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Role of electron microscopy in the study of mercury contamination of soil

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- David Joy, and Larry Allard

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OAK RIDGE National Laboratory

U.S. DEPARTMENT OF ENERGY

Collaboration with MSU

- Carl Boehlert, Mechanical materials of structural materials
- Yue Qi, Microstructure of energy materials (battery and fuel cells)
- Chong-Yu Ruan, Dept. of Physics, Ultra-fast electron microscopy

Toronto, Canada

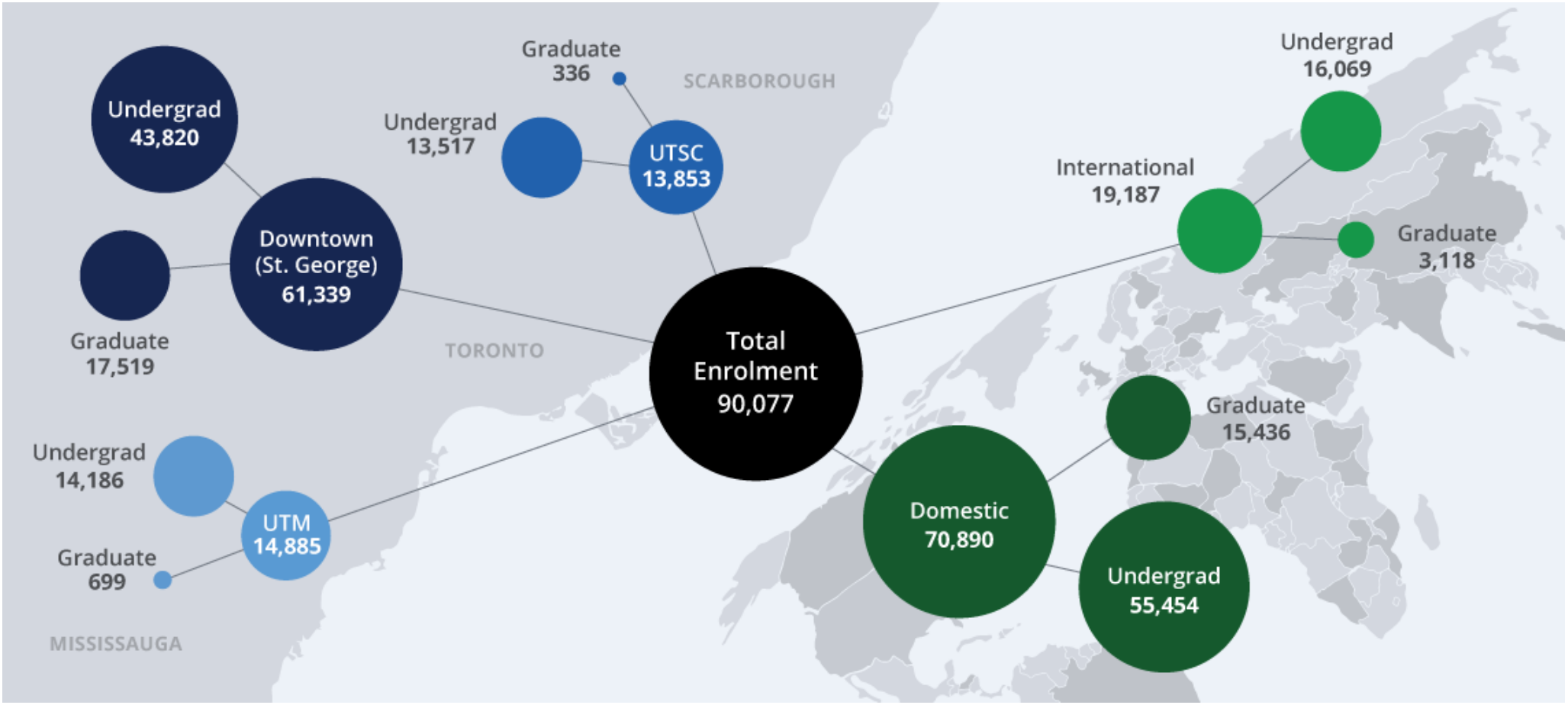
Canada's Leading University

University of Toronto

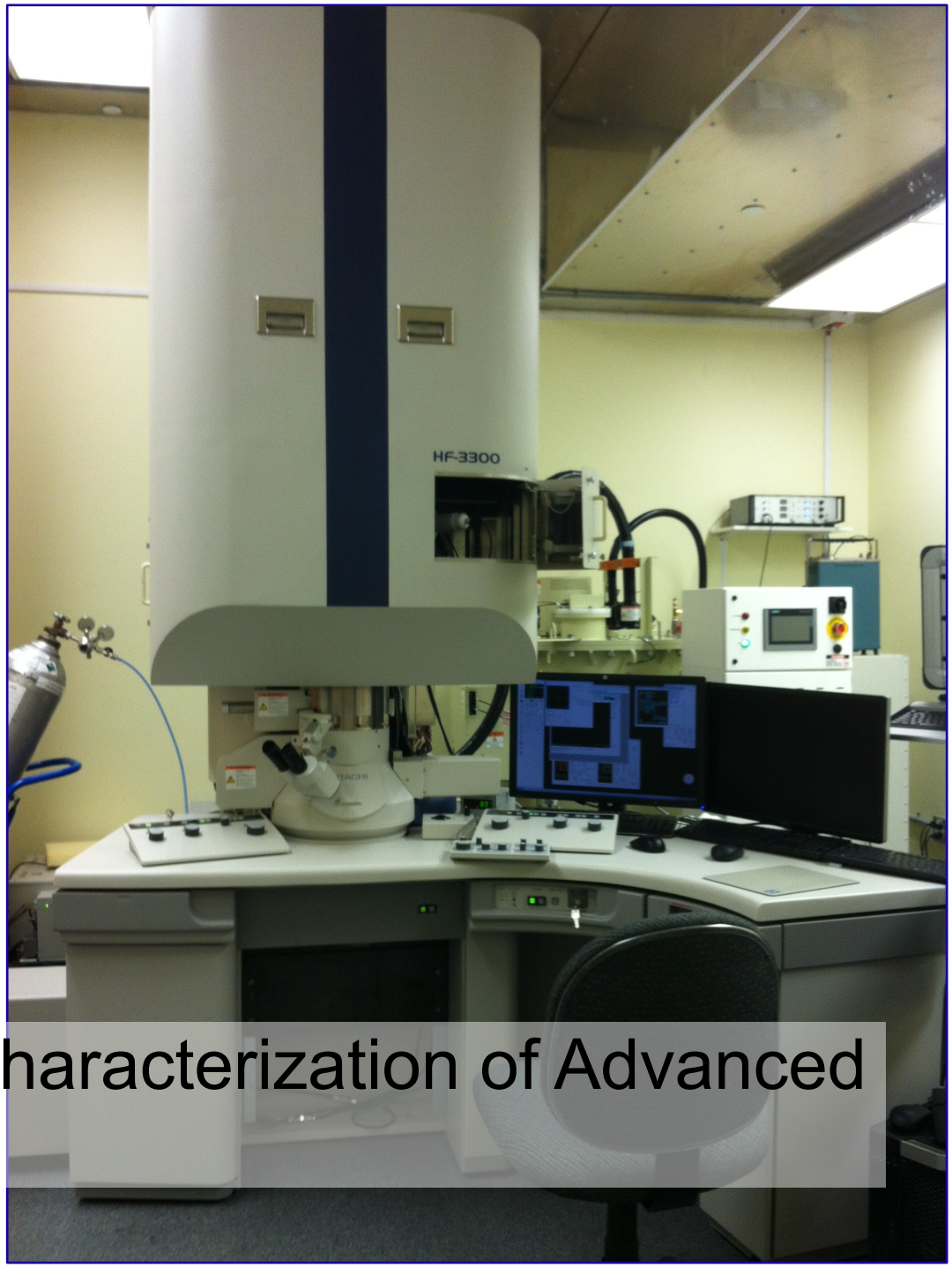
- Founded in 1827 King's College (Church of England)
- 1850 University of Toronto
- Canadian Confederation on July 1, 1867

UNIVERSITY OF TORONTO

Alumni 537,000



- Environmental TEM
- Dual FIB/SEM
- 4 SEMs
- sample preparation accessories



Ontario Center for the Characterization of Advanced Materials (OCCAM)

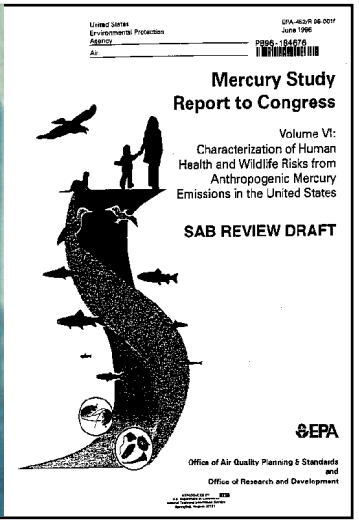
Application of scanning electron microscopy (SEM)

- Mercury contamination
- Environmental remission

The Mercury Problem

- Mercury – Global pollutant, highly toxic, readily transported/recycled.
- Methymercury – bioaccumulates and concentration magnifies in higher organisms. Poisoning is not reversible.
- World-wide Fish Consumption Advisories: 6 oz tuna/wk
- Industrial pollutant: mines, chlor-alkali plants, and power plant emissions, etc
  - Globally in all industrial countries, and airborne particulate Hg(II) crosses borders with jet streams.
  - US DOE sites:
    - Paducah, Kentucky
    - Savannah River, South Carolina
    - **Oak Ridge, Tennessee**

Minamata disease: neurological syndrome



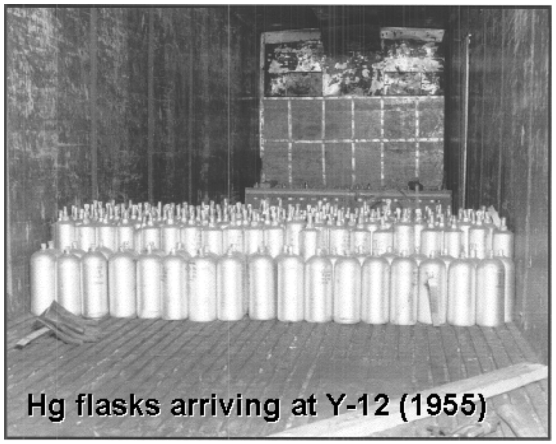
Mercury contamination spreads along waterways

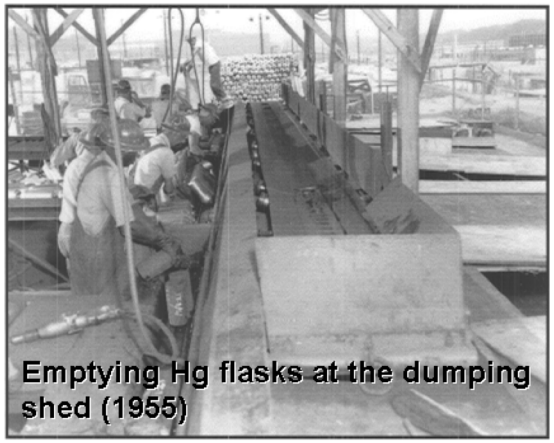
Hg in fish exceeds EPA's Ambient Water Quality Criteria in all six Oak Ridge environmental managed streams, shown in red (>0.3 µg/g)

First priority: dealing with Hg contamination on the Oak Ridge Reservation, Tennessee, USA

Mercury at Y-12 National Security Complex (Oak Ridge, Tennessee)

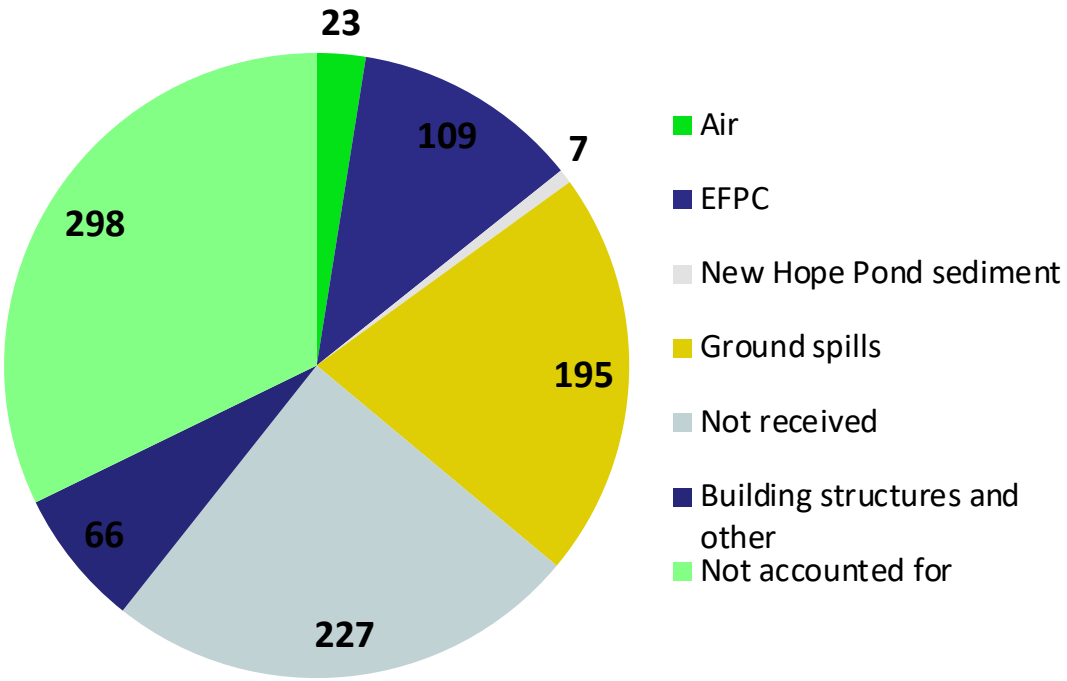
- From 1950-1963 Li isotope production at Y-12 utilized >10 million kg Hg


Hg flasks arriving at Y-12 (1955)


Emptying Hg flasks at the dumping shed (1955)


Mercury retort building (1983)

Mercury Loses at Y-12 (1000 kg)



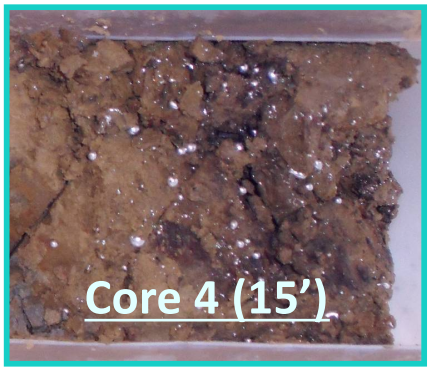
* data from the 1983 UCC-ND Task Force Study

- Hg present in soils/sediments
- High rainfall (>127 cm annual precipitation) transports mercury

- Facilities modernization exacerbates Hg export to streams

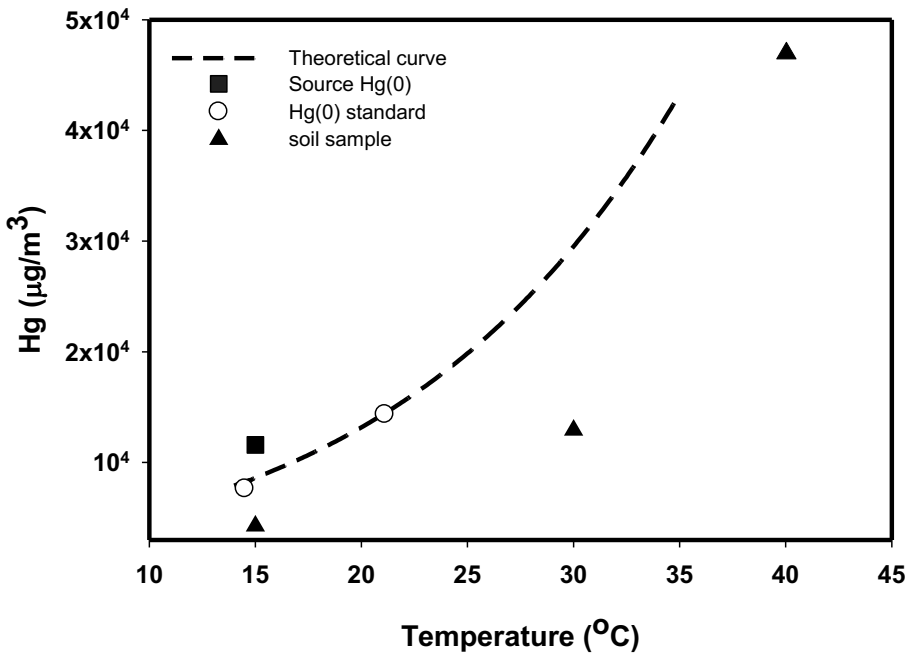
Depending on location, beads of Hg are widely distributed

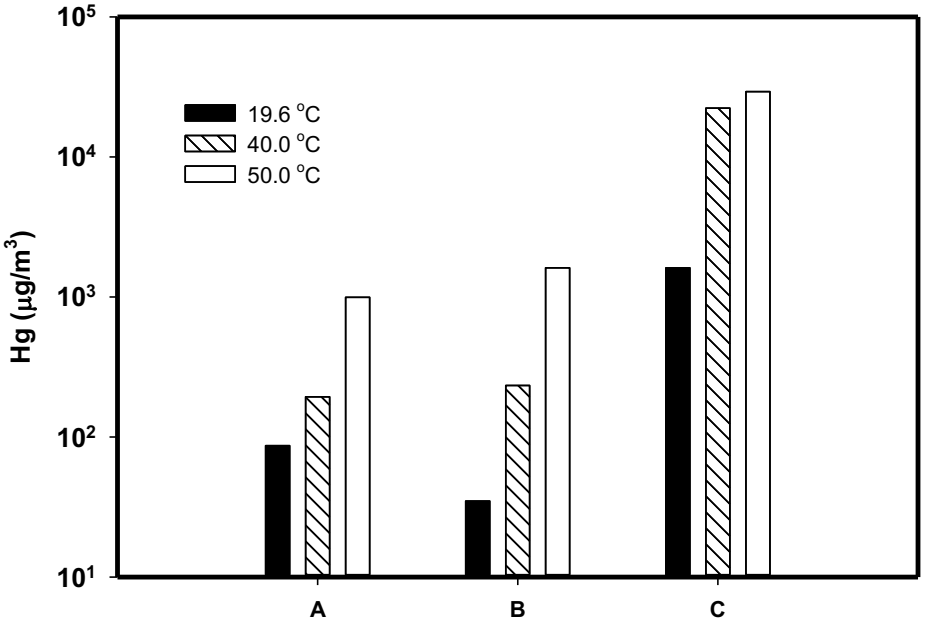
Pools of Hg detected @15' associated with gravels overlying clay



- Why do we need microscopy study?
  - The unearthed mercury beads have dull appearance and low vapor pressure
  - What is on the surface of the Hg beads?
    - Hydrocarbon (oil)?
    - HgO crystals?
    - Clay minerals?
- We use a scanning electron microscope at low voltage for this work at 200-500V
- The information is then used for the clean-up effort

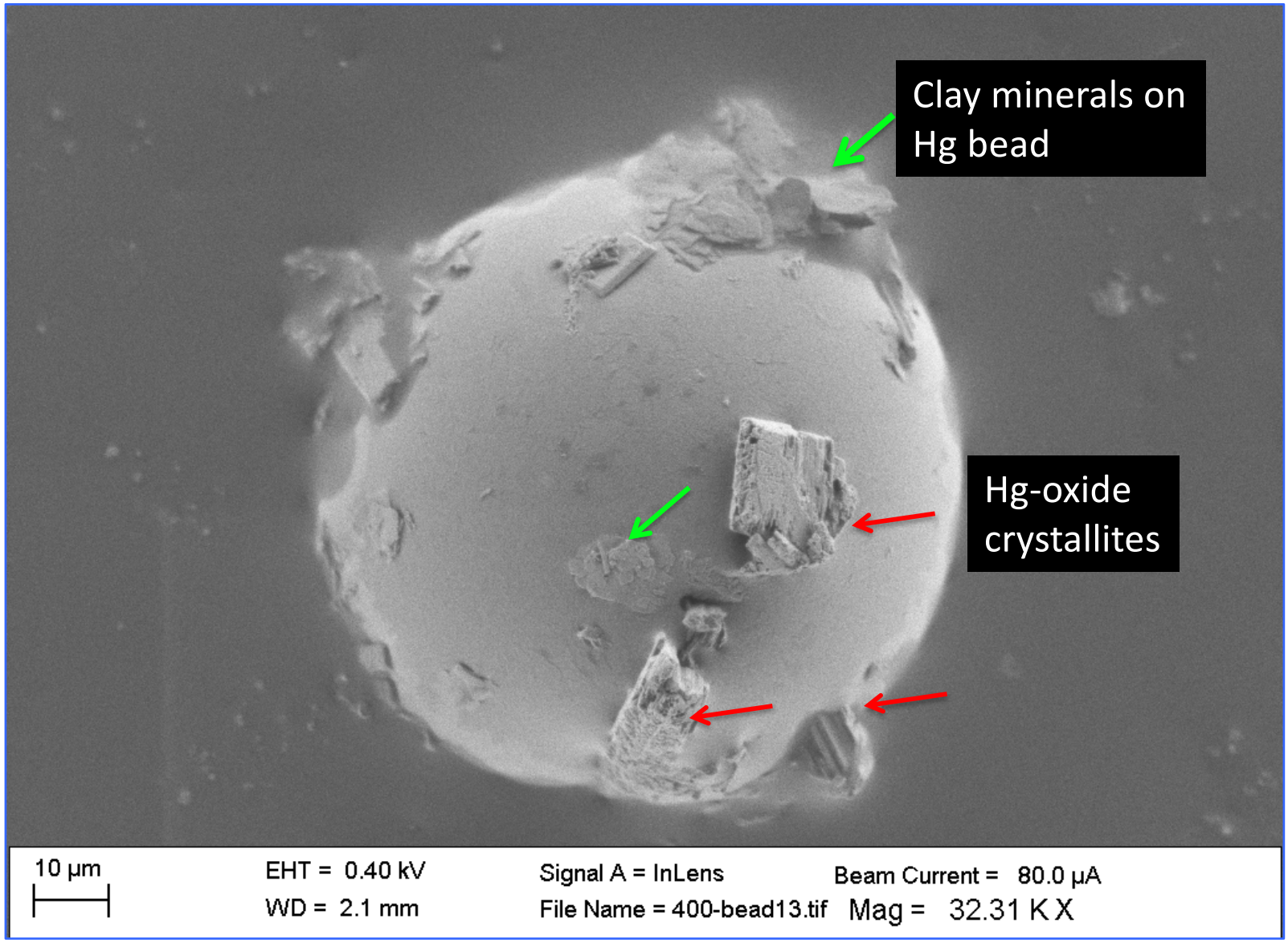
Sediment Hg does not have as high gas pressure as pure Hg(0): coating developed





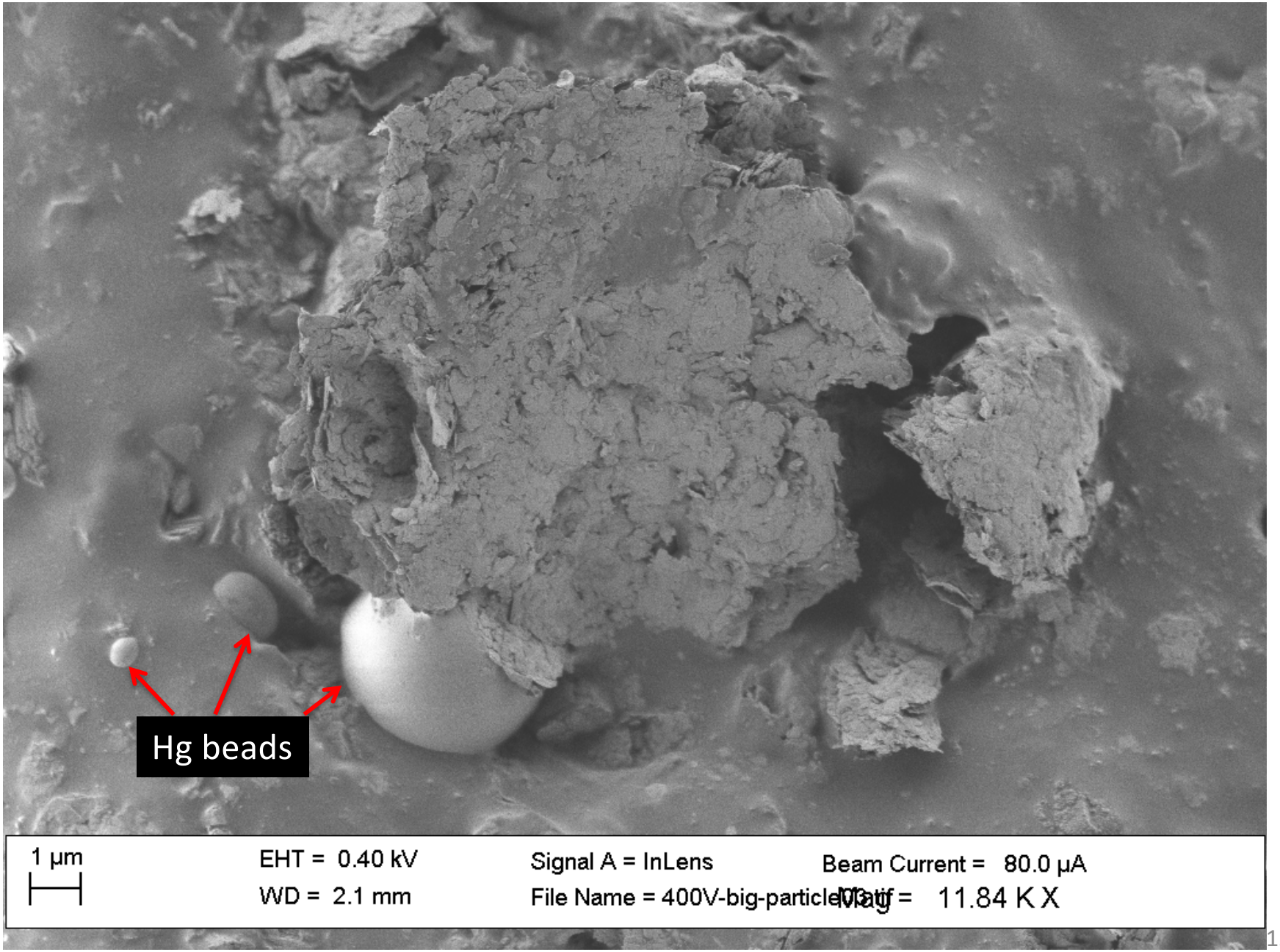
- Sediment Hg beads responded to temperature as measured by headspace Hg(0)
- Most samples show lower than predicted Hg(0) levels in headspace, but the concentrations increased with temperature
- Pulverizing sample increased headspace Hg; indicates presence of coating on Hg(0) beads
- 74 of 186 samples had detectable Hg(0)

Mercury beads in sediment: clay minerals and HgO crystallites:

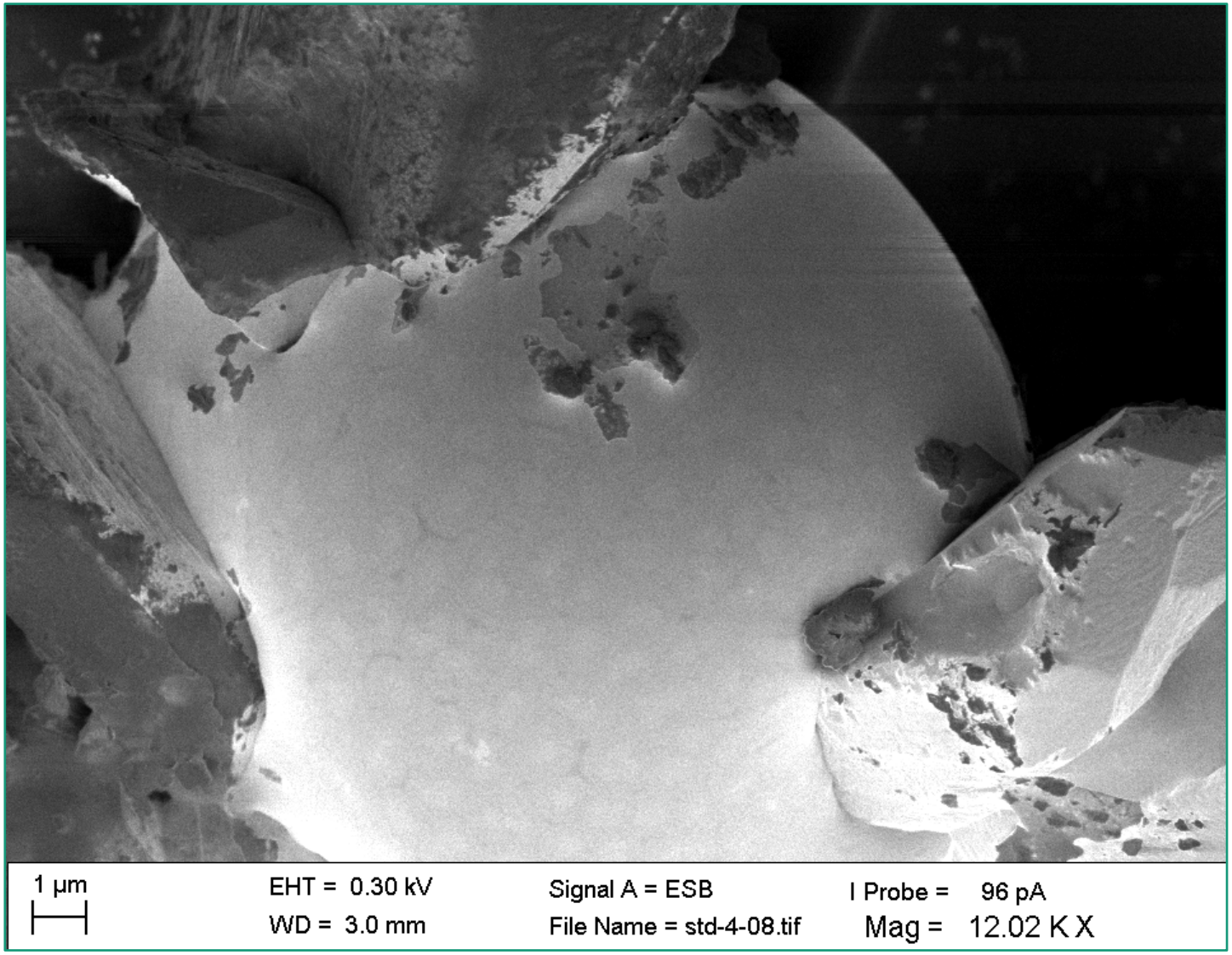


- Green arrows point to the clay minerals
- Red arrows point to the Hg oxide crystallite

Hg beads of submicron to mm sizes, imbedded in aluminum silicates



Sediment Hg does not have as high gas pressure as pure Hg(0): organic matter on the surface



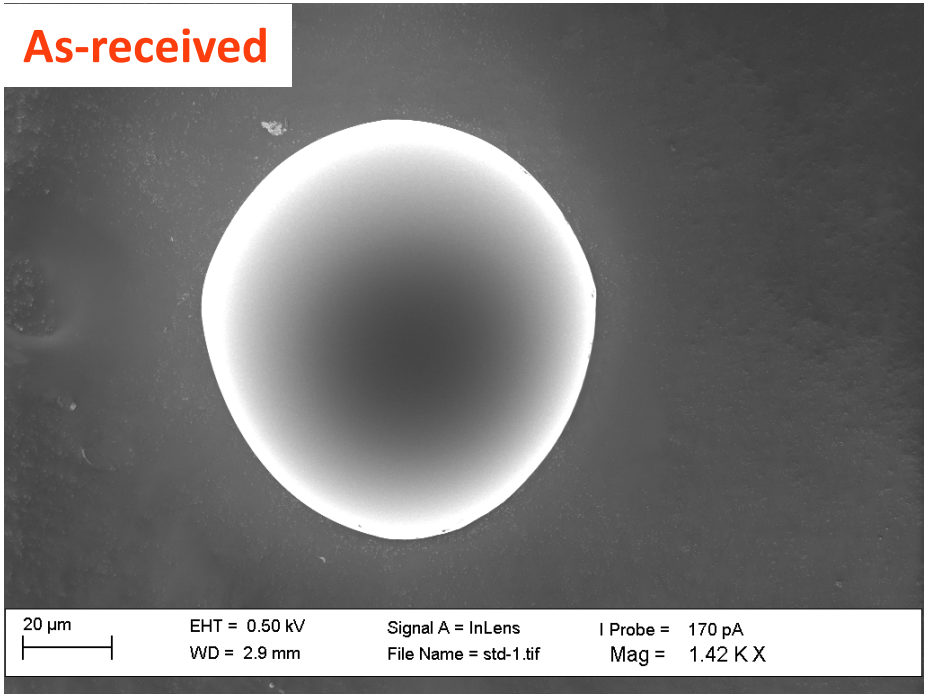
- Using an energy-selective backscattering detector, the contrast suggest the presence of a thin layer of organic matter.

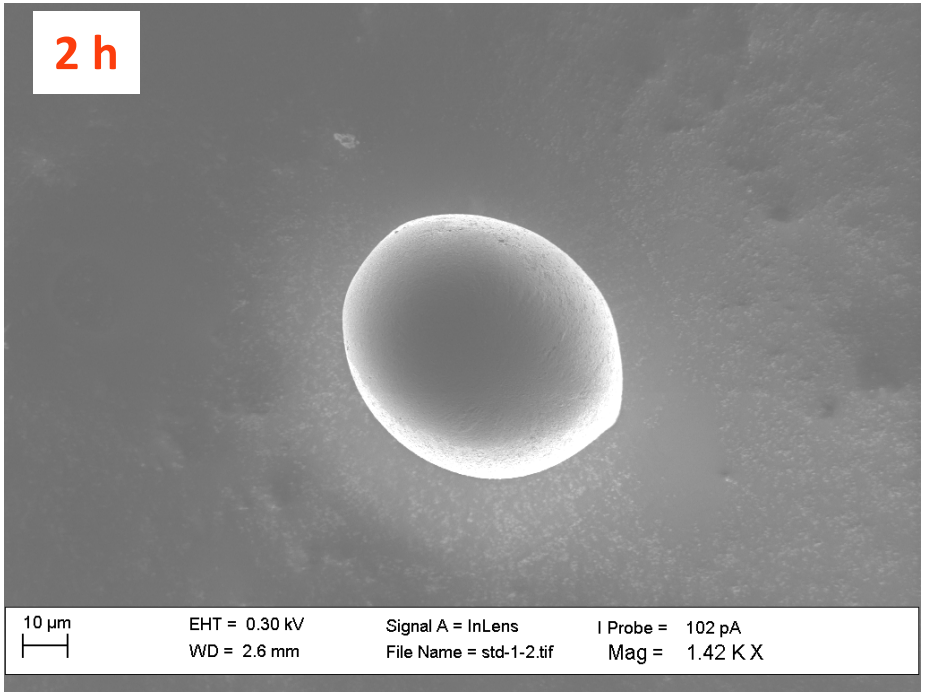
What is the fate of Hg(0) following 50 years in the subsurface?

- Based on coring, spectroscopy analyses, various extractable Hg fractions, and SEM characterization:
  - ✓ In unsaturated oxidizing areas, Hg(0) is contained in beads with HgO coatings, and with mineralogical associations (oxides, clays)
  - ✓ Hg binding with organic matter was observed
- Implications: coating facilitate Hg dissolution in water?

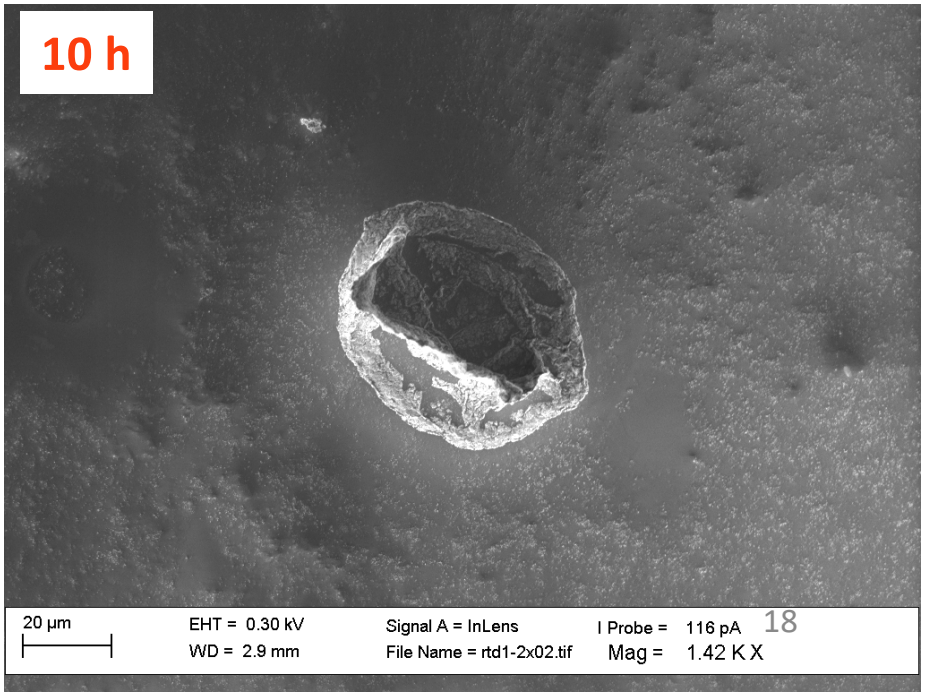
- Testing new mercury removal methods
- Stabilize mercury by forming HgS
  - ✓ filtering contaminated water with sulfur-containing resin beads
  - ✓ by Zn-doped bio-magnetite nanoparticles
  - ✓ by H_2S gas reacts with Hg beads (*Ex situ* SEM analysis)

Ex situ SEM: Mercury beads reacting with H_2S gas





- Reduced volume of Hg(0) and increased amount of nanocrystals containing Hg-S-O



Thank you!