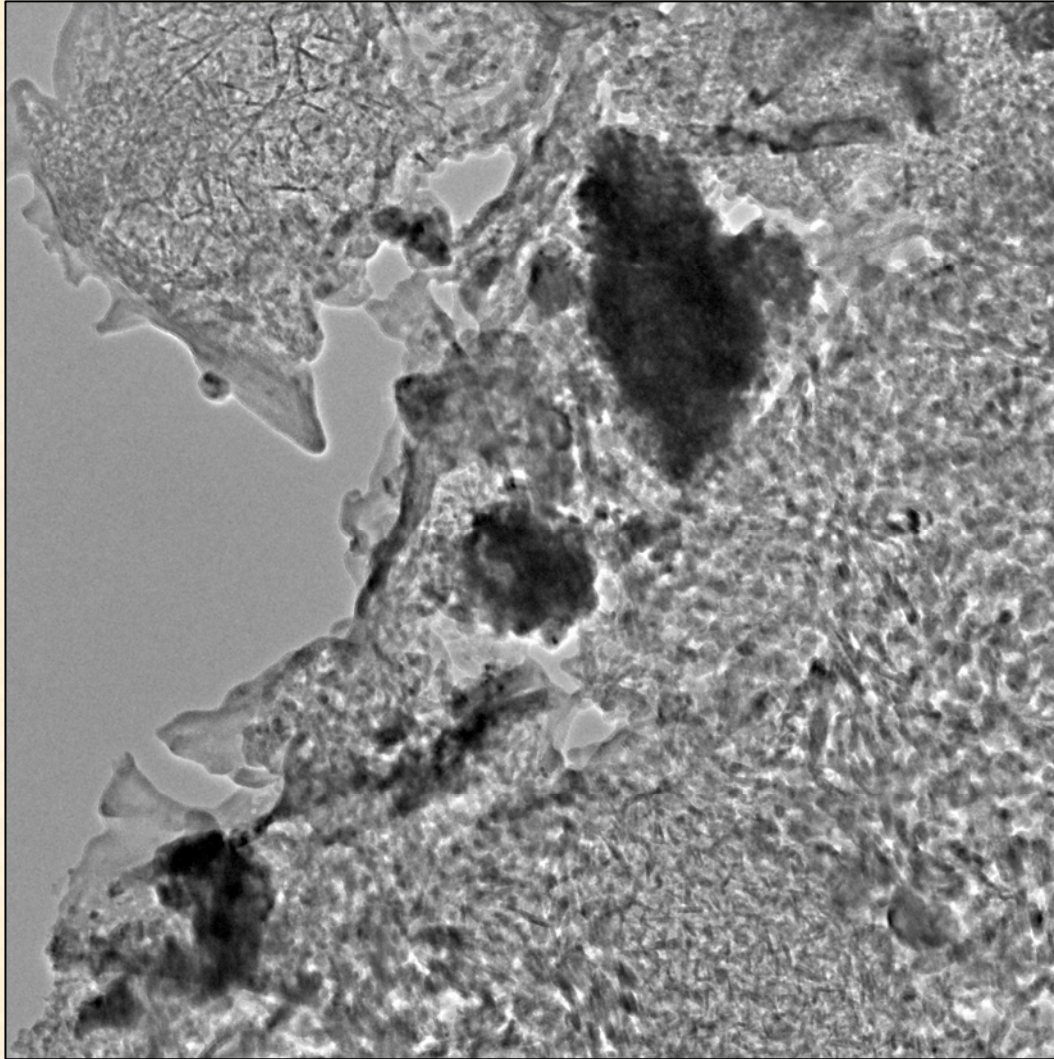
Umicore  
LNT fresh



E and F primarily Alumina, Pt also present (see next)



Umicore  
LNT Fresh

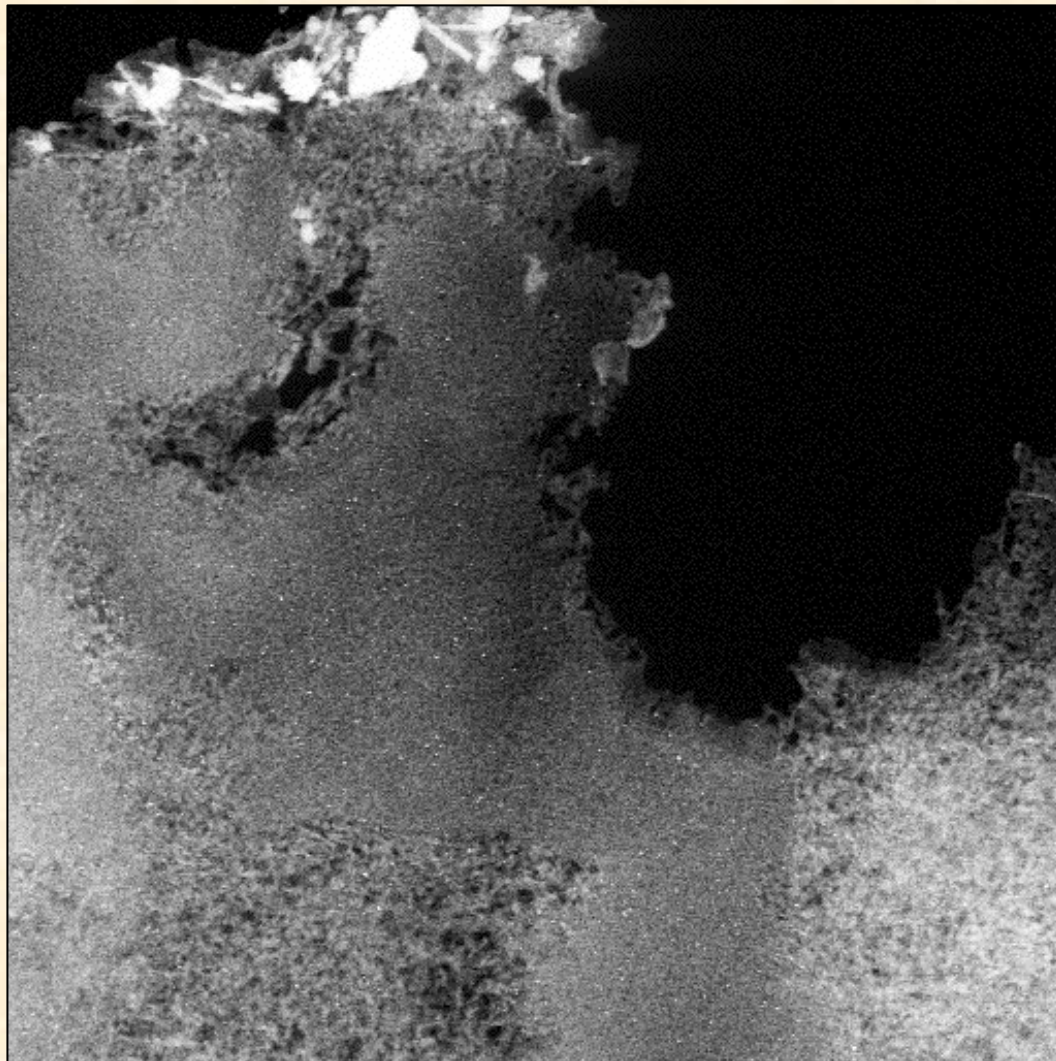


BF ACEM

(Remaining slides all ACEM)

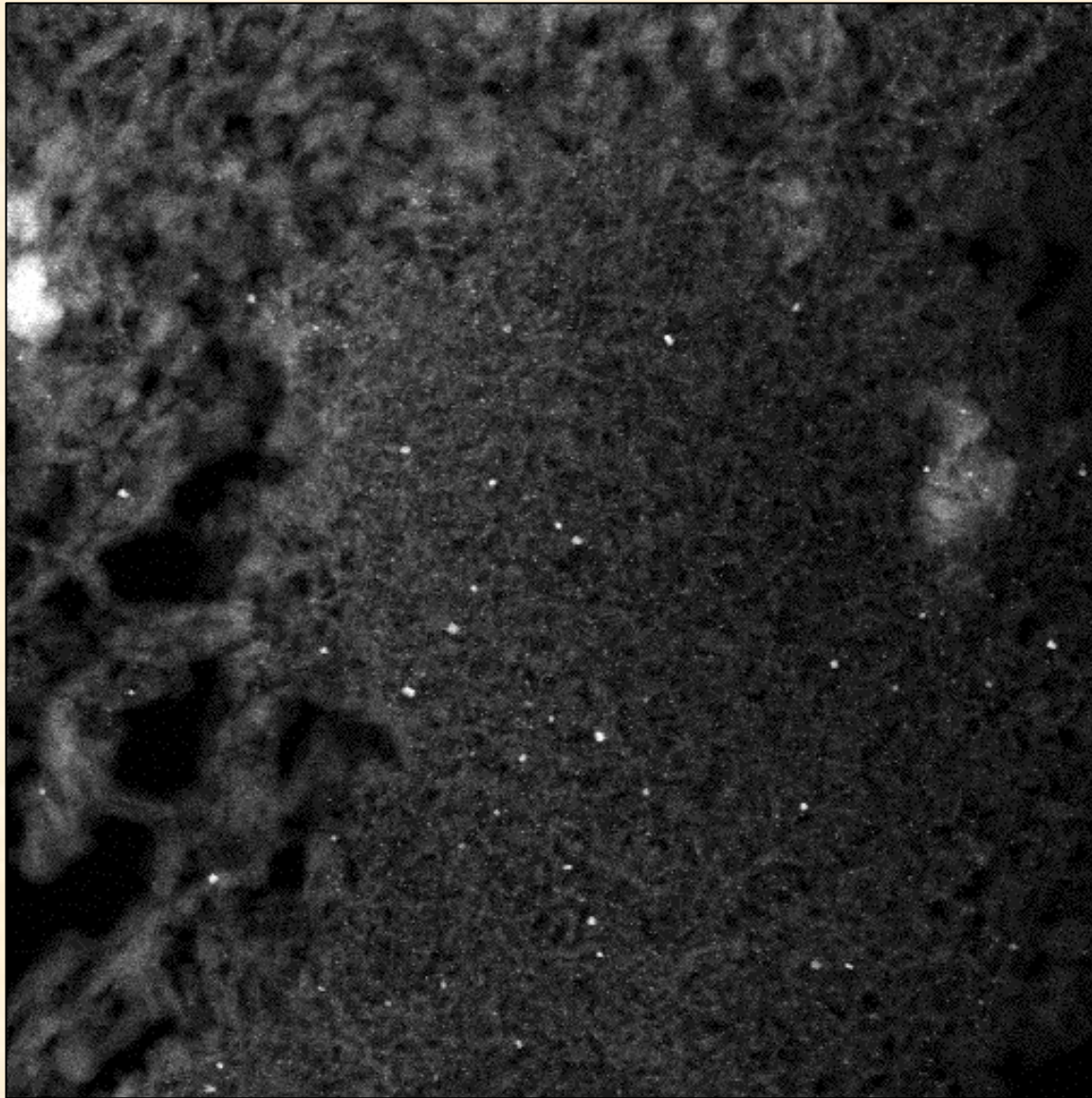


Umicore  
LNT fresh



ADF STEM ACEM

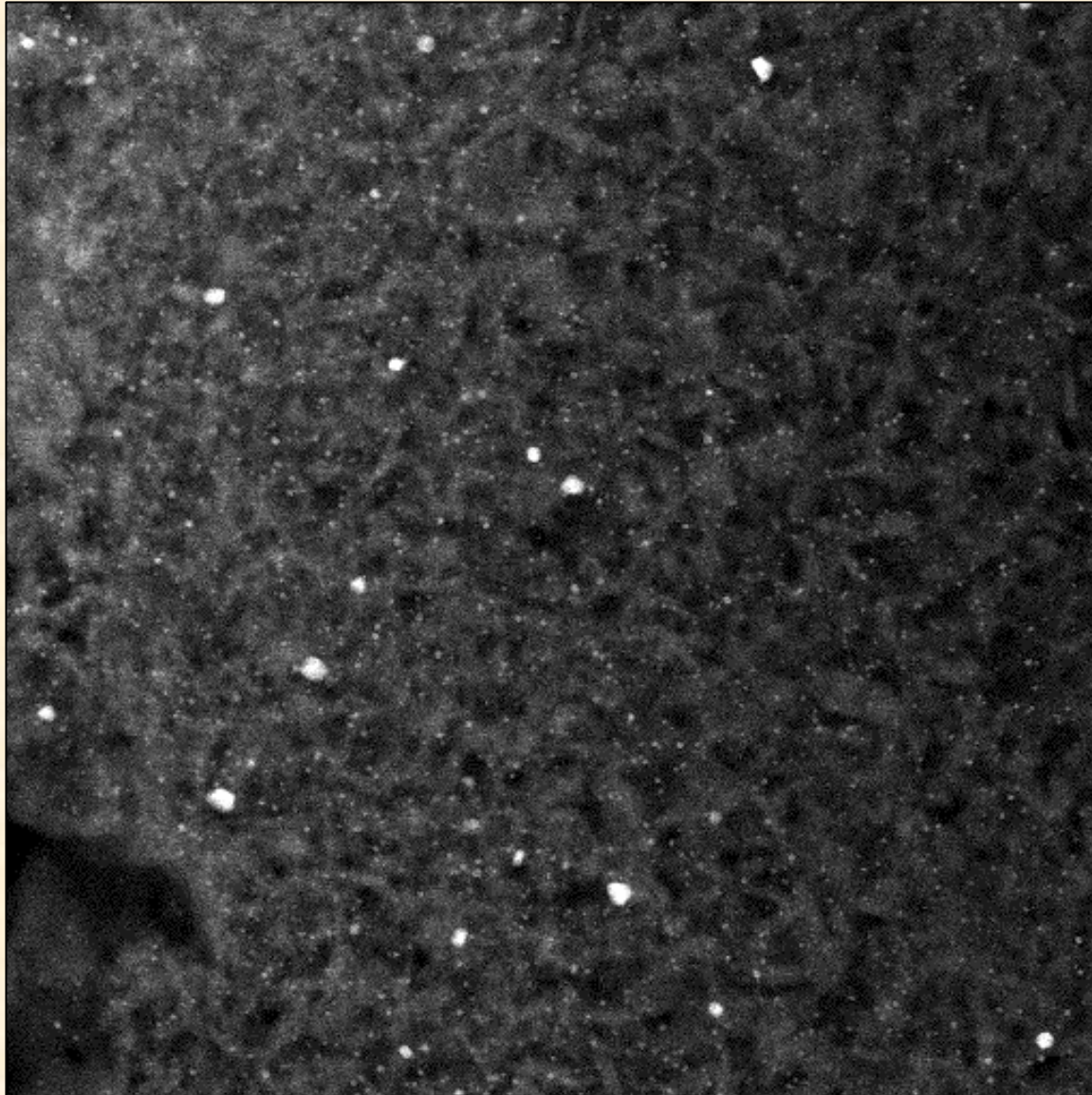
Umicore  
LNT Fresh



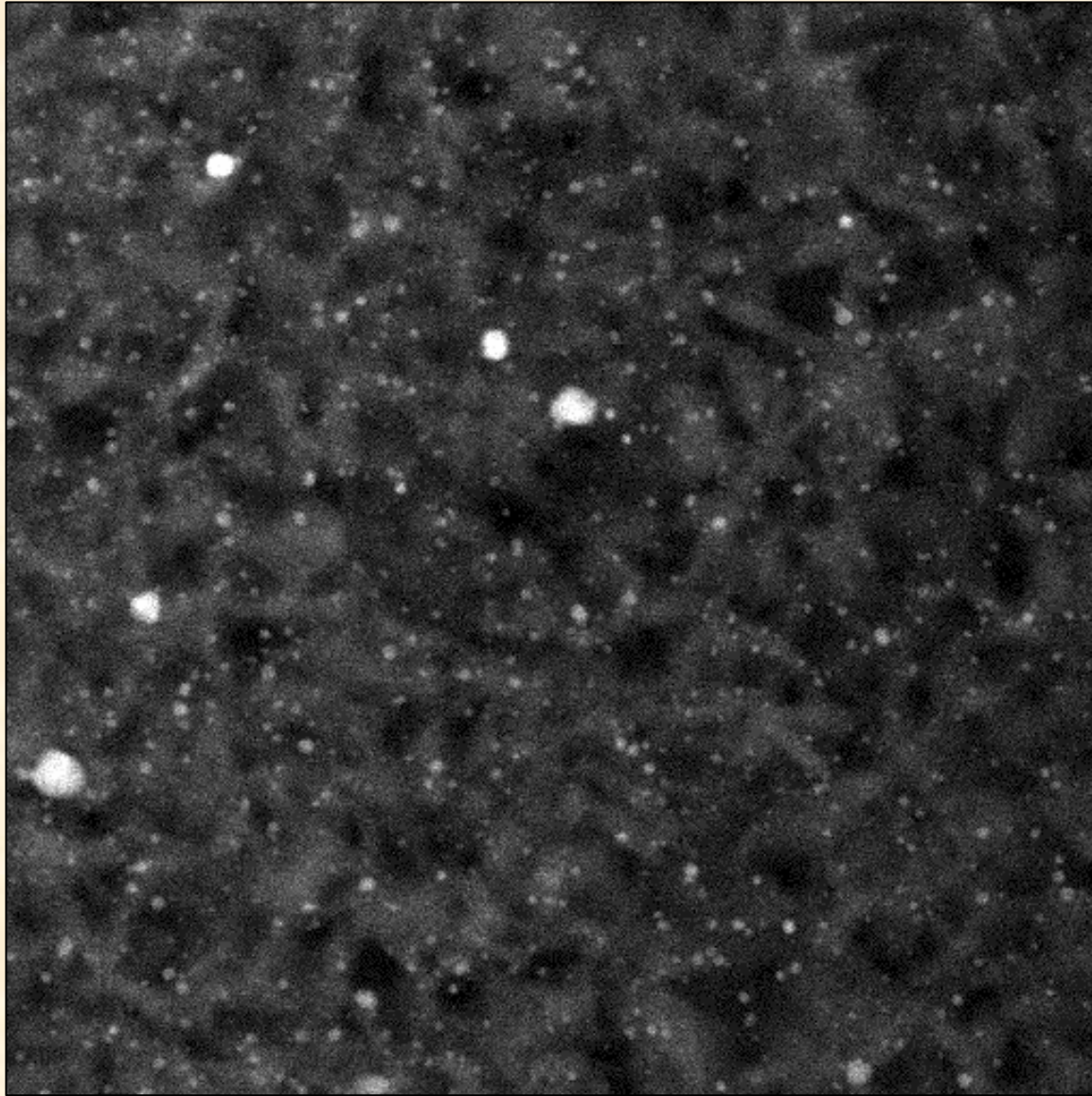
Mag series: 2



Umicore  
LNT Fresh

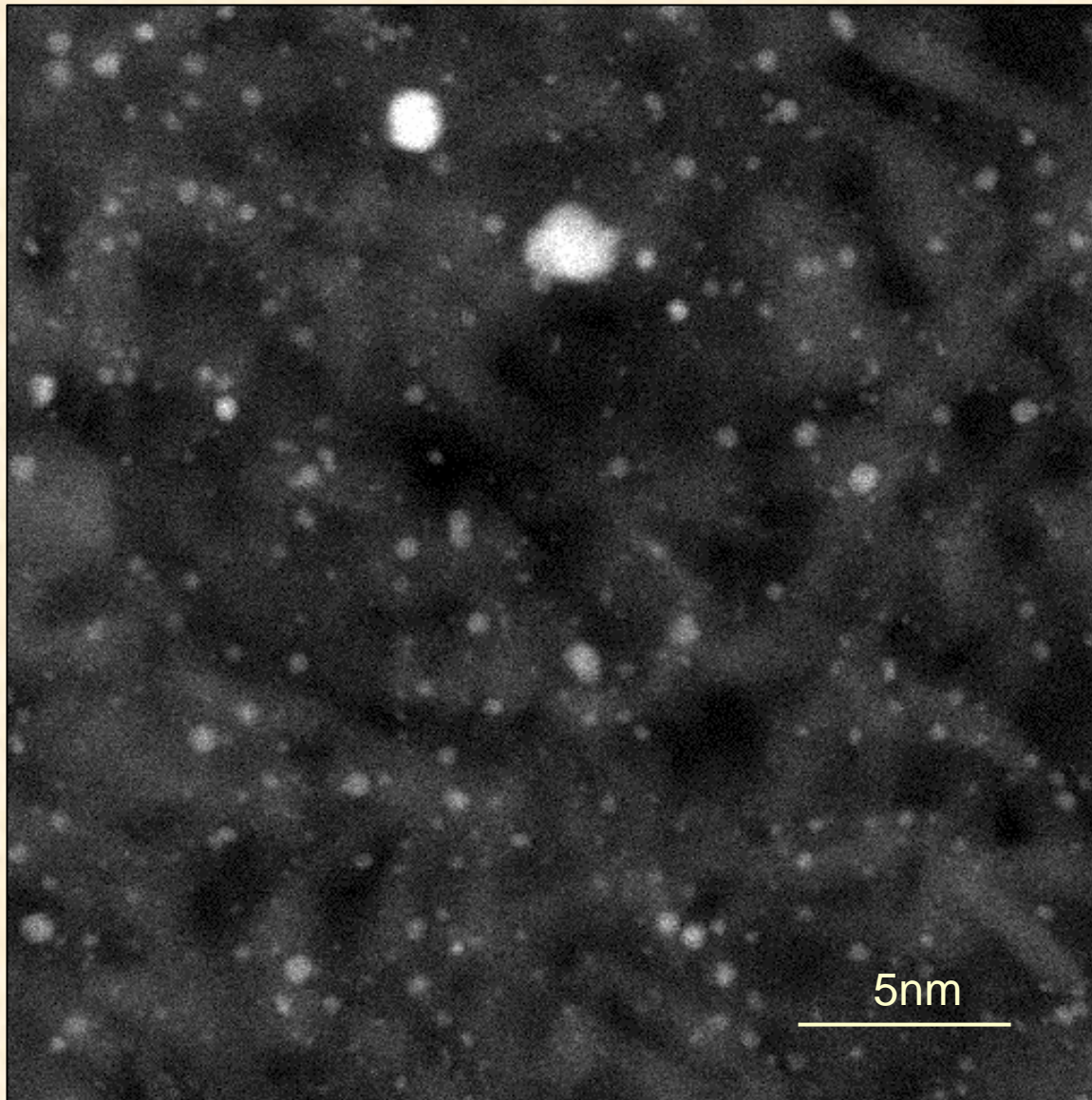


Umicore  
LNT Fresh



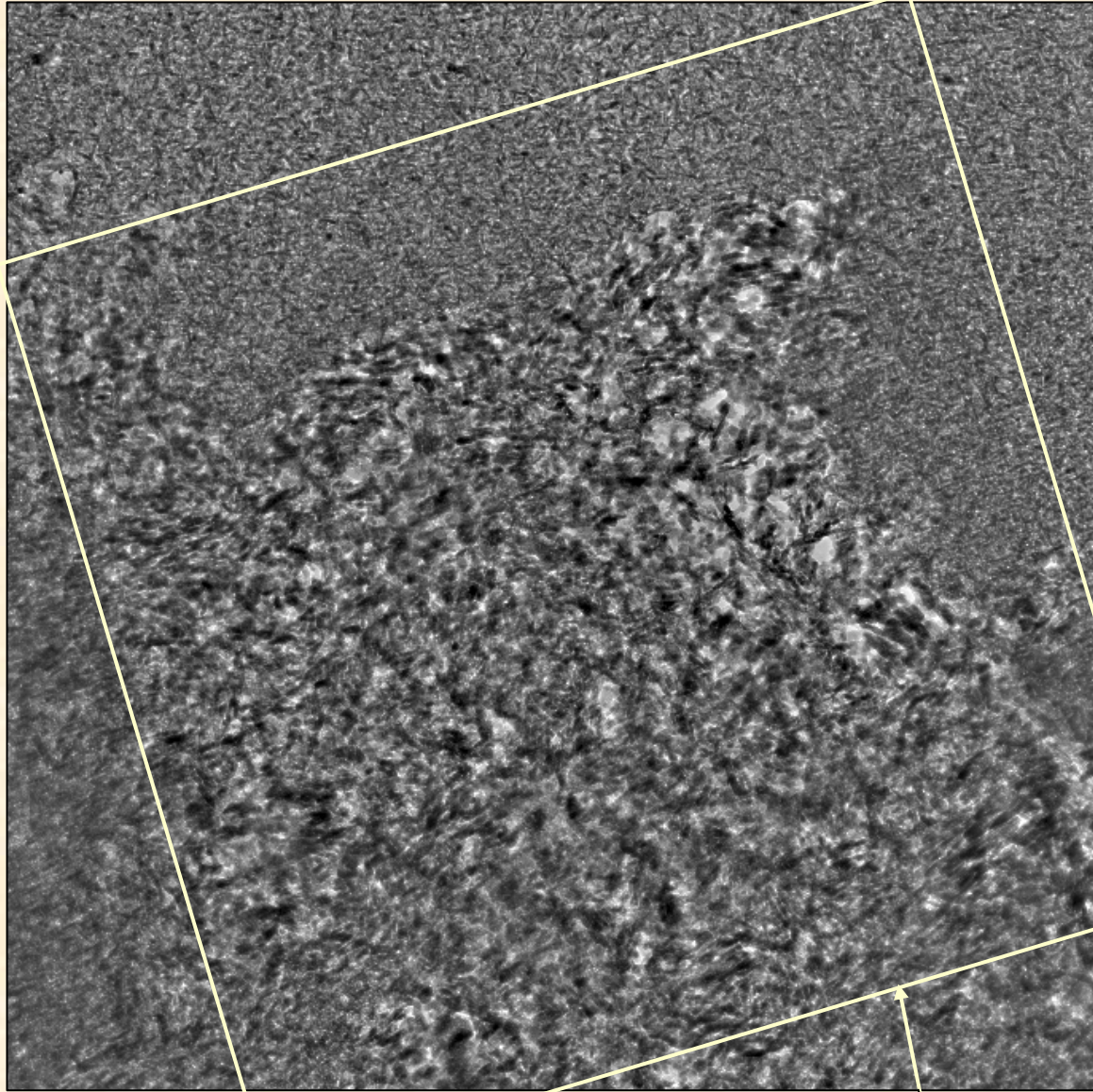


Umicore  
LNT Fresh





Umicore  
LNT Fresh

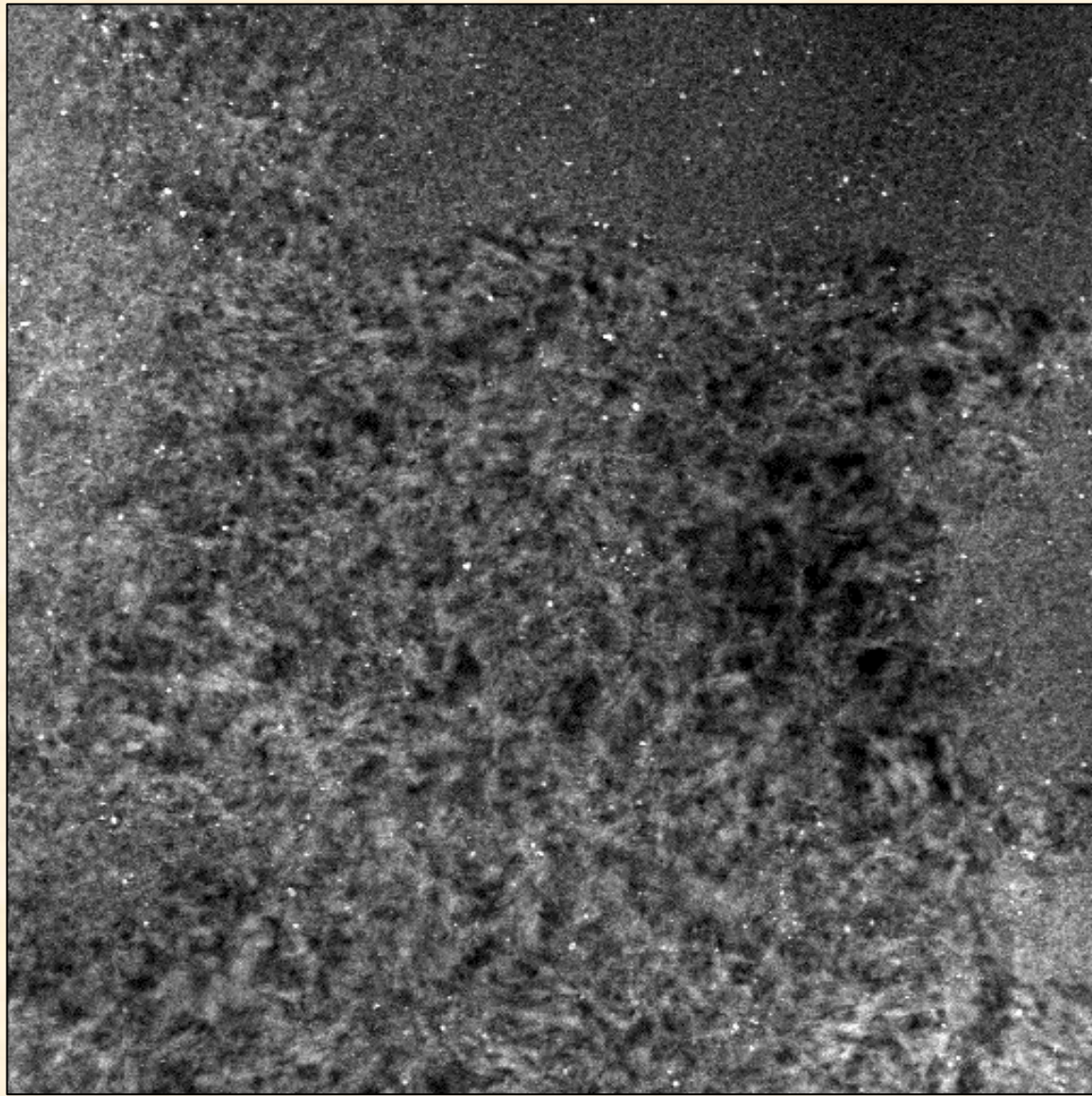


Pt particles  
cannot be  
unambiguously  
located

BF ACEM

Area for next image

Umicore  
LNT upstream

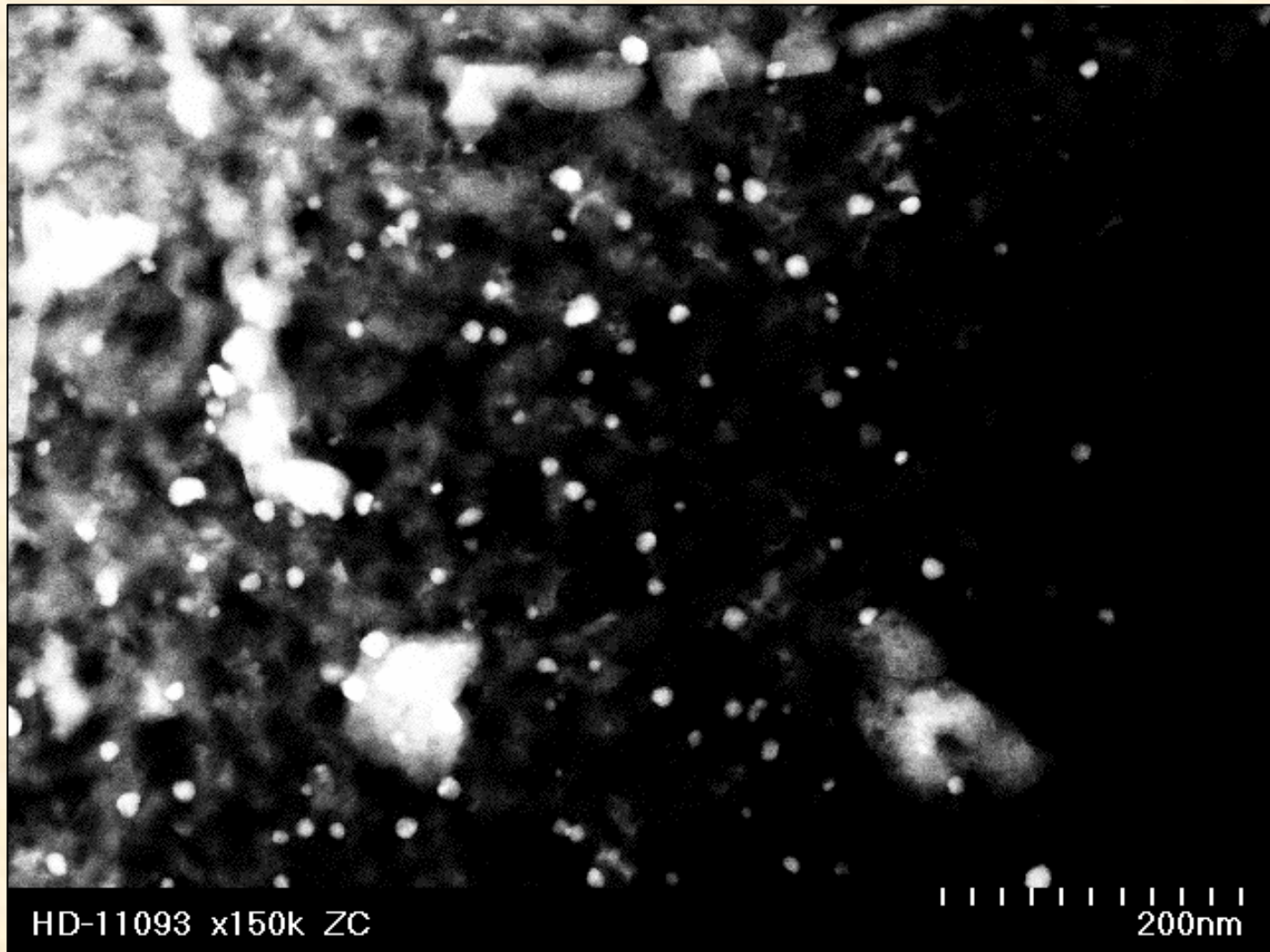


ADF ACEM

Pt particles clearly seen in bright contrast



Umicore de-greened, Pt particles 5-20nm in size



HD-2000 HA-ADF "Z-contrast" image

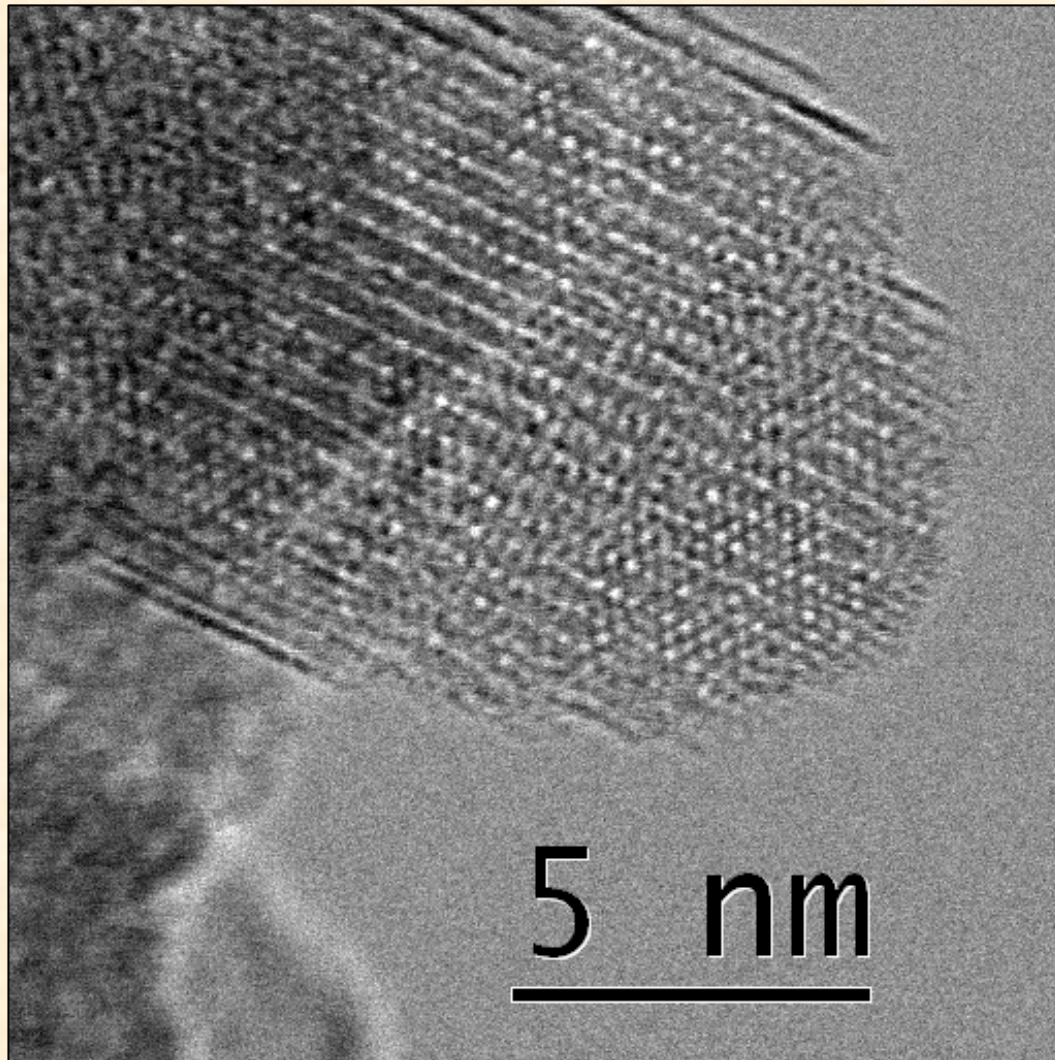
# Tri-rhenium carbonyl clusters on $\gamma$ -alumina

(Work with Prof. Bruce Gates and students, UCalDavis, and Drs. Melanie Moses and Chaitanya Narula, ORNL)

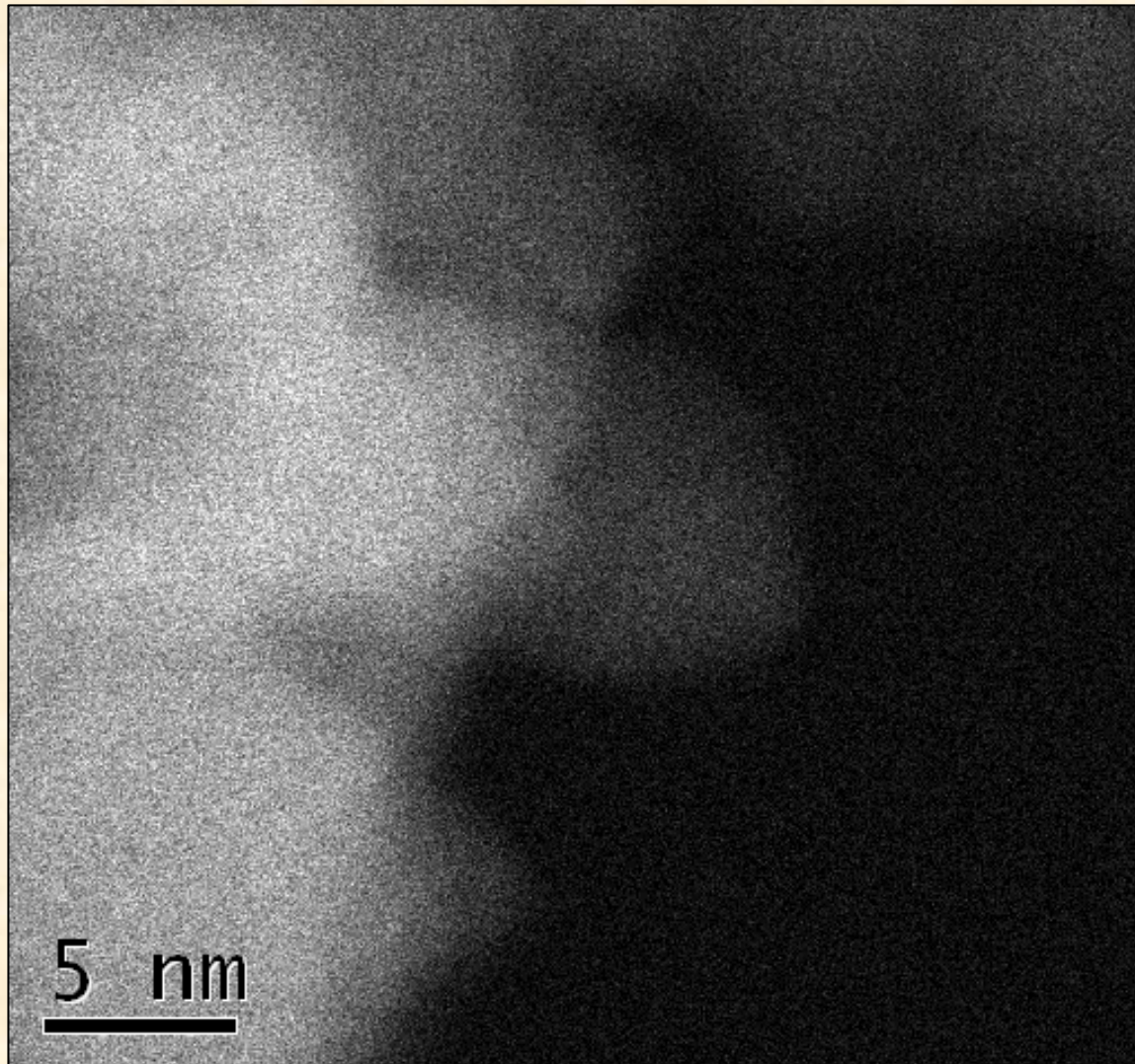


# Noble Metal on Support: $\text{H}_3\text{Re}_3(\text{CO})_{12}$ /commercial $\gamma\text{-Al}_2\text{O}_3$ System

- $\text{H}_3\text{Re}_3(\text{CO})_{12}$  was synthesized by literature methods and adsorbed on commercial  $\gamma\text{-Al}_2\text{O}_3$  powder
- IR and EXAFS indicate that rhenium tricarbonyl clusters are present on the sample

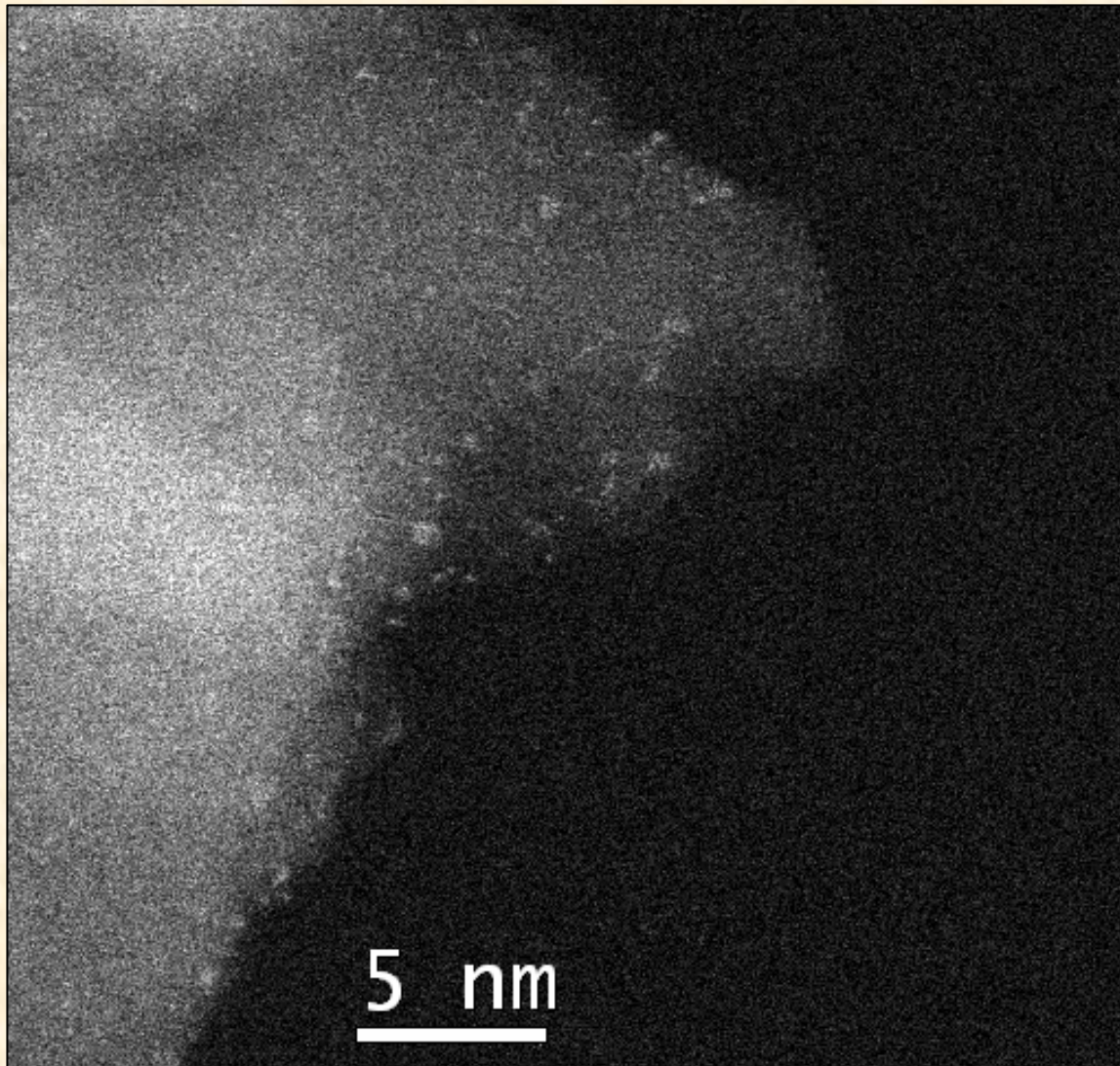


BF STEM image of bare alumina



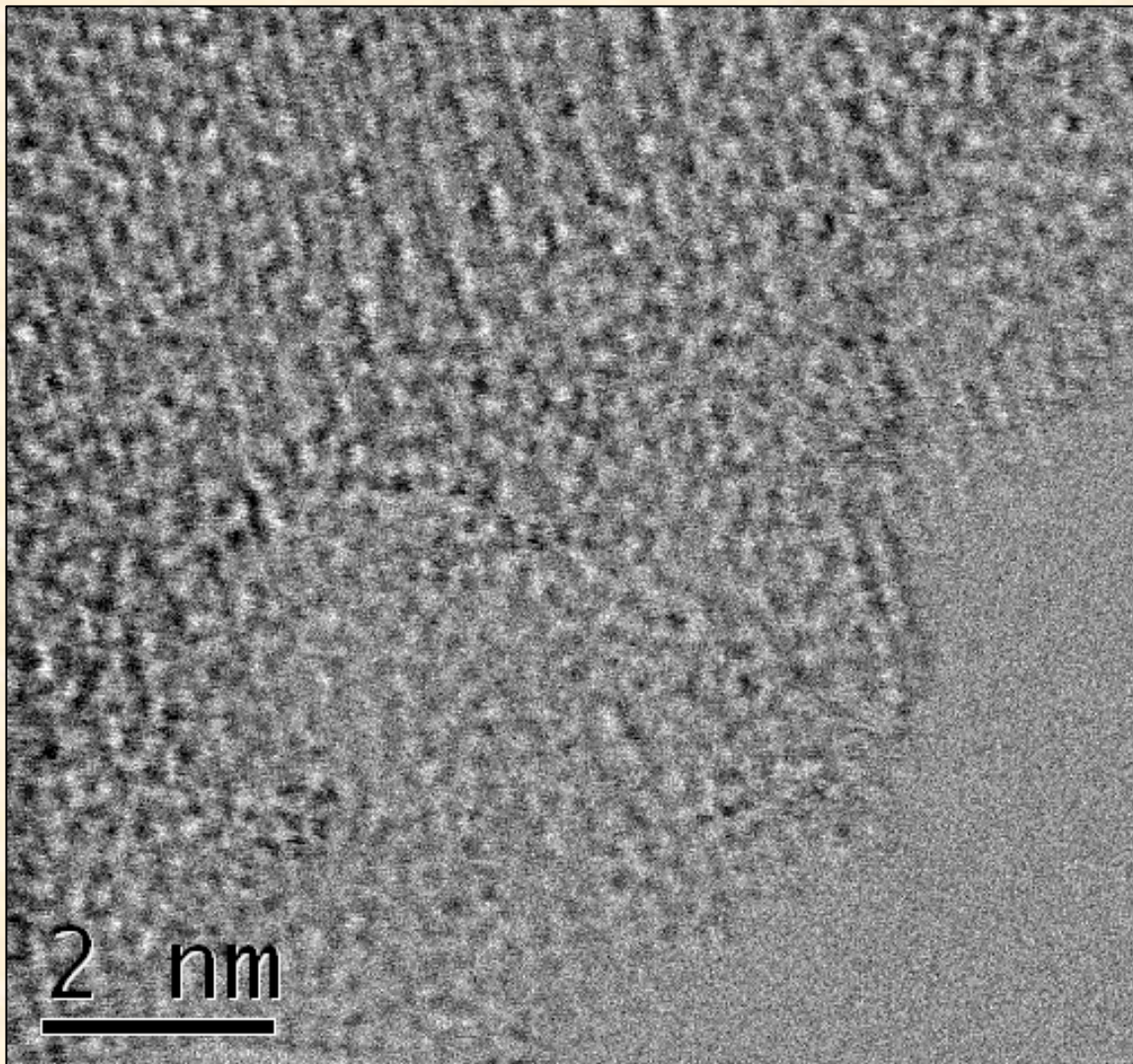
HA-ADF image of same area





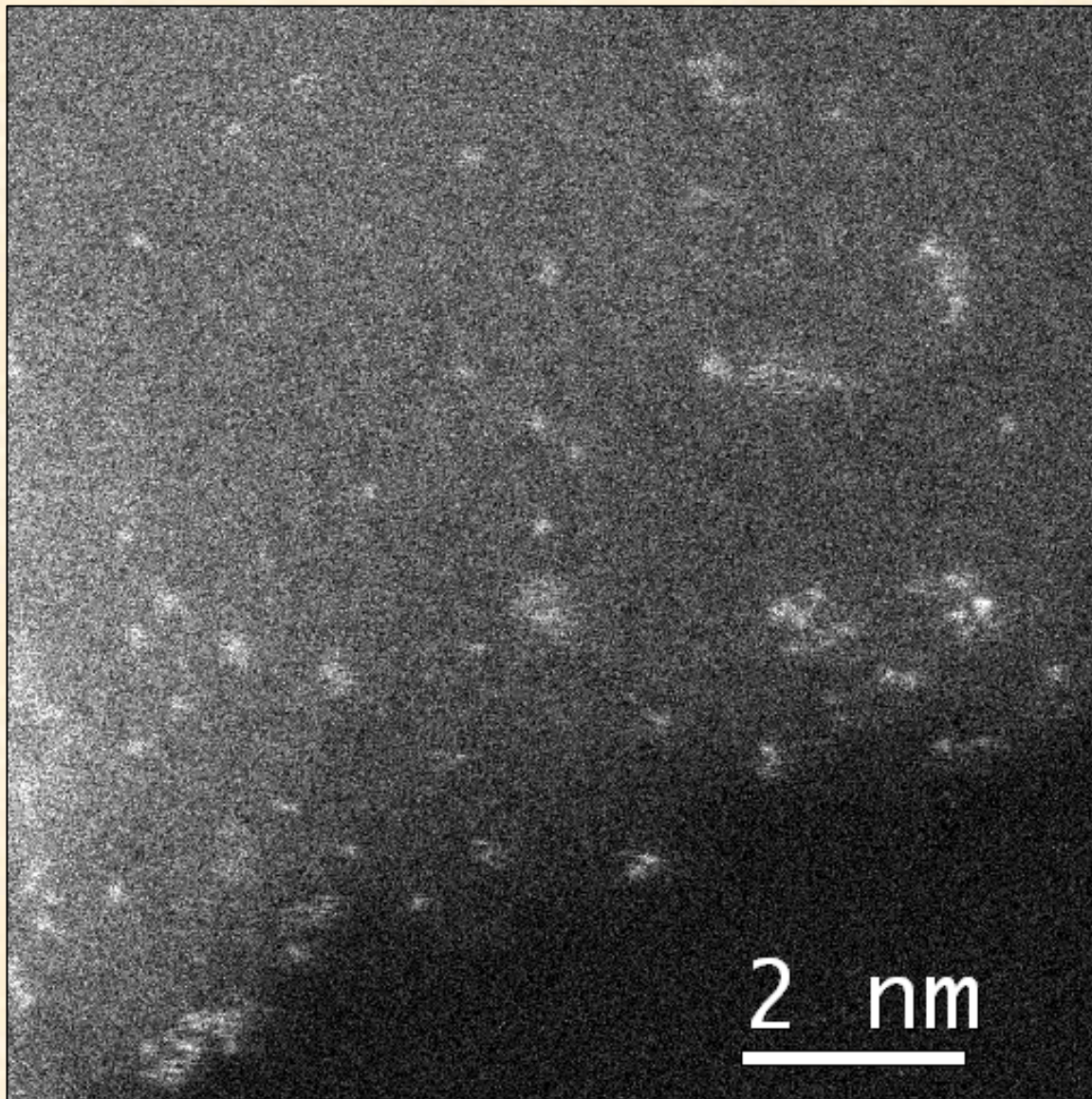
Alumina with tri-rhenium carbonyl clusters deposited





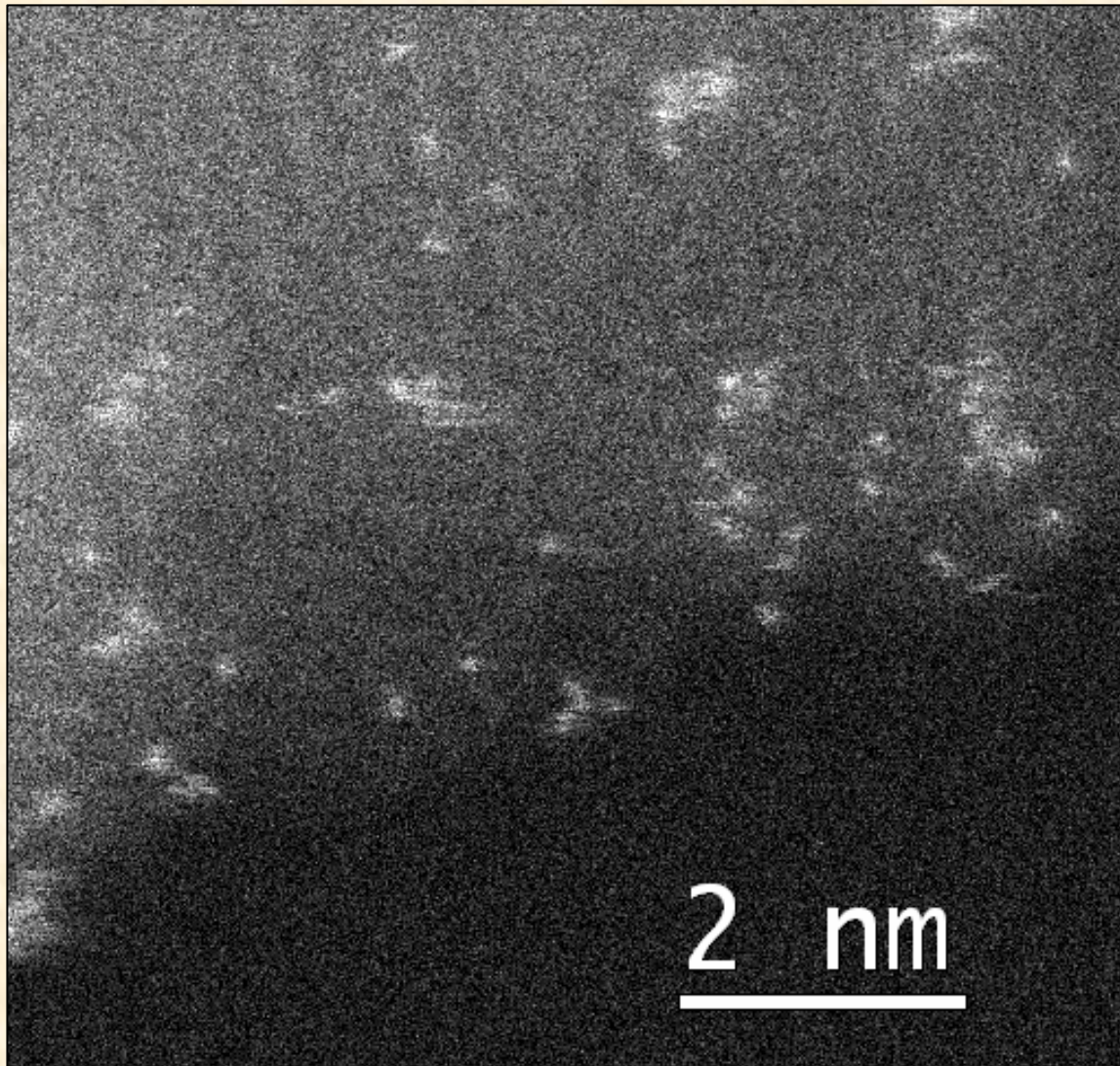
BF STEM image of thin edge of alumina plate, with tri-rhenium clusters present.





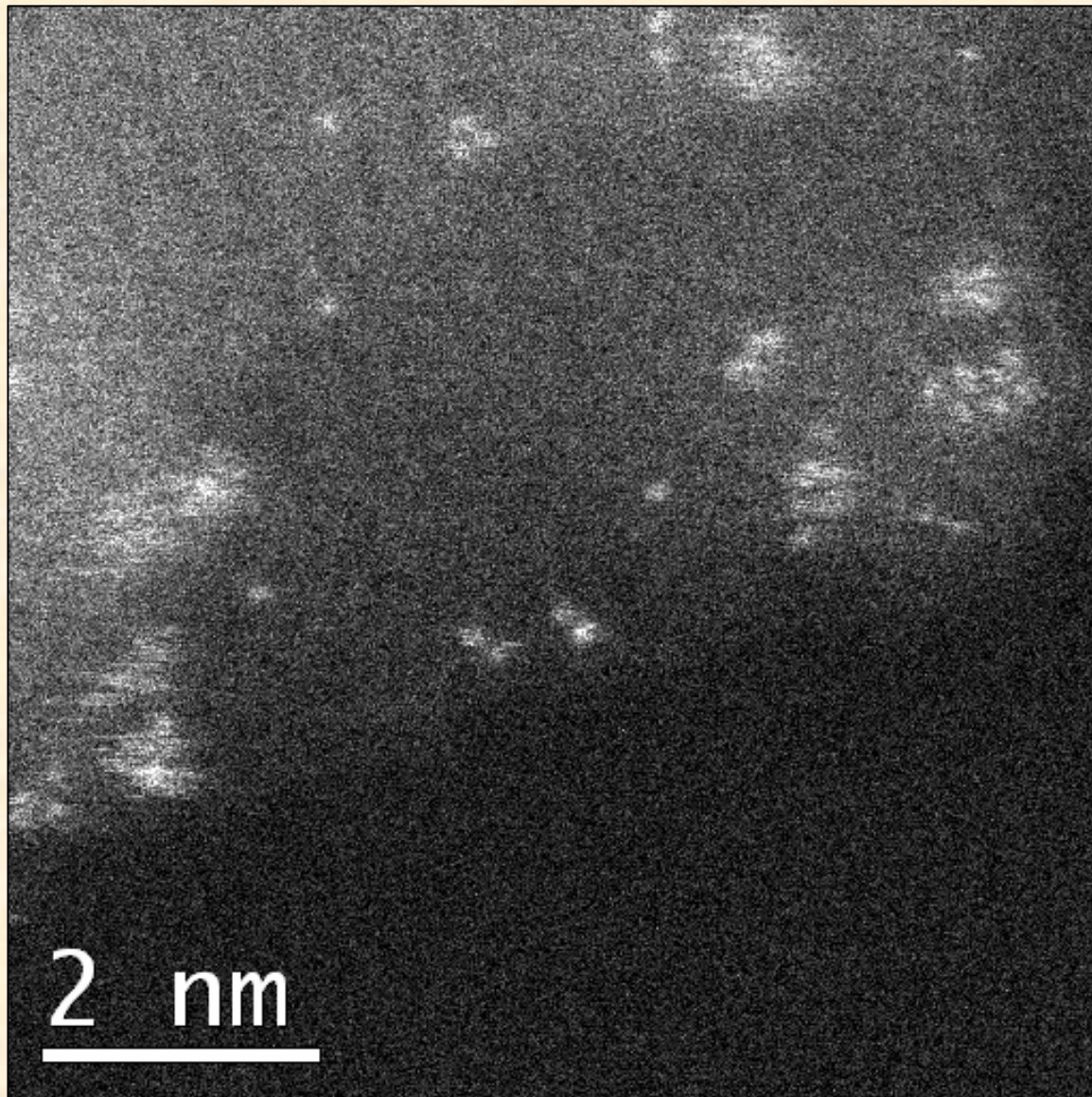
HA-ADF STEM image of same area





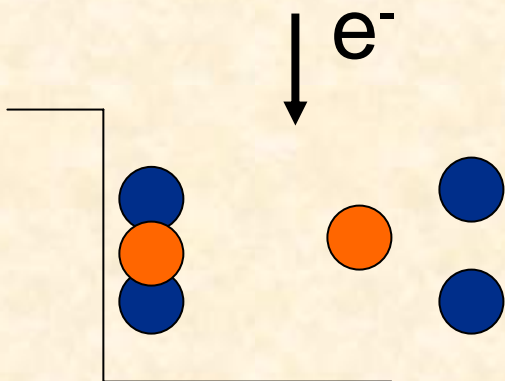
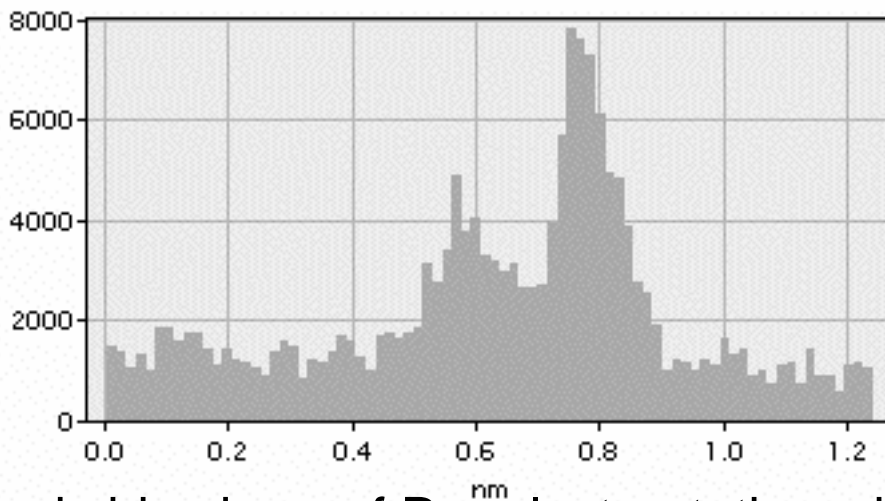
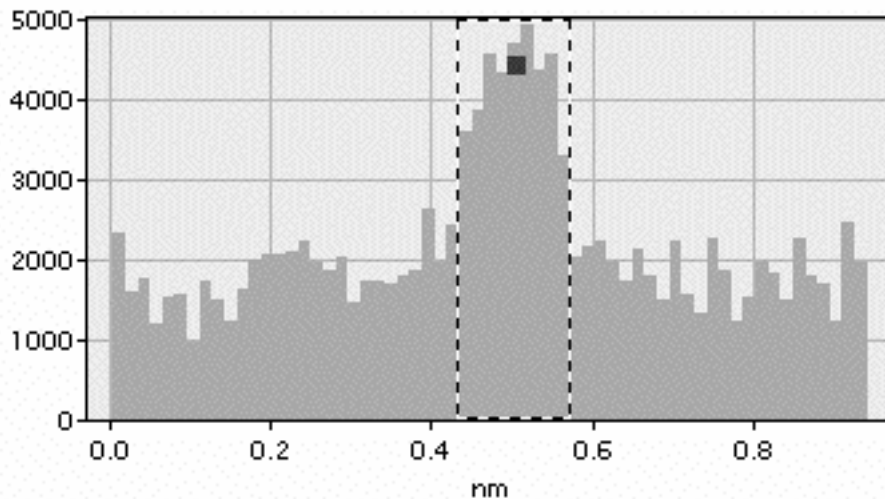
Same area, after some time; note movement of atoms and clusters.





Final ADF image



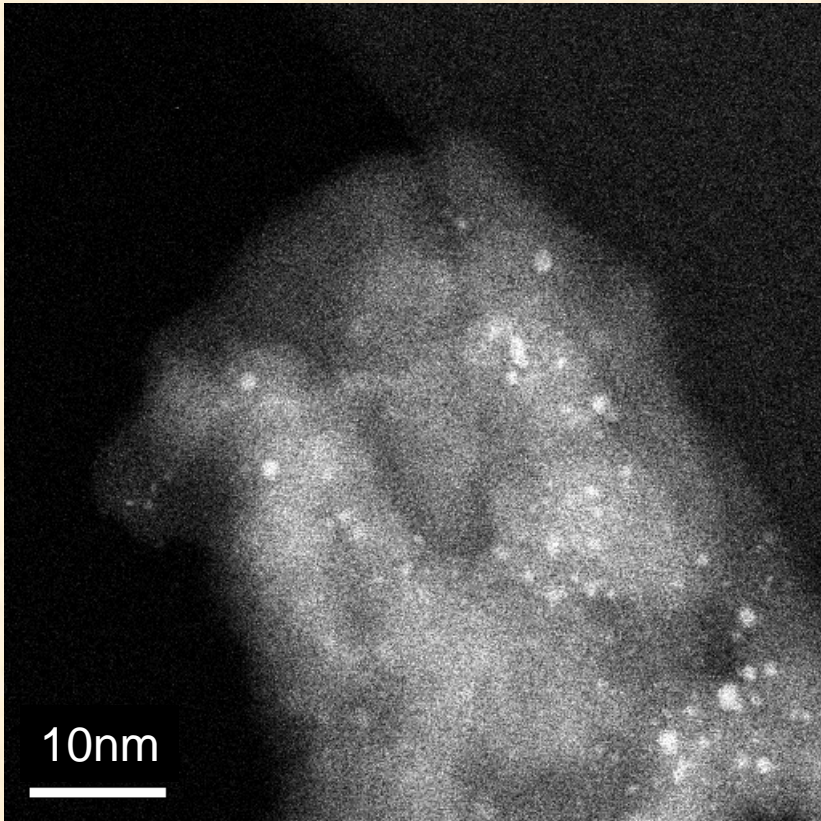


Front and side views of  $\text{Re}_3$  cluster, tethered to a ledge parallel to the beam direction. Above trace is consistent with this cluster orientation.

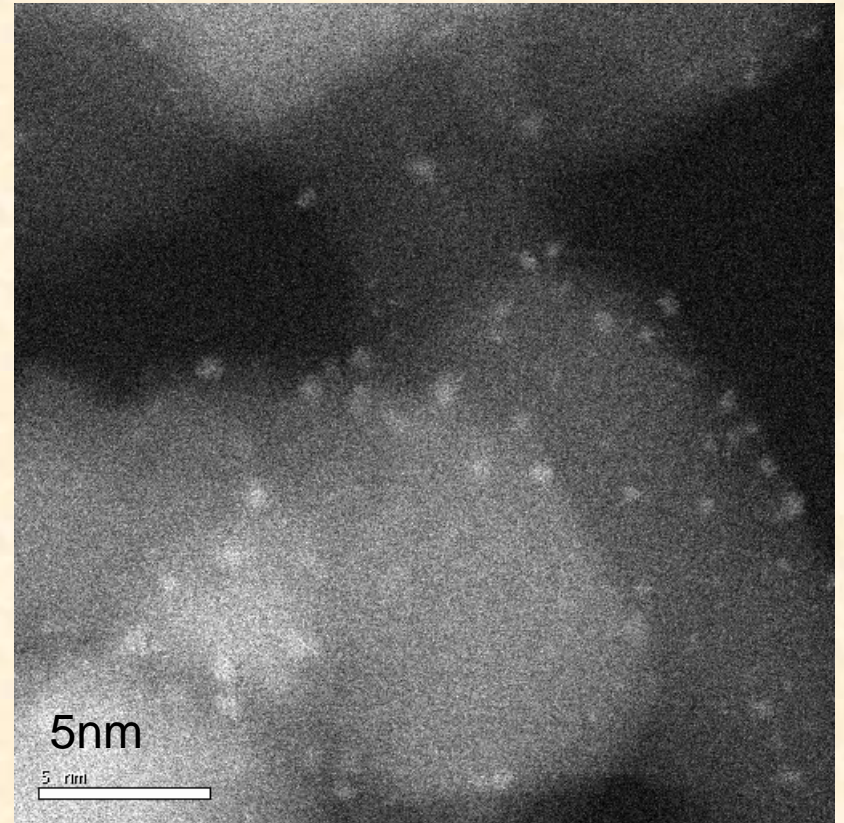
*Decarbonylated Rhenium*  
 $[H_3Re_3(CO)_{12}]/Al_2O_3$   
treated in  $H_2$  at  $400^\circ C$

**JEOL 2200FS-AC “ACEM”**  
**27 April 2005**

# Contains Nanoparticles



Magnification = 2 Mx



Magnification = 5 Mx

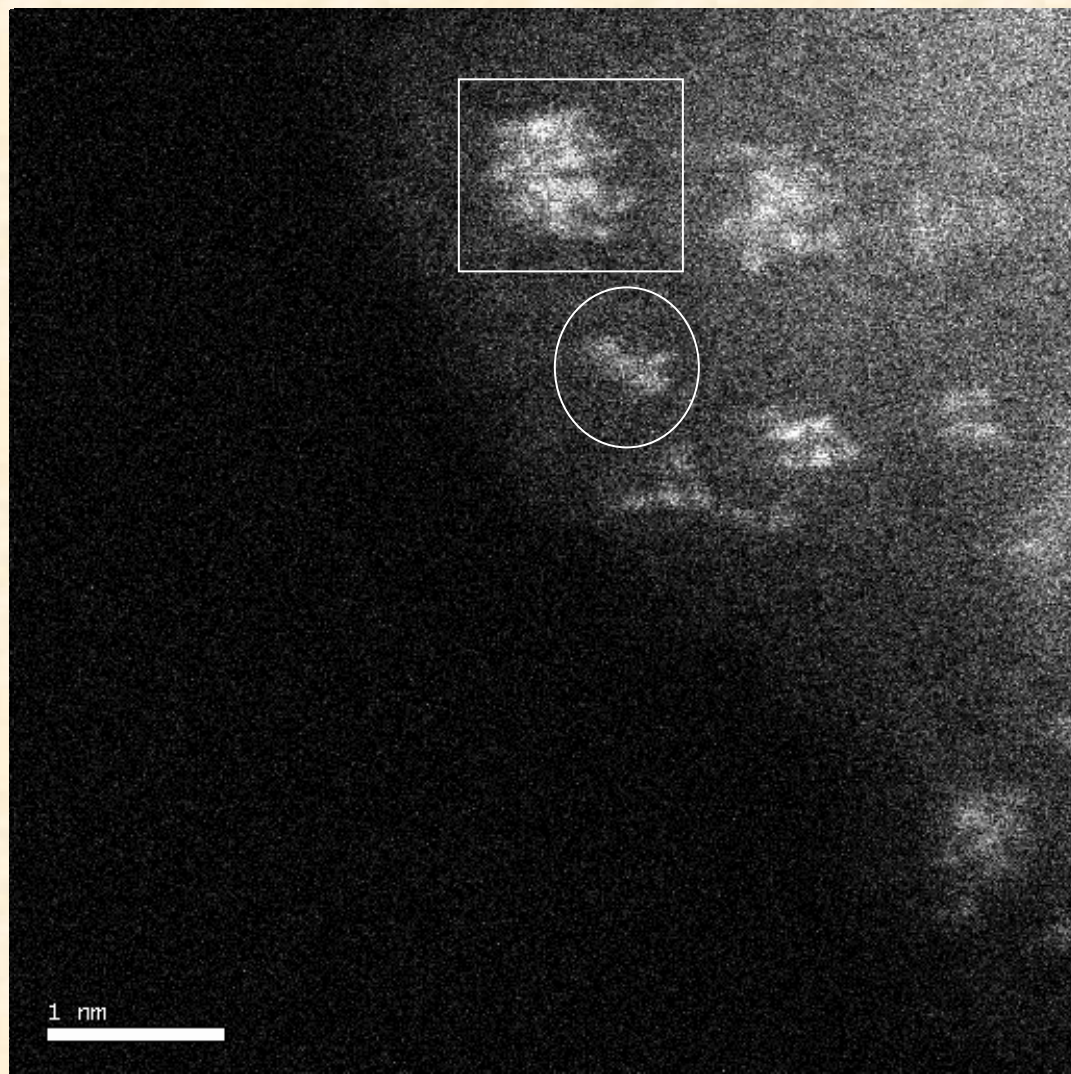


# Re Atoms constantly moving

## **DIRECTIONS:**

Go To Slide show and scroll through consecutive images of the same area using the arrow keys

All at a magnification of 20Mx



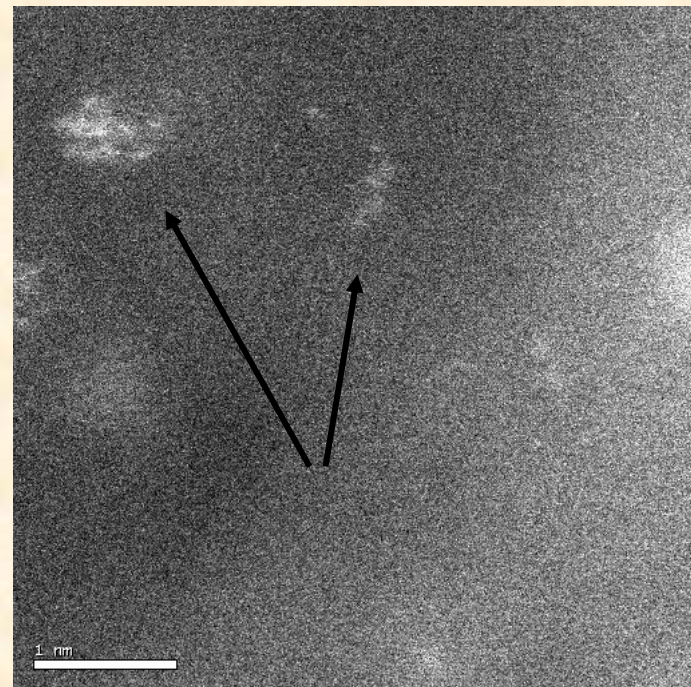


## Re Atoms Cluster Growth

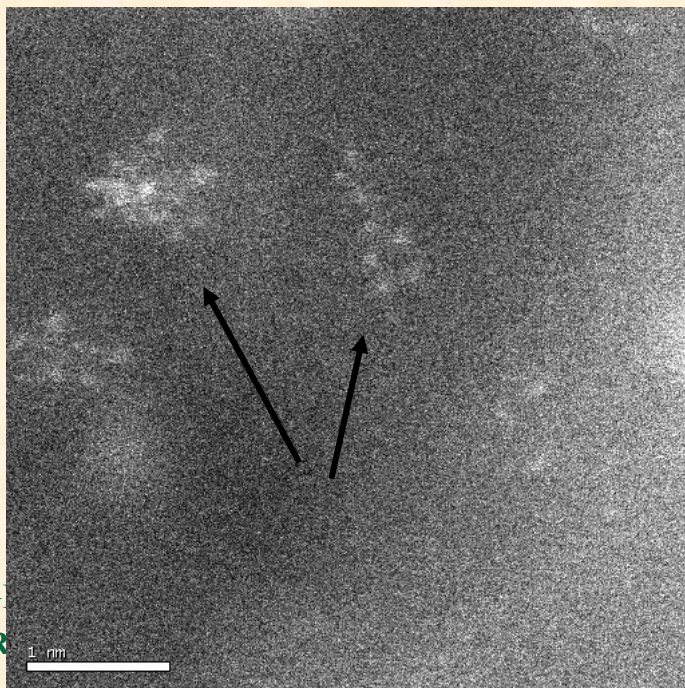
All at a magnification of 25Mx

Single Re atoms and Re clusters  
are present.

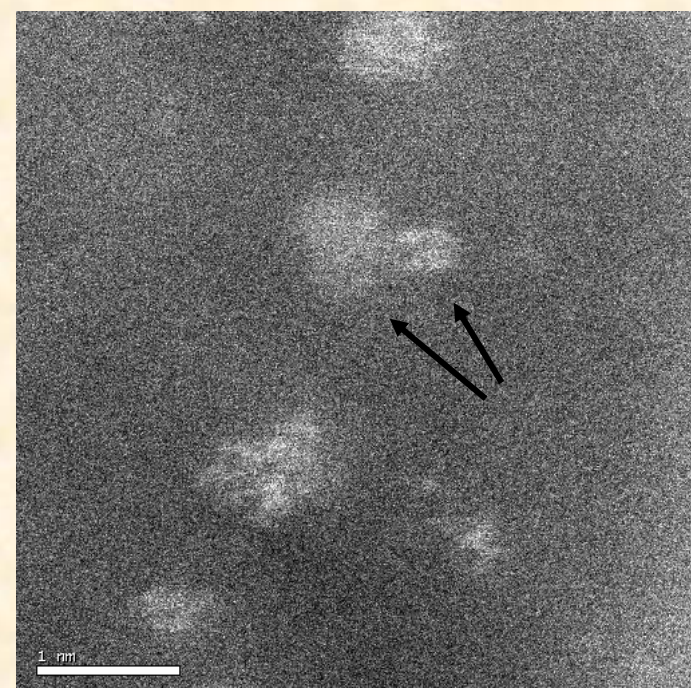
1



2



3

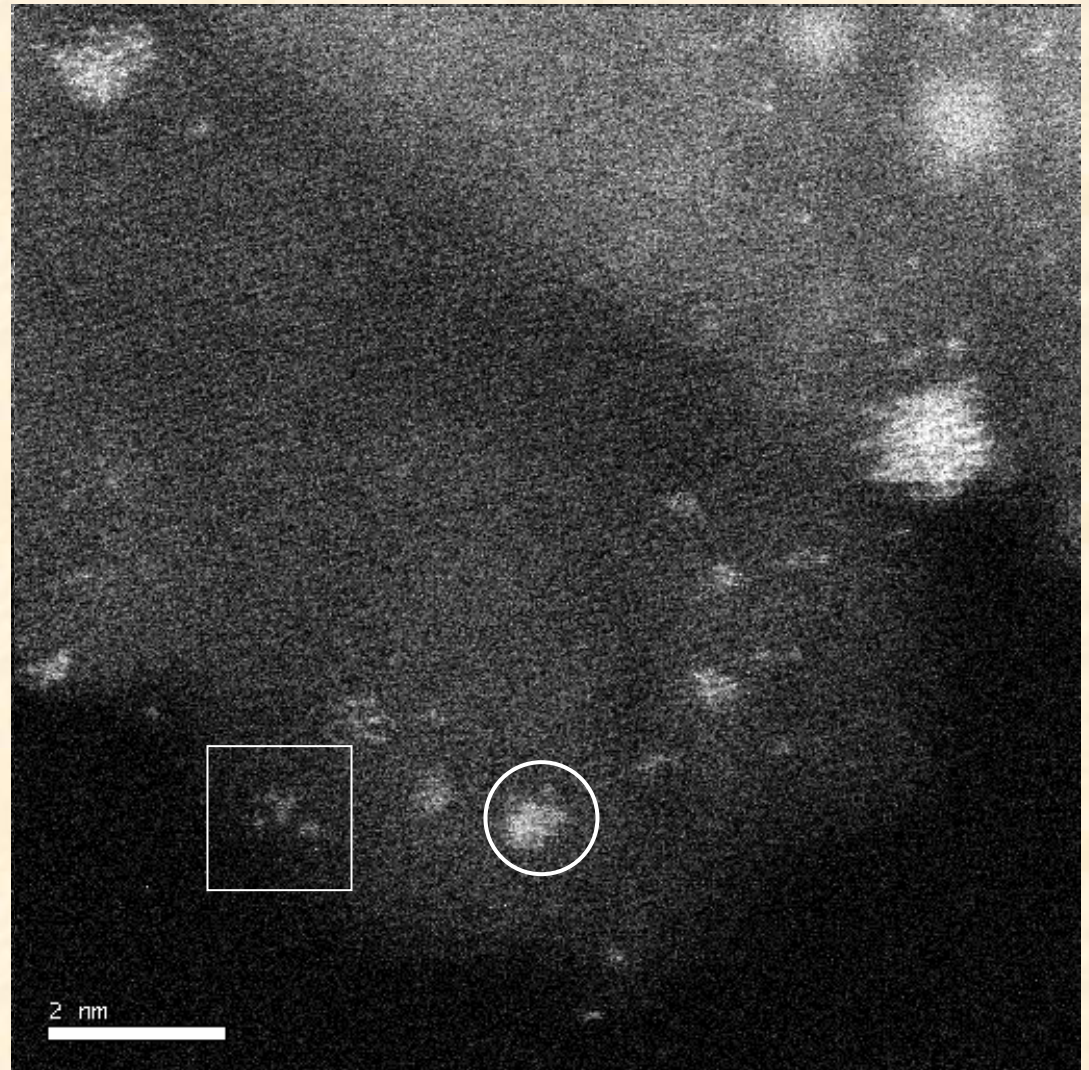




## Crystal Growth Orientation along Alumina Lattice Planes

### **DIRECTIONS:**

Go To Slide show and scroll through consecutive images of the same area using the arrow keys



# Conclusions

The new JEOL 2200FS-AC aberration-corrected STEM/TEM, coupled with an excellent laboratory environment, offers great promise to provide “routine” sub-Å imaging capabilities.

## Acknowledgement

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