Opportunities for Earth and Environmental Science at Diffraction Limited Storage Rings

community insights from May MBA workshop

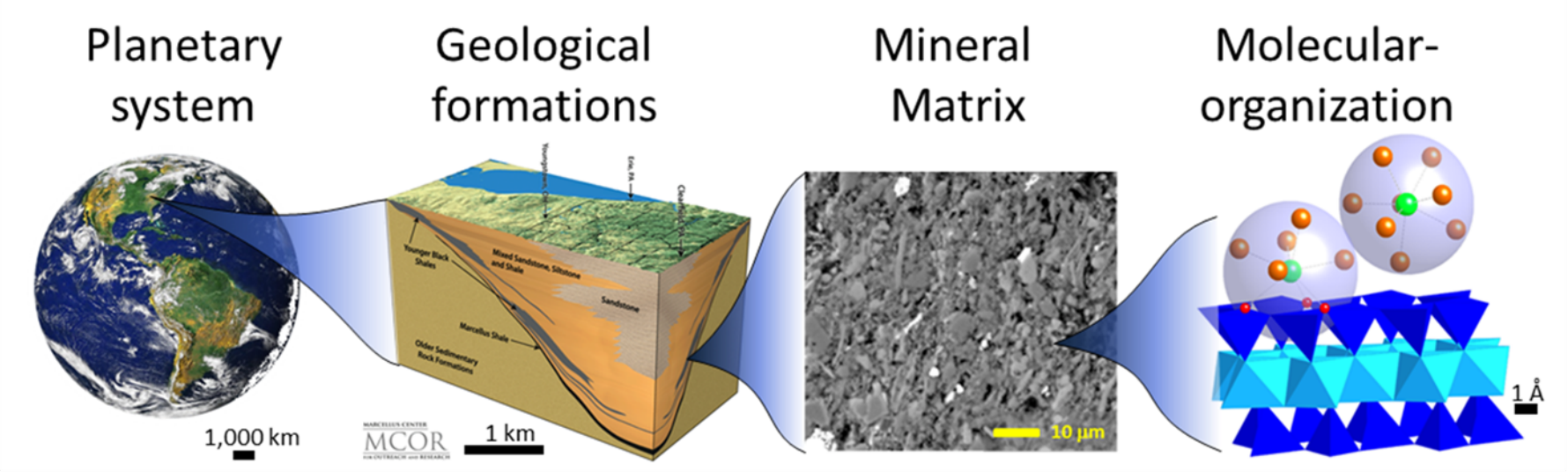
E^3 APS-MBA Workshop

- Meeting gathered members of Earth, Enviro, Extreme Conditions (E^3) community to identify compelling science that will take advantage of APS-U properties. Report from group will be part of APS-U early experiments document.

E^3 highlighted the broad scope of synchrotron enviro- / geo-science research

- Crystalline to amorphous solids – stability, role in reaction processes
- Solutes in liquids – aqueous complexes, nucleation/precipitation
- Properties of fluids in confined pores, geometries (incl. nanopores)
- Fluid flow and transport processes at pore and sub-pore scales
- Nanoparticles and colloids – stability, transport and cycling
- Mesoscale transport and bioavailability of contaminants and nutrients
- Chemical speciation of contaminants – esp. beyond model systems
- Time-resolved studies of dynamic processes – nucleation/precipitation, ripening and shape change
- In-situ studies and integration of useful sample cells – mimic real conditions
- Also coupled studies with life sciences: Environmental genomics – gene modification to direct biologic interaction with contaminants, nutrients, etc. Medical mineralogy. Rhizosphere chemistry.

Extreme inherent heterogeneity of Geosystems



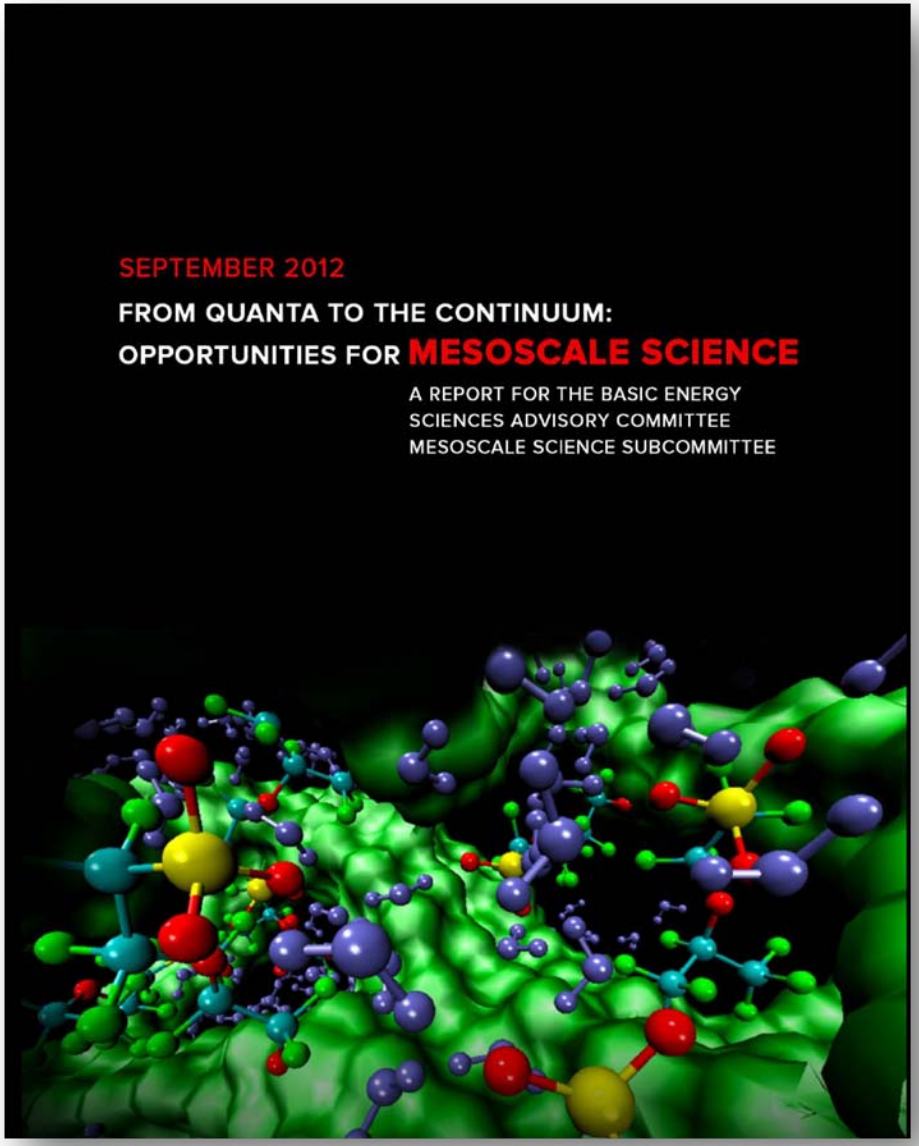
- Geosystems inherently display extreme inherent heterogeneity ranging from molecular to planetary length-scales.

- The use of coherent, high brightness X-ray sources enables a robust understanding of the complex reactivity in these systems.

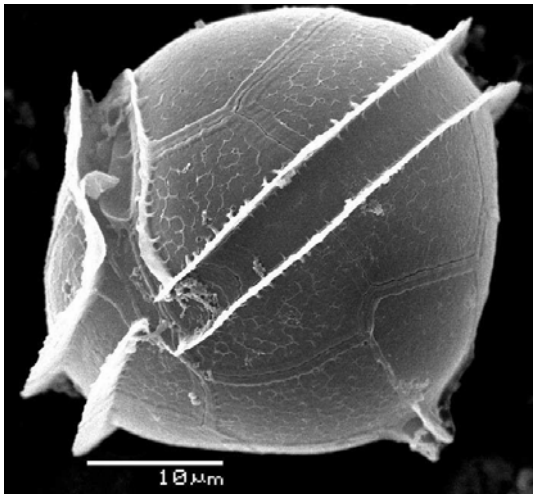
High Brightness is the Key Parameter

- Reduce emittance to pm-rad range
- Unique for hard X-rays (~5 to 100 keV)
- Allow production of intense, 10s of nm-sized, X-ray probes
- Analyses at lower concentrations in smaller samples and/or voxels
- Faster interrogation of large samples at high spatial resolution, transient phenomena

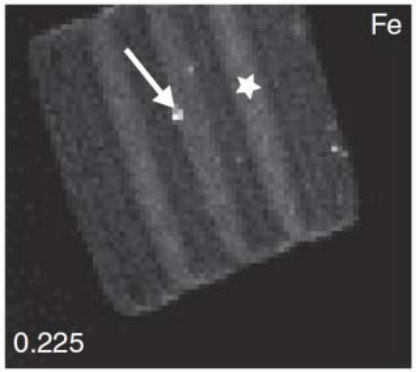
• **Nanoscale** resolution, applied over the **mesoscopic length scales**, allow us to understand how the atomic, molecular, and nanoscale hierarchy of architectures organize to define their more familiar bulk macroscopic behavior at **geologic and planetary scale** (*BESAC Subcommittee on Mesoscale Science*, 2012; *BER Molecular Science Challenges Workshop Report*, 2014).

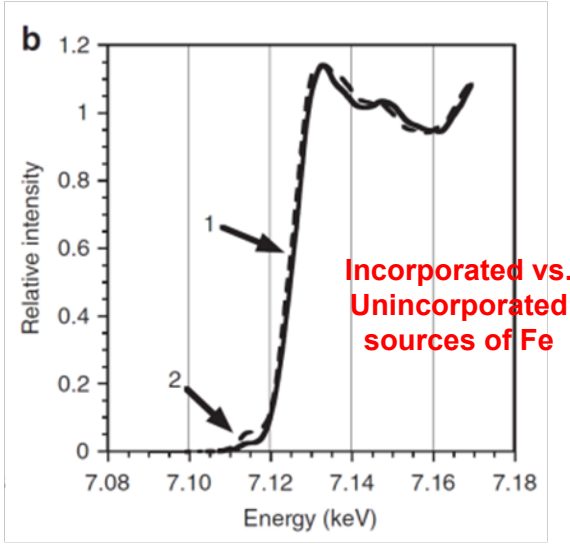


Trace Metals in the Oceans: Constraining Iron Cycling in Marine Systems



- Trace metals, notably Fe, play key roles in controlling biological production in the Southern Ocean, yet the mechanisms regulating metal availability in marine systems are incompletely understood.
- Since phytoplankton are responsible for about half the photosynthetic fixation of carbon (primary production) on Earth, this has significant control on atmospheric CO_2 levels.
- High resolution elemental maps of phytoplankton can reveal morphologically distinct metal pools associated with biogenic silica.
- *MBA upgrade will allow rapid, high quality XAFS to define the speciation and impact of these potentially significant metal sinks.*

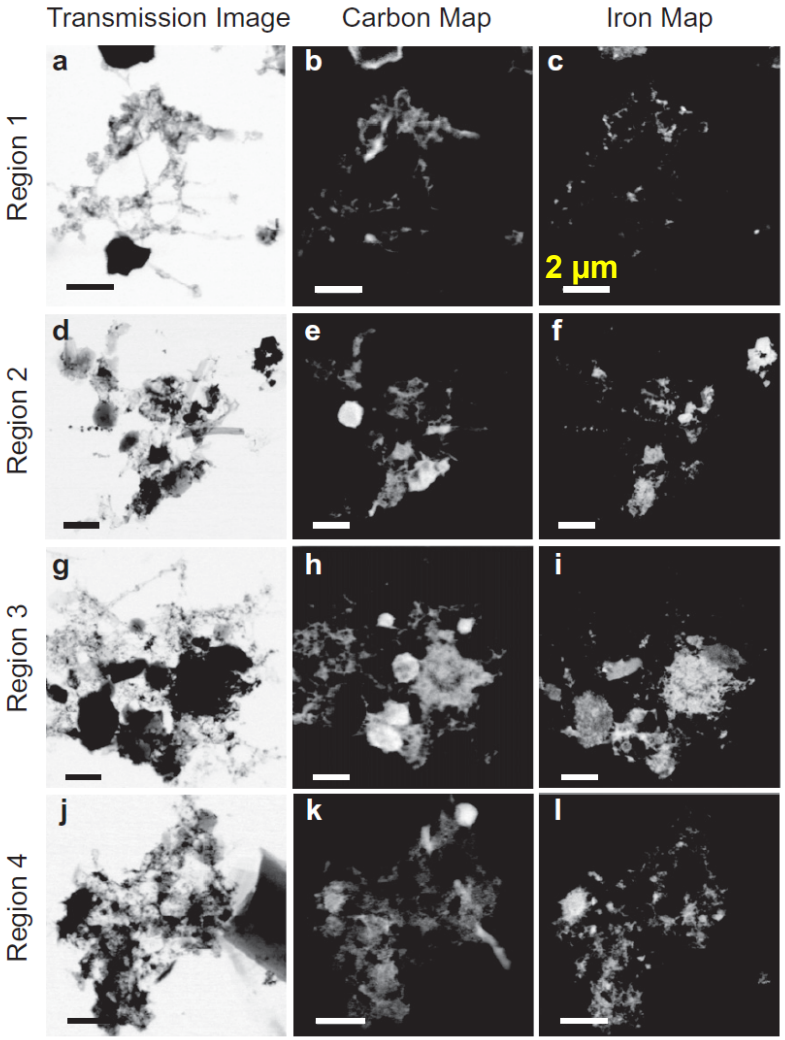




Ingall, E.D., et al. (2013) Nature Communications, v. 4.

Trace Metals in the Oceans: How far can hydrothermal iron travel from a vent?

- Deep-sea hydrothermal plume particles are known to sequester seawater trace elements and influence ocean-scale biogeochemical budgets .
- How biotic versus abiotic oxidation–reduction impact particle chemistry and mineralogy at small scale unknown (Å, nm, µm)
- Chemistry can differ over oceanographic scales (1000s km)
- *MBA upgrade will allow rapid, high quality XAFS of large number of samples with high spatial and spectral resolution.*
- Critical to understanding the net effect of hydrothermal fluxes on ocean and sedimentary trace element budgets.



Breier et al. 2012 GCA

Analysis of metals in atmospheric particulates

Fine- and ultrafine particles in aerosol samples from urban Detroit show heavy metals, including U. Mostly HRTEM studies.

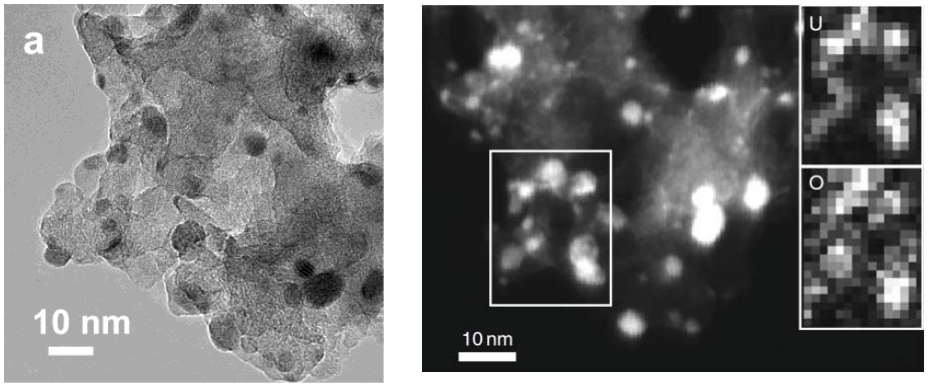
Most of the trace element enriched particles detected within a range of **0.01-1.0 *μ*m** in size, which has the longest atmospheric residence time (100 days).

These ultrafine particles are much more inflammogenic per mass dose than larger-size particles, the inflammatory response of the observed heavy metal particles may be increased.

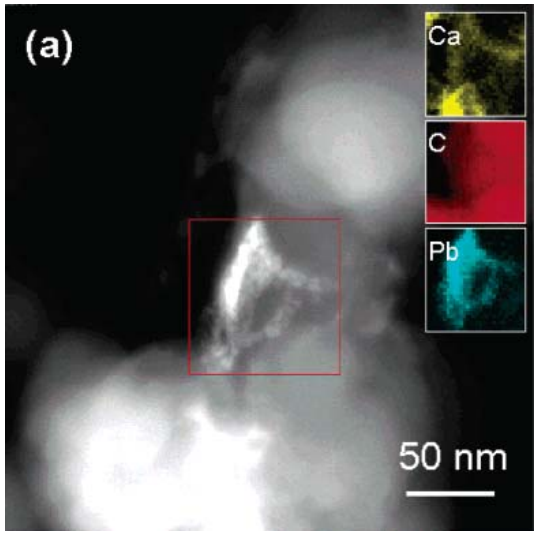
Chemical toxicity, inflammatory potential, environmental stability of metal particles may influenced by **speciation**.

MBA upgrade will allow XAFS of nm sized metal-rich domains in atmospheric dust.

Utsunomiya et al. (2002, 2004)



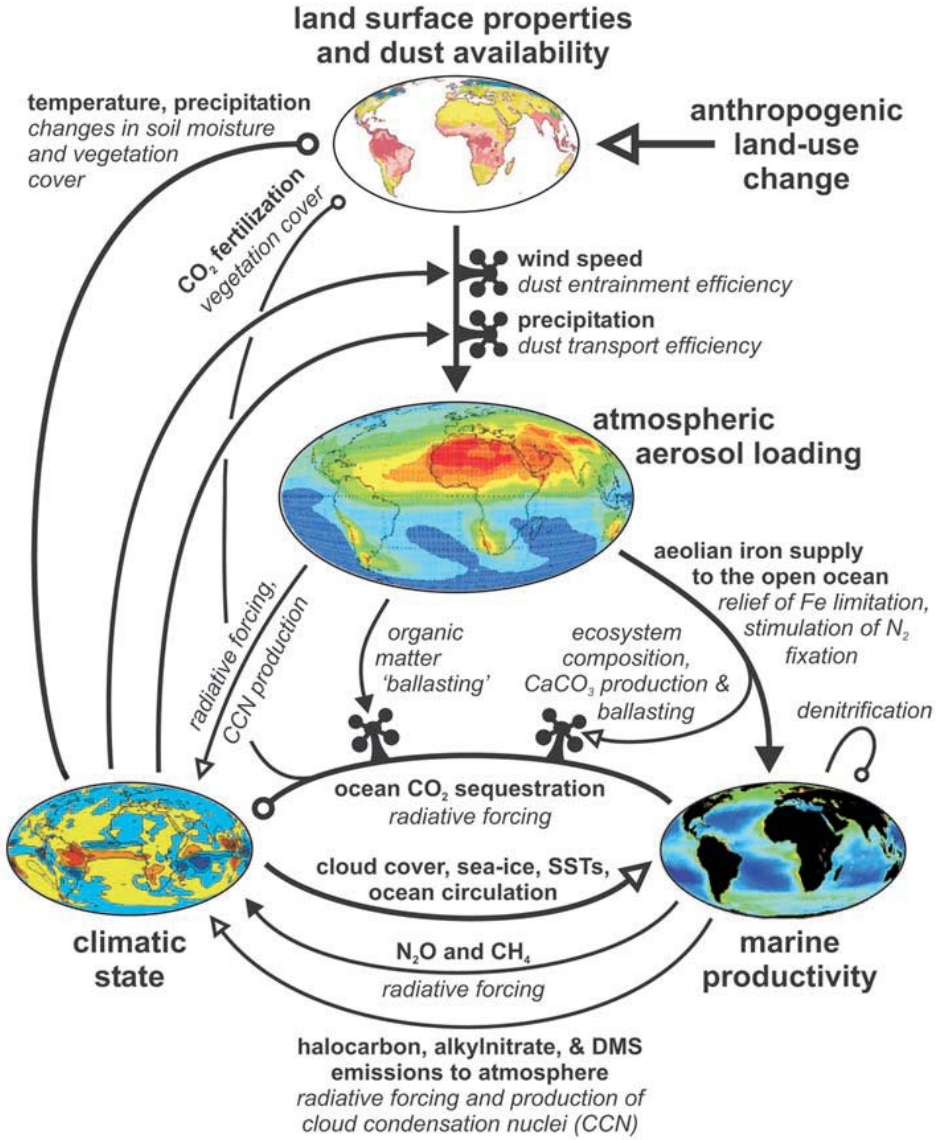
Uraninite nanoparticles in atmospheric particulates (a) BF-TEM shows small heavy particles within the carbonaceous matter of soot less than 10 nm in size. Insets are elemental maps of U and O by STEM-EDX.



- HAADF-STEM image of Pb-bearing particle on the surface of carbonaceous matter.
- 50 nm-size Pb-rich domain consisting of <5 nm-size nanocrystals.

The speciation of Pb in the atmosphere is crucial with respect to its potential health effects.

Nanoscale spectroscopies to understand global cycles



Jickells et al.(2005) Science

The Global Iron Cycle

- Environmental conditions of Earth, including the climate, are determined by physical, chemical, biological, and human interactions that transform and transport materials and energy.

- **Global Iron Connections**: land surface and dust availability, atmospheric <u>aerosol loading</u>, <u>geologic fluxes</u>, <u>marine productivity</u>, climatic state.

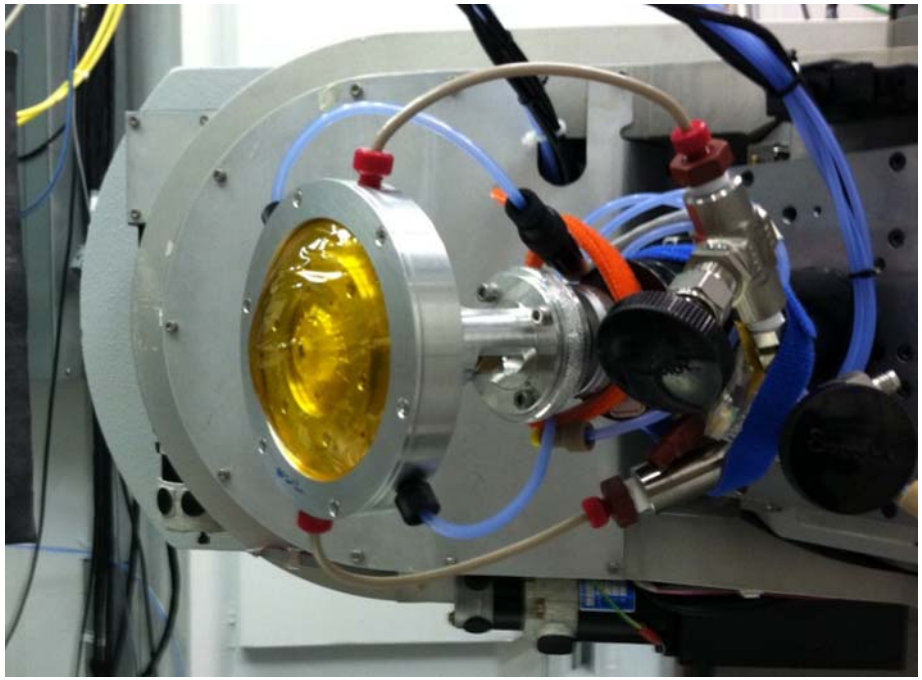
- increased atmospheric aerosol loading
  ⇨ increased marine productivity

- increased marine productivity
  ⇨ lower CO_2 and a colder climate

MBA upgrade directly impacts global scale studies of climate chemistry

MBA opportunities in mineral interface studies

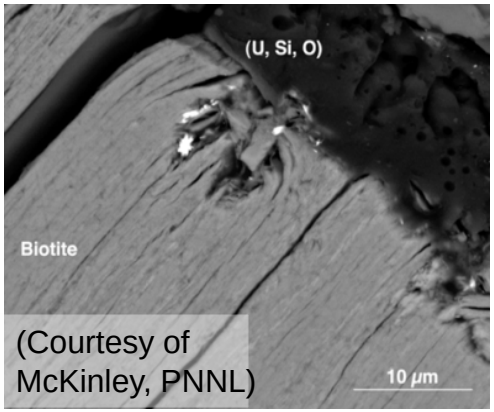
- Today, we can put most of the undulator beam on a sample for CTR/XSW analysis to determine interface structure and composition
- Small intense MBA beams will allow higher resolution studies of heterogeneous samples
- Advance us further along the path from model compounds to real rocks.
- Improved coherence (XPCS, CDI) allows study of the kinetics of surfaces during growth/reactions including buried structures.
- Applying multimodal probes (XRIM, CDI, optical, LEED) to extract information on different length scales (Å to µm) from a single sample.



Understanding Complex Reactivity in Heterogeneous Systems:

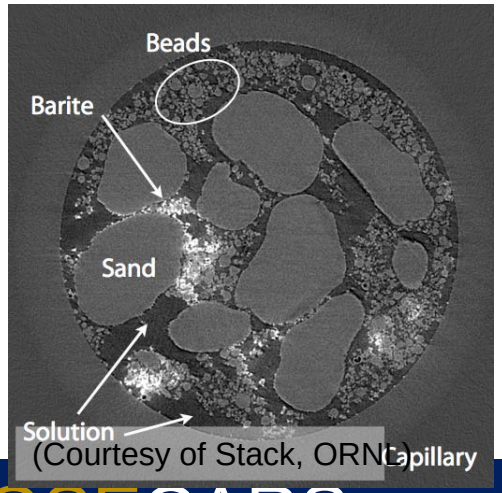
Reactivity (e.g., precipitation) on mineral surfaces is highly heterogeneous. Principle controls governing reactivity are not well understood.

Precipitation of uranium in Hanford sediments:



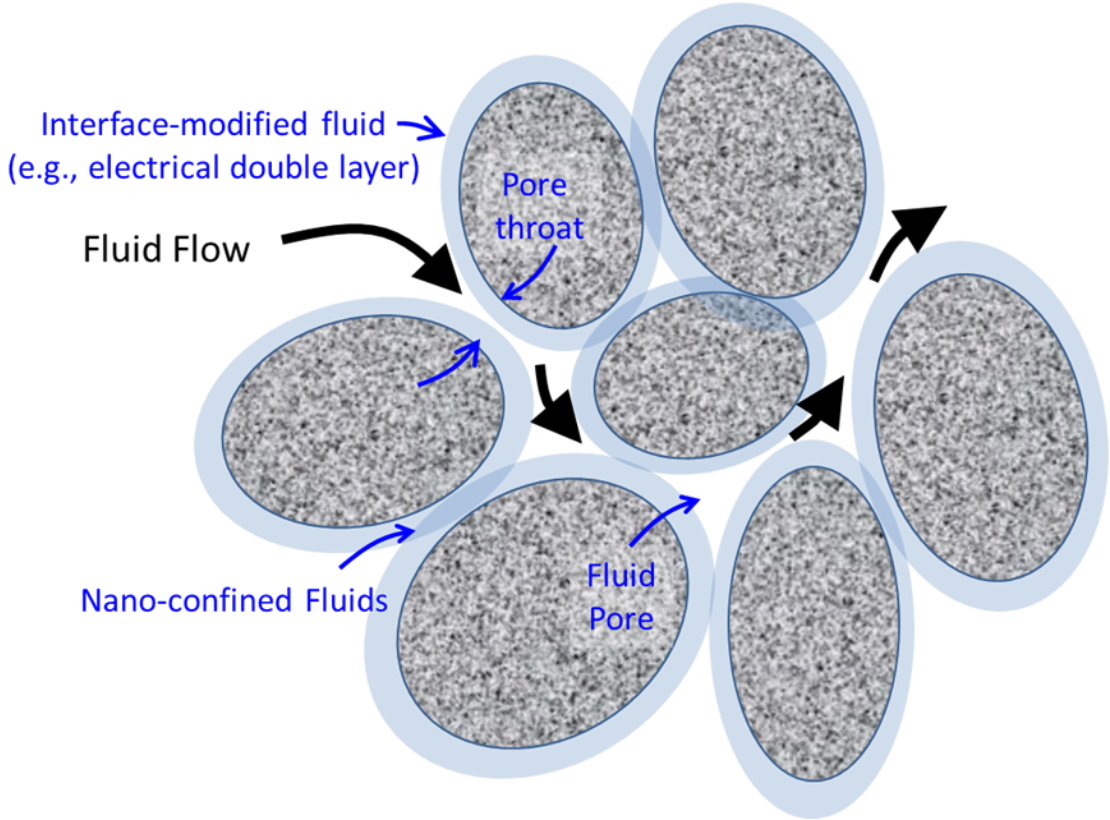
(Courtesy of McKinley, PNNL)

Precipitation of barium sulfate (barite) in a simulated mineral matrix:



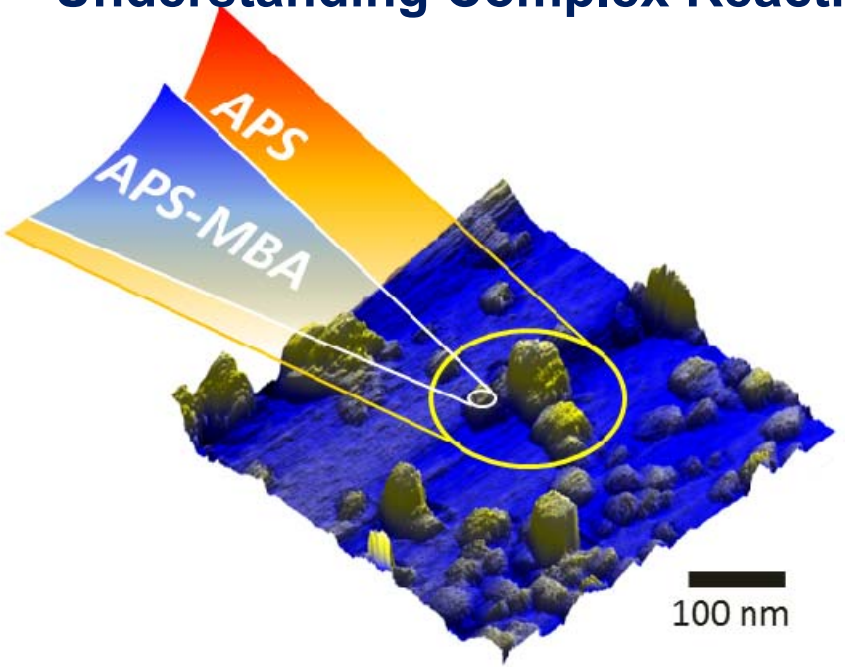
(Courtesy of Stack, ORNL)

Schematic of Nano-porous Media:



→ Complexity in observed behavior likely due to a combination of confinement effects: - flow, interfacial curvature (in pores), local interfacial structure…

Understanding Complex Reactivity in Heterogeneous Systems:



Complex contaminant-mineral reactions

Ex-situ atomic force microscopy image of PuO_2-nanoparticles formed spontaneously at the muscovite-water interface.
(From Schmidt et al., *Environ. Sci. & Tech.,* 2013)

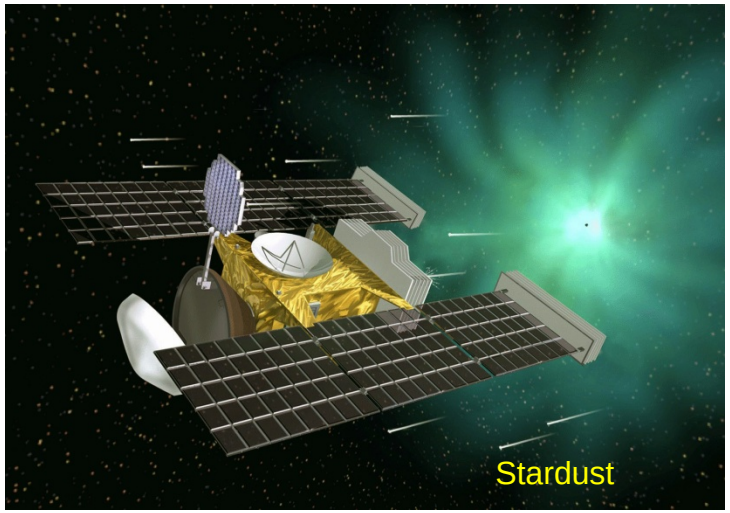
Current interfacial X-ray microscopy limited to ~100 nm (orange circle). The APS-U will achieve a substantially improved spatial resolution through coherent diffraction (<20 nm, in blue).

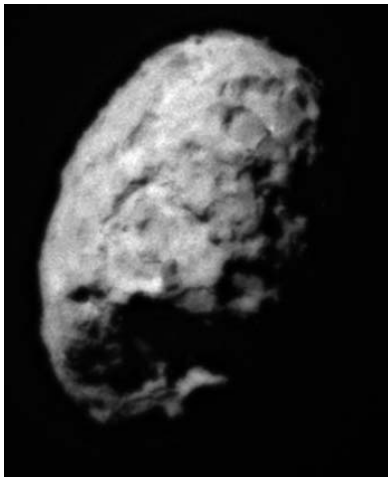
- This will allow the discovery of the principles governing nucleation and growth of individual particles through direct in-situ observations (e.g., under confinement, flow, etc.) and to resolve the structures within a given particle.

- Test and validate predictive capabilities for understanding transport in geologic repositories of energy-related materials (e.g., CO_2, radiological waste, etc.)

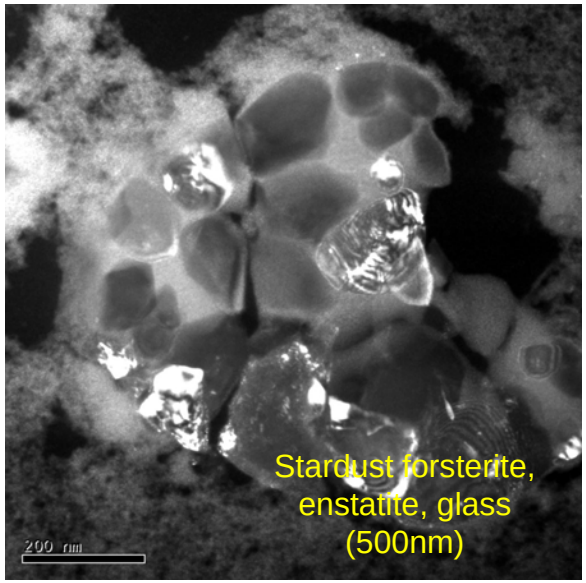
Synchrotron Radiation Studies of Extraterrestrial Materials

- Stardust mission, first sample return mission since Apollo, returned only ~1 microgram of comet dust.
- Properties of synchrotron radiation (brightness, tunability, etc.) allow detailed characterization of such minute samples.
- Synchrotron analyses are nearly non-destructive allowing multiple techniques to be applied to the same specimens.
- Such analyses are used as the first step in preliminary examination programs.

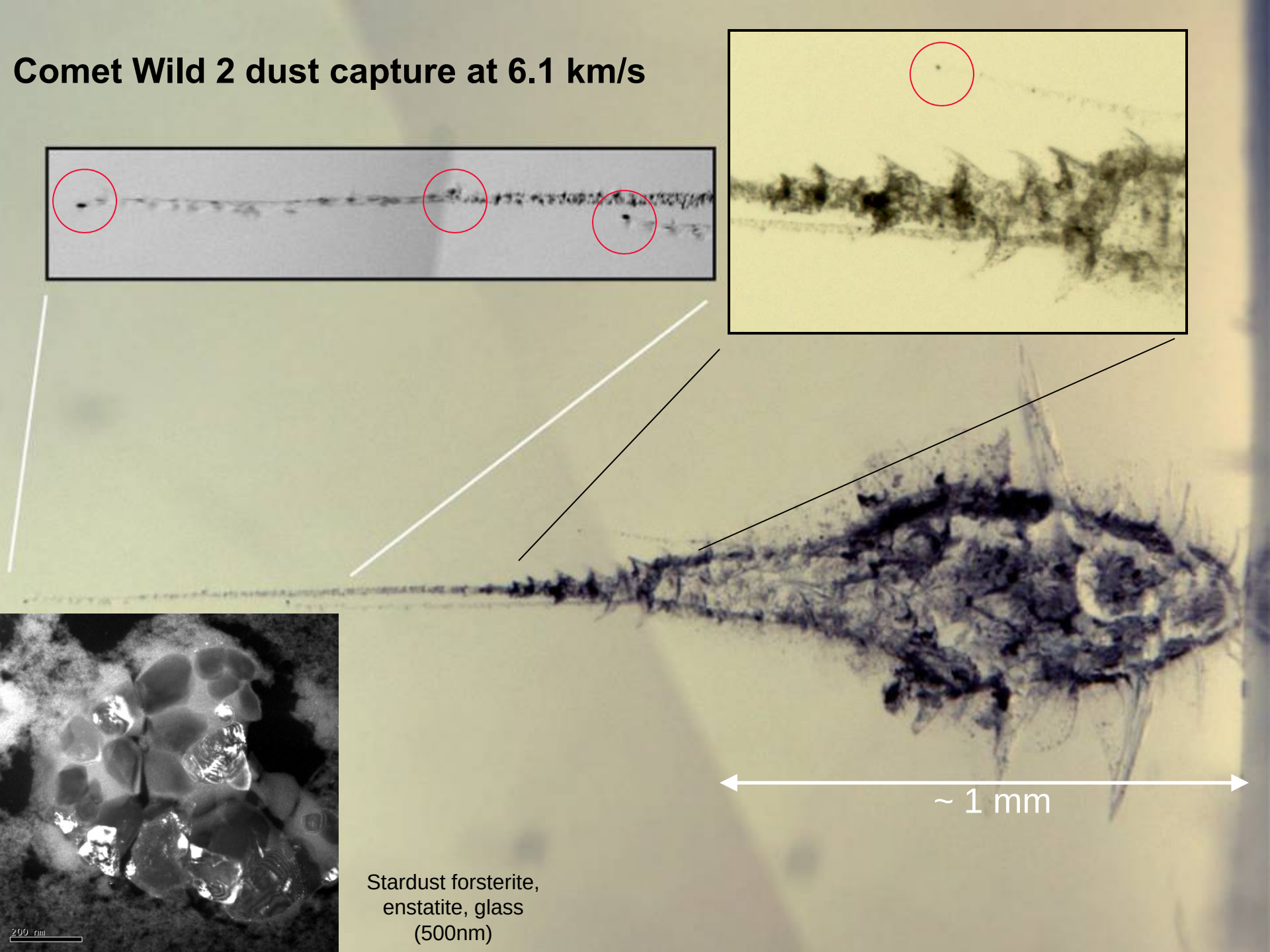




Comet Wild 2



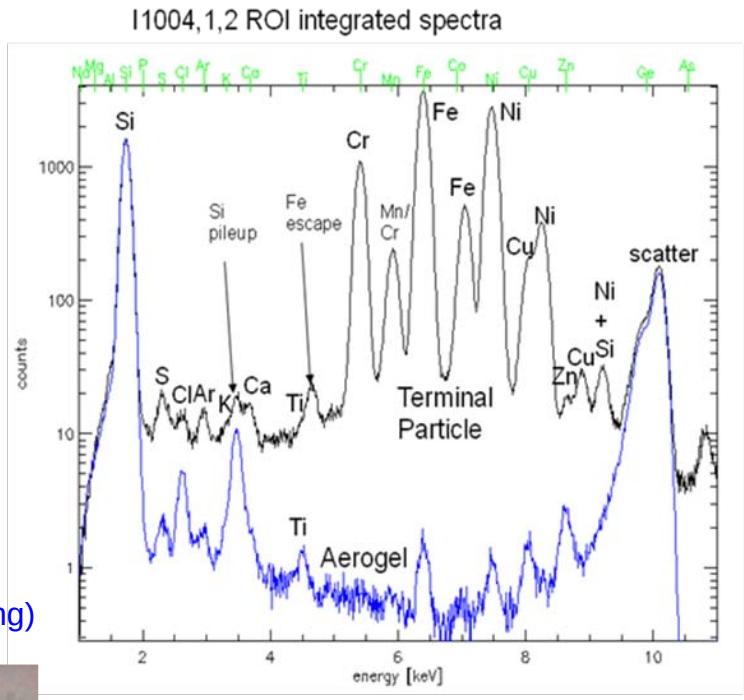
Comet Wild 2 dust capture at 6.1 km/s



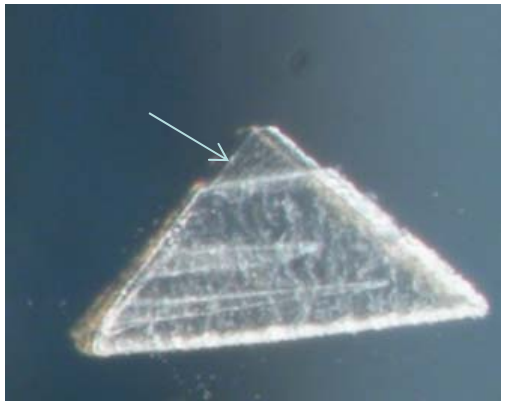
Stardust forsterite, enstatite, glass (500nm)

Stardust Interstellar Grains: Smaller, Harder to Find

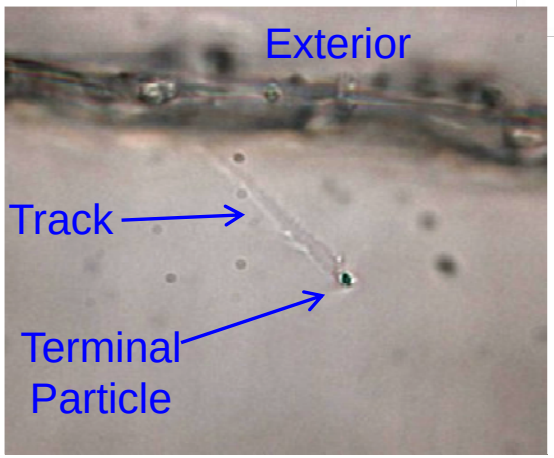
- Objective: Characterize interstellar candidates and to compare the compositions with the expected properties of interstellar dust and spacecraft hardware (secondaries).
- First challenge is to find them! Search by
- Stardust@home identified ~30,000 “dusters”, ~1 µm tracks.
- Of these to date, ~70 candidates have been identified. Many of these are secondaries (solar cells).
- Probes today provide “bulk” analysis only. We want the composition of sub-components.



Pico-keystone in a Si_3N_4 sandwich. The window is 1.5 mm square

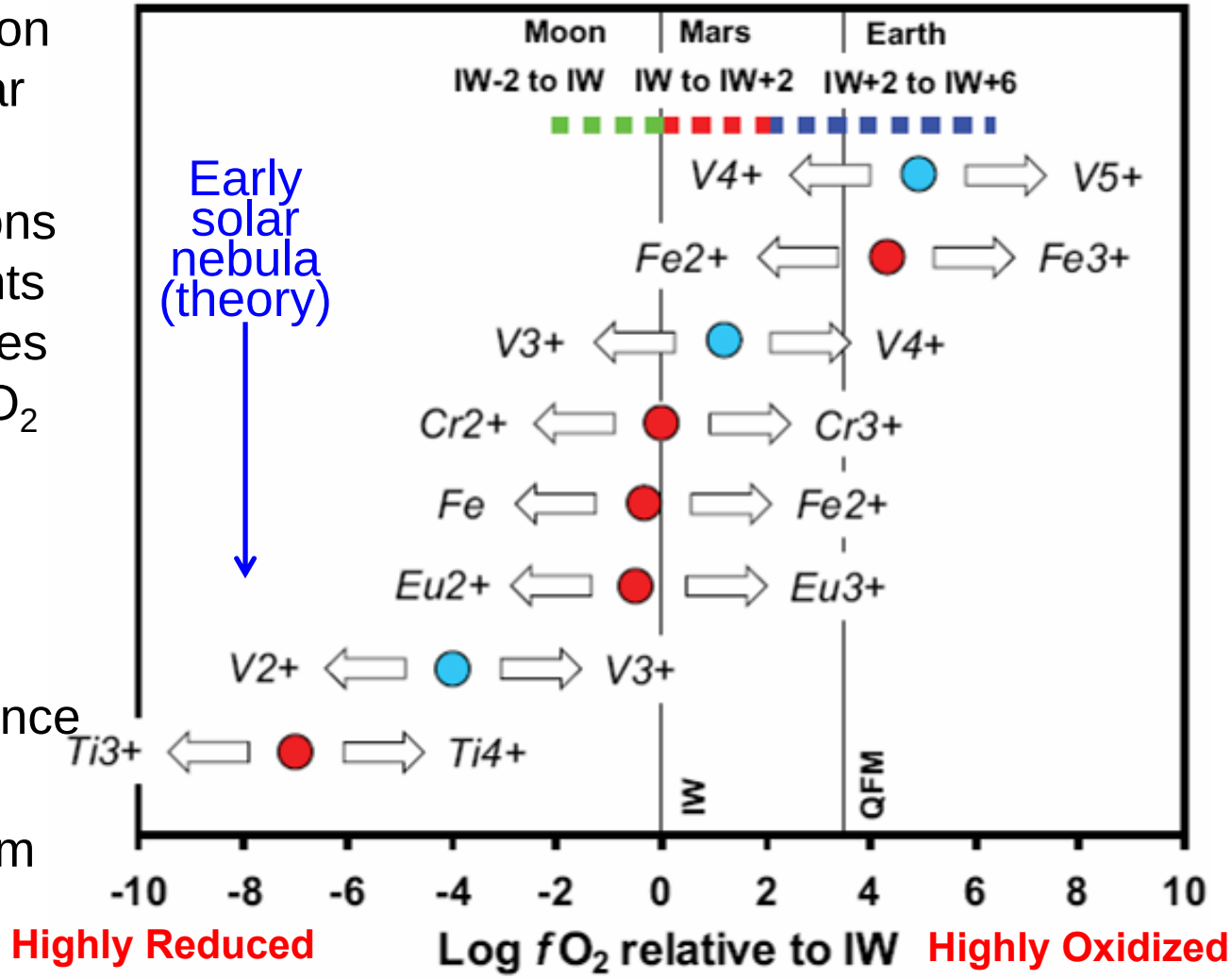


Track 2 optical image (~ 20 µm long)



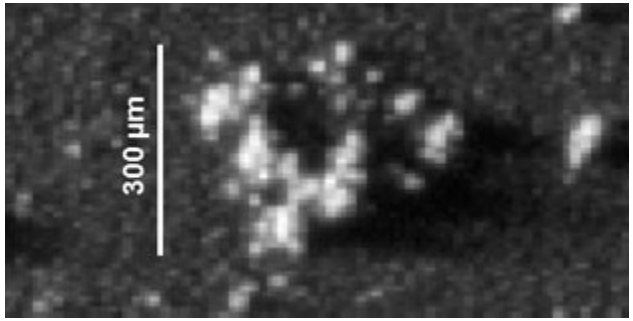
Valence Determinations of Minerals in Extraterrestrial Materials

- What was the oxidation state of the early solar nebula?
- Valence determinations of multivalent elements can be used as proxies for oxygen fugacity fO_2 (~partial pressure).
- Synchrotron X-ray analyses provide a means for direct measurement of valence states.
- Challenging at sub-µm resolutions!!



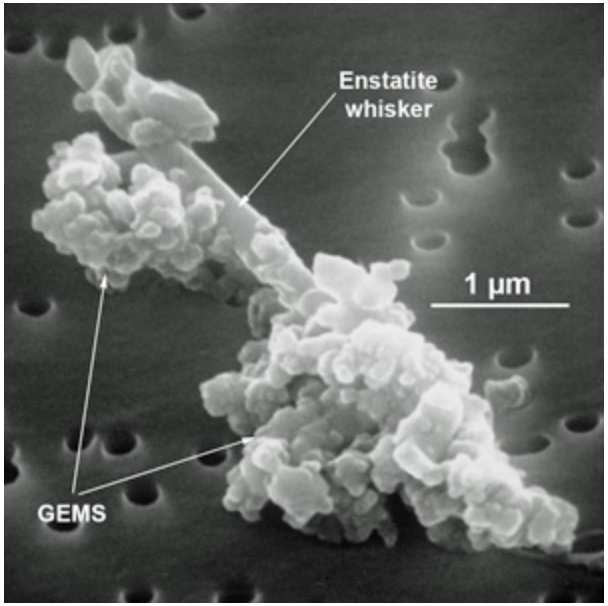
Papike et al. (2005) Am. Min. 90, 277-290

Comet (Rosetta)



Rosetta COSIMA (COmetary Secondary Ion Mass Analyzer) image shows a dust particle that shattered (named Arvid)

Stratosphere

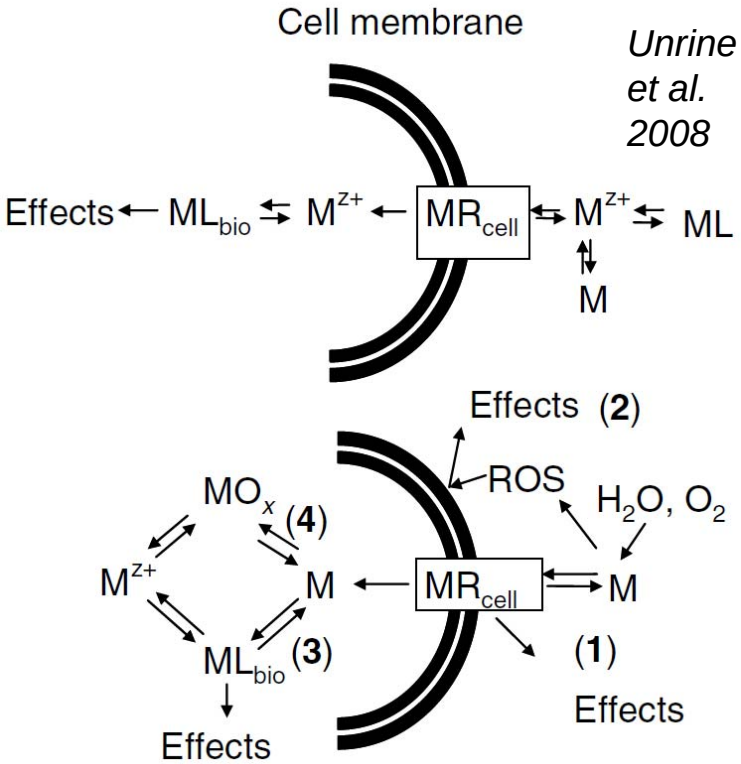


A secondary electron image of a typical chondritic Interplanetary Dust Particle (IDP) collected from the Earth's stratosphere.

- MBA upgrade will provide the intense, nanometer beams needed to make **XRF** measurements of sub-micron components in extraterrestrial materials feasible.
- APS MBA will allow better sensitivity (more detected elements) and possibility of **XANES** determinations of valence states at these resolutions.

Long term environmental impacts of engineered nanomaterials (ENMs)

- Little work on potential ecological effects and risks of ENM's in terrestrial environments. What data exists is often contradictory.
- Deposition of CeO_2 from diesel exhaust (a few ppm) reportedly disrupts N fixation by legumes. Conclusions based on model systems where exposure doses **4-5 orders of magnitude higher than found in nature**.
- Current models for metal bioavailability in the environment assume a biotic ligand model (BLM); relates toxicity to speciation and competition between environmental / biotic ligands.
- Nanoparticulate metals may violate BLM.

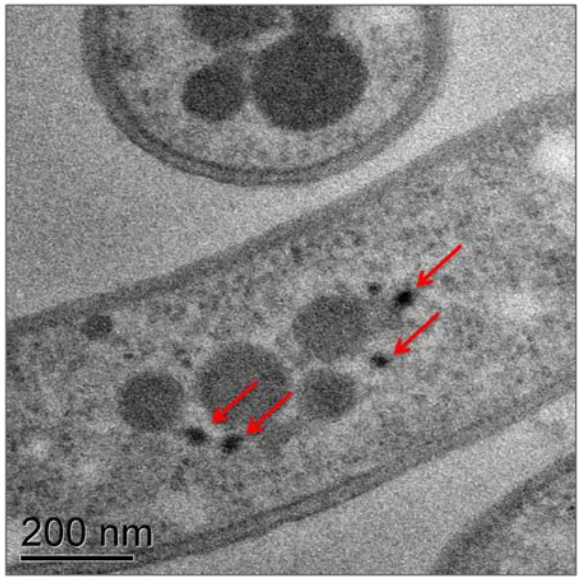


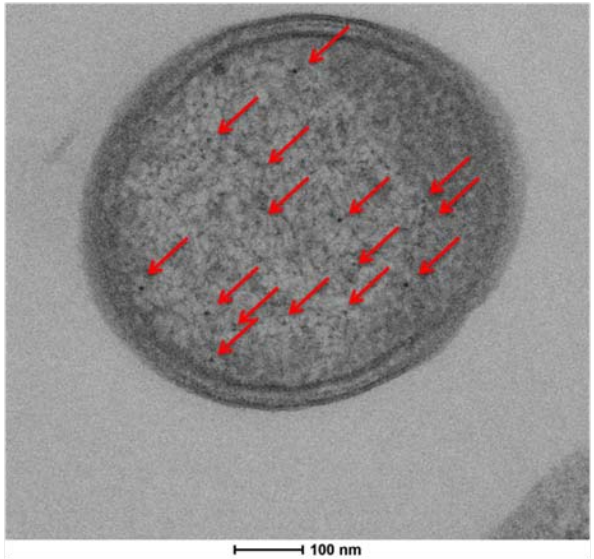
Unrine et al. 2008

ENM's may (1) bind directly to cell surface receptors, (2) generate reactive oxygen species intracellularly or intercellularly, (3) bind directly to sensitive biotic ligands, (4) uptake of intact metal particles into cells with subsequent intercellular oxidation and release of free metal ions.

Long term environmental impacts of engineered nanomaterials (ENMs)

- APS MBA upgrade will allow nanoscale imaging over a large, mesoscale area with ppm sensitivity.
- Determination of metal speciation of ENMs in soils, sediments, biological organisms, and plants.
- High spatial resolution X-ray based ptychographic and XRF imaging of ENM's conjugated to nutrients will provide fundamental understanding of the relationship between inter/intra cellular exchange between nutrients and nanoparticles within biofilms, roots, soil and colonizing symbiotic microbes.
- Ability to conduct all these experiments tomographically 3-dimensionally.





Quantum dots within soil bacteria. Kemner (ANL)

Full Chemical State Information in a Single Shot

Challenge:

- Determining chemical states at 30 to 100 nm scale is difficult.
- Energy scanning for XANES is time-consuming, requires high spatial stability as energy changes, and a large resultant radiation dose.

For spatial resolution below 20 nm on dilute sample, conventional XANES may be impossible.

Opportunity for Next-Generation Emission Spectroscopy:

- High energy resolution XRF (~1 eV at 6 keV) allows chemical/spin state determination without scanning incident energy.
- Could get chemical state information for **~all** elements in illuminated spot simultaneously
- Currently, need <u>crystal analyzers with low efficiency</u>: measurements photon flux limited , slow, can only measure one element at a time.
- Recent developments at APS and NIST with superconducting XRF detectors promise ~1 eV resolution at 10^5 Hz.
- Coupled with a high flux nano-probe beam from an MBA APS, this will allow chemical state determination for **multiple elements** simultaneously, without moving anything, and much less susceptible for radiation damage.
- Allow currently impossible nano-scale mapping of chemical states.
- Scanning spectroscopies still vital and will need ID improvements!

Mn Kb spin state determination

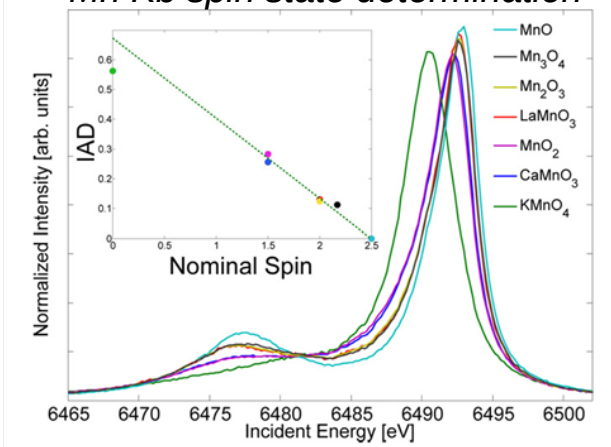
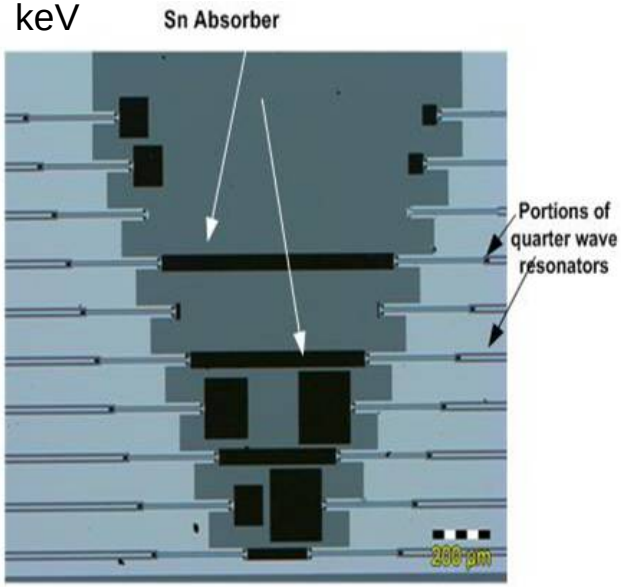


Fig. 6. Kβ main X-ray emission spectra normalized to the spectral area of manganese oxides, $K^{VII}MnO_4$ and perovskites $CaMn^{IV}O_3$ and $LaMn^{III}O_3$; (inset) IAD values with MnO as reference as a function of formal spin state with linear fit that considered MnO, MnO_2 and perovskites. The statistical error is smaller than the symbols.

Superconducting XRF Detectors in development at APS and NIST should achieve 1 eV resolution at 6 keV



Conclusions

- The Earth, Environmental and Extreme Conditions Science (E^3) community directly benefits from the continued improvement in brilliance afforded by next-generation X-ray storage rings. APS-MBA will further expand the E^3 community (atmospheric, oceanographic, and marine science, surface and sub-surface colloidal chemistry).
- Perhaps more than any other scientific discipline, E^3 research is highly challenged by the extremely heterogeneous nature of materials studied.
- The unparalleled brightness and coherence afforded by the planned APS MBA upgrade will allow for dynamic, in-situ, and multimodal analysis of heterogenous Earth materials that is not currently possible.
- To make best use of the potential provided by APS-U, investment now is required in **new detectors**, **optics**, and **undulator designs**.