Impact of the Local Environment and Electron-Transfer Initiated Transformation of the Structure and Chemical Properties of Mineral and Contaminant Microparticles

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Team Meeting for Science Focus Area:

"Role of Microenvironments and Transition Zones in Subsurface Reactive Contaminant Transport"

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PNNL-SA-65077

This project developed from a ERSP project that was linked to a BES Geochemistry Project, "Reaction Specificity of Nanoparticles in Solution" aimed to establish fundamental understanding of the mechanisms that control overall reactivity, reaction pathways and fate of iron micro- and nanoparticles.

Some of the reactivity studies Lee Penn mentioned are from this project.

- *Among the things we have learned using synthetic "model" particles*
  - *Small changes in particle composition can significantly alter reactivity*
  - *Particle reactivity varies with time as the particles change*
- *Move from model systems to isolated components of Hanford sediments*
  - *Materials Separation and Characterization – many ways of doing it*
  - *Quick probe of reactivity differences*
  - *Mechanistic Study of reaction processes*

Objective and Scope

- Objective
  - Obtain fundamental information about reactivity and structural, chemical and compositional transformations of sediment-derived and biogenic metal oxide microparticles that are induced by electron transfer reactions and other interactions with their local environment.
- Scope
  - Isolate, identify and characterize Fe(II), Fe(II/III), Mn(III/IV) and Ti containing microparticles in Hanford sediments of different ages, facies types, etc. (a census)
  - Conduct mechanistic reactivity studies on isolated microparticles using probe molecules such as carbon tetrachloride and Tc(VIII) to probe electron transfer reactions and particle transformations. Surface precipitation and surface passivation will be examined (impacts of reactions and time dependence of reactivity).
  - Studies to understand dissolution, reactivity and structural transformations of other Hanford relevant biogenic/abiogenic contaminant particles containing Tc, U and Pu.

Hanford particle collection and characterization

Isolate, identify and characterize Fe(II), Fe(II/III), Mn(III/IV) and Ti containing microparticles in Hanford sediments of different ages, facies types, etc.

- *Assemble and summarize existing information about Hanford sediments.*

- ***Develop and the apply a separation approach to isolated the relevant mineral phases.***

- *Coordinate with other sediment collection activities and reactivity needs. (e.g Ward, Zachara, and Liu)*

- *Apply needed characterization methods (including microscopy, diffraction, and surface measurements).*

Project Components

•Measurements of particle reactivity and particle transformations

Conduct mechanistic reactivity studies on isolated microparticles using probe molecules (including carbon tetrachloride and Tc(VIII)) to probe electron transfer reactions and particle transformations. Surface precipitation and surface passivation will be examined.

• Compare the reactivity of "similar" and "dissimilar" isolated particles.

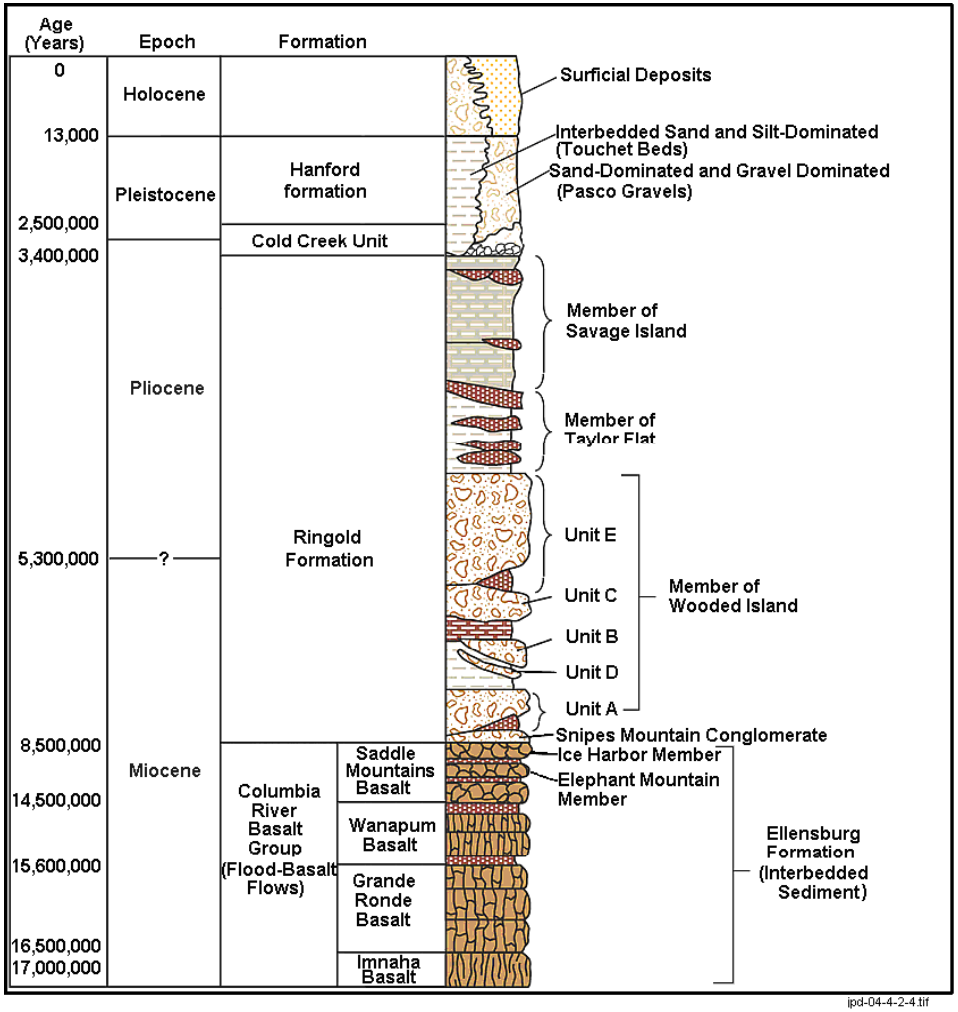
•Develop a quick screening test that can indicate in at least a semi-quantitative way oxidative and reductive capacity (Clock Reaction)

•Probe one electron and two electron process reaction processes

• Examine time dependence of reactions with probe molecules, impacts of adsorption, coatings and passivation on

Assembling existing information for Fe- and Mn-containing minerals

- Information being assembled and summarized
  - PNNL's Vadose Zone Characterization and Integrated Disposal Facility (IDF) projects
  - EMSP-, ERSP-, and Hanford S&T projects completed at PNNL and other sites in support of Hanford Site missions
  - Subsurface Science SFA project
  - Hanford IFC (Hanford's 300 Area Uranium Plume) project
  - Hanford 100 Area remediation studies



Generalized Stratigraphy of the Pasco Basin and Vicinity

Separation of Fe- and Mn-Containing Minerals from Hanford sediment Samples

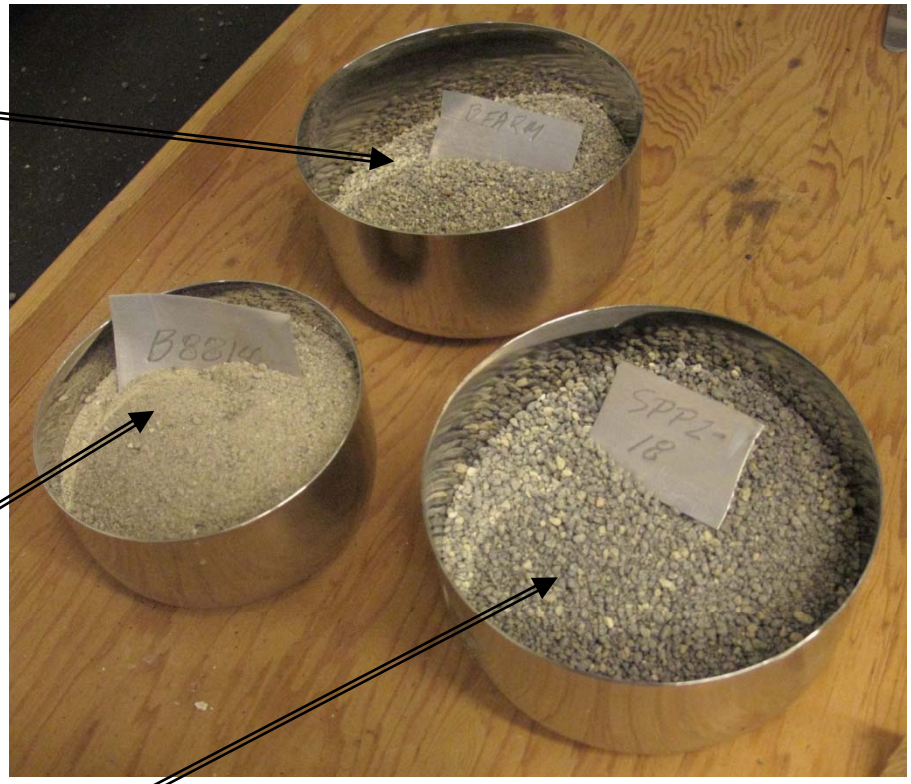
- Demonstration of separation processes and use of Frantz magnetic barrier separator by Andrew Grosz at mineral processing laboratory at USGS in Reston, Virginia
- Tested methods on three Hanford sediment samples
  - 300 A SPP2-18 < 2mm
  - B Tank Farm, lower composite (200E) < 2 mm
  - Hanford fine sand composite (B8814) (200W) < 2 mm
- A summary will follow as a basis for discussion of planned follow up
- Includes additional visit to USGS and possible equipment purchase

Three Hanford sediment samples

B Tank Farm, lower composite (200E) < 2 mm
Composite sediment sample from 10 samples from depths of 75 through 120 ft bgs (below ground surface) from Hanford RCRA borehole 299-E33-337

Hanford fine sand composite (200W) < 2 mm
B8814 corresponds to Hanford RCRA borehole 299-W22-50. Composite includes vadose zone sediment recovered from borehole bore samples

300 A SPP2-18 <2mm
From excavation of South Process Pond Pit #2 (SPP2)



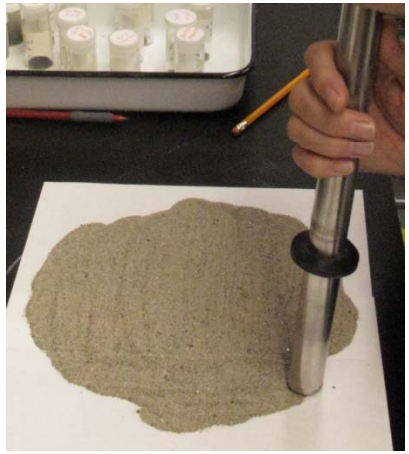
Material Separation Process at USGS

Split and weigh

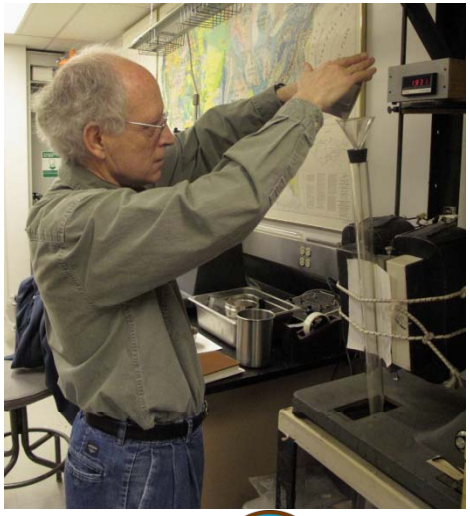
Wash

Dry and Weigh

Remove Mag Mat #1



Remove Mag Mat # 2



Separate material into four initial groups

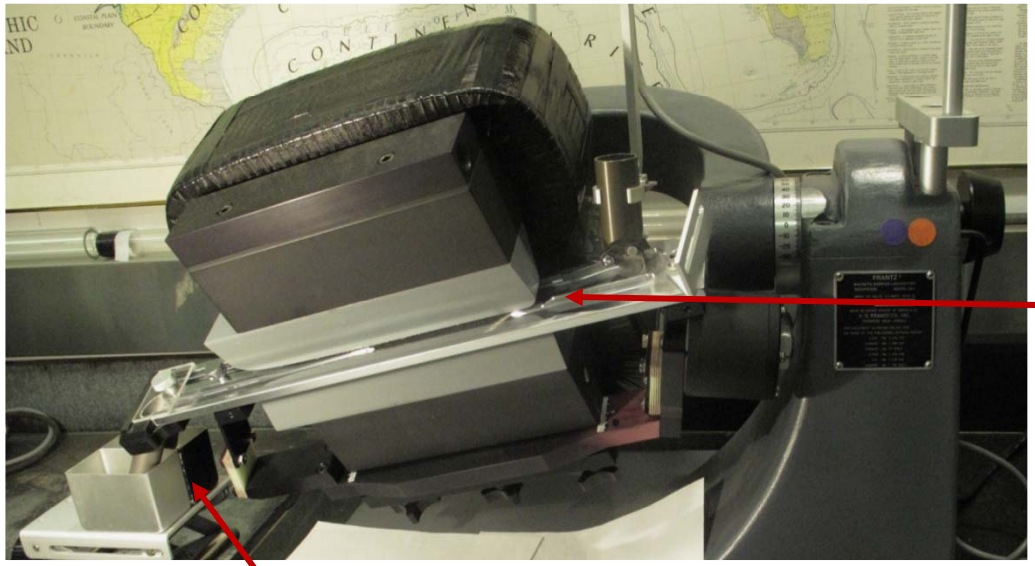
- Hand-held and drop magnetic (highly-magnetic)
- Drop magnetic, hand held non-magnetic
- Hand-held magnetic, drop-non-magnetic
- Non-magnetic

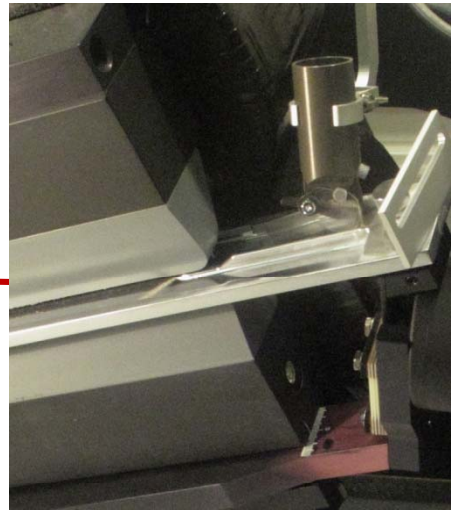
Processes Used for Test Analysis of Hanford Sands at USGS 19-Feb-09

1. Riffle split dry bulk samples
2. Weigh splits
3. Elutriate off clay/silt particle size fraction (i.e., fine size fraction) with DI water
4. Retain fine size fraction in separate containers
5. Apply ultrasonic treatment to greater than clay/silt size fraction (i.e., coarse size fraction) to help remove additional fines
6. Dry coarse and fine size fractions dried at 150 °C
7. Weigh coarse size fraction
8. Use hand held magnet to separate ferromagnetic fraction from coarse size fraction
9. Use free fall magnetic separation on coarse size fractions
10. Use LB-1 Frantz Magnetic Barrier Laboratory Separator on **non-magnetic** portions of coarse size fraction
    - Complete separation using different currents
    - Each set of magnetic separation conditions produces three samples - magnetic susceptible, nonmagnetic and effectively ferromagnetic (stuck to pole piece)
11. Store, or weigh and store separated fractions

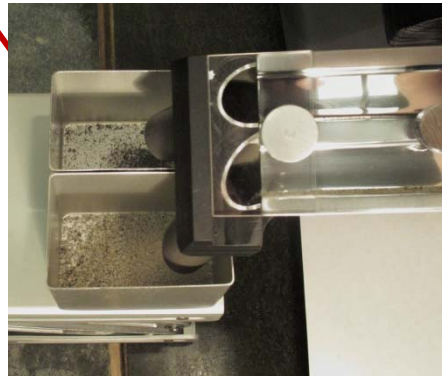
The Frantz® Magnetic Barrier Laboratory Separator Model LB-1

Diamagnetic Separation/Barrier Separation/ Paramagnetic Separation/



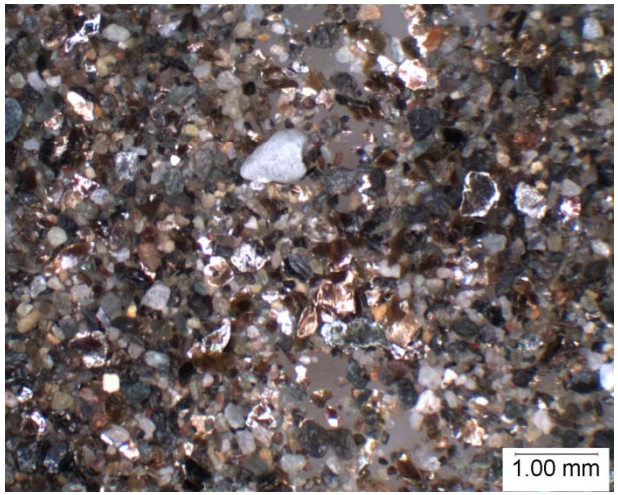


Stronger (top) and Weaker (bottom) Paramagnetic Fractions

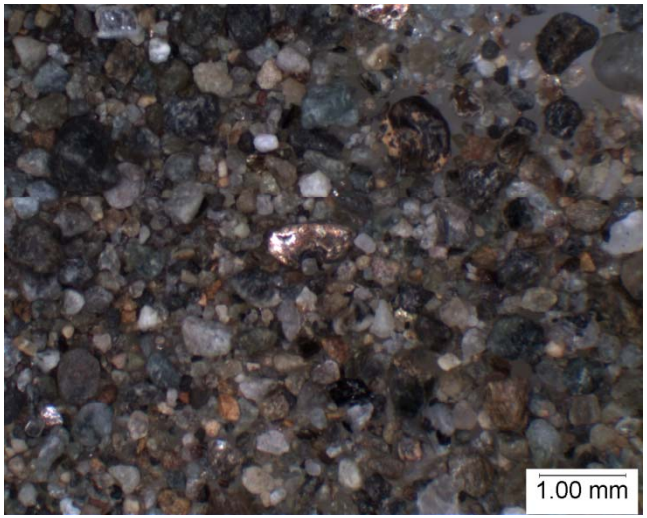


Non-Magnetic Fraction

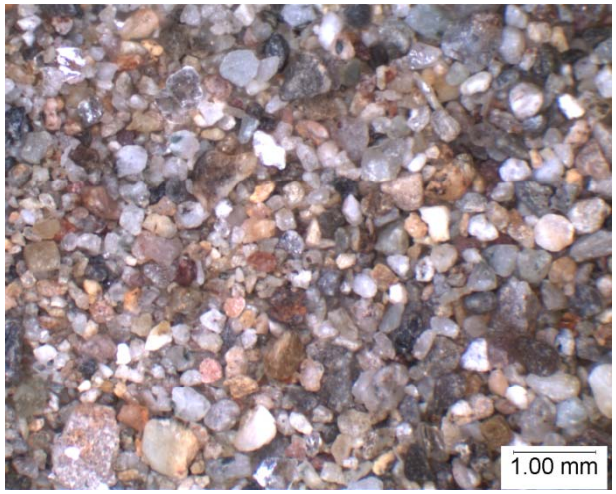
Paramagnetic Materials
Separated at different magnetic field strengths



Magnetic at 0.5A



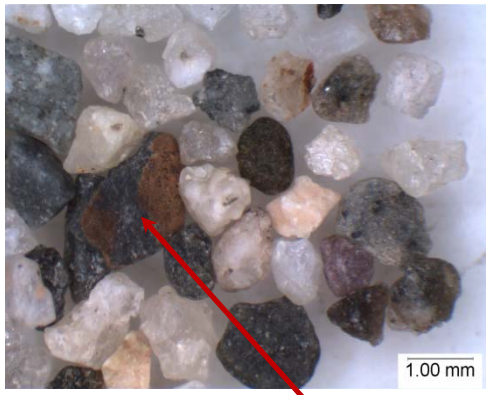
Magnetic at 0.8A



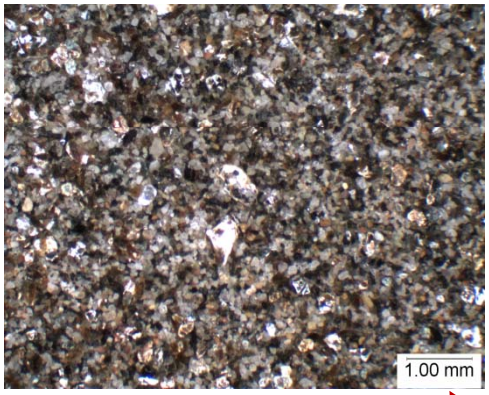
Magnetic at 1.3A

Separation Issues

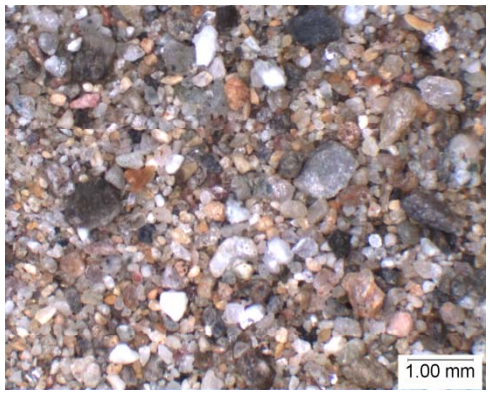
- Partial processing of three types of sediments produced approximately 30 separate samples
- Size and/or density separation will assist selectivity of magnetic separation
  - Panning for dense particles increased the ability to separate Fe phases and allowed quick identification
  - Use of aggressive ultrasonic treatment allowed removal of coatings of fine particles from some larger grains and improved separation of silt/clay fraction
- For reactivity studies want to minimize alterations of particles due to heating or solution interaction
  - What liquids are acceptable?
  - Is aggressive ultrasonic treatment acceptable?
- Need to optimize process to collect amounts of materials needed for some studies
  - Capabilities to be implemented at PNNL?
- Recommendations for consideration
  - Apply a form of gravity/density separation as initial step
  - Apply water sieving for particle size selection
  - Consider use of heavy liquids to selective separate dense Fe, Mn, and Ti mineral components



B8814
Non Magnetic, >710µm



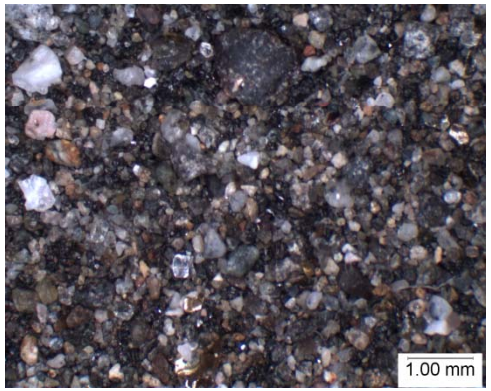
B8814
Ferro (hand)Magnetic



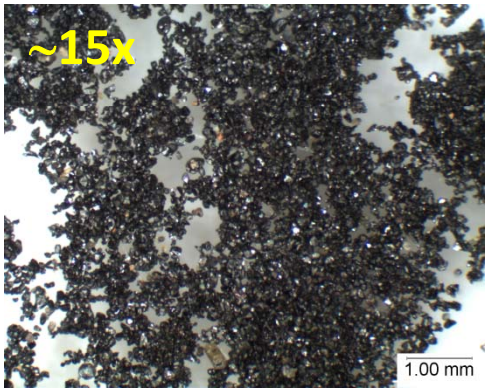
B8814
Magnetic at 1.3 A

Fe Oxide Coating

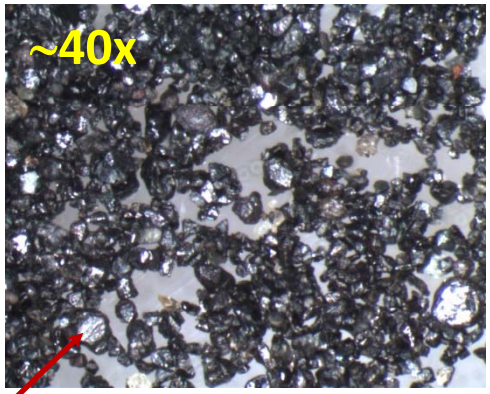
Micas (reflective in micrograph)



B8814
Magnetic, Magnetic



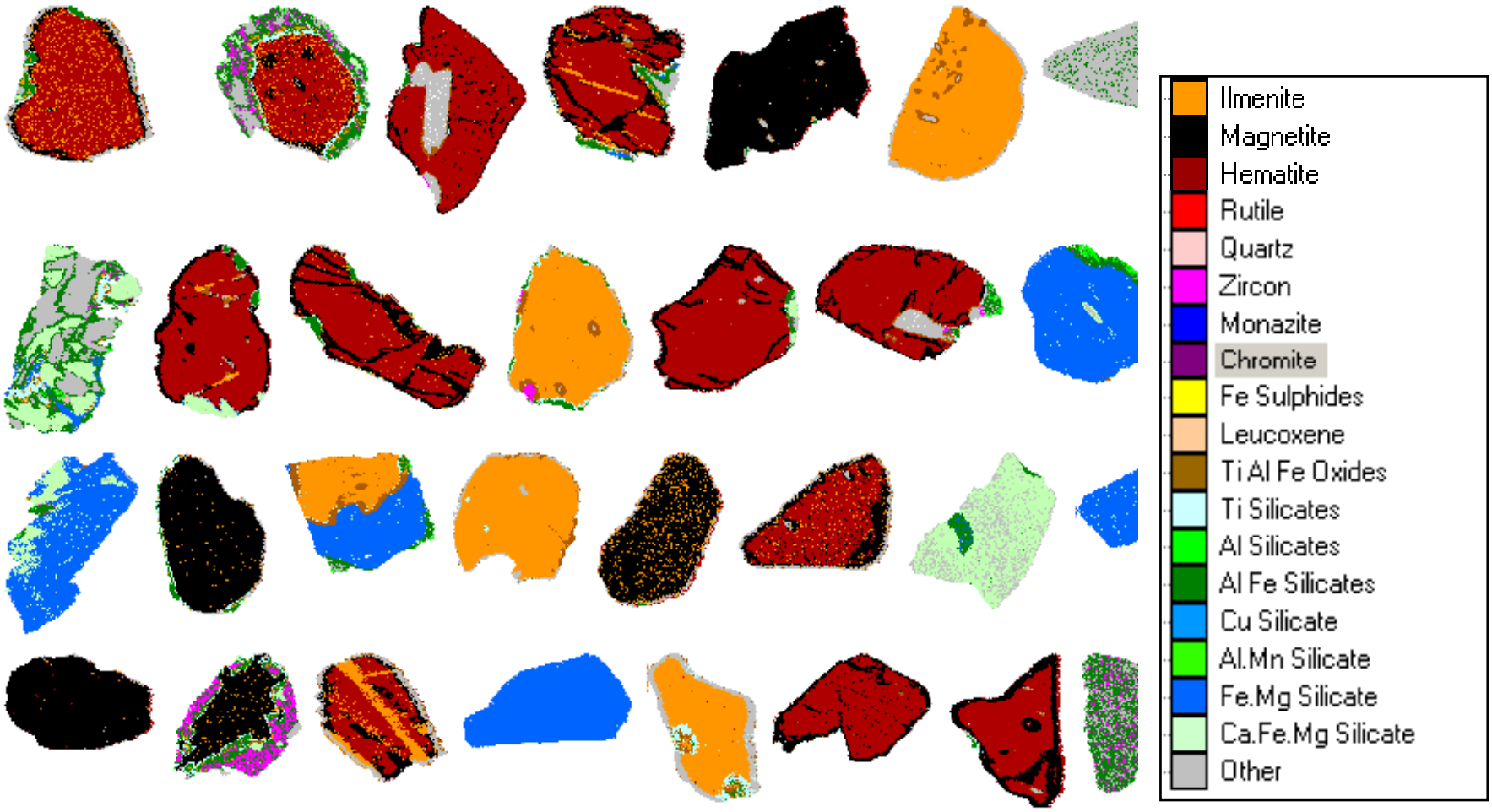
B8814
Panned, Magnetite Conc



B8814
Panned, Magnetite Conc

Magnetite

QEMSCAN



~100 μm Particles

Office of Science
U.S. DEPARTMENT OF ENERGY

Environmental Remediation Sciences

William R. Wiley EMSL

Pacific Northwest NATIONAL LABORATORY

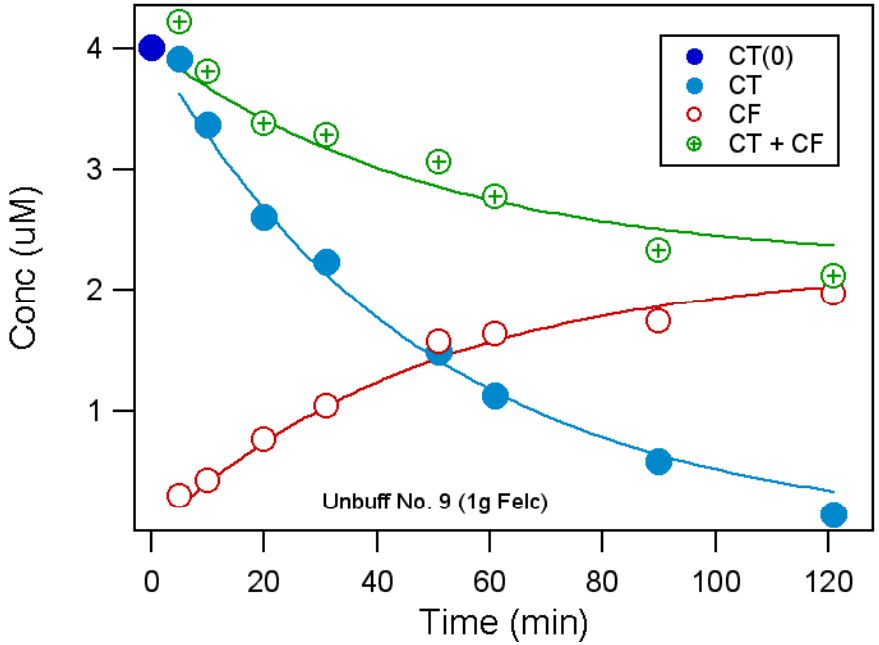
Clock Reaction as Screening Test for Reactivity Differences

Two types of color change reactions to be tested to determine if differences can be systematically observed:

Reduction of copper sulfate (an industrial QC test)

Use quinones and identify a suite of related molecules, with the goal of finding the redox pair that enables QUICK and VISUAL assessment of reactivity of both oxidation and reduction.

Reactivity Studies with CCl_4



Toxic Breakdown Products

CCl_4 (CT) $\xrightarrow{+1\ e^- \ -1\ Cl^-}$ $\bullet CCl_3$

$\bullet CCl_3$ $\xrightarrow{+\bullet H}$ $HCCl_3$ (CF)

$\bullet CCl_3$ $\xrightarrow{+1\ e^- \ -1\ Cl^-}$ $:CCl_2$ $\rightarrow$ HCOOH, CO, etc.

Benign Breakdown Products

Planned Activities

- FY2009
  - Assemble existing data catalog Fe, Ti and Mn containing microparticles from Hanford sediments
  - Develop separation process
  - Select round of sediments for separation
  - Characterize separated sediment samples
  - Screen characterized Fe phases for major reactivity differences
  - Select specific microparticles for detailed mechanistic study and examine
  - Start mechanistic reactivity and transformation kinetics studies for selected microparticles
  - Develop specific scope and plan for contaminant transformation studies

- FY2010
  - Expand and fill critical gaps in oxide phase census
  - Add additional size/phase to detailed mechanistic study
  - Conduct initial experiments for contaminant transformation studies

Research Team

- Don Baer – Project lead
  - Interface and surface chemistry, nanoparticle characterization, reactivity and stability
- Ken Krupka and Jeff Serne
  - Hanford data assembly and assistance with separation
- Jian Liu (Jenny) New Postdoc
  - Particle characterization, solution reactivity
- R. Lee Penn and Student
  - Microscopy, reactivity, clock reactions, transformations

This project is also linked to a BES Chemistry Project, "Reaction Specificity of Nanoparticles in Solution" which is seeking a fundamental understanding of the mechanisms that control overall reactivity, reaction specificity and fate of iron-based nanoparticles.

Expected Science Accomplishments

- Determine characteristics of natural metal oxide microparticles that influence particle reactivity
- Obtain kinetic information about how particle changes – including surface passivation and surface precipitation – alter reactivity
- Determine how organic and inorganic coatings alter the reactivity of contaminant particles.

Collaborations with other activities

- *Microparticulate characterization and reactivity studies will link with the BES Reaction Specificity of Nanoparticles in Solution Program (Baer), the electron transfer project (Rosso), Microscope Mass Transfer (Liu) and Reactive Transport (Zachara) Studies.*

- *U and Tc nanoparticle studies will be developed that will link with electron transfer (Rosso) and the pore/molecular scale research projects (Fredickson, Beliaev, Shi)*

- *Pu nanoparticulate studies will link with the Pu transformation project (Felmy)*