Uncovering Fundamental Ash-Formation Mechanisms and Potential Means to Control the Impact on DPF Performance and Engine Efficiency

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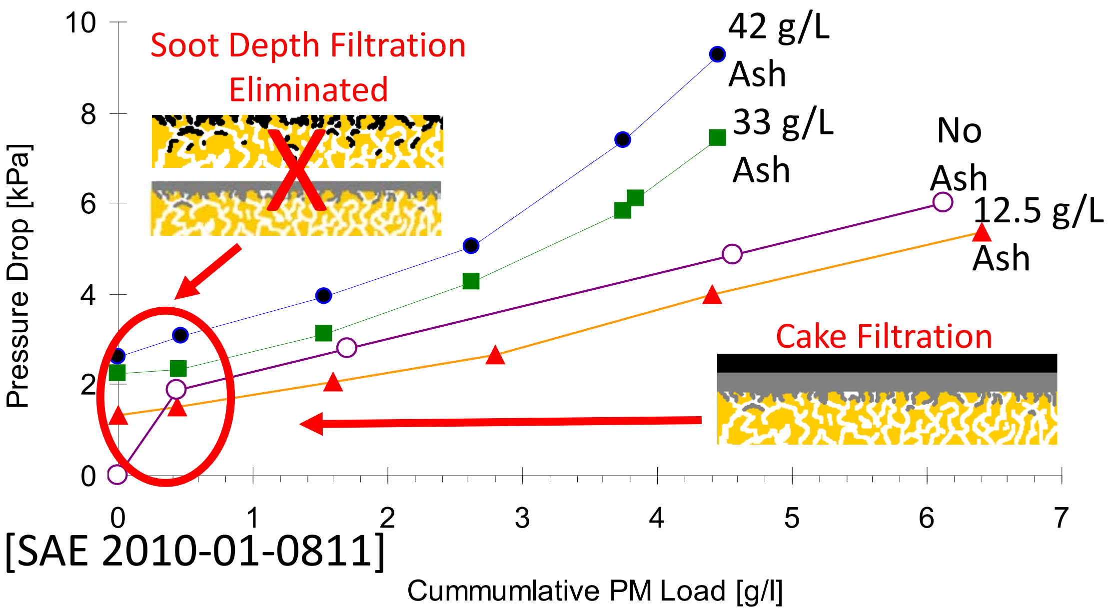
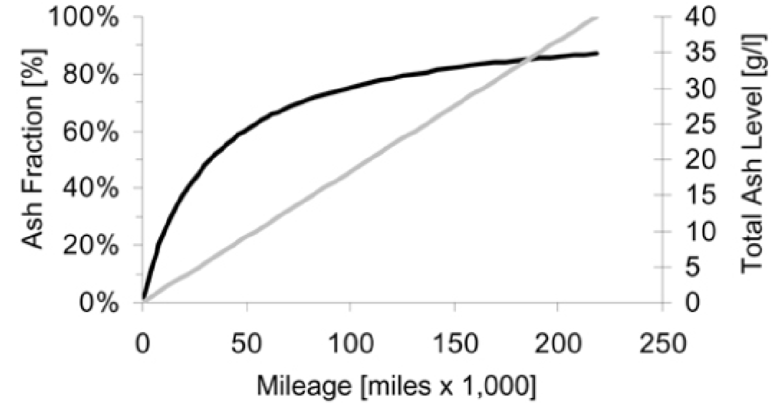
DEER 2012

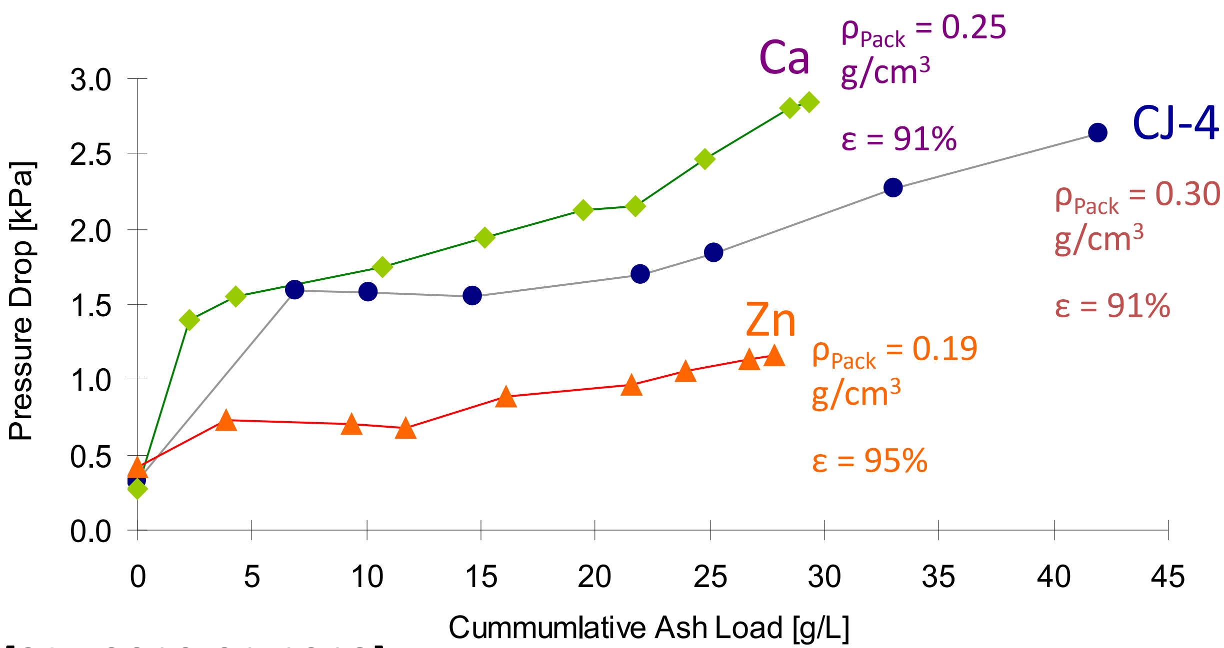
Ash Affects DPF Performance



[SAE 2010-01-0811]



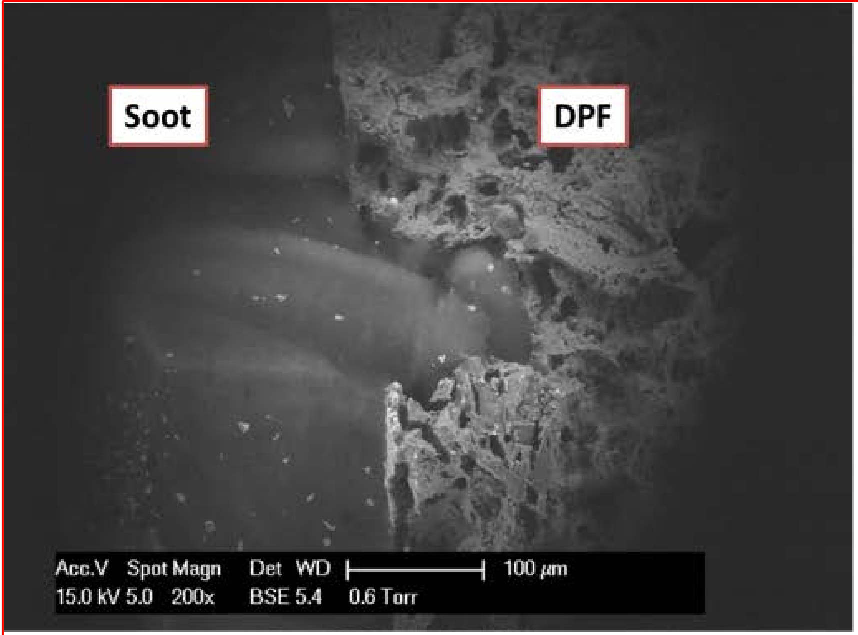
[SAE 2007-01-0920]



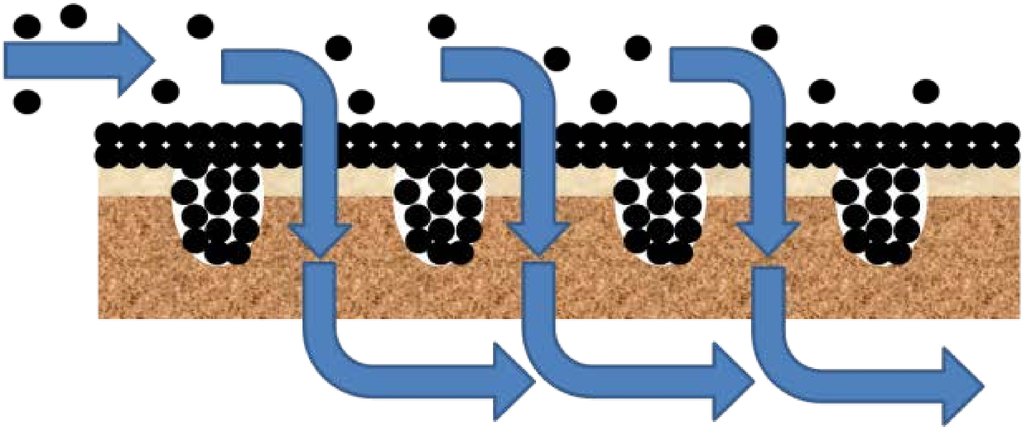
[SAE 2010-01-1213]

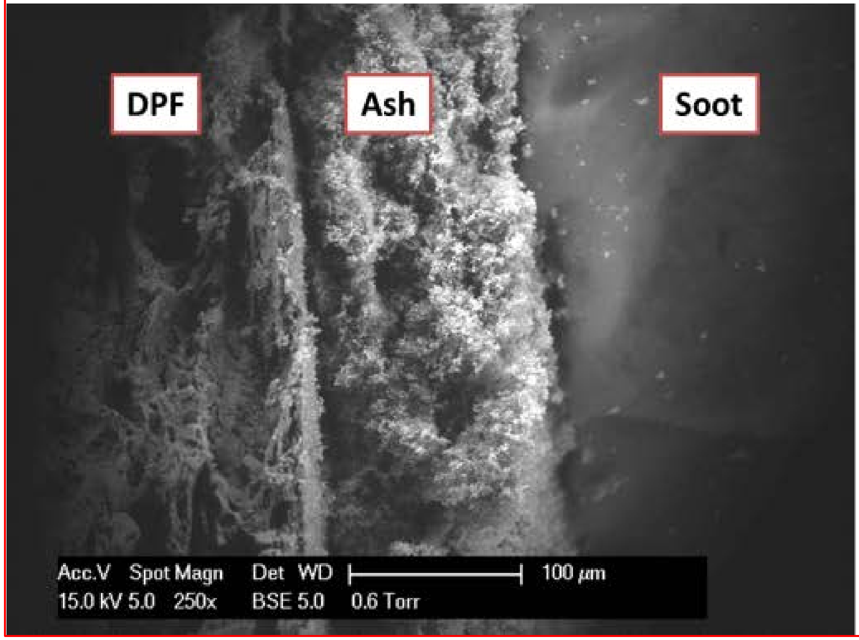
- **Ash accumulates in the wall flow-through filter and raises ΔP**
- **Ash fills DPF surface pores and forms a cake layer**
- **ΔP plot shows accumulation mode**
- **Lubrication chemistry shows and effect on ΔP**

Filtration concepts

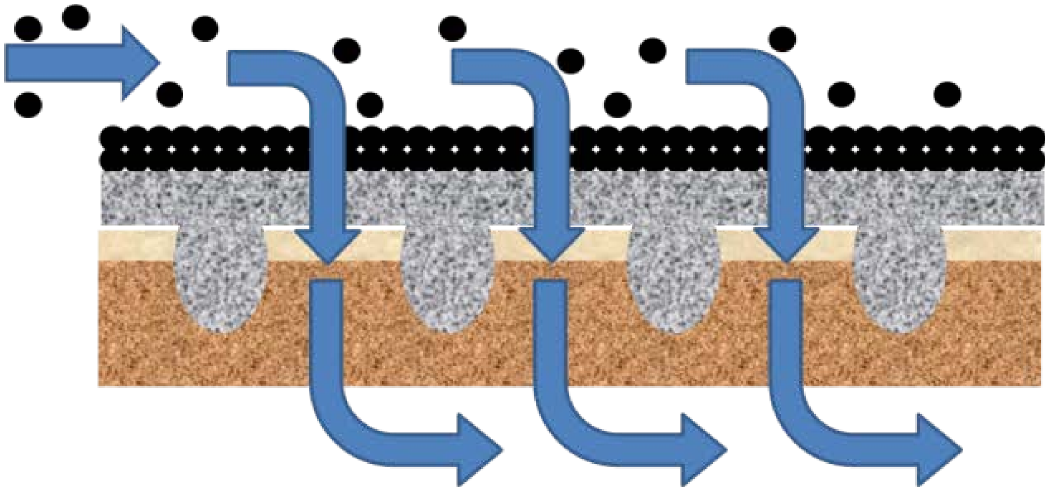


Depth filtration

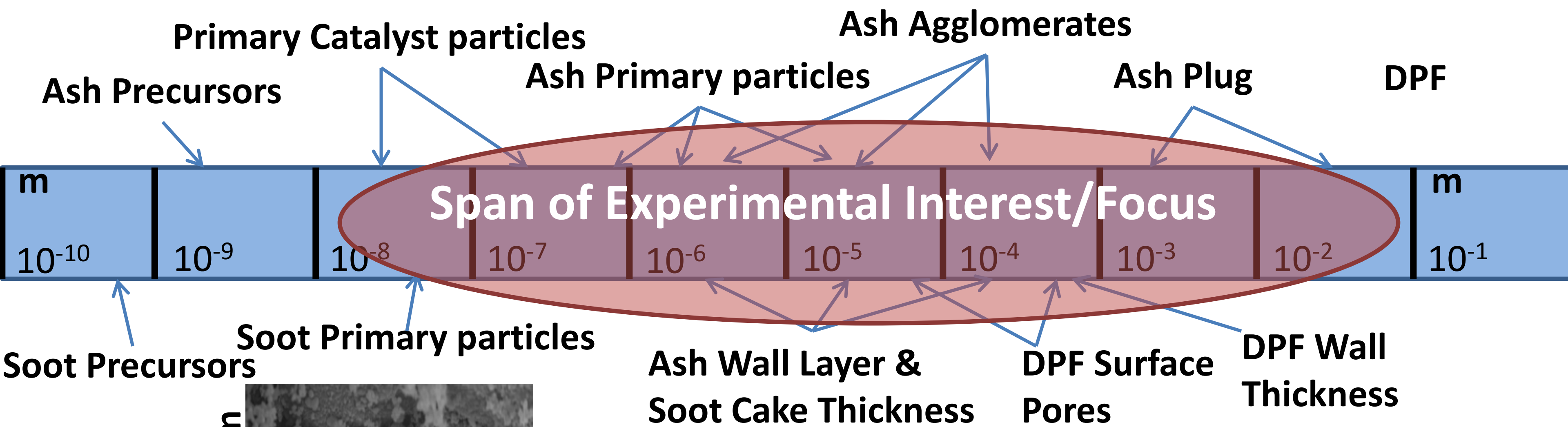


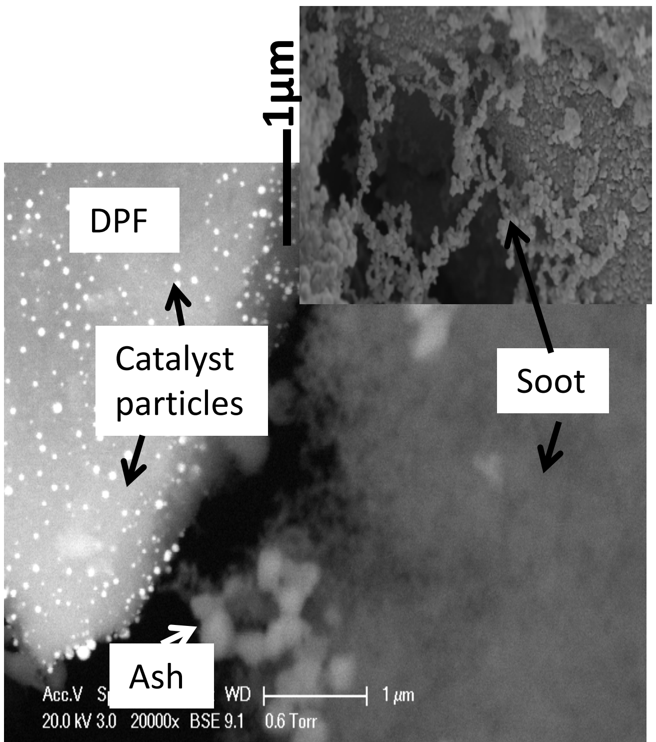


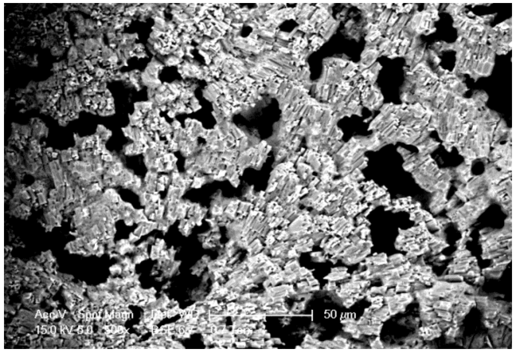
Cake filtration

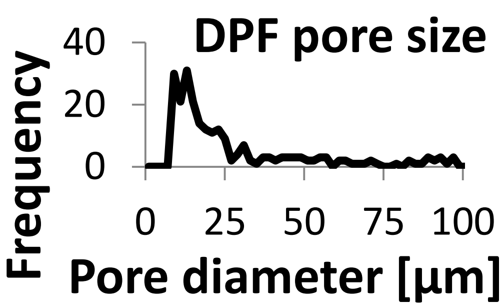


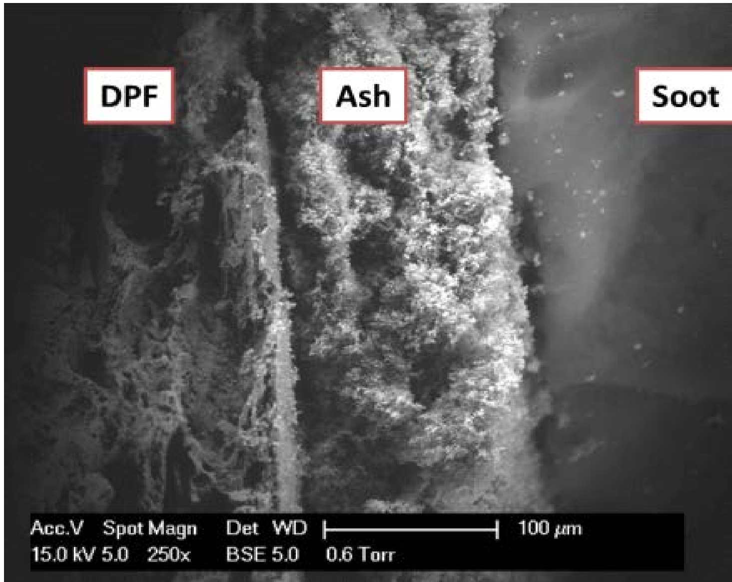
DPF/Ash/Soot at Scale



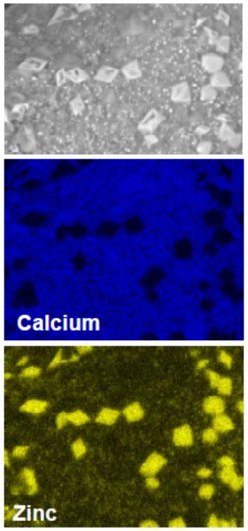








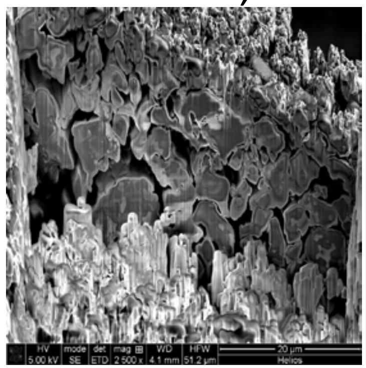
Coupled Experimental System

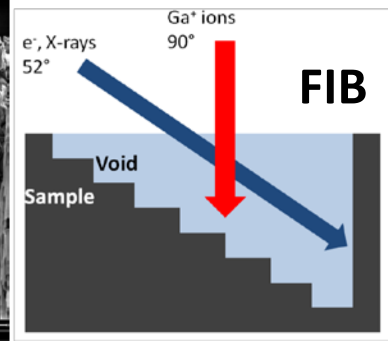


Elemental mapping

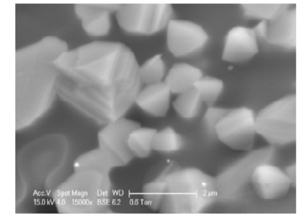
EDX

Sub-surface, interfacial information





FIB

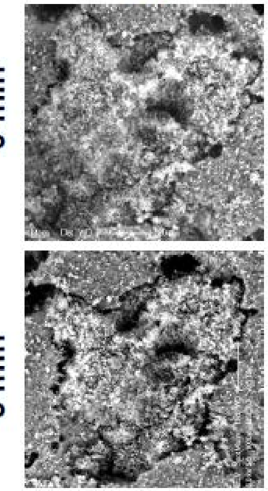


HR-ESEM/BSe⁻

Hi-res imaging

Ca

0 min

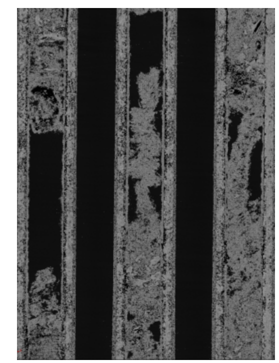


5 min

1. High Resolution Environmental Scanning Electron Microscopy with Back-Scattered Electron and Energy Dispersive X-Ray imaging (**HRSEM/BSe⁻/EDX**)
2. Focused Ion Beam milling (**FIB**)
3. Quartz Crystal Microbalance with Dissipation (**QCMD**)
4. X-Ray Diffraction (**XRD**)
5. X-Ray Computed Tomography (**X-Ray CT**)
6. Temperature Programmed Oxidation (**TPO**)
7. X-Ray Fluorescence (**XRF**)
8. Small Angle X-Ray Scattering (**SAXS**)
9. Atomic Force Microscopy (**AFM**)
10. X-Ray Photoelectron Spectroscopy (**XPS**)

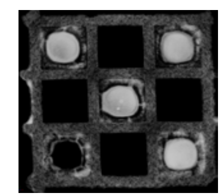
Aged samples:

- Lab
- Field



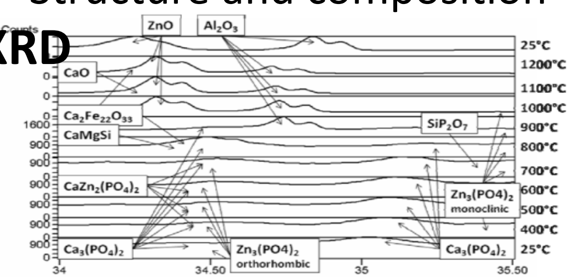
X-Ray CT

3D imaging



Structure and composition

XRD

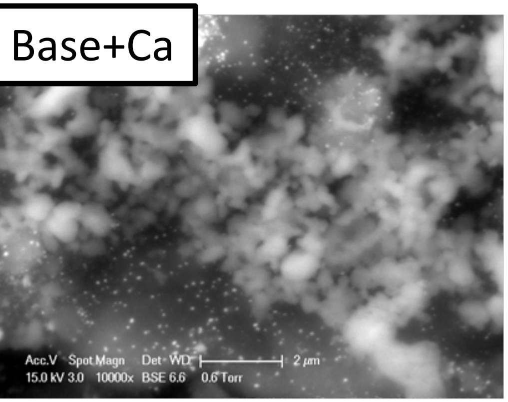


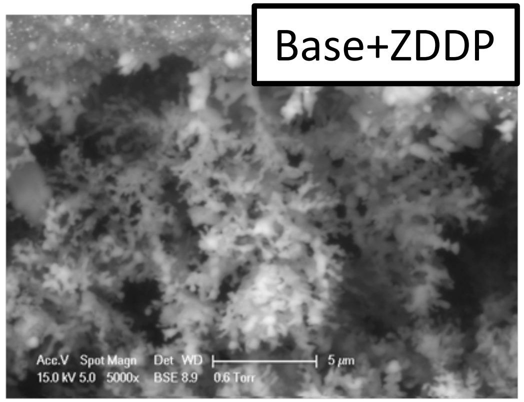
Lubrication-Derived Ash

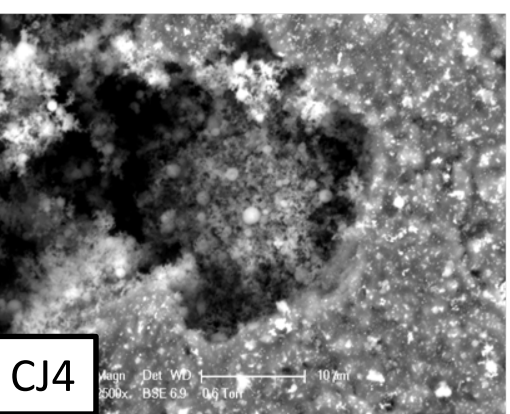
- Incombustible, inorganic, ionic compounds
- In general, high melting temperatures and low solubilities
- Ca, Zn, Mg in the form of sulfates, phosphates and oxides
- Trace: Fe, B, Mo, Al, Si, Na(biofuels)
- ≈0.5-1% by mass of soot, bound to soot
- Enter as Å-nm size, grow to 100's of µm
- Oil consumption ≈ fuel consumption/1000

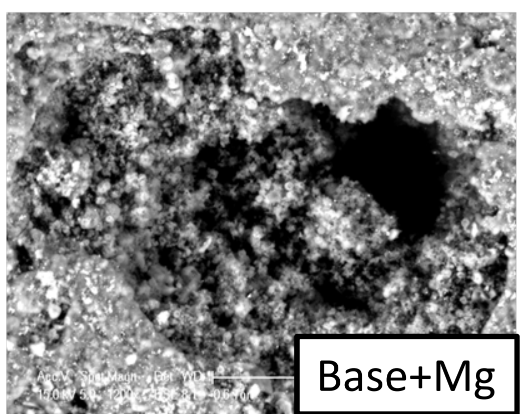
Zn	Ca	Mg
$Zn_2P_2O_7^{\star}$ $Zn_2P_2O_7^{\dagger}$	$CaSO_4$ $Ca_3(PO_4)_2$	$Mg_3(PO_4)_2$ $MgSO_4$
CaZn	**CJ4**	**Field**
$CaSO_4$ $Zn_3(PO_4)_2$ $Ca_3(PO_4)_2$ $CaZn_2(PO_4)_2$	$CaSO_4$ $Zn_3(PO_4)_2$ $Ca_3(PO_4)_2$ $CaZn_2(PO_4)_2$ $Ca_{2.6}Mg_{0.9}(PO_4)_2$	$CaSO_4$ $Zn_3(PO_4)_2$ $Ca_3(PO_4)_2$ $CaZn_2(PO_4)_2$ $Mg(PO_3)_2$ Fe_3O_4 ZnO

$Ca_3(PO_4)_2$ $\rho = 3.14 g/cm^3$ $T_{melt} = 1394°C$	$Zn_3(PO_4)_2$ $\rho = 3.998 g/cm^3$ $T_{melt} = 900°C$	$Mg_3(PO_4)_2$ $\rho = 2.74 g/cm^3$ $T_{melt} = 1353°C$
$CaSO_4$ $\rho = 2.96 g/cm^3$ $T_{melt} = 1460°C$	$ZnSO_4$ $\rho = 3.54 g/cm^3$ $T_{melt} = 680°C$	$MgSO_4$ $\rho = 2.66 g/cm^3$ $T_{melt} = 1124°C$
CaO $\rho = 3.35 g/cm^3$ $T_{melt} = 2572°C$	ZnO $\rho = 5.61 g/cm^3$ $T_{melt} = 1975°C$	MgO $\rho = 3.58 g/cm^3$ $T_{melt} = 2852°C$

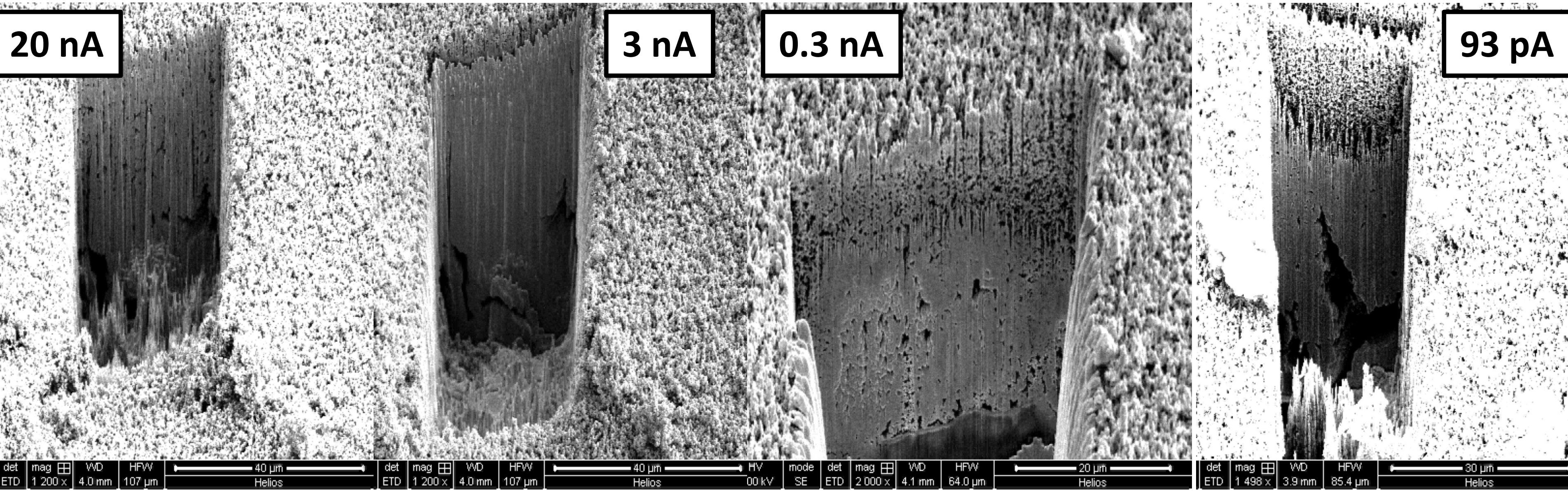




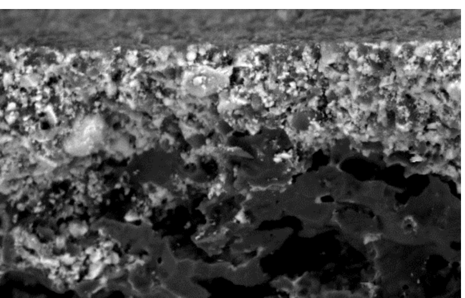




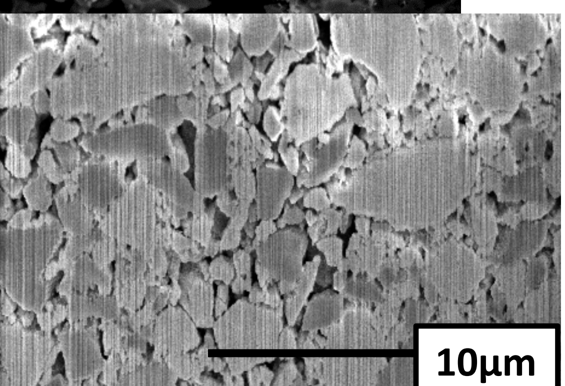
Focused Ion Beam



[SAE 2012-01-0836]

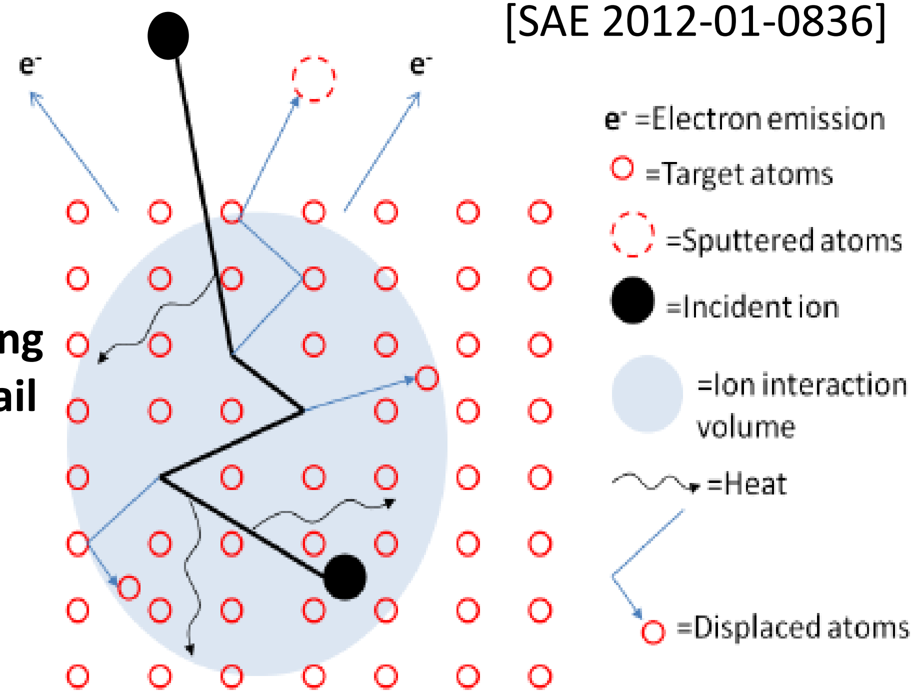


'Broken' WC



FIB milled WC

- FIB+SEM+EDX
- Useful for observing interfaces, structure
- nm-µm
- Ga^+ ions at 5-50 keV
  - Forced sputtering
  - Subsurface detail



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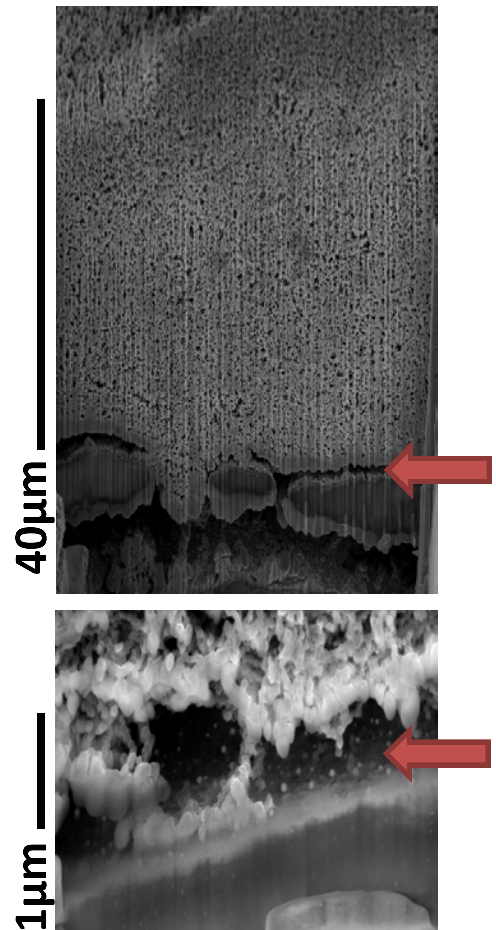
Interfacial observations

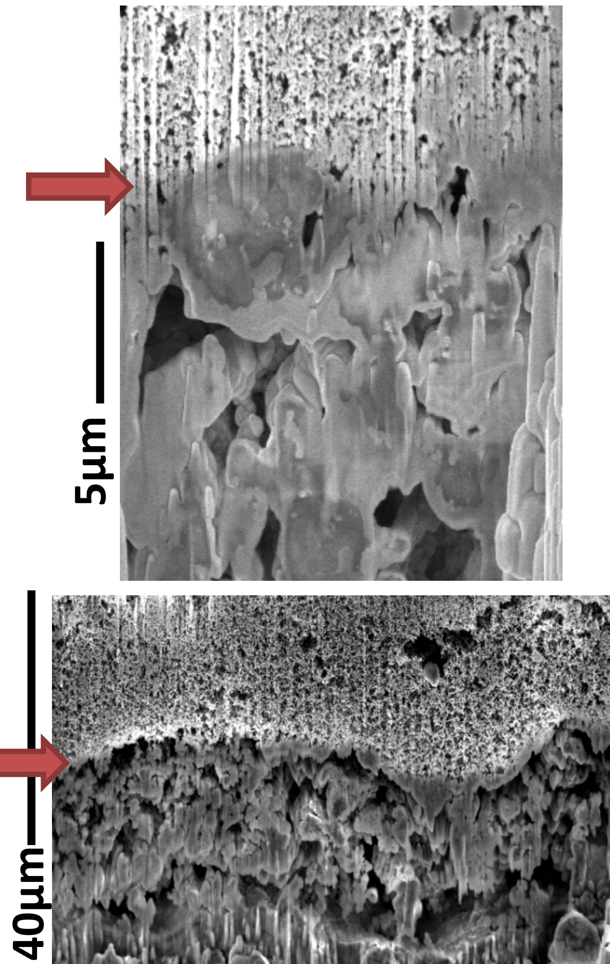
Ash-DPF: Some gaps observed, Ca and Zn ash appears to form bound layer
Soot-DPF: Gaps observed at interface
Soot-Ash: Tight interface, ash acts as filter surface, very little soot penetration
[SAE 2012-01-0836]

= Interface

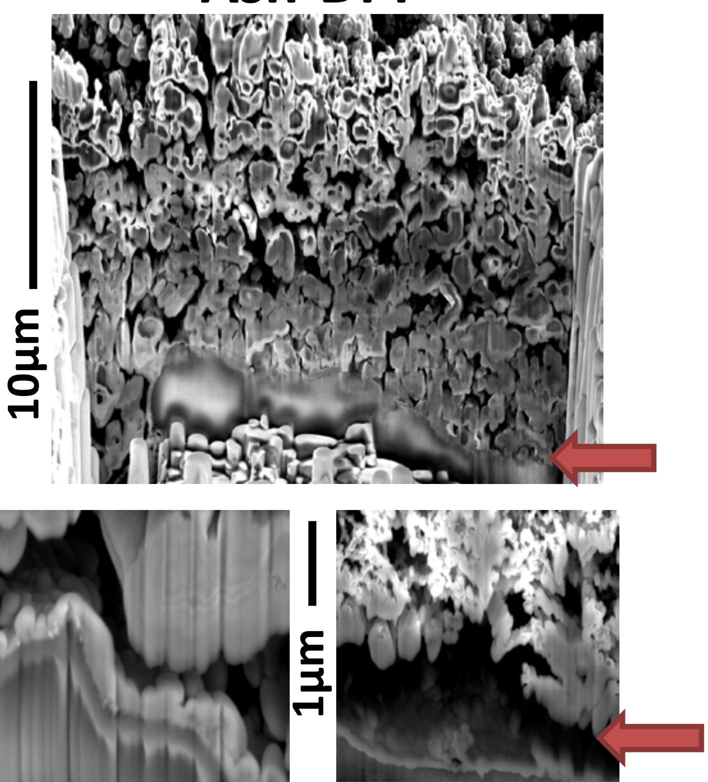
Soot-DPF



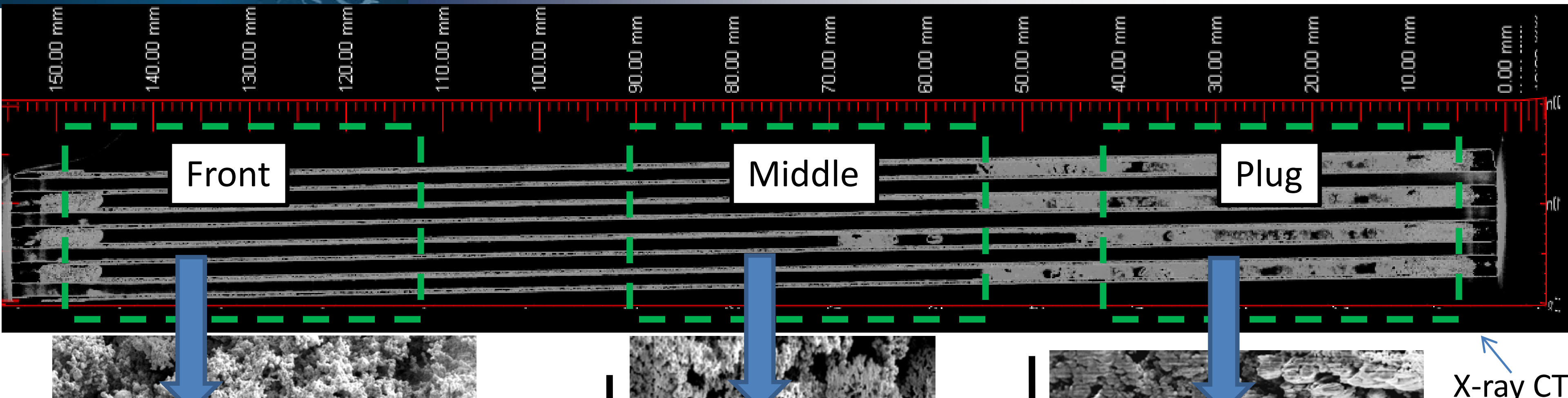
Soot-Ash

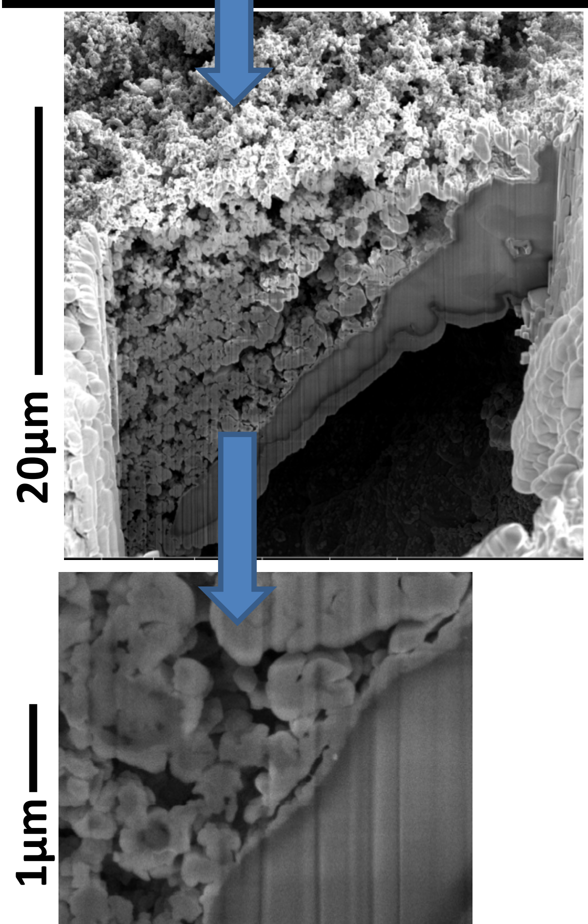


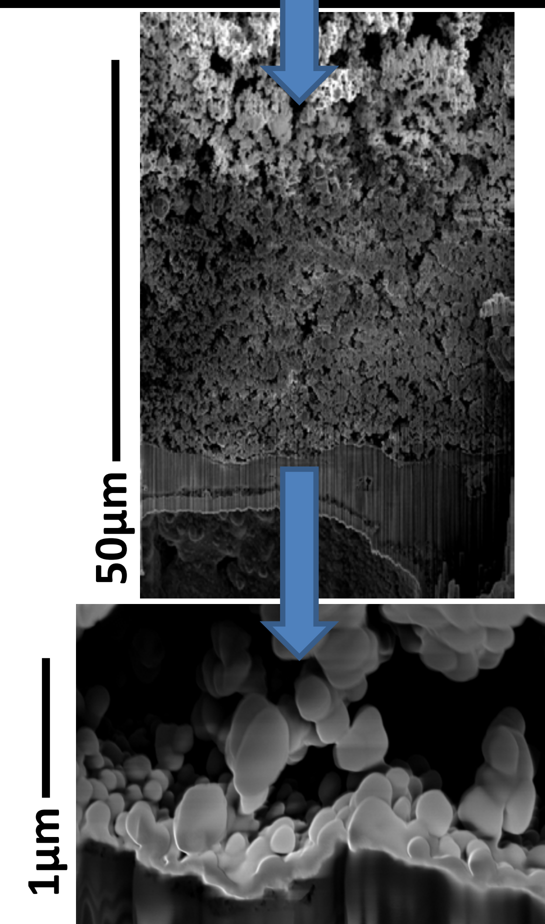
Ash-DPF

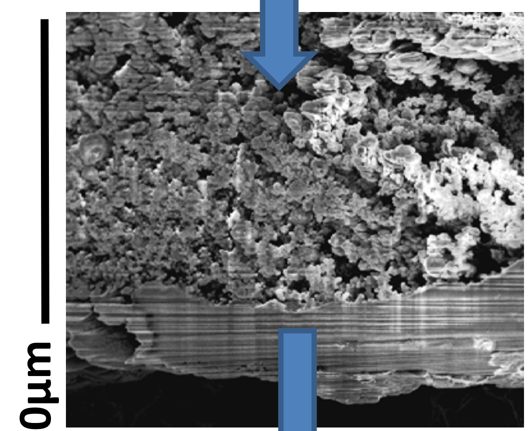


Ash Distribution







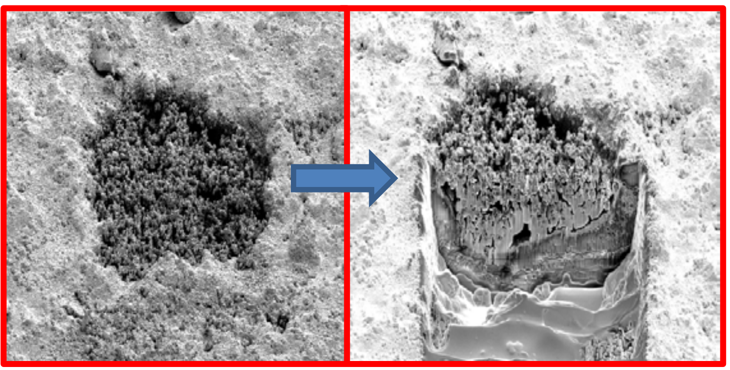


- **FIB milling shows similar nm- and µm-scale ash-DPF interactions at F, M and P axial positions**
- **Ash layer thickness has been shown previously to vary with axial position**

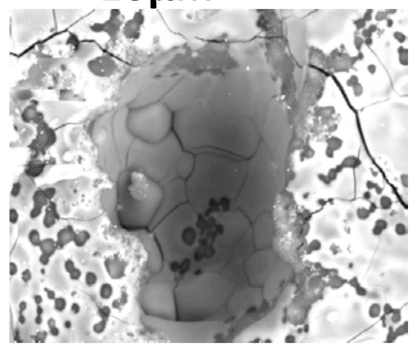
DPF Surface Pores

- FIB milling shows ash trapped in DPF surface pores
- Little to no ash penetration into filter substrate
- Illustrates ash depth filtration
- Suggests that ash particle size/shape may affect ΔP

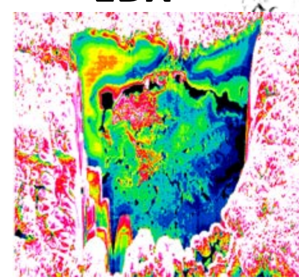
40µm



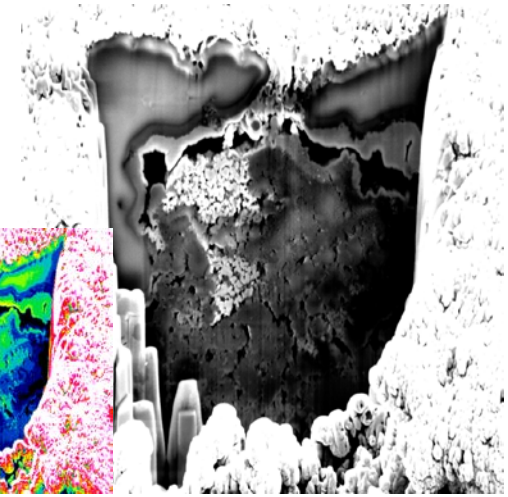
10µm



EDX

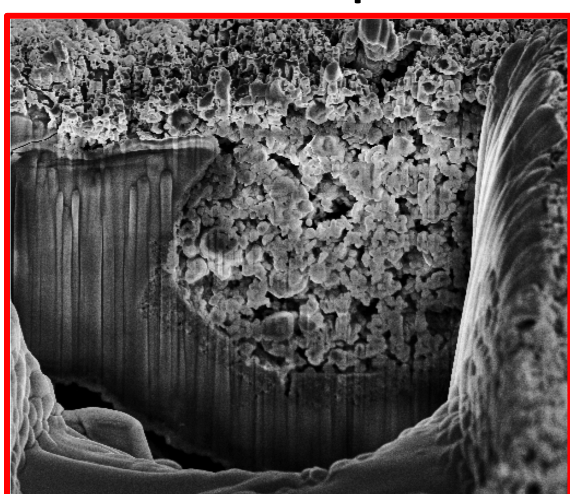


5µm

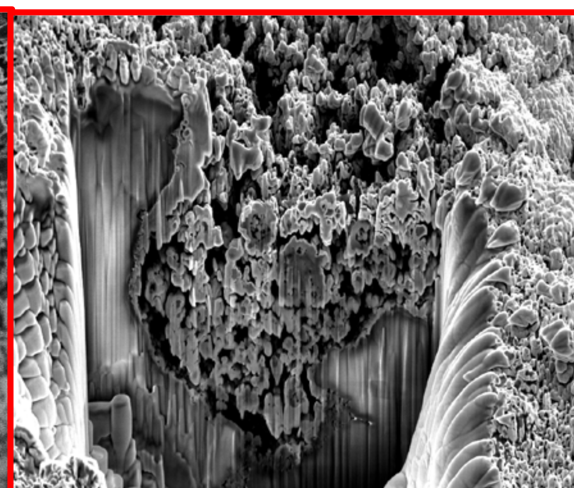


[SAE 2012-01-0836]

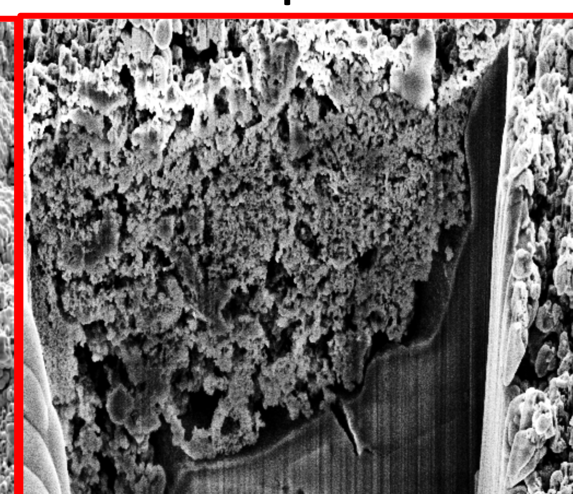
5µm



10µm

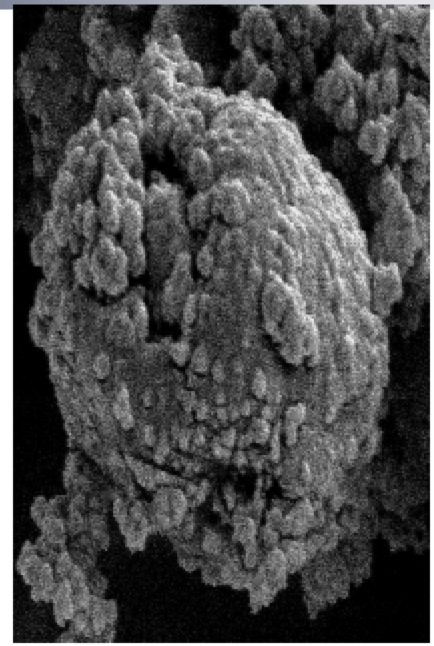


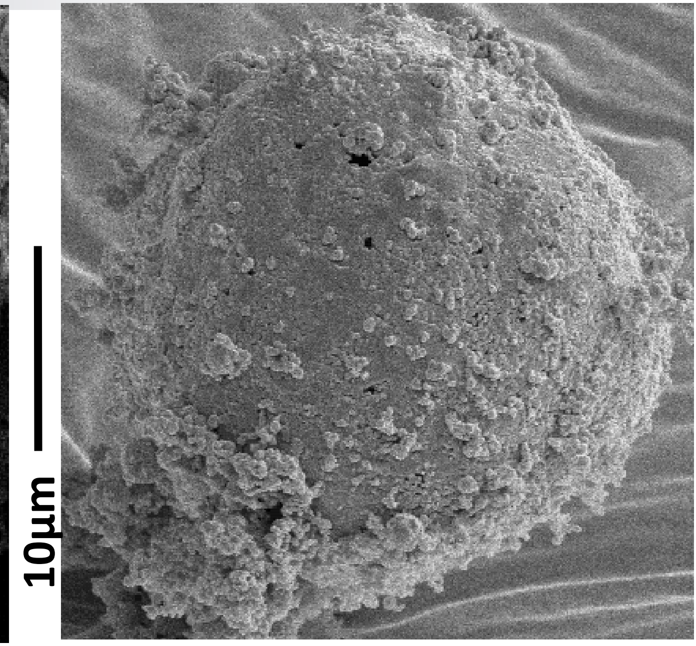
5µm

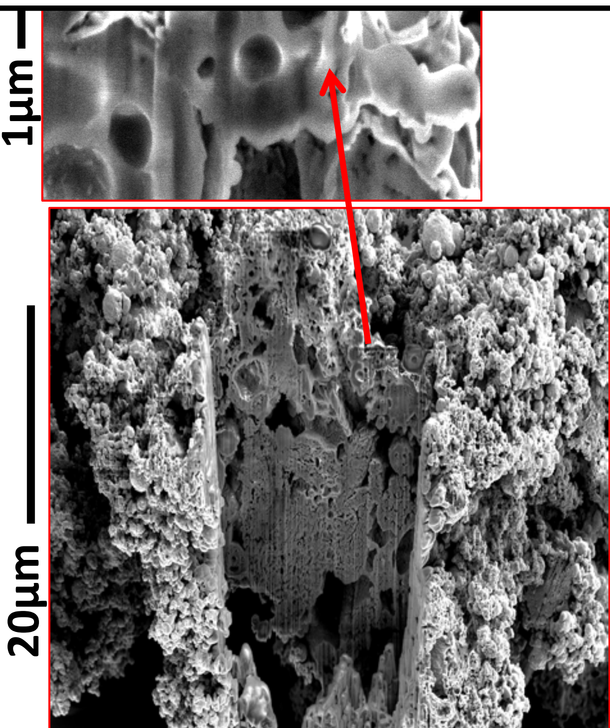


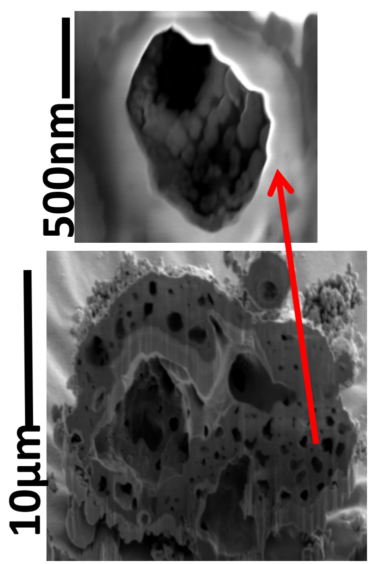
Porous Primary Ash Particles

- EDX shows large porous particles include Ca, Mg, S, P
- Adds to understanding of formation mechanisms
- Motivates a multiscale interpretation of ash porosity
- Manipulation of primary ash particles may significantly reduce bulk ash volume in DPF









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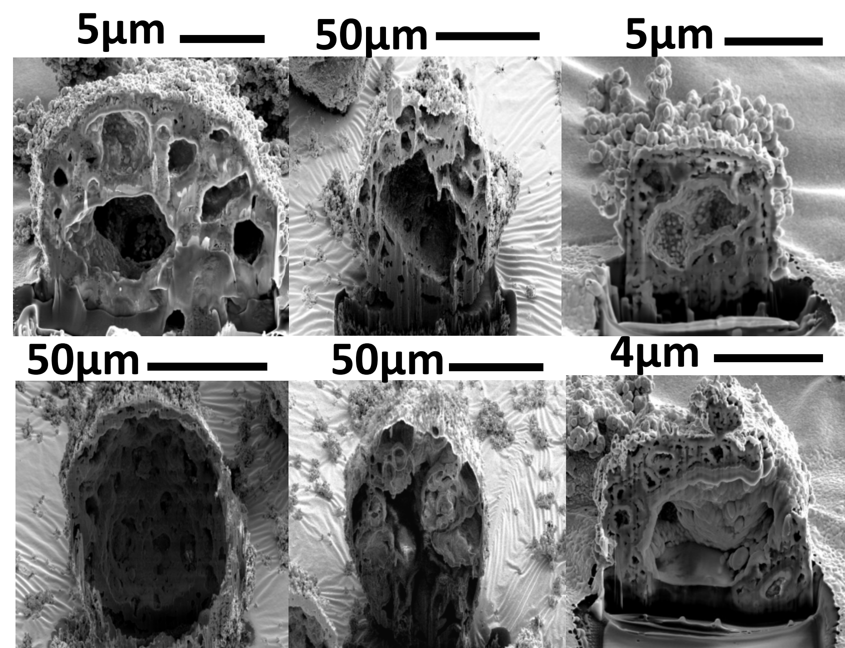
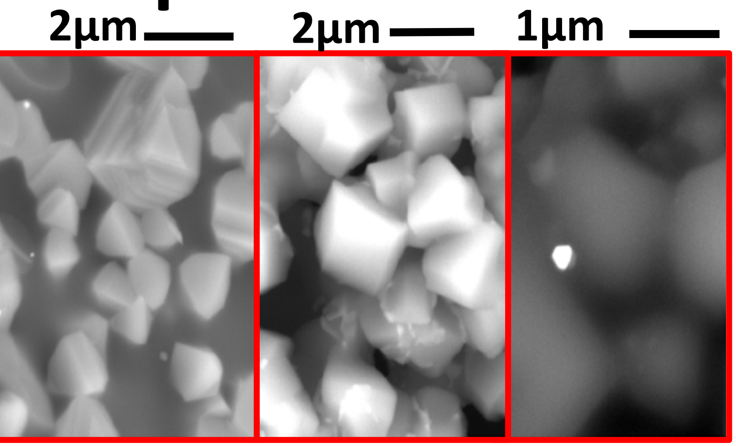


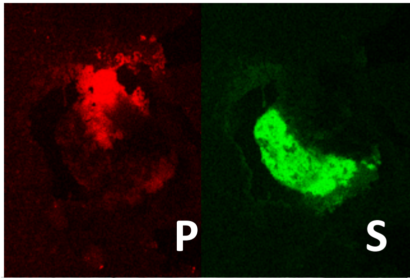
Temperature induced structural and chemical changes

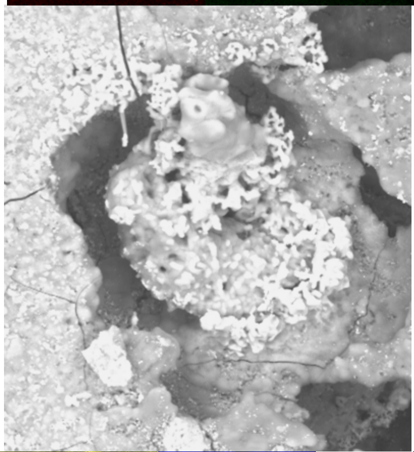


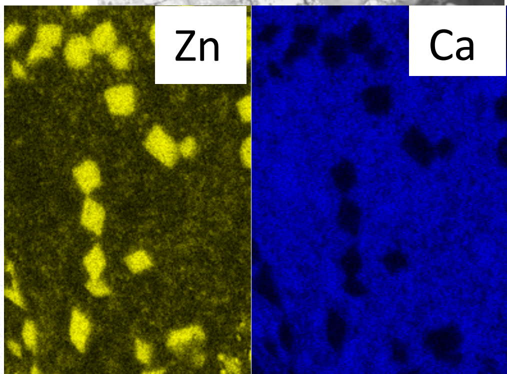
Observed thermal effects

[SAE 2012-01-1093]

- Crystal growth
- Chemical separation
  - Ca/Zn, P/S
- Catalyst sintering
- Ash particle growth and sintering
- Bulk ash volume reduction in pores

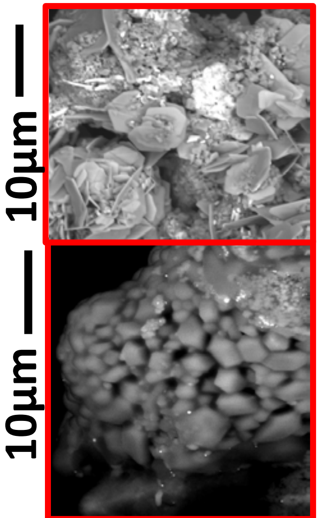


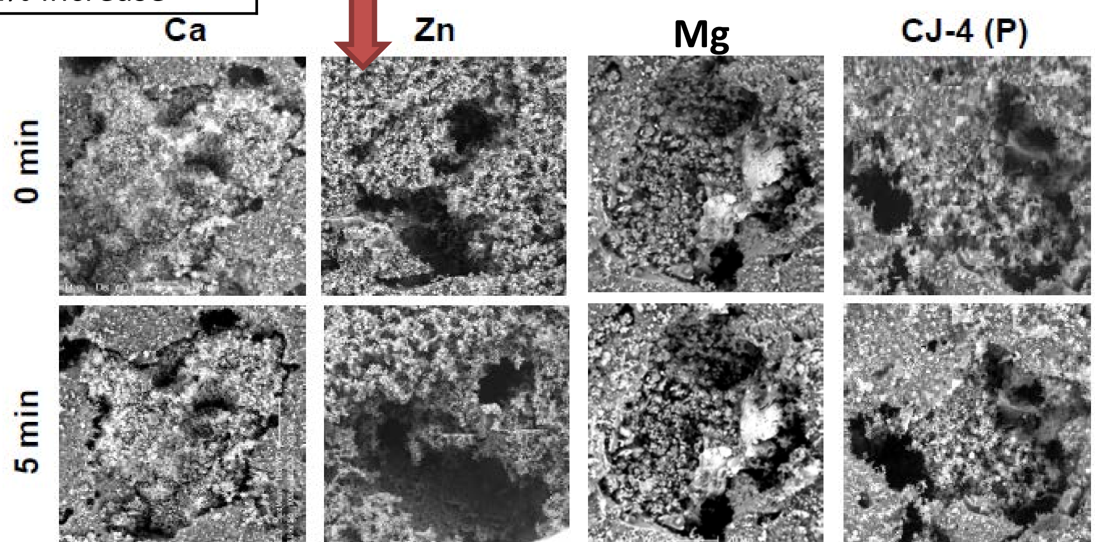




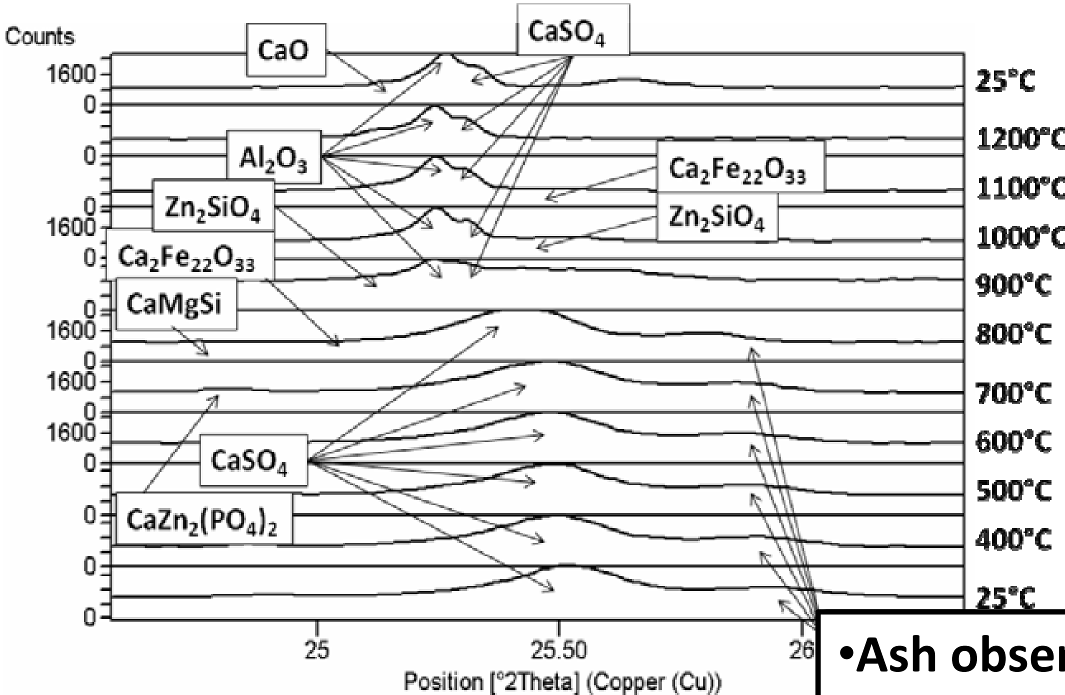
Ash Type	Pore area change
Base+Ca	102% increase
Base+ZDDP	196% increase
Base+Mg	23% increase
CJ4 (Periodic)	21% increase

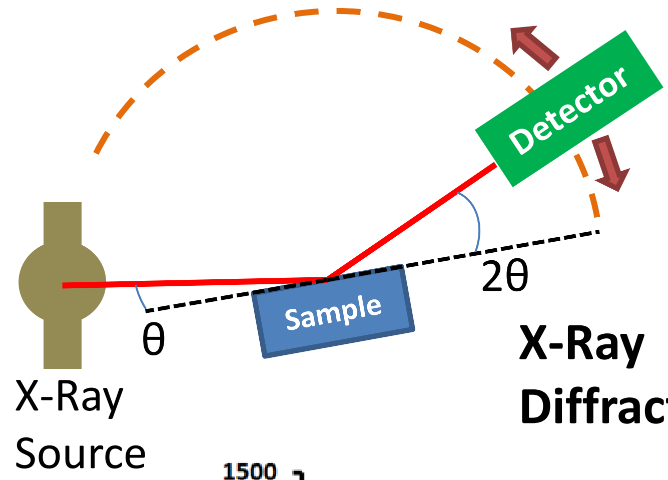
5 min at 880°C



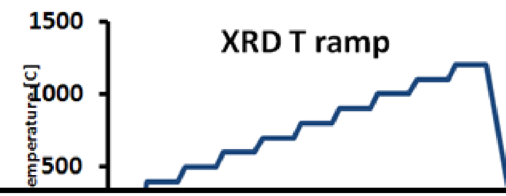


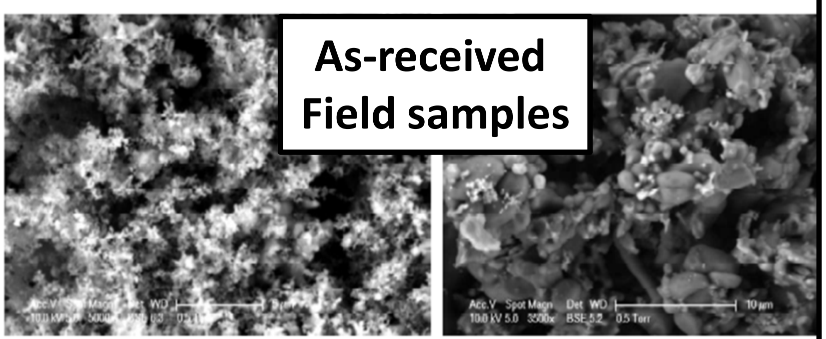
Ash composition and structure





X-Ray Diffraction





$CaSO_4$
$Ca_3(PO_4)_2$
$CaZn_2(PO_4)_2$
$Mg(PO_4)_2$

$CaSO_4$
$Mg(PO_4)_2$
$MgAl_2S_4$

$Zn_3(PO_4$
Ca_2SiO_4
Fe_2O_3

•Ash observations from XRD:

- Structural and chemical effects from high T
- Oxide formation
- Ash species with multiple structures/phases
- Ash species chemical interaction with DPF substrate
- Approximate thermal history of field samples
- Most chem/phys changes occur <5 min.
- Higher thermal resistance after heating
- Irreversible chem/phys changes with T

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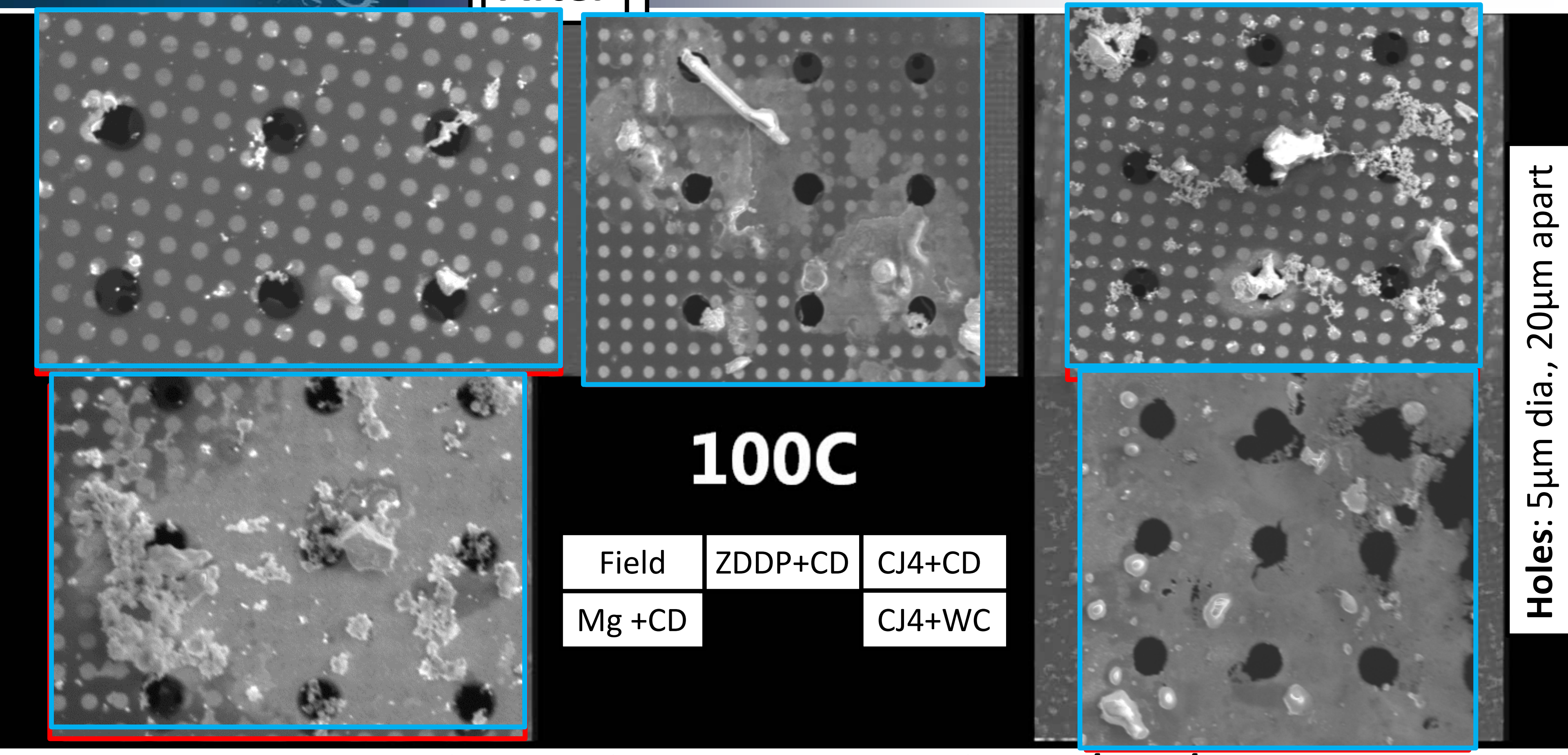
Heated SEM Stage

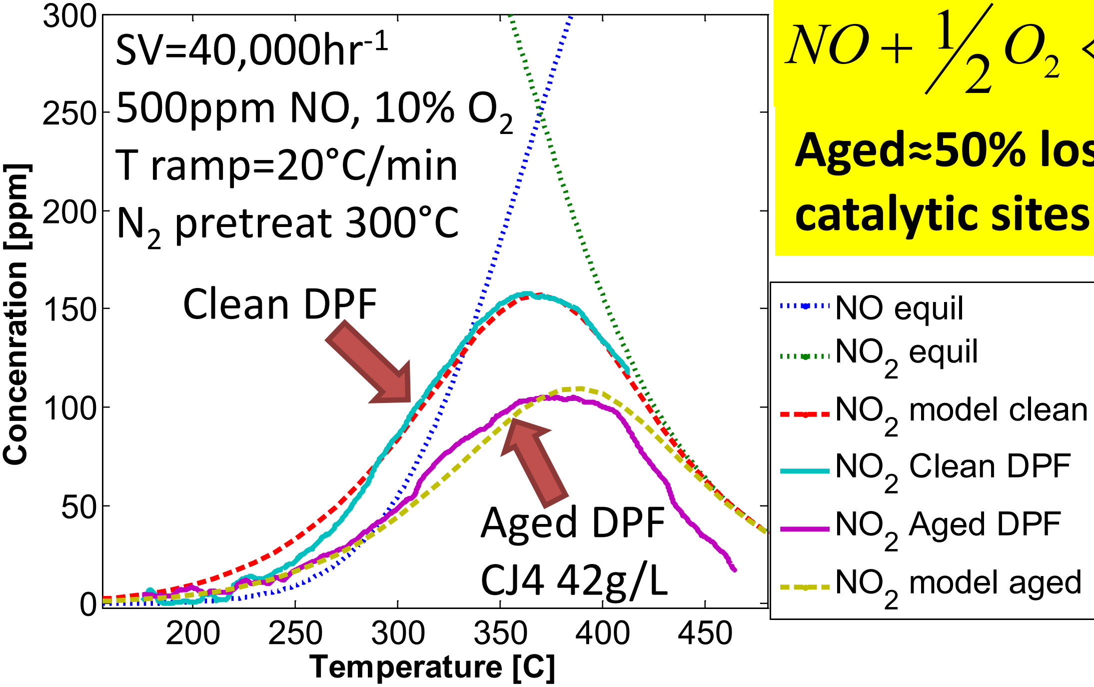
After



- **Initial data shows usefulness of heated SEM stage for ash/soot/DPF**
- **Clear differences seen between ash types**
  - **Zn-ash melts first, Mg-ash melts last**
  - **Passive ash melts before active ash**
- **Gas release from ash!**
- **Melting onto DPF surface**

- **100-1000°C at 50°C/min + 10min at 1000°C**
- **Hitachi S-3400N ESEM with Protochips stage**
- **Special thanks to ORNL's HTML (M. Lance, J. Howe)**

Ash Effects on DPF Catalyst



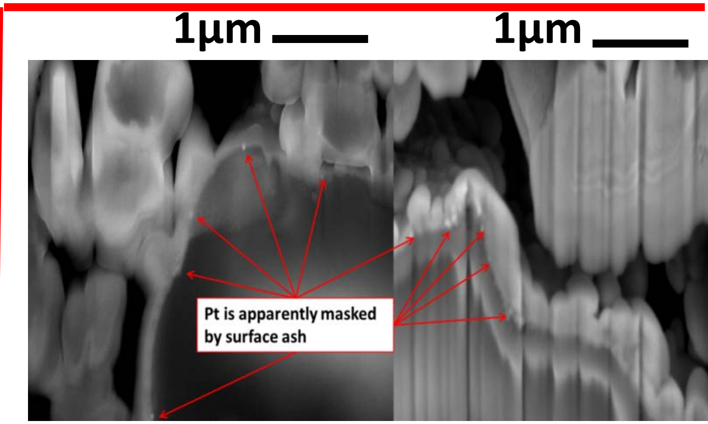
$$NO + \frac{1}{2} O_2 \Leftrightarrow NO_2$$

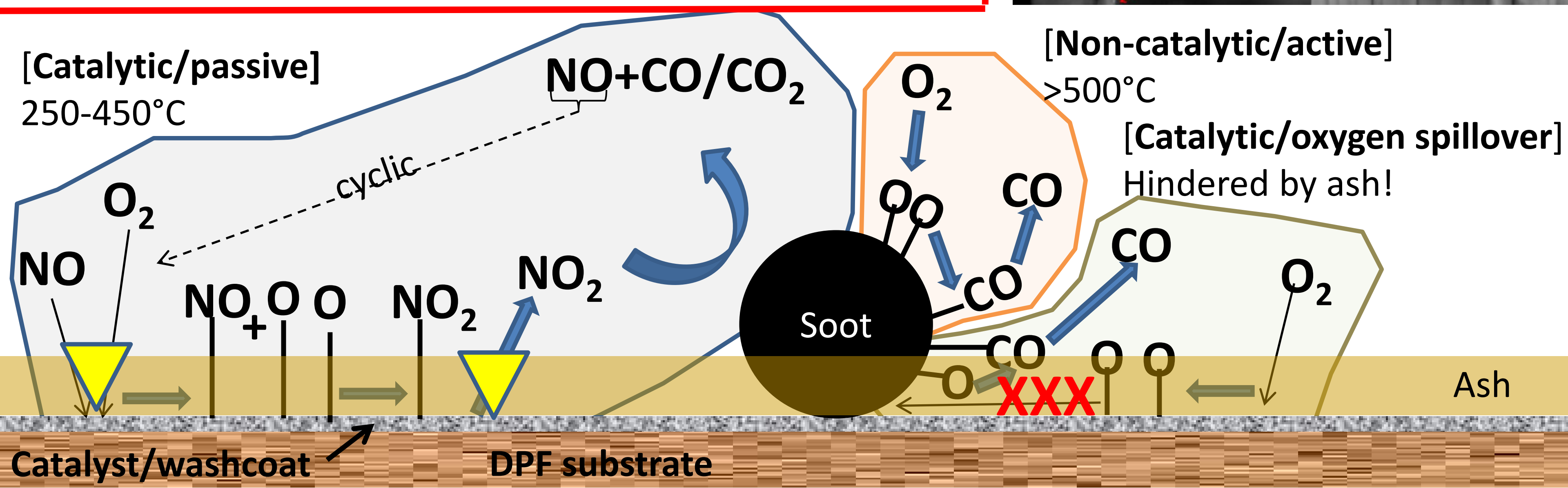
Probe reaction

Aged≈50% loss in catalytic sites

$$r_{NO,ox} = k_{NO,ox} C_{NO} C_{O_2}^{1/2} - \frac{k_{NO,ox}}{K_{eq,NO,ox}} C_{NO_2}$$

[Ind. Eng. Chem. Res., 44, 2005, 3021]

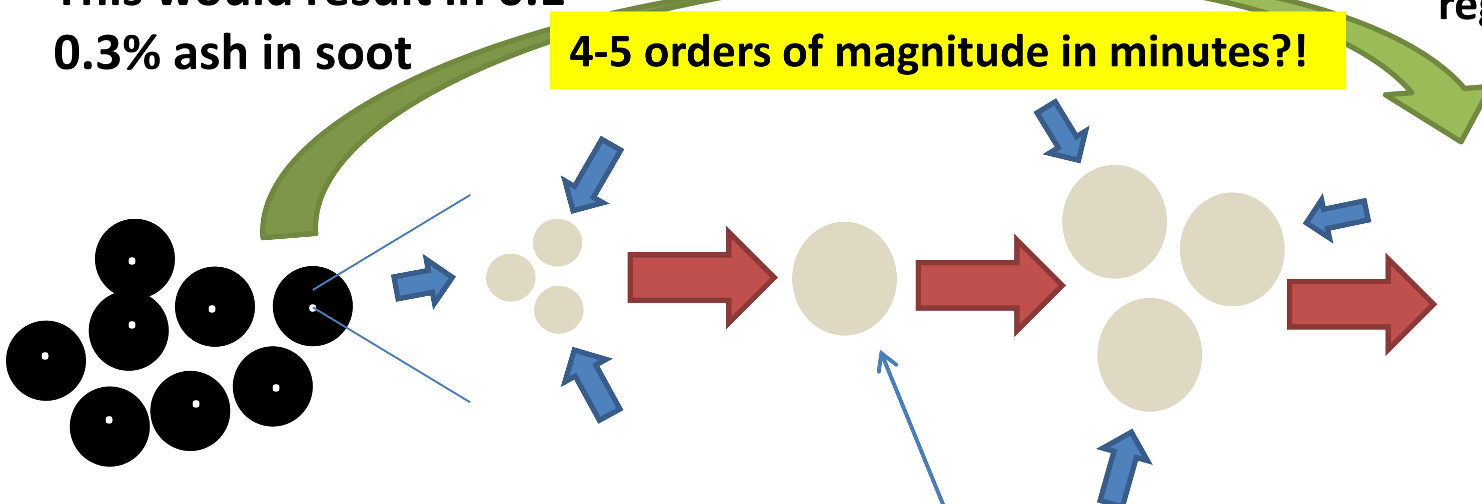




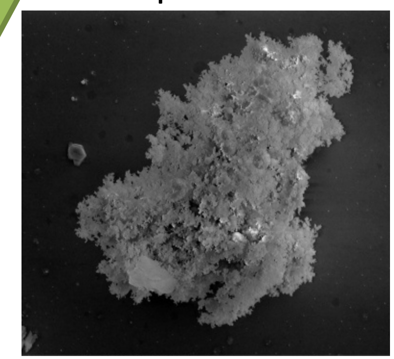
Ash Formation

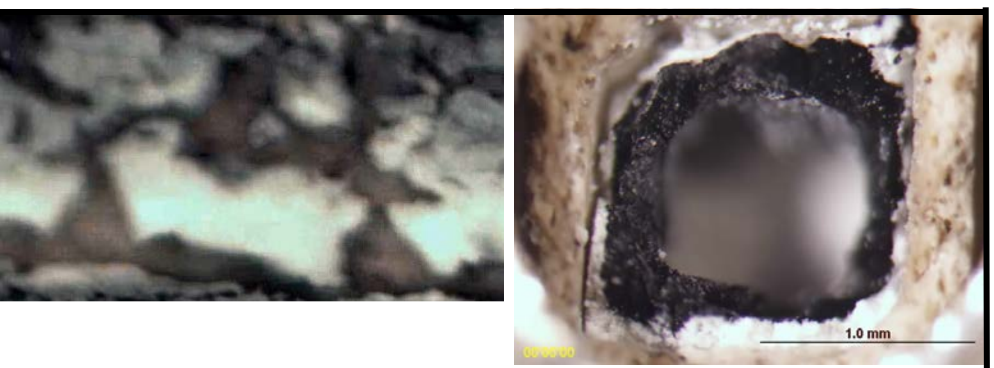
- <u>SAXS data</u> hints at a 3.5nm diameter particle in soot
- This would result in 0.1-0.3% ash in soot

- <u>10-20µm</u> ash particles observed after 1 regeneration



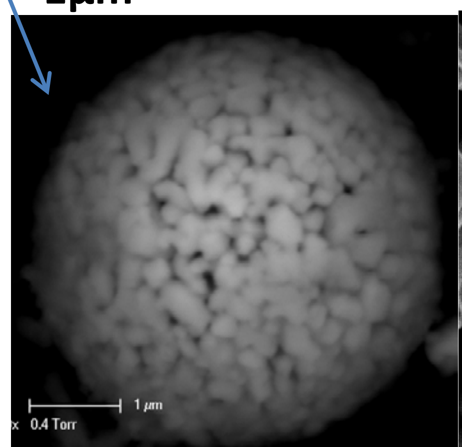
10µm



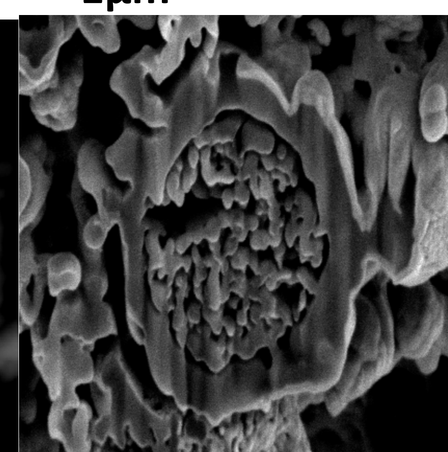


[Sappok, DEER 2011,2012]

1µm



1µm



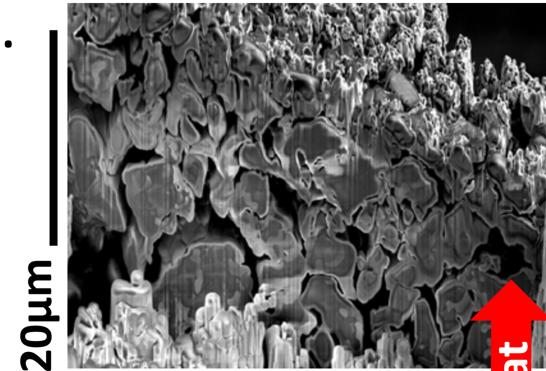
Ash Manipulation

Potentially controllable ash properties:
- Particle size
- Porosity
- Inter-particle attractive forces
- Structure
- Composition
- Agglomeration

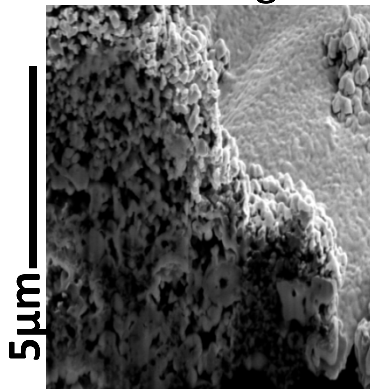
Theory considerations:
- ΔP_{ash} = ƒ(permeability, layer thickness)
- Permeability = ƒ(porosity, particle size)
- Layer thickness = ƒ(inter-particle attraction)

Potential strategies:
- Hybrid active/passive regen
- Post-engine additives
- Porous wall ash, dense plug ash
- Thermally resistant ash
- Increased permeability

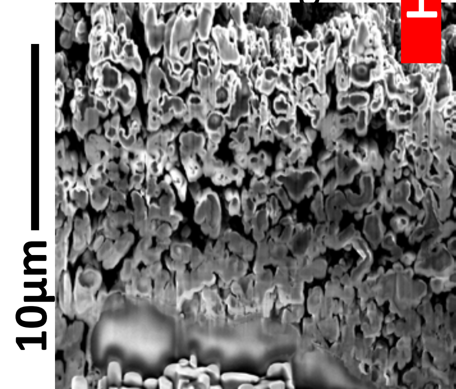
Passive regen.
d_{part}≈100nm
Active regen.
d_{part}≈1.5µm
High T treat.
d_{part}≈ 5.5µm



Passive regen.



Active regen.



Summary

- We have the tools to potentially 'solve' the ash problem
- The ash/soot/DPF/catalyst system is very complex
- Currently we are at the point of observing/measuring/modeling some of the fundamental mechanisms which relate nm-μm scale phenomena with emissions systems-aging and performance
- Tools and approach suitable for other aftertreatment components (DOC, SCR, DPF+SCR, etc.)
- Current goals: understand interfacial attractive forces (Ash-DPF, ash-soot, soot-DPF) and manipulate them

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- Valvoline	**- US Department of Energy**	
- Ciba	***- Ford***	***- Lutek***

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