Dynamic Reactivity of Mafic Materials Due to CO_2 Acidified Brines

NATIONAL ENERGY TECHNOLOGY LABORATORY

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08/07/2024

U.S. DEPARTMENT OF ENERGY

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WVU

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Pennsylvania Bureau of Geological Survey

- **John Neubaum**

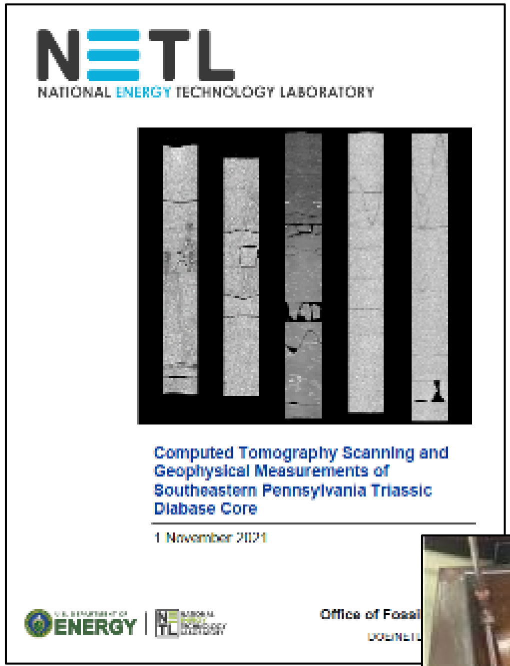
#Now with Rystad Energy (CCUS Data Analyst)

*Now with Carraig Nua Geoscience

Task Overview

Project Goal: Visualize and describe dynamic evaluation of rocks due to dissolution and mineralization of CO_2 through fractured seals and reservoirs

1. Core characterization report with West Virginia University and Pennsylvania Geological Survey.
2. Examine and describe the rapid mineralization of east coast mafic sills due to CO_2/brine exposure.
3. Examine the dynamic changes in flow properties of this material using NETL's new TESCAN DynaTOM system.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Computed Tomography Scanning and Geophysical Measurements of Southeastern Pennsylvania Triassic Diabase Core

1 November 2021

ENERGY | NETL

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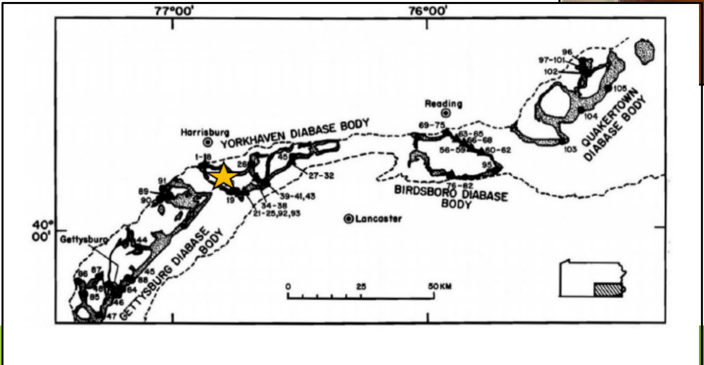
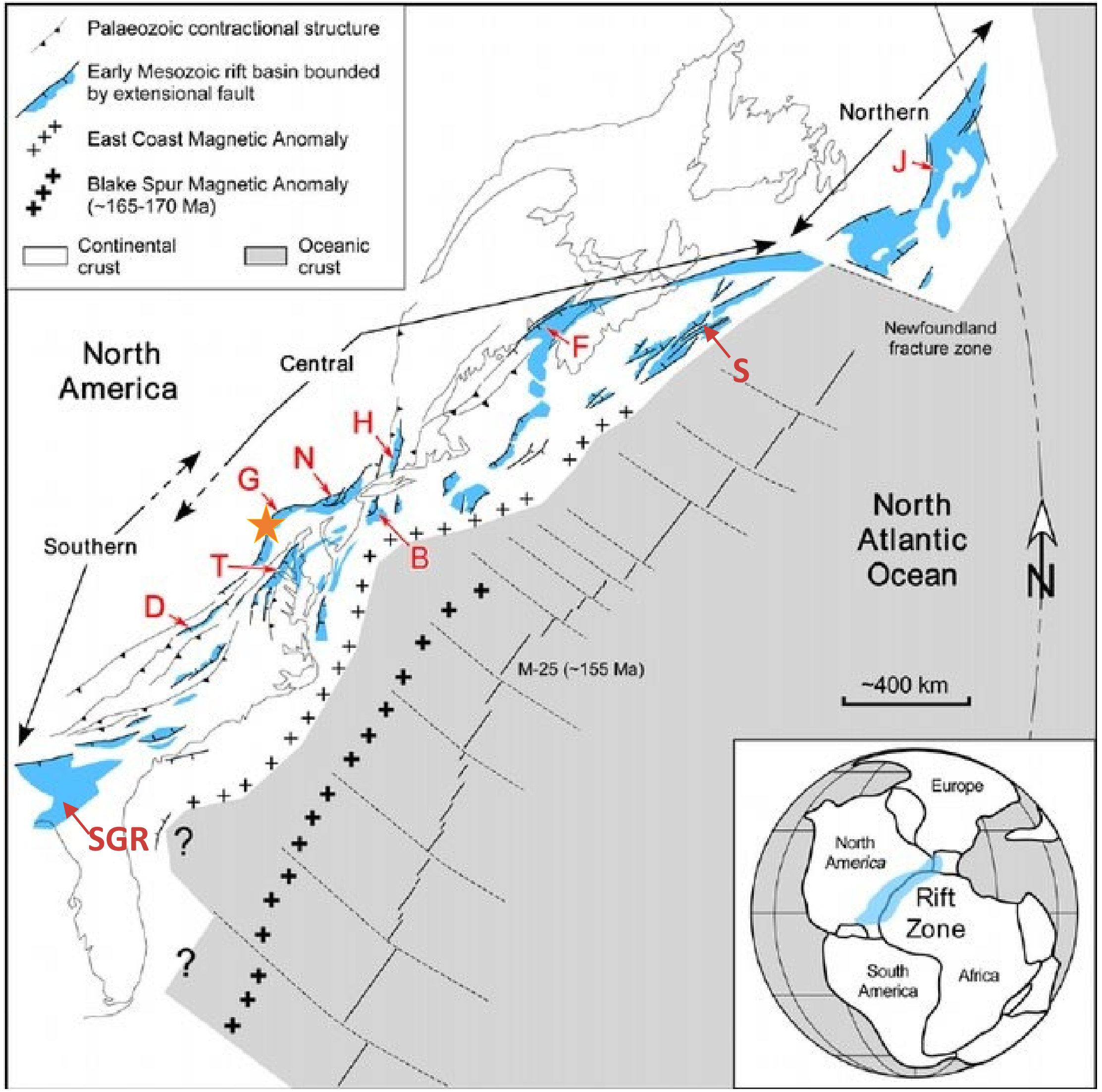


Figure 2: Diabase bodies map adapted from Beck (1972) to show the location of the cores in this study indicated with a gold star.

Potential for Utilization Along the East Coast



(Withjack et al., 2013)

- **Half-graben basins present from Georgia to Nova Scotia, and even offshore into Greenland.**

  In the US:
  - South Georgia Rift (SGR)
  - Dansville Basin (D)
  - Taylorsville Basin (T)
  - **Gettysburg Basin (G)**
  - Newark Basin (N)
  - Hartford Basin (H)

  Outside US or Offshore:
  - New York Bright Basin (B)
  - Fundy Basin (F)
  - Scotia Basin (S)
  - Jeanne d'Arc Basin (J)

East Coast Onshore Locations of Interest

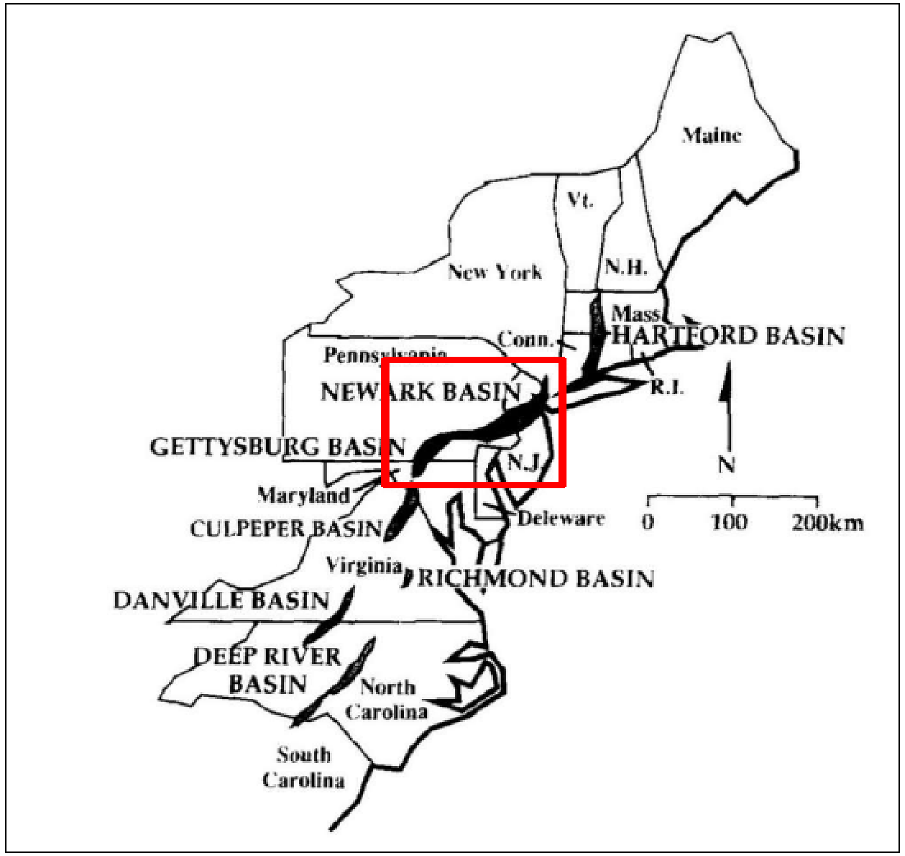
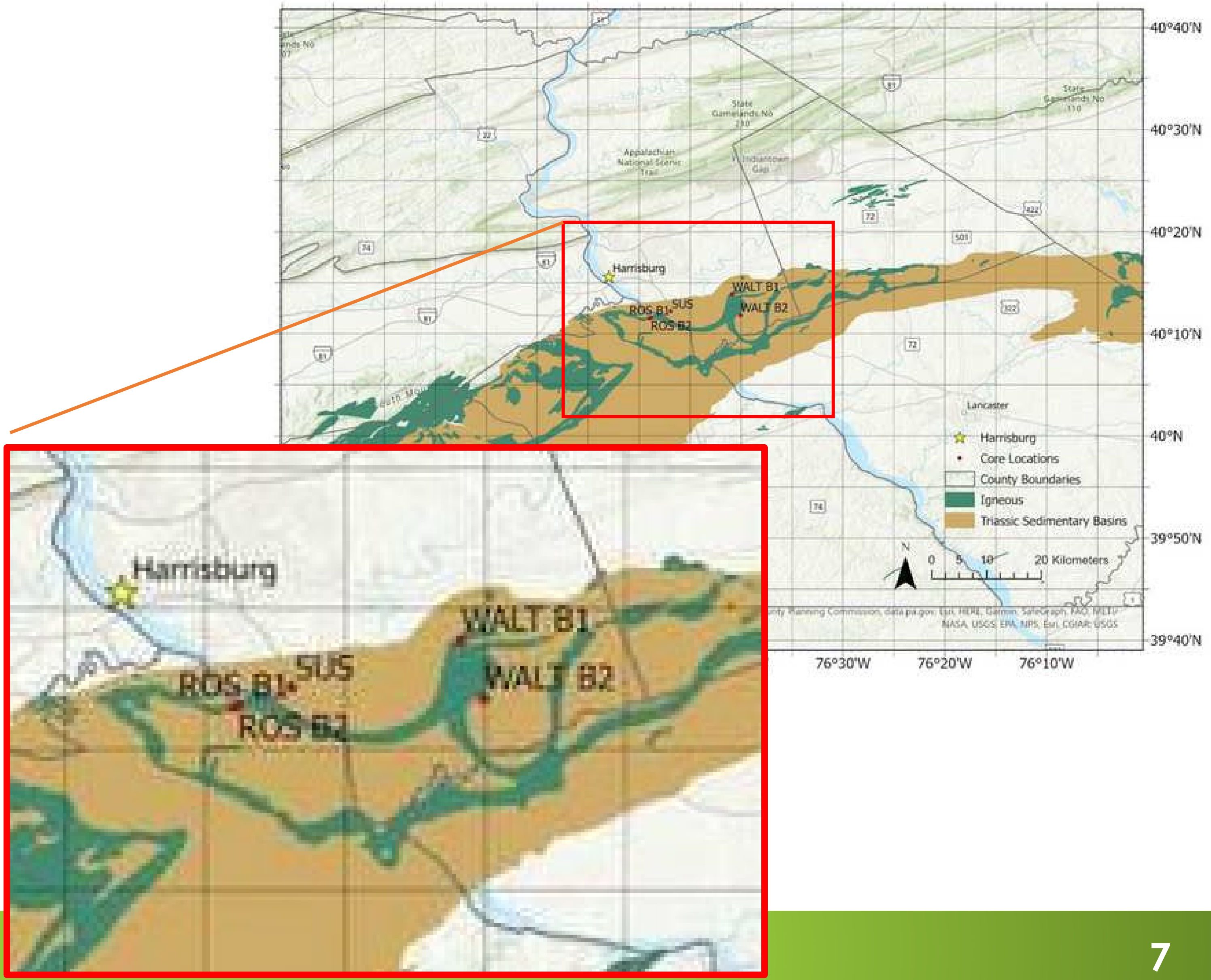


Figure 3: Triassic basins of the Mid-Atlantic region adapted from Woodruff et al., 1995. The Newark-Gettysburg basin, which is of particular interest, is outlined with a red box.

- **Focus on samples from the Gettysburg-Newark Basin for this current work**
- **Future studies looking at the Deep River Basin (Durham Basin) as well**
  - Geothermal test well being drilled at Duke University and examining through collaboration with Dr Laura Dalton

Sample Locations

- Near surface bore holes outside of Harrisburg PA were identified by the PA Geological Survey
  - Susquehanna River,
  - Rosser Road (1 and 2)
  - Waltonville Road (1 and 2)
- Bore holes from gas pipelines under the Susquehanna River
- Simplified geological map of south-central Pennsylvania and the middle Susquehanna River valley, showing the surface extent of Triassic sedimentary rocks of the Gettysburg sub-basin and intruding dolerite of the Yorkhaven (center) and Gettysburg (southwest) sill complexes.



Data from Core Characterization Report

Figure 75: 2D image from industrial CT scan of the Susquehanna River core at 129.2 ft. where the red arrow indicates a mineralized fracture.

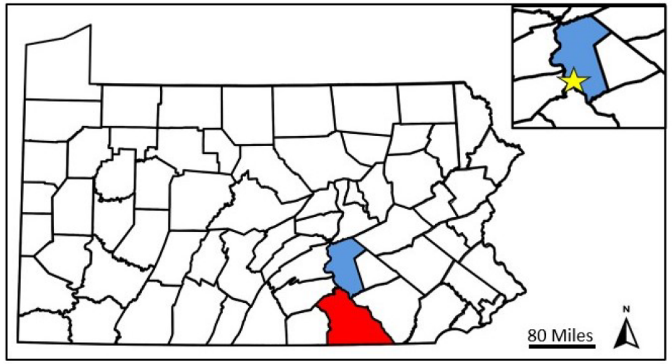
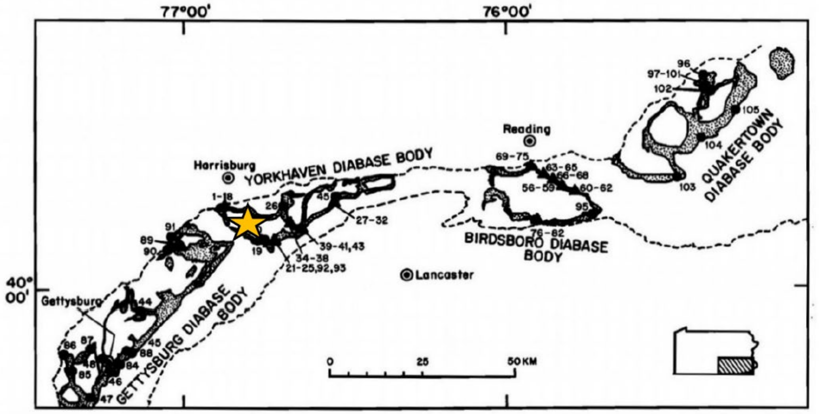


Figure 1: County map of Pennsylvania highlighting York County (blue) and Dauphin County (red). Diabase cores were obtained from the Pennsylvania Geological Survey, near Harrisburg, Pennsylvania (indicated with a yellow star).



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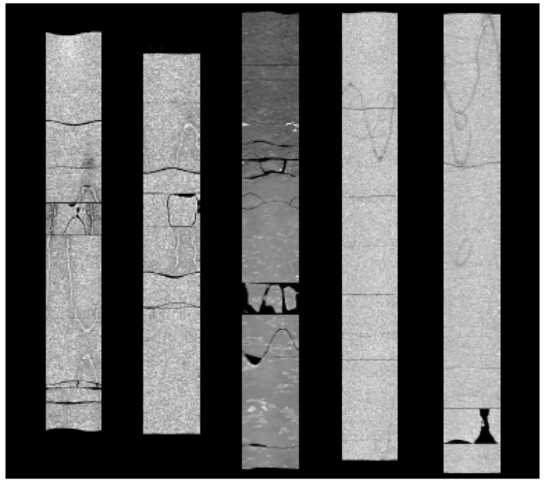

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Computed Tomography Scanning and Geophysical Measurements of Southeastern Pennsylvania Triassic Diabase Core

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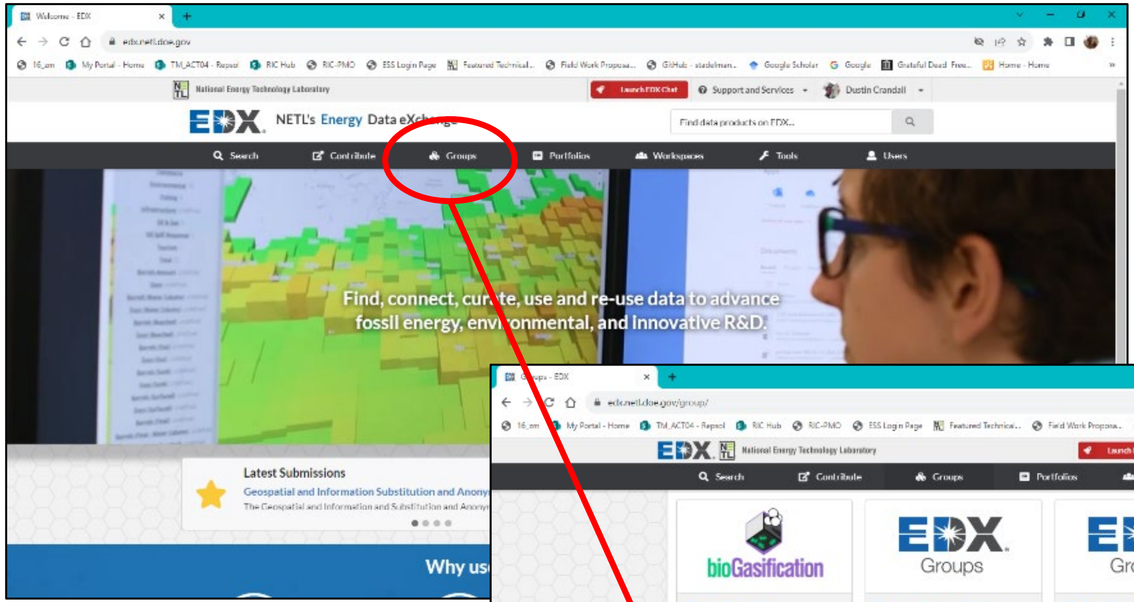
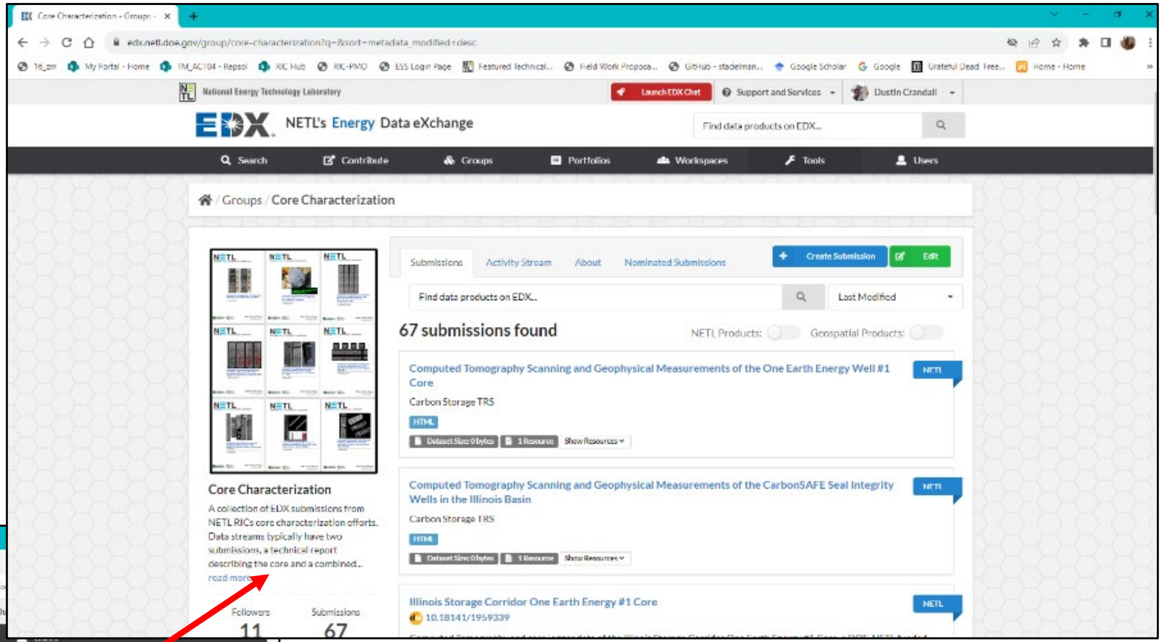
DOE/NETL-2021/2843

Data Publicly Available on EDX

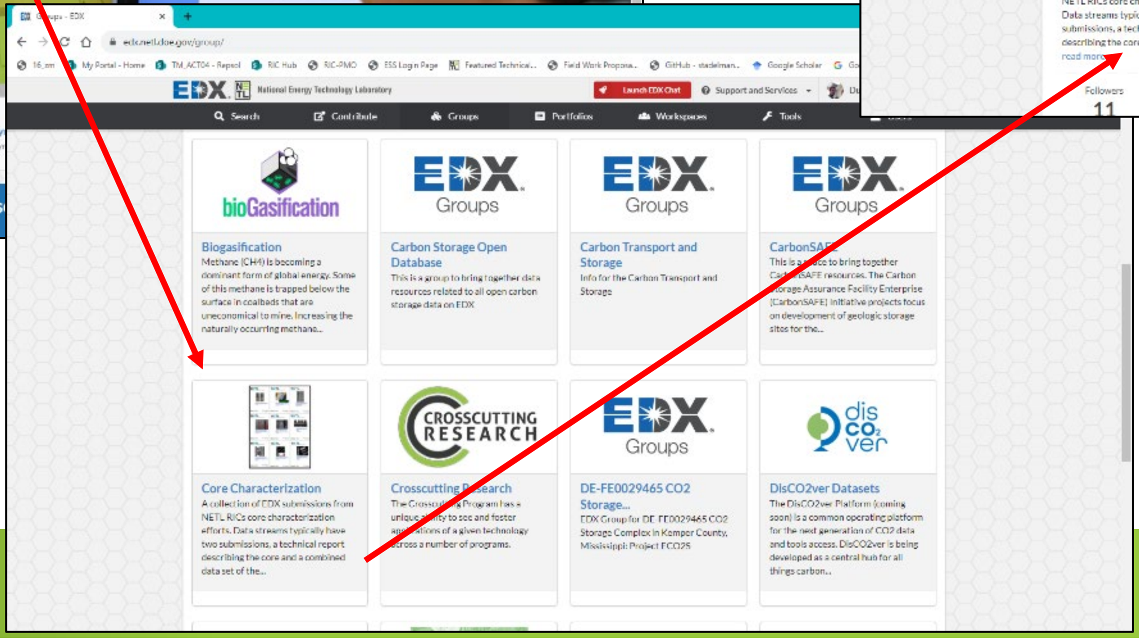
Not on RokBase yet…

- **Start in the "Groups" at https://edx.netl.doe.gov/**





Links to reports, the raw data, and any processed data are here



Scroll down to the "Core Characterization" group

Multi-Scale CT and Core Flow Facility

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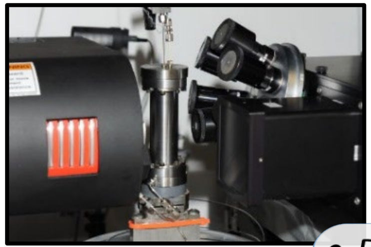
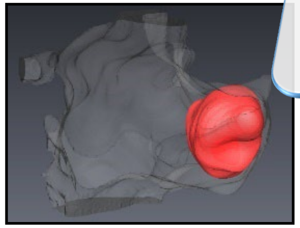
Unique Capabilities: Four computed tomography scanners with 3D resolution from microns to millimeters, all with ancillary core flow capabilities. Able to performed controlled multiphase flow in cores from 0.25" to 2" in diameter at conditions up to 10,000 psi and 200 ˚C. Full time technical staff to assist with rock preparation, experimentation design, setup, execution, and analysis. Plus, controlled flow systems for long term tests, and GeoTek multi-sensor core logger.

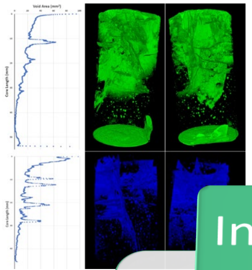
Opportunities: Direct examination of rocks from carbon storage sites under *in-situ* conditions with supercritical CO_2. Stressing of samples to understand mechanical behaviors. Examination of relationships between rock properties, geochemical alteration, and permeability (or structural properties). Scanning to complement other experiments, or to digitally and non-destructively preserve core from relevant locations.

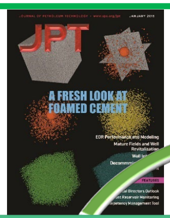




Micro-CT

- *Pore Scale*
- *Small Samples*
- *Dynamic Flooding*



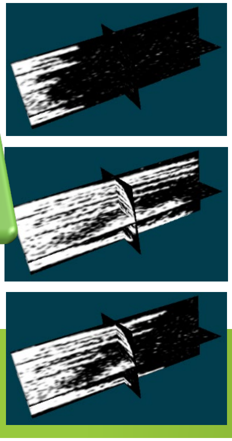


Industrial CT

- Pore & Core scale
- 1" Diameter plus Samples
- Highest Pressures

Medical CT

- Core Scale
- Large Samples
- Dynamic Flooding



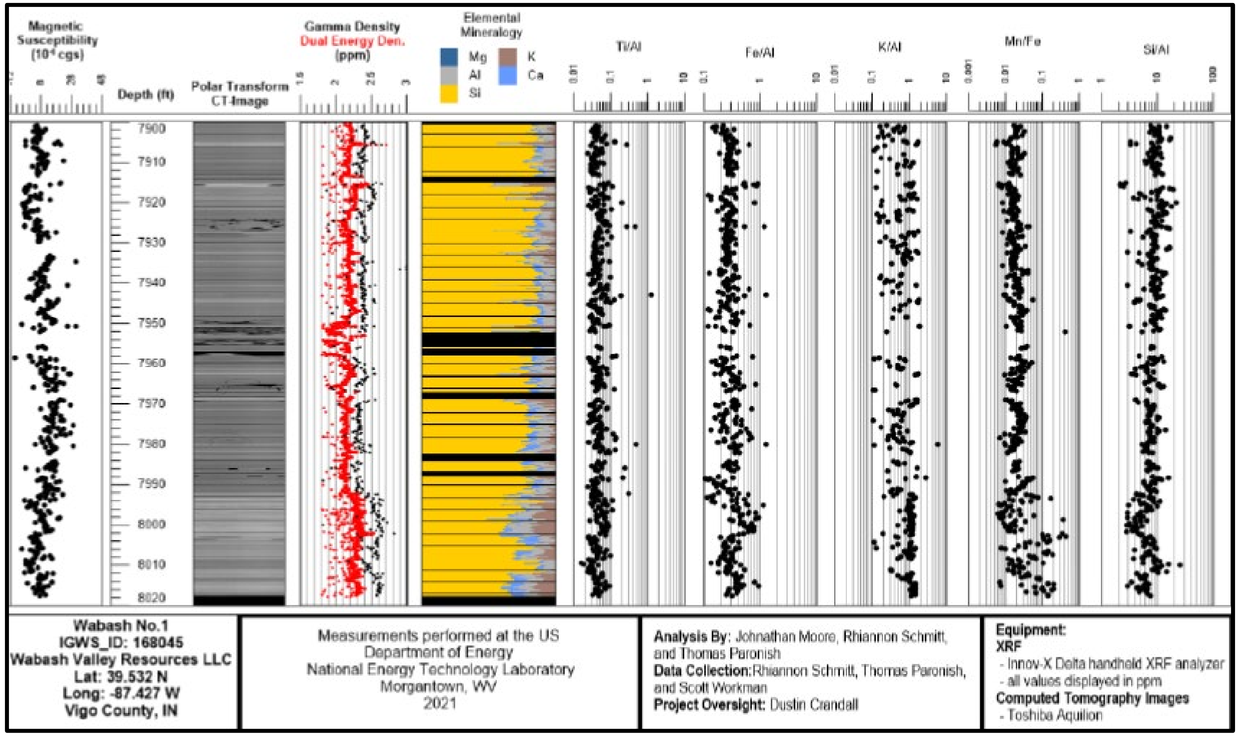
For More Information:

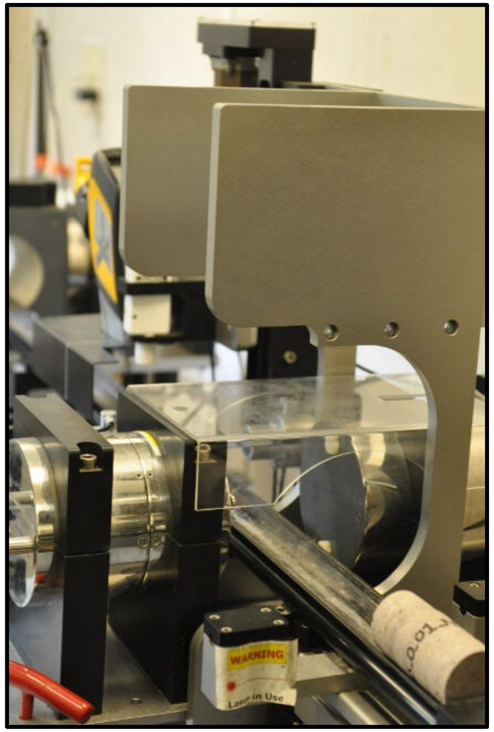
- Equipment/Lab Factsheet (link)
- Core characterization EDX Data Group (link)
- Core characterization YouTube Video (link)
- CO_2 Brine Relative Permeability Accessible Database (link)

GeoTek Core Logger

POC: Thomas.Paronish@netl.doe.gov

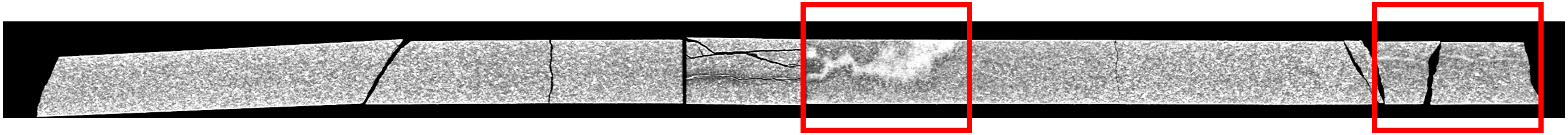
The GeoTek Multi-Sensor Core Logger at NETL obtains high-resolution p-wave velocity, gamma density, natural gamma, resistivity, magnetic susceptibility, and handheld X-ray fluorescence spectrophotometry on whole-round and split-core samples. Analyses including XRF have been performed on almost 2 miles of core and available on EDX (link) and www.rokbase.org.



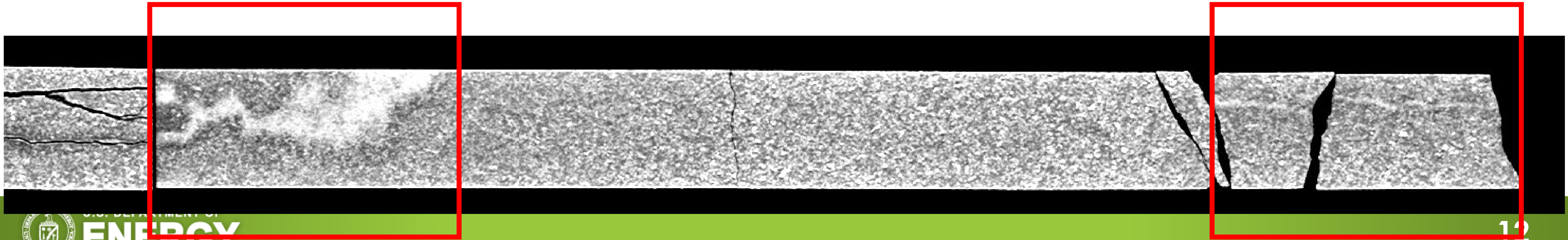


Fracture Identification with Computed Tomography

- Mostly homogenous core with a few mineralized fractures
- Focused on sampling for reaction work in bulk representative locations, as well as around fractures.



Roser Road Bore Hole 1 Core, 55 to 59 feet, with two fractures identified. Note core is 2-inch diameter



High Resolution CT Scans

- Further visualization with Industrial CT scanner
- Three-fold improvement in resolution (95 microns)

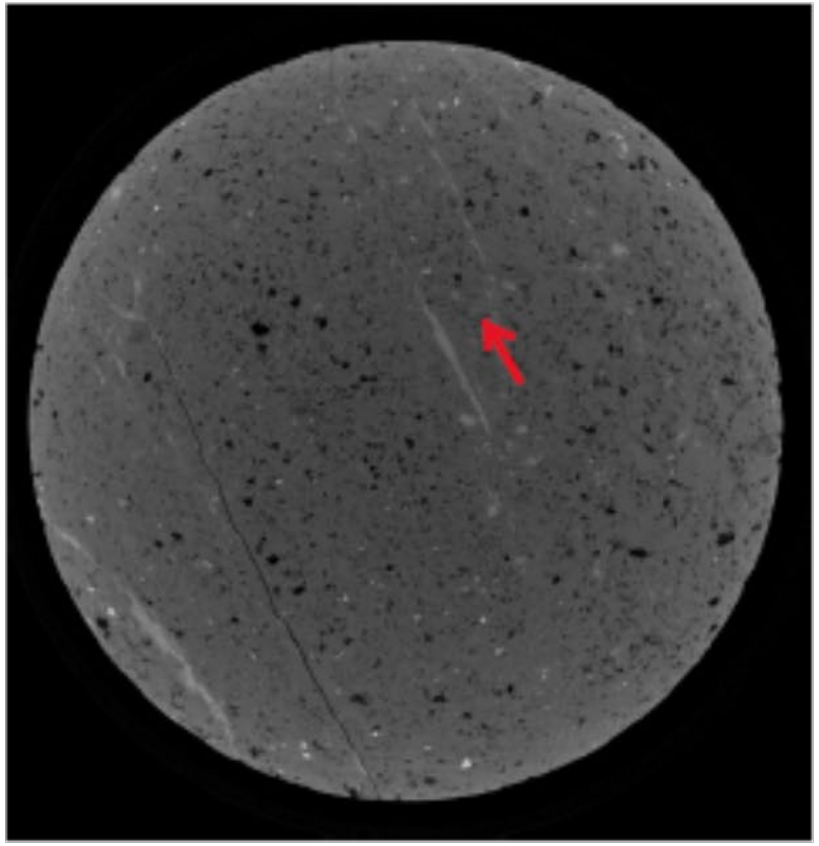
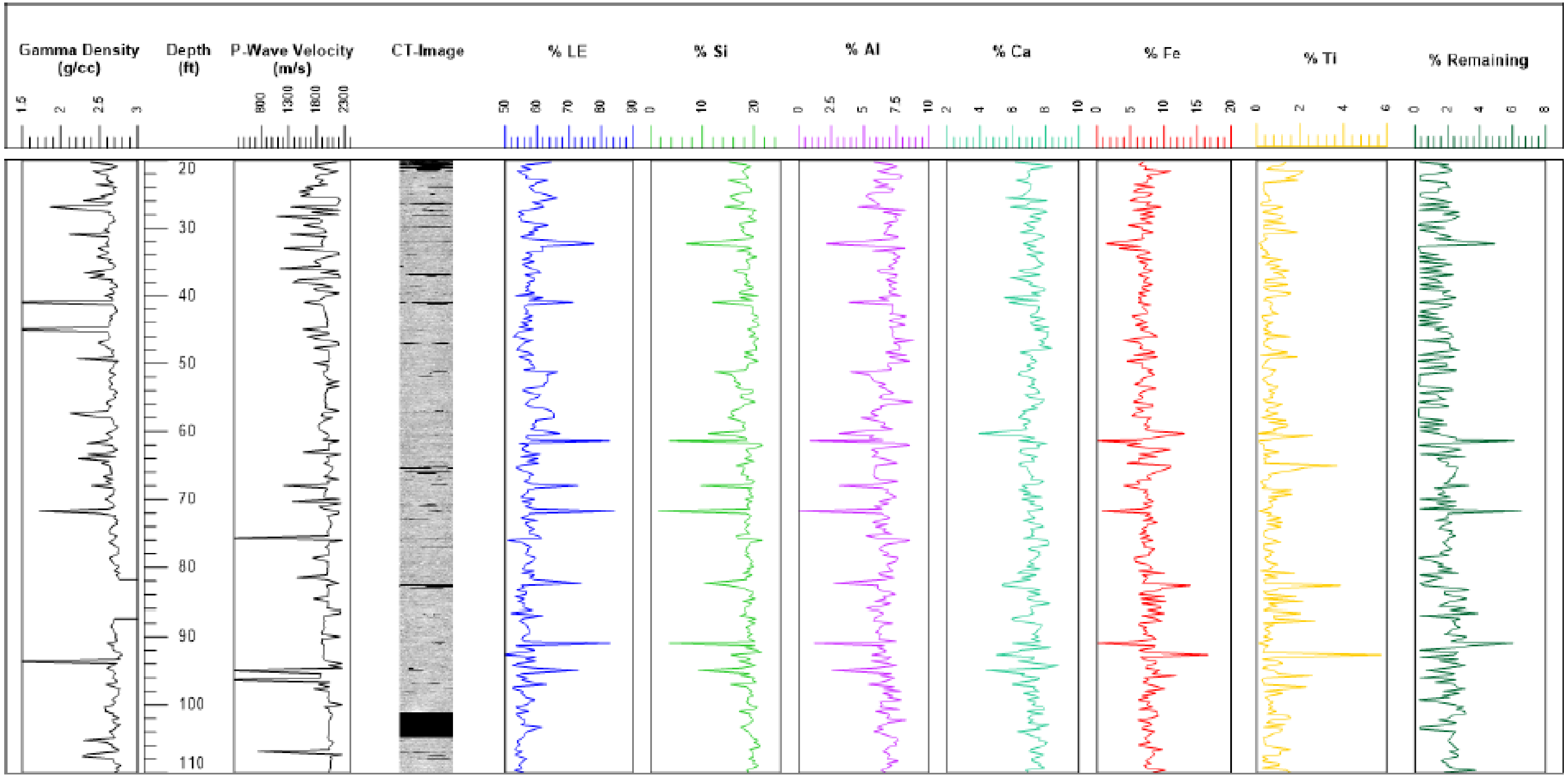


Figure 75: 2D image from industrial CT scan of the Susquehanna River core at 129.2 ft. where the red arrow indicates a mineralized fracture.

Core Logger Measurements Every 6 cm

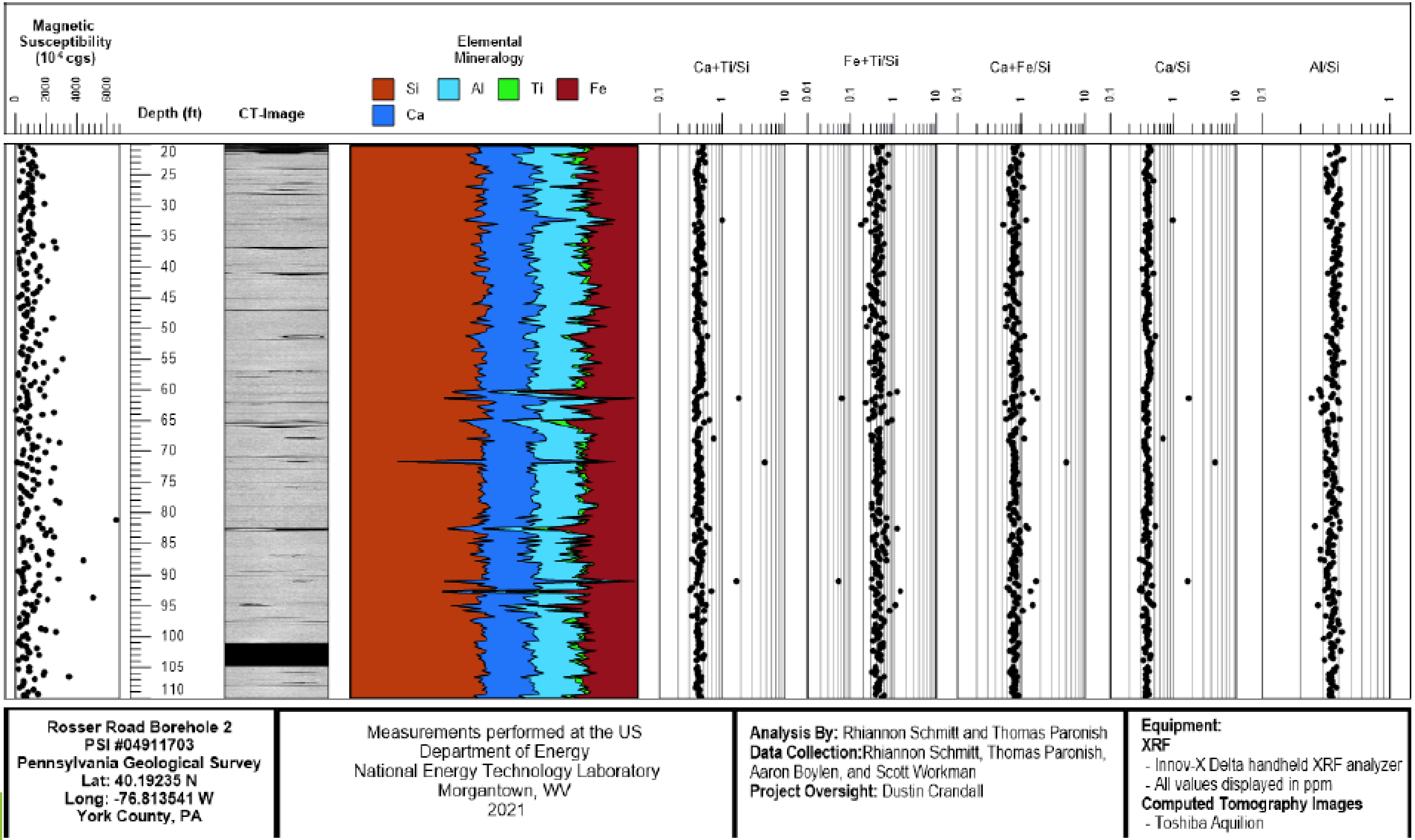
- **Gamma density**
- **P-Wave**
- **Handheld XRF**



Rosser Road Borehole 2 PSI #04911703 Pennsylvania Geological Survey Lat: 40.19235 N Long: -76.813541 W York County, PA	Measurements performed at the US Department of Energy National Energy Technology Laboratory Morgantown, WV 2021	**Analysis By:** Rhiannon Schmitt and Thomas Paronish **Data Collection:** Rhiannon Schmitt, Thomas Paronish, and Scott Workman **Project Oversight:** Dustin Crandall	**Equipment:** **XRF** - Innov-X Delta handheld XRF analyzer - All values displayed as percent **Computed Tomography Images** - Toshiba Aquilion

Elemental Mineralogy from hhXRF

- **Silica rich throughout, with little variation along core lengths**



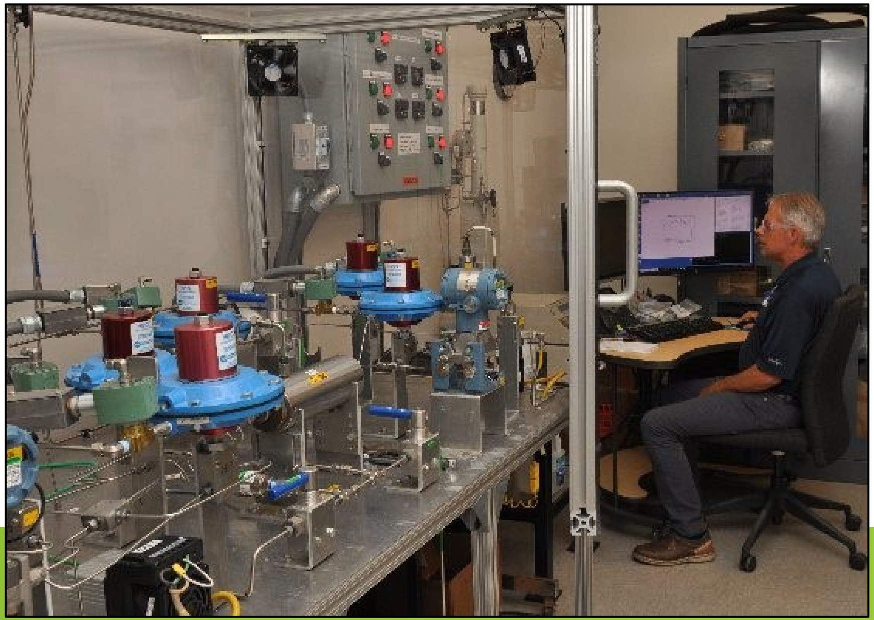
Permeability Measurements of Subcores

Most well below 50 nD

- **High-precision fluid permeability was measured for select samples with the Randolph Steady-State Core Analysis Laboratory (RaSSCAL) low-permeability direct measurement system.**

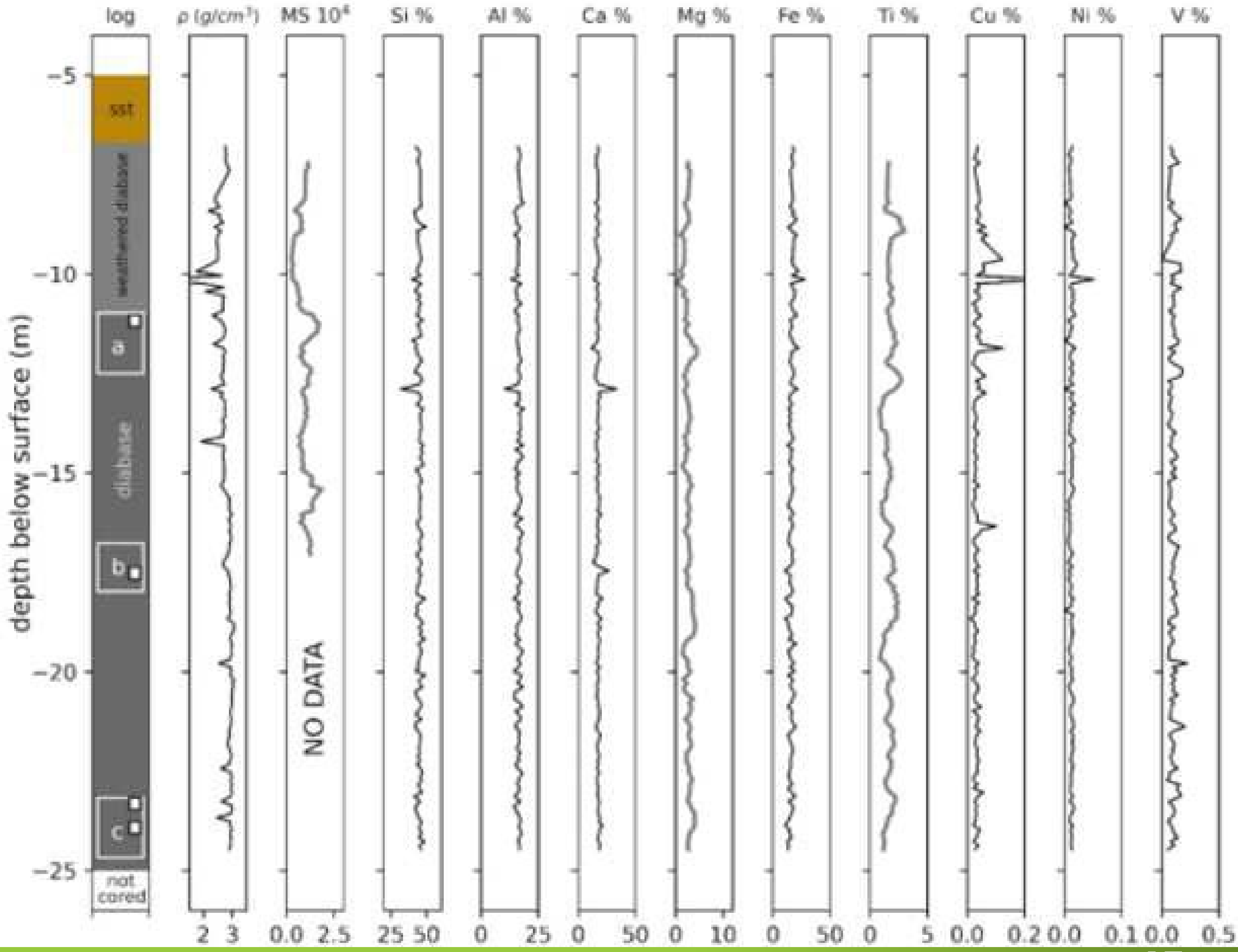
Table 4: Permeability Measurements of Diabase Core Plugs at Selected Depth

Well	Depth	Borehole	k (nD)
ROS	36	B1	52.60
ROS	57	B1	2.91
ROS	76	B1	2.00
ROS	78.4	B1	37.66
SUS	53	B1	1.60
SUS	325	B1	0.03
SUS	327	B1	0.54
SUS	357	B1	0.07
WALT	57	B1	15.59
WALT	101	B1	34.59
WALT	81.6	B2	< 0.05
WALT	86.1	B2	< 0.05



Subsampling

- **Data analyzed and combined in logs (ROS B-1 shown)**
- **Lithological, and selected petrophysical and geochemical results.**
  - ρ: gamma density.
  - MS: magnetic susceptibility.
- **Labeled white boxes are the locations of higher resolution CT scans.**
- **White dotes are the locations of sub-samples aqueous-CO_2 reaction experiments.**

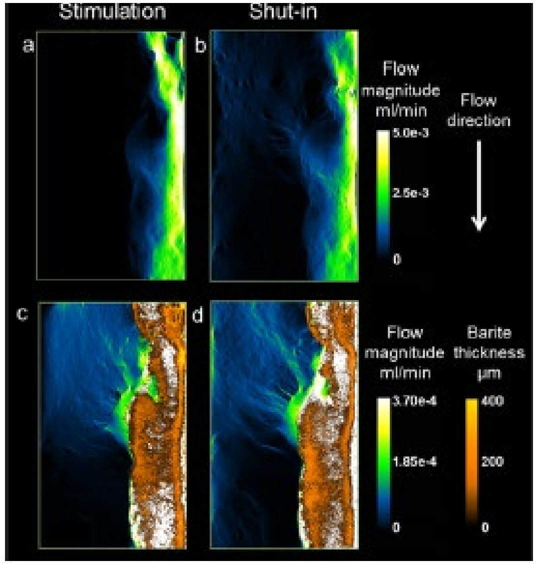


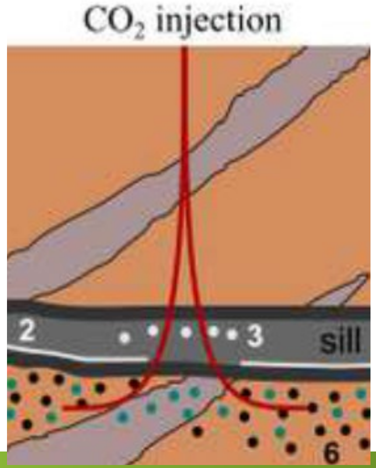
Water-CO_2 Reactions at elevated T&P

- **Characterization of five Triassic Diabase wells**
  - Rosser Road Borehole 1, Rosser Road Borehole 2, Waltonville Road Borehole 1, Waltonville Road Borehole 2, and Susquehanna River well
  - Included first pass non-destructive measurements (Medical CT imaging, multi-sensor core logger, and whole core Industrial CT imaging)
- **Diabase plugs were collected from representative regions**
  - Additional characterization (XRD, SEM, high-resolution CT images)
- **Samples were crushed and exposed to an aqueous CO_2 solution at representative subsurface pressure and temperature for 45 days**
  - 50 °C (122 °F)and 25 MPa (3,625 psi)
- **Following aqueous CO_2 exposure samples were examined for mineralogy changes using XRD.**
- **Findings showed rapid carbonate mineralization in the diabase samples**

Questions from the characterization work

- **Eight samples from across two representative cores (Rosser Road B-1 and Susquehanna Rover B-1)**
  - Range of dolerite, veins and some fractures; but very uniform!
- **Very low permeability, less than 50 nD …**
- **Rapid mineralization observed**
  - In 10-day experiments; pressure stabilized in batch reactions in hours
- **What is the potential for these to be 'self-healing seals'?**
  - Slow leak of slightly carbonated brine through fractured diabase to reduce permeability under what conditions?





Initial Plan with NETL's DynaTOM CT Scanner

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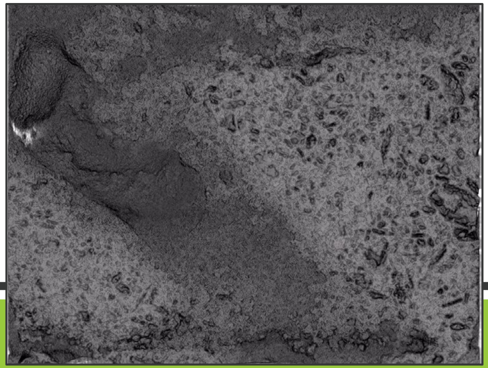
High speed CT with ~10-micron resolution

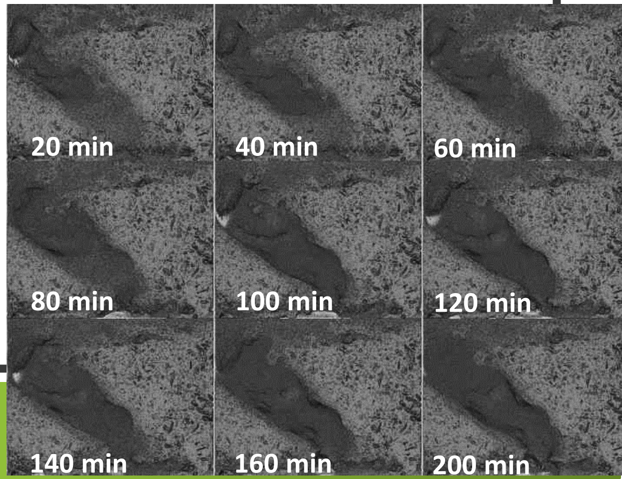
- First of its kind in the US
- Installed 2021

Unique rotating gantry enables CT source and detector to spin around sample

Reconstruction software to map low resolution scans to higher resolution base images

Structural changes due to geochemical alteration tested with a weak acid injection in limestone





Pivoting to Medical and Other systems

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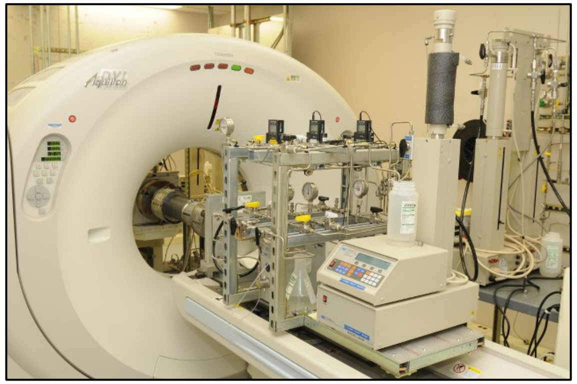
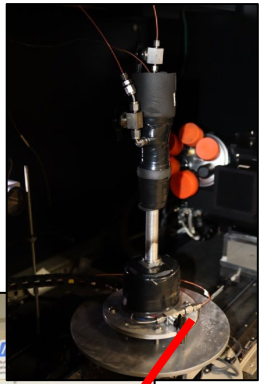
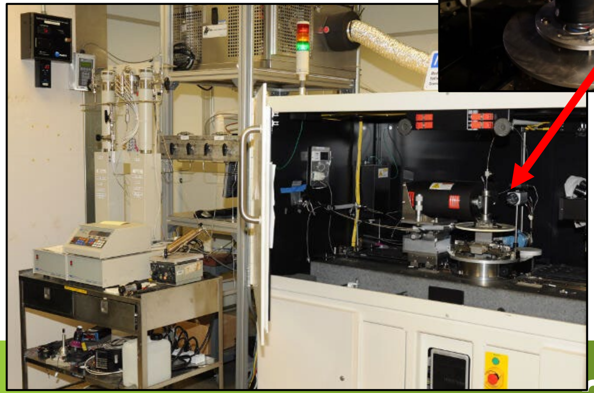
- **Due equipment issues have not been able to ramp up direct study with the DynaTOM yet.**
- **Pivoted to using a combination of our other scanners to get moving, develop workflow**
- **Medical CT scanner – multi-day/week flow with high precision DAQ and low-resolution imaging. 1” D composite core.**
- **Industrial CT scanning – Pre/post imaging of flow core.**
- **Micro-CT scanning – Several mm diameter composite core with micron scale imaging over weeks long exposure.**







Description of Medical and Micro experiments

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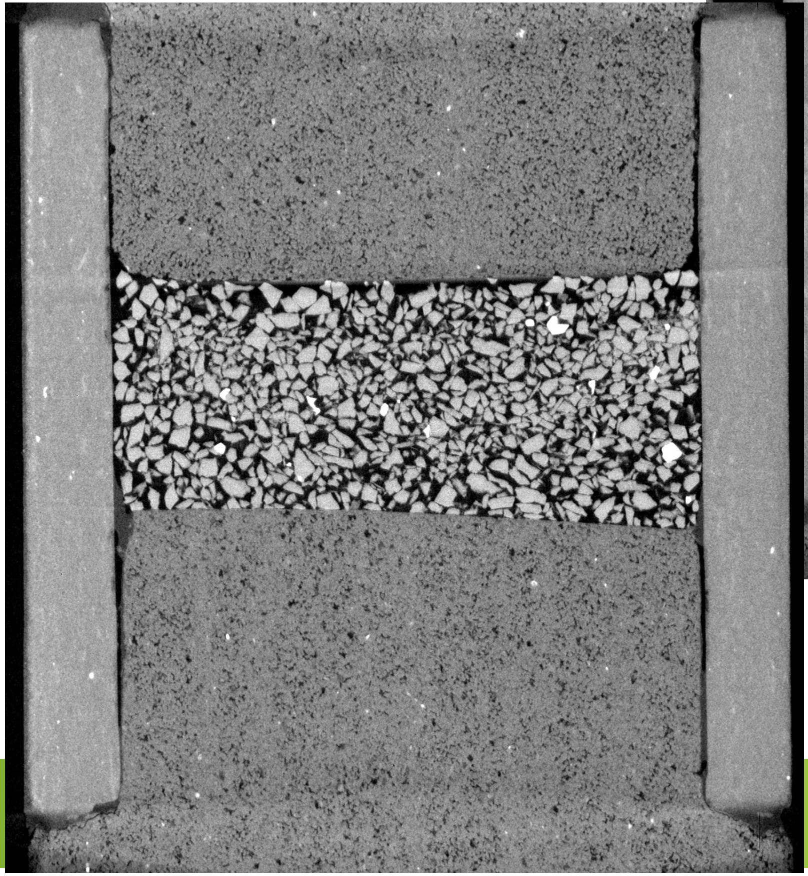
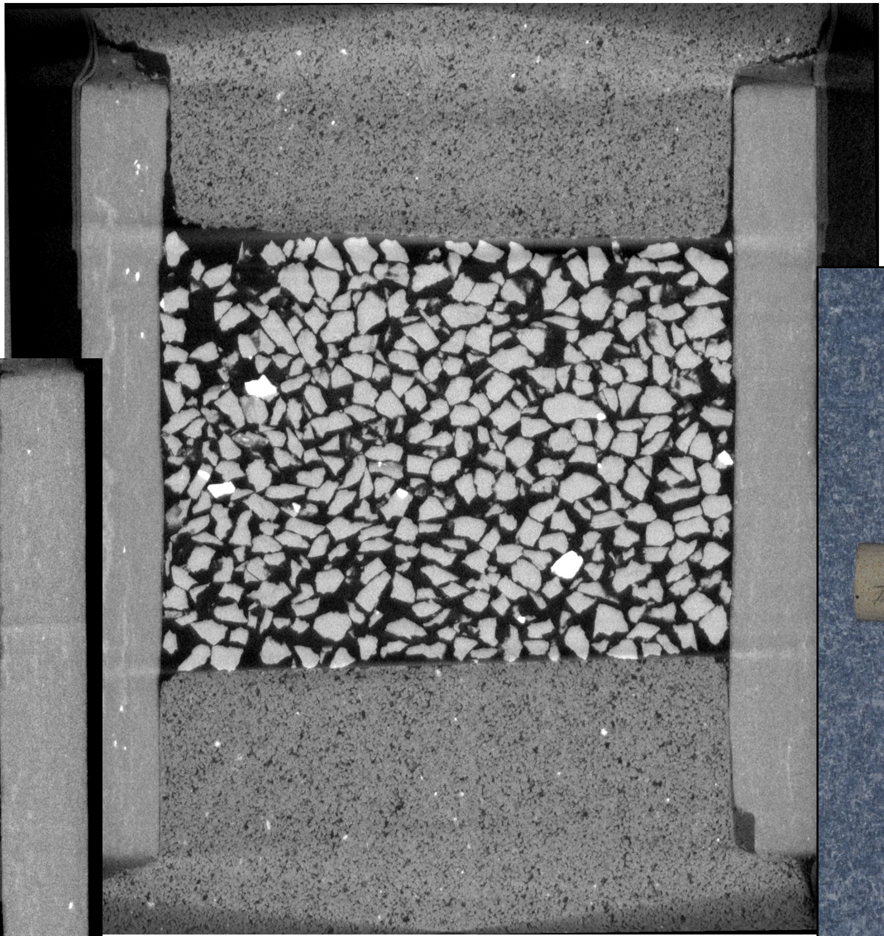
- **For methodology, prior to use of PA diabase samples, tested olivine reaction rates with low heated carbonated brine flow**
  - In order to get rapid interaction, ground samples used.
  - To use in existing core flow facilities in the micron and medical CT scanners, had to develop a unique composite core.
- **Hollow shale cylinder prepped and filled with ground olivine. Berea sandstone injection/effluent plugs fitted to the shale and epoxied in place.**
  - Worked very well to enable the ground sample to be under proper P&T and experience flow

Composite core system

- High-resolution cross-sectional images.
- 1” diameter

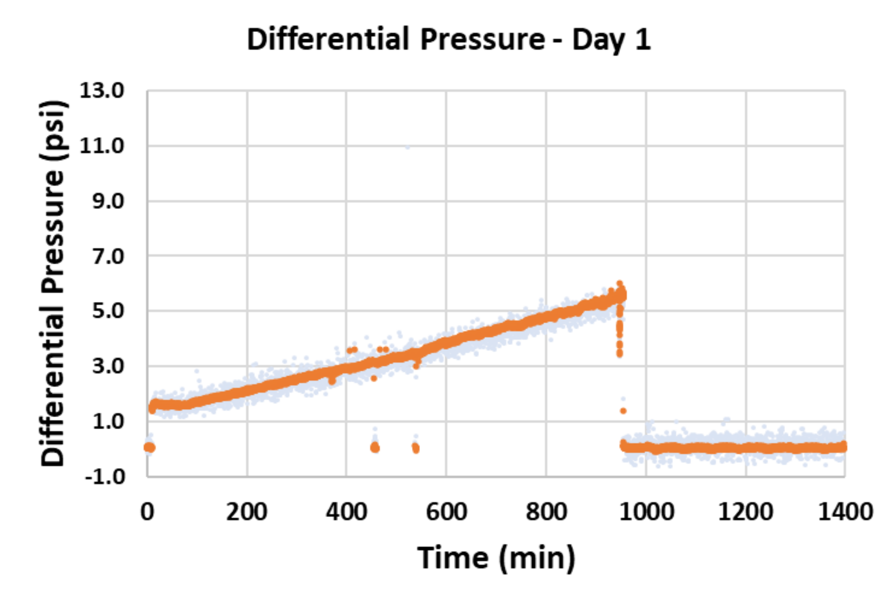


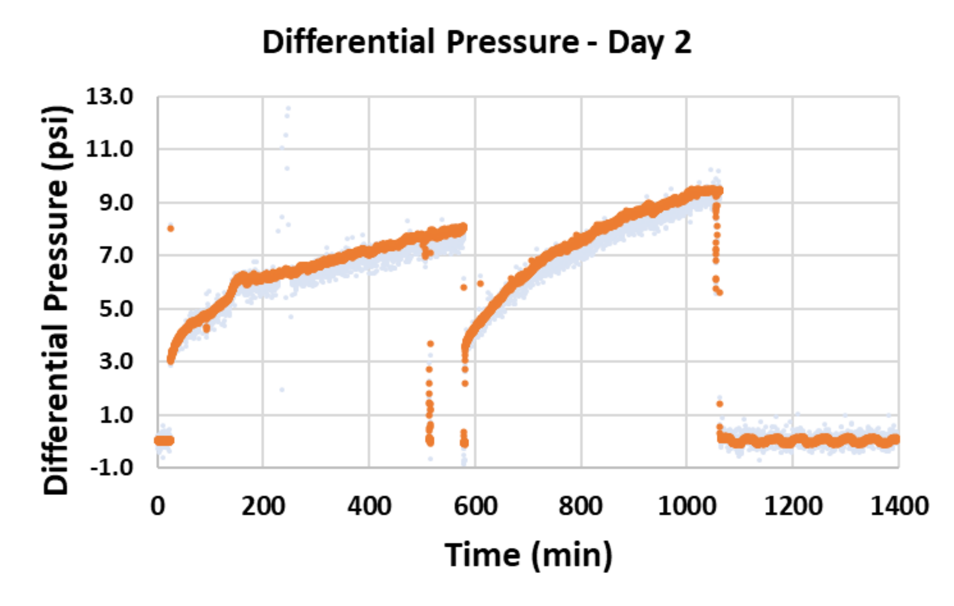


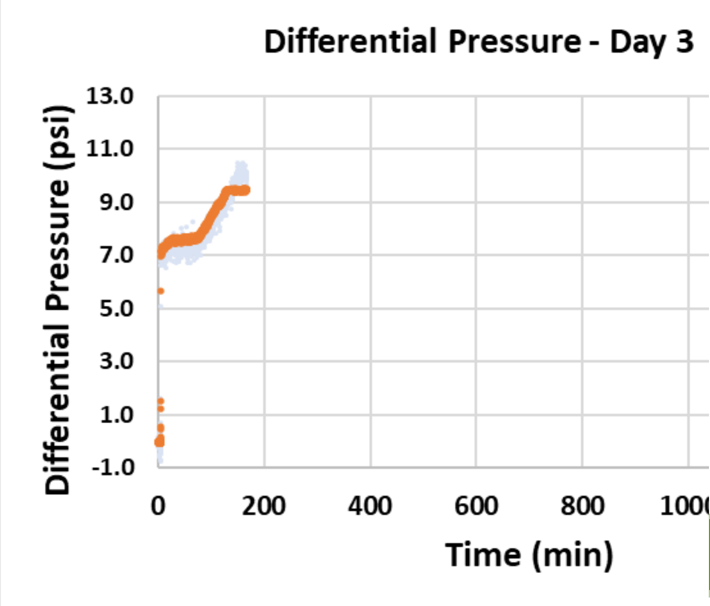
Changes in Medical CT Measured Permeability

Work in progress!

- Brine at temperature and pressure sparged with CO_2 for 24-hours
- P_{pore} = 3350 psi, T = 150 °F, Flow rate = 1 $^{ml}/_{min}$
- Preliminary examination shows rapid increase in differential pressure across core, for first examination from ~1 psi to 10+ psi 3 days (~2L injected)

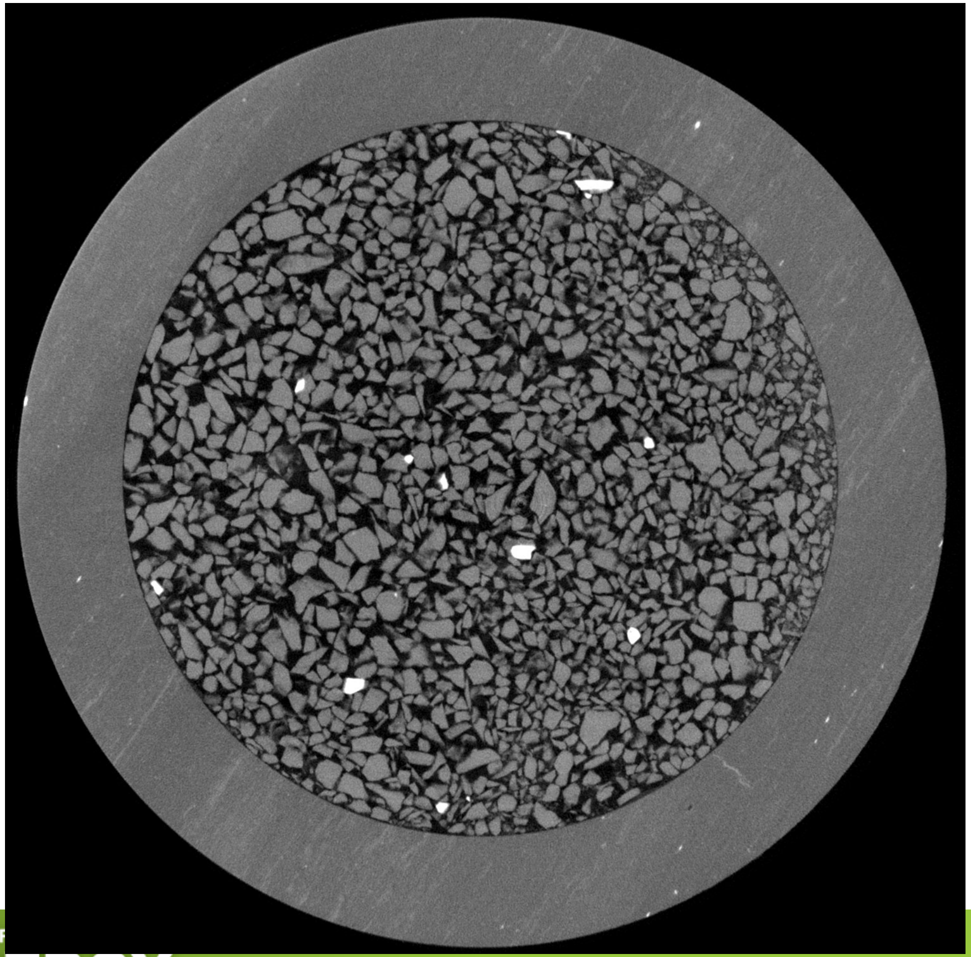




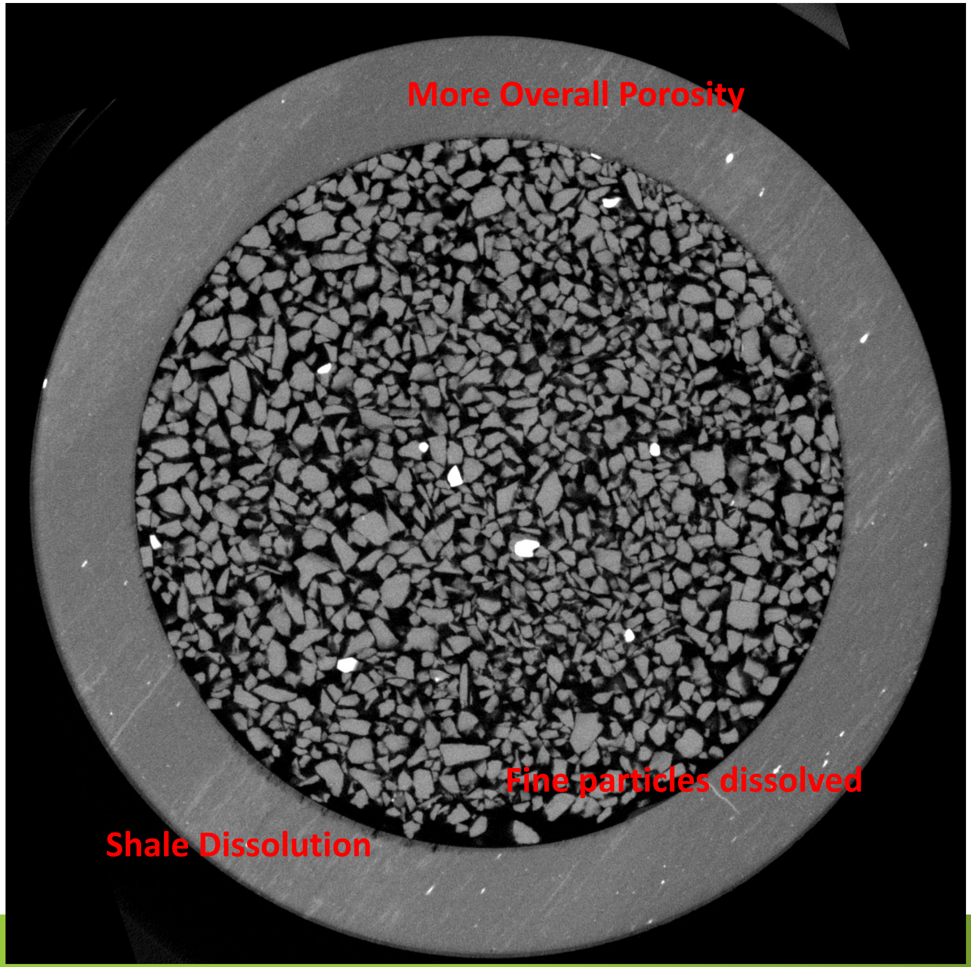


Pre/post industrial CT scans of medical tests 1

- **Pre flow – Slice 1229 near inlet**

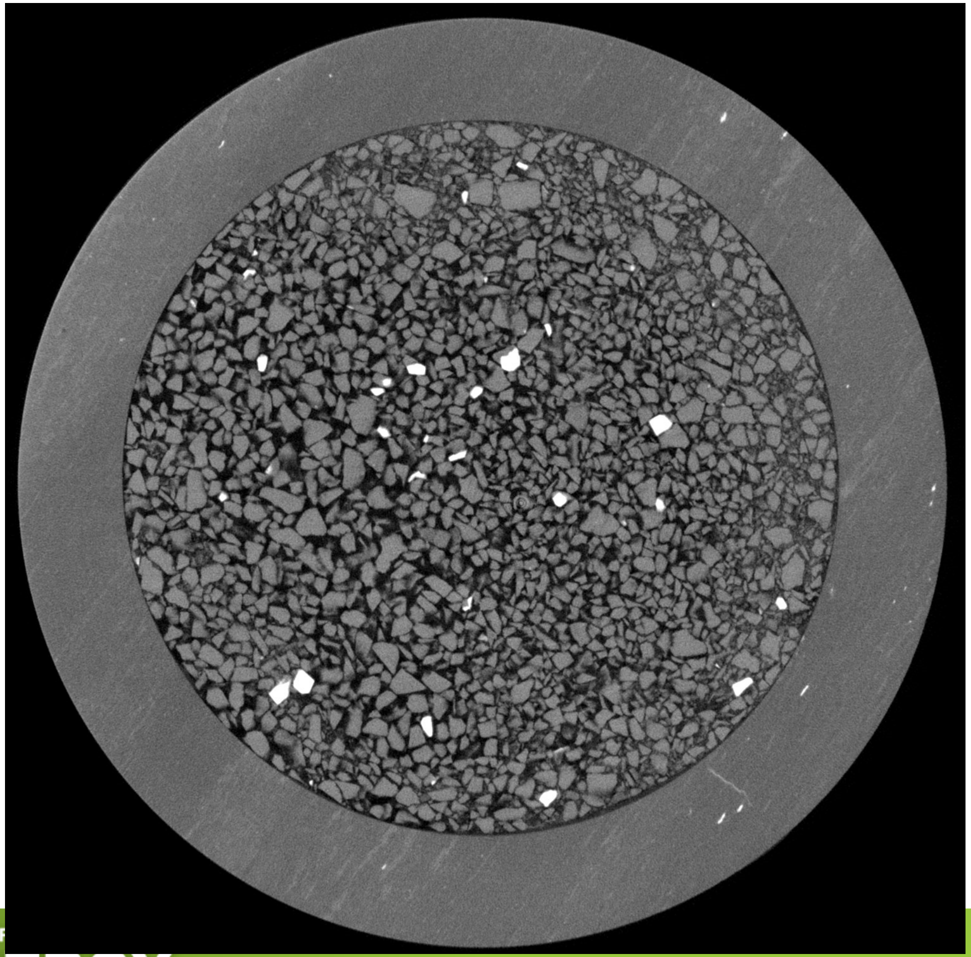


- Post flow – Slice 1215 near inlet

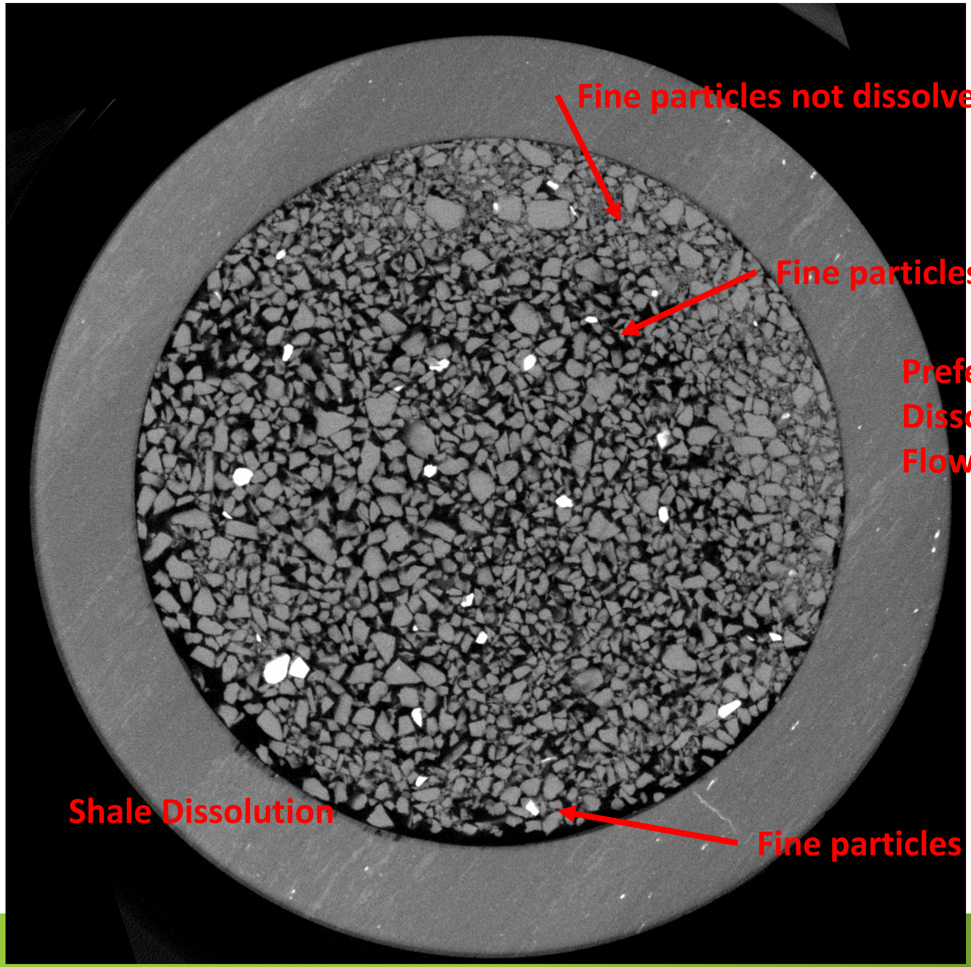


Pre/post industrial CT scans of medical tests

- Pre flow – Slice 1178 mid-inlet

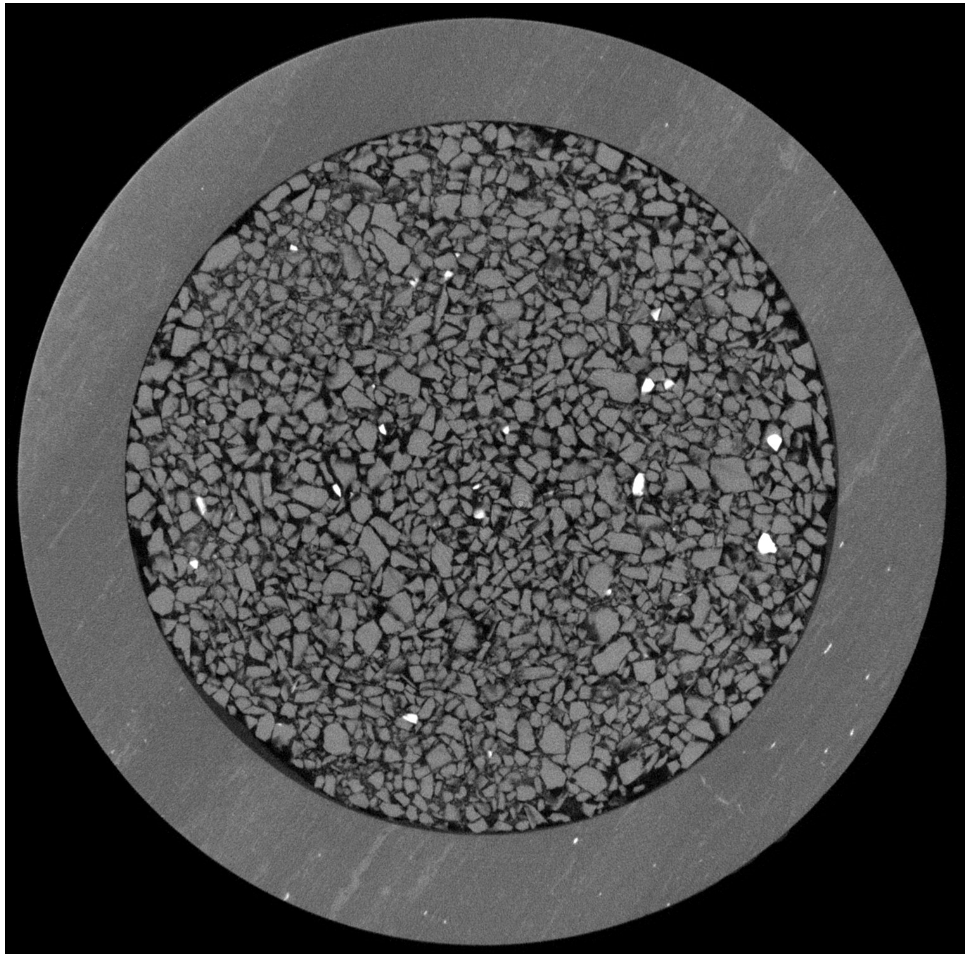


- Post flow – Slice 1147 mid-inlet

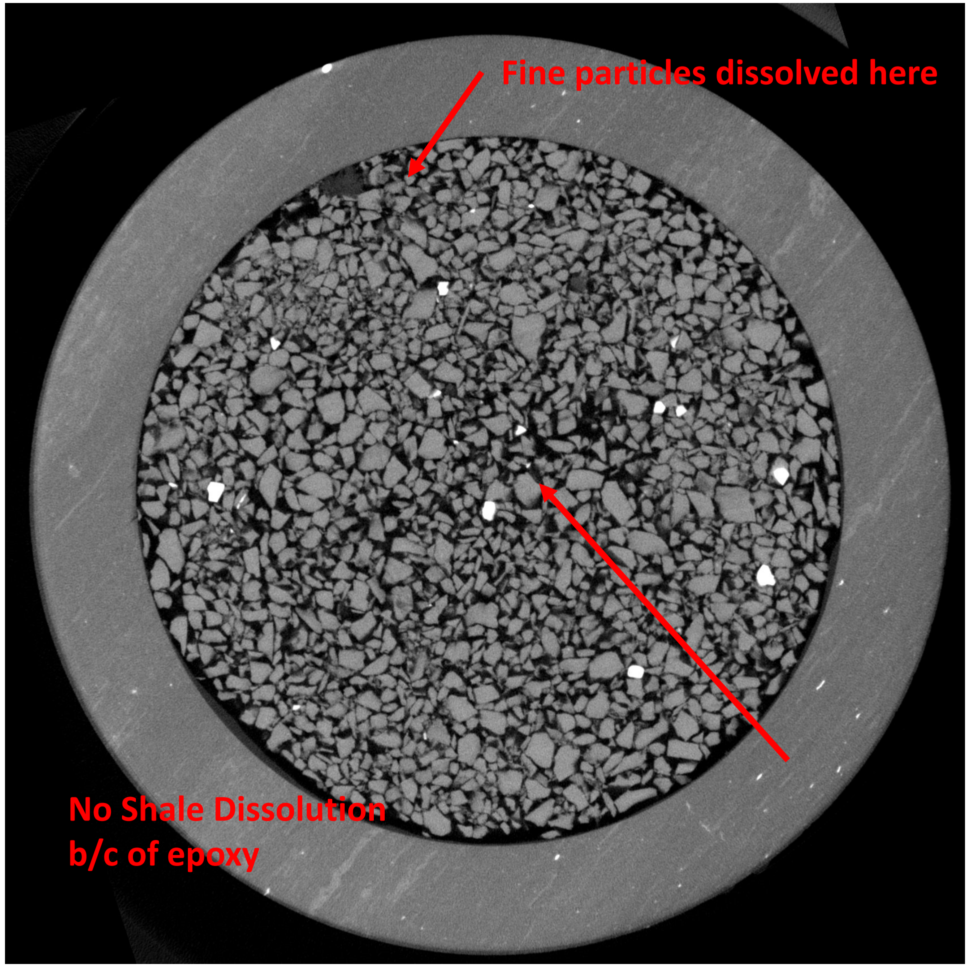


Pre/post industrial CT scans of medical tests

- Pre flow – Slice 1123 mid

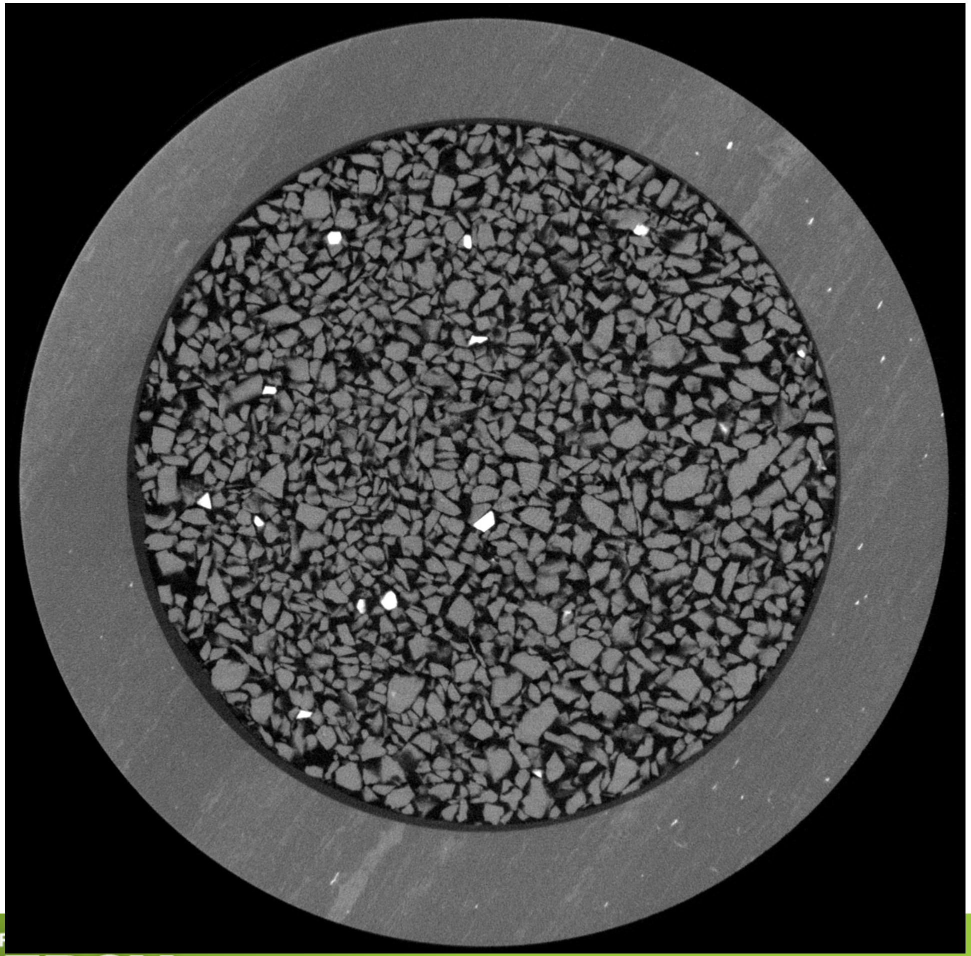


- Post flow – Slice 1180 mid

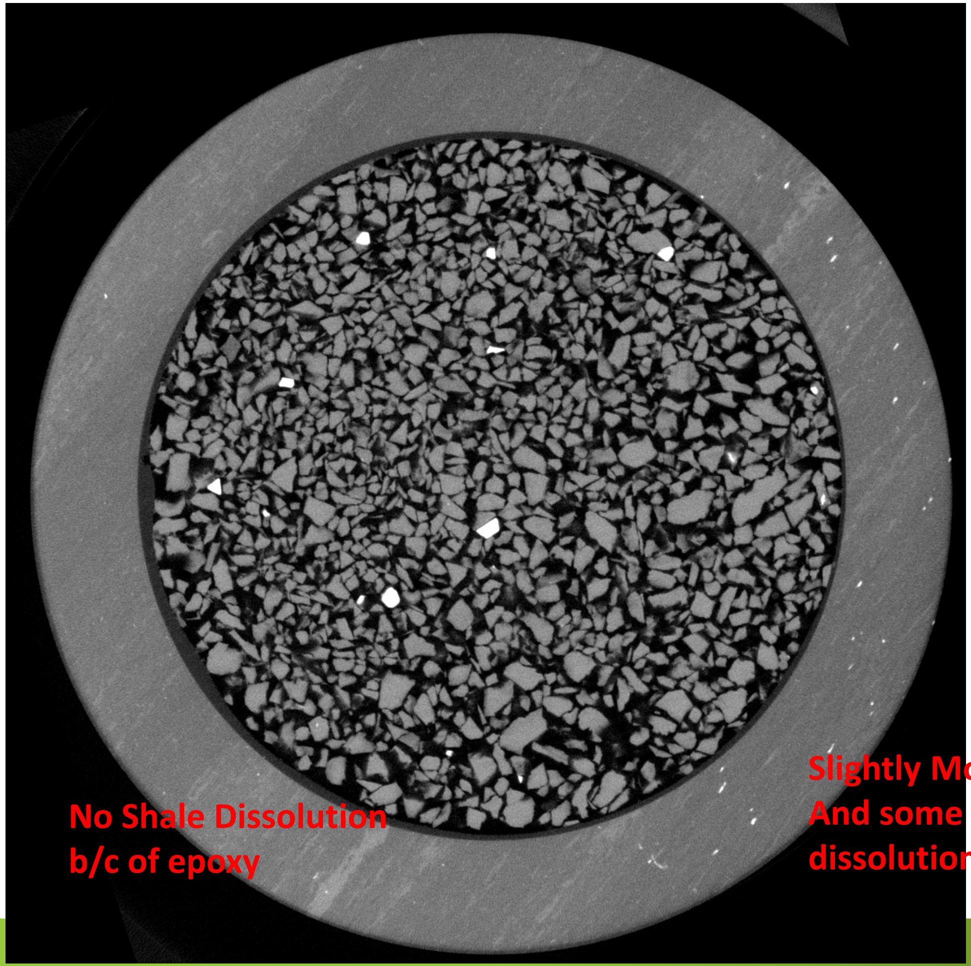


Pre/post industrial CT scans of medical tests

- **Pre flow – Slice 862 – Near outlet**

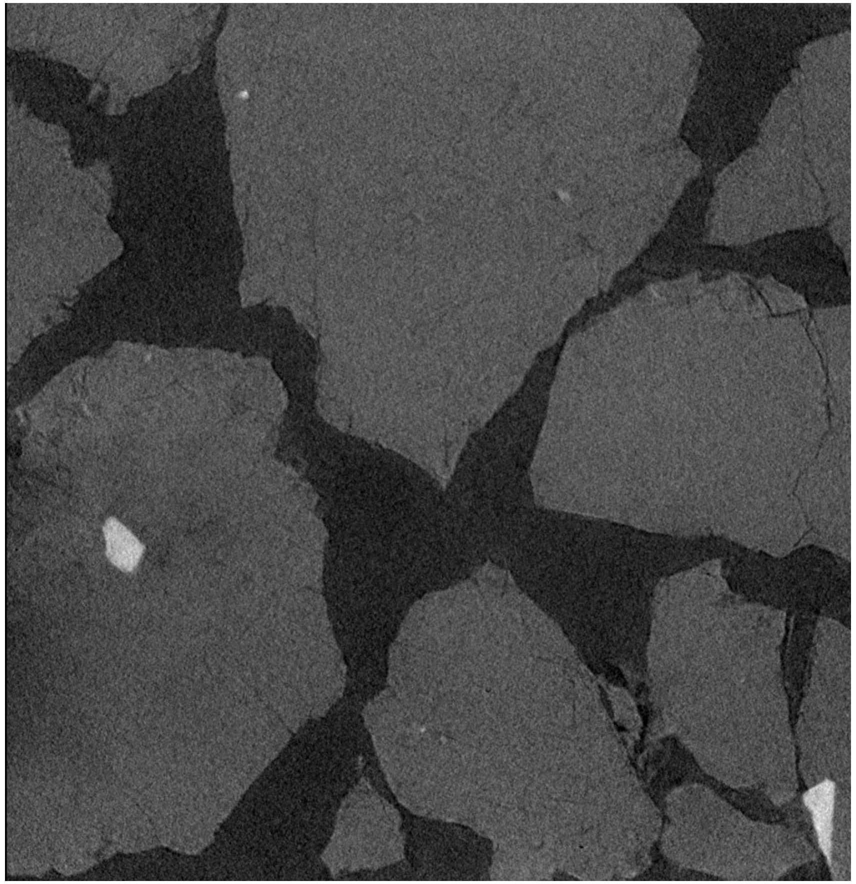


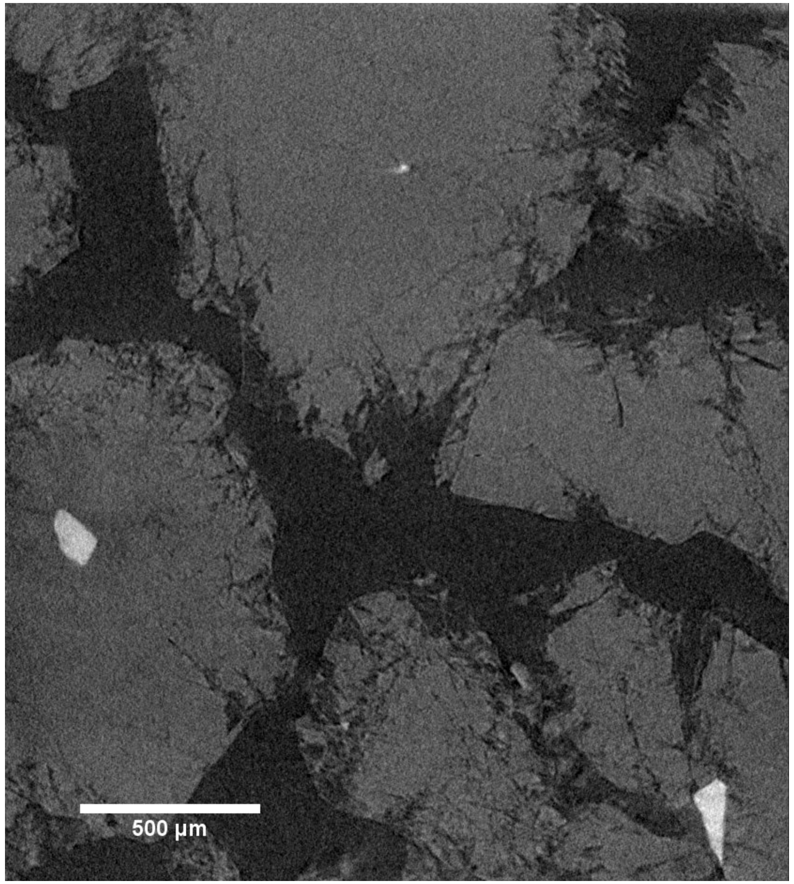
- Post flow – Slice 796 – Near Outlet



Pore-scale olivine dissolution from Xradia MicroCT

- Dissolution around grain edges
- Pre-existing fractures and weak zones are primary sites for initial dissolution
- Some shifting of smaller grains as they lose structural integrity





Following CO_2-water flow for 30 days

Overall summary

- **We've got the systems in place to examine fracture sealing dynamically for these potential self healing seals**
- **DynaTOM may be functional later this year, but we're also not going to fully rely on this moving forward.**
  - Can hope! But also need to make sure we're moving.
- **Analysis of rates of changes in permeably with change in sieved size of olivine samples to constrain the rates of injection for diabase samples**
- **Schmitt, R.R., Andrews, G.D.M., Moore, J., Paronish, T., Workman, S., Gumowski, L.M., Brown, S.R., Crandall, D., Neubaum, J. (2022) Self-Sealing Mafic Sills for Carbon and Hydrogen Storage, *Geological Society, London, Special Publications Vol 528* https://doi.org/10.1144/SP528-2022-43**

Thank you!

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Questions?

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Data available on Energy Data eXchange edx.netl.doe.gov

Published Technical Reports available on Osti.gov

Data available on RokBase.org