Resource, Technology, and Infrastructure

Jaeheon Lee
Colorado School of Mines

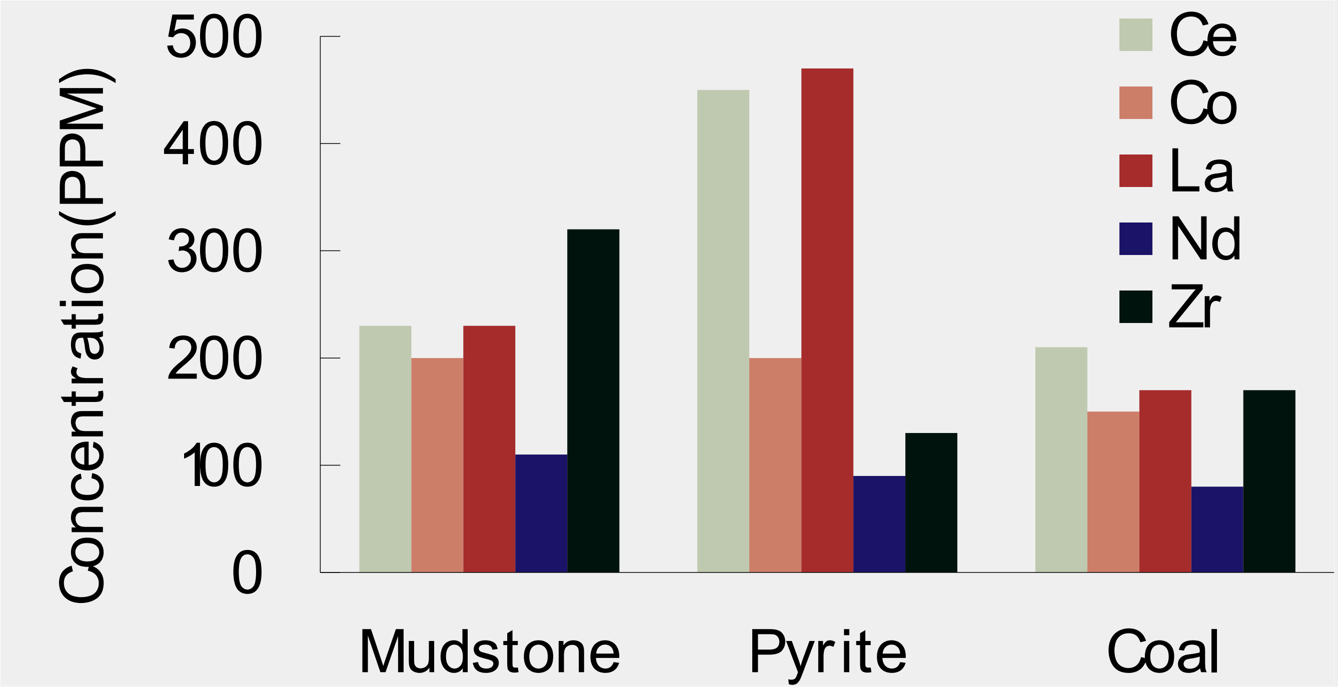
Samples Received

- Mudstone sample
- Pyrite sample
- Coal sample

Characterization

- ICP analysis
- XRD analysis
- Automated Mineralogy

Chemical Characterization

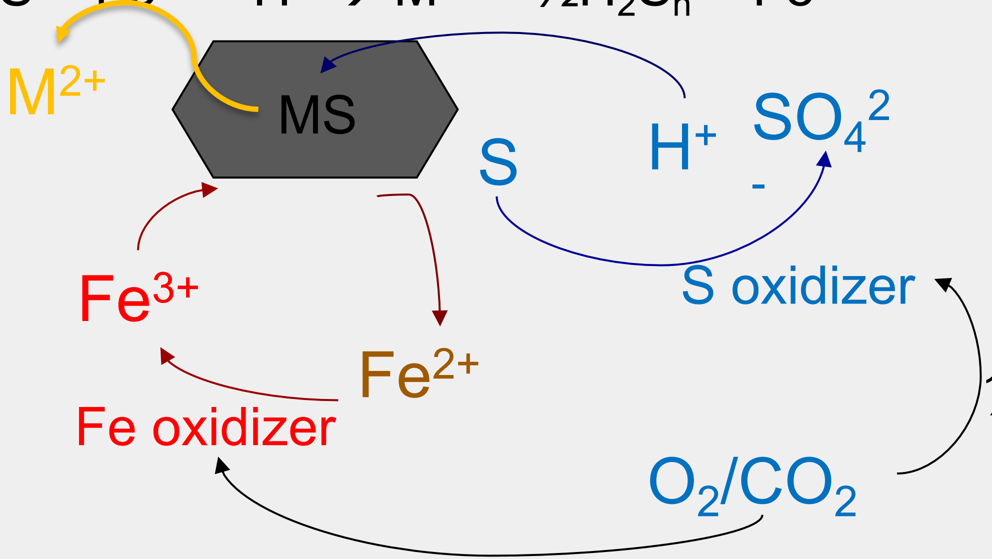


Automated Mineralogy, %

	Mudstone	Pyrite	Coal/clay
Quartz	64.78	13.36	17.08
Illite/Muscovite/Kaolinite	25.42	1.04	77.44
Biotite	2.62	0.18	2.02
K-feldspar	2.49	0.70	0.58
Albite	0.51	0.07	1.92
Chlorite	0.11	0.01	0.26
Pyrite		84.17	

Bioleaching/Biooxidation

$$MS + Fe^{3+} + H^{+} \rightarrow M^{2+} + \tfrac{1}{2}H_2S_n + Fe^{2+}$$



$$\tfrac{1}{4}S_8 + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^{+}$$

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^{+} \rightarrow 2Fe^{3+} + H_2O$$

Bioleaching/Biooxidation

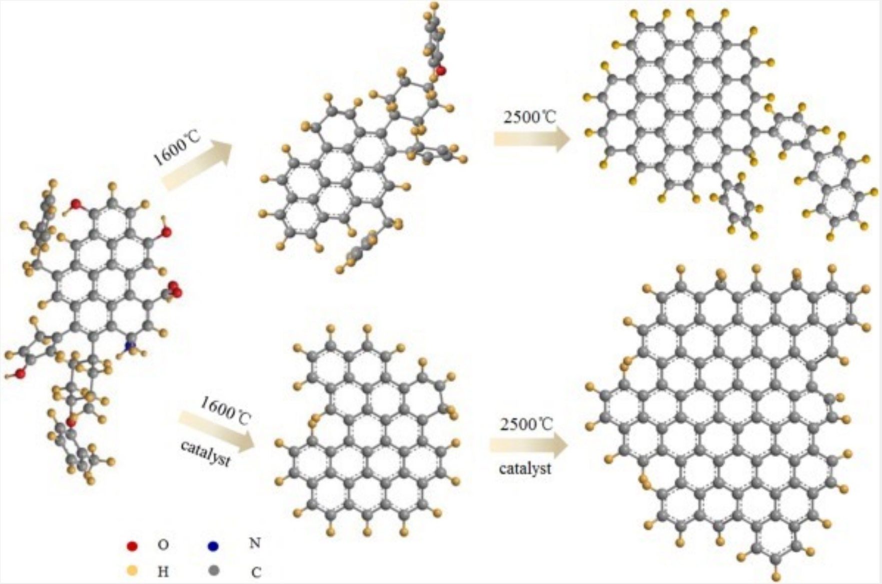
- The leach agent in the process is regenerated, leading to less chemical addition → Environmental advantage

- Provide routes to handle low grade materials

- Other lixiviant can be generated microbially

High Temperature Coal Treatment Review

Graphite conversion



Simple graphitization of coal is possible by high temperature treatment above 2800 C

B_2O_3 addition increases the degree of graphitization and reduces required temperature

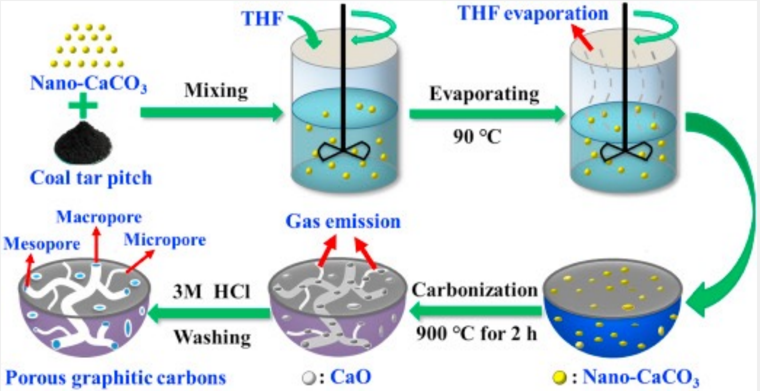
Can produce graphite with excellent properties for use as battery anodes

Shi, 2021. https://doi.org/10.1016/j.fuel.2021.120250
Camean, 2011. https://doi.org/10.1016/j.jpowsour.2011.01.041

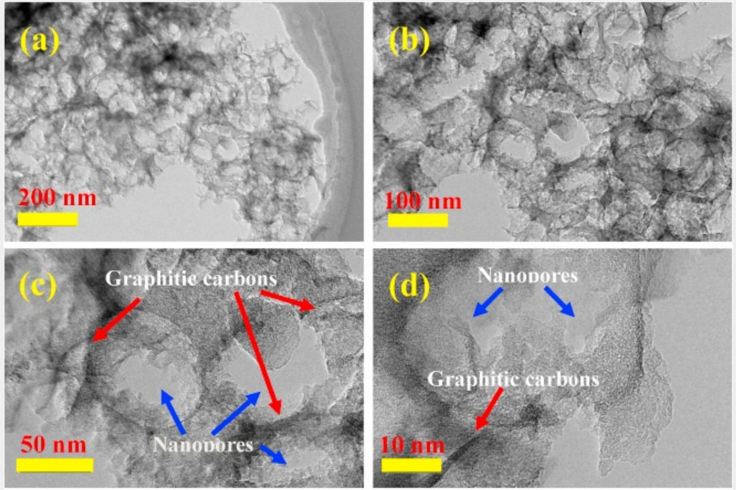
Developments in energy efficiency

Coal tar pitch mixed with $CoCO_3$ and tetrahydrofuran (THF)

Porosity can be controlled to balance surface area and side reactions



Xing, 2019. https://doi.org/10.1016/j.jallcom.2019.04.300
Han, 2020. https://doi.org/10.1016/j.powtec.2020.12.052



Activated carbon

High adsorption performance activated carbon composite can be made from coal mine discard and waste slurry

Synthesized alone by heating with KOH

Composite with zeolite has high adsorption affinity for Cu and Rh

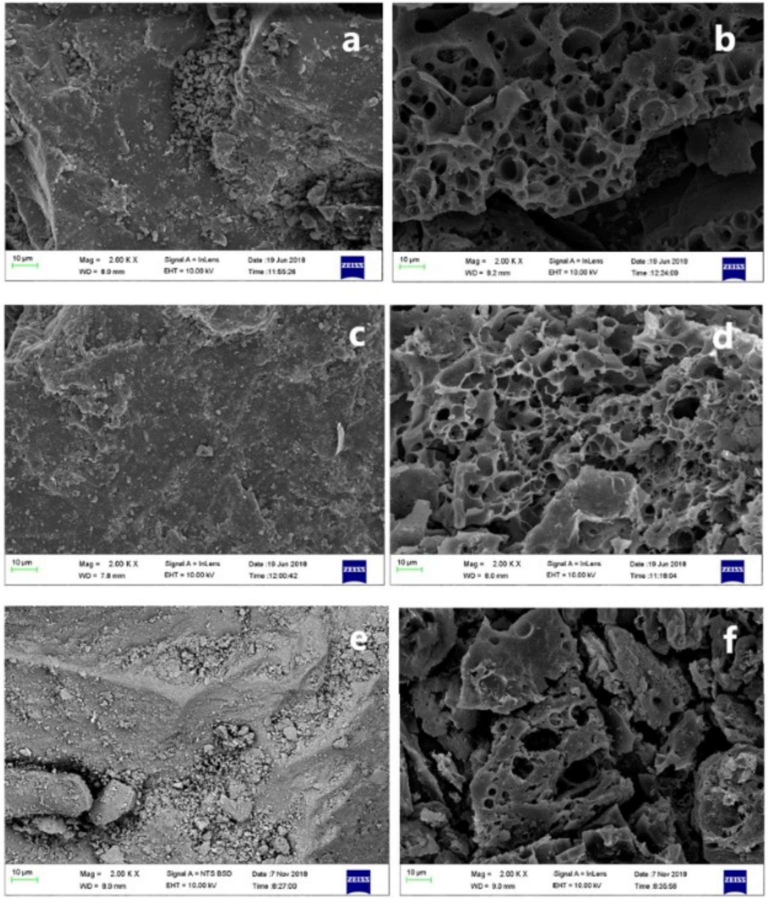


Fig. 4. SEM images of (a) run of mine coal (b) ACR (c) discard coal (d) ACD (e) Slurry coal (f) ACS.

Abdulsalam 2020. https://doi.org/10.1016/j.fuel.2020.117157
Li, 2020, https://doi.org/10.1016/j.cej.2020.124513

Microwave assisted conversion

Very low energy and low temperature method of graphitic conversion of coal

Multilayer graphene growth occurs by placing coal powder on metal foil and exposing to microwaves in a reducing atmosphere

Currently only effective at very small production quantities

Masi, 2020. https://doi.org/10.1016/j.nanoso.2020.100660

Solvent extraction

All coal has some proportion of naturally occurring crystalline carbon

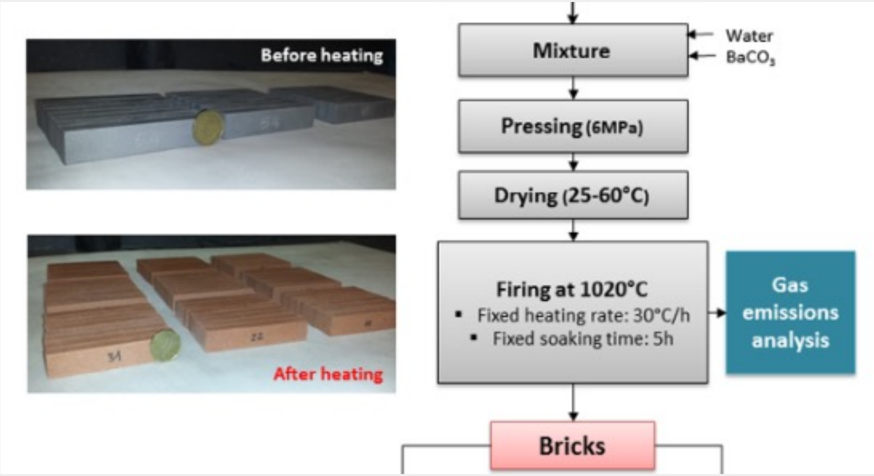
Solvent extraction can be used to extract the graphite in needle coke as a replacement for, or a supplement to converting amorphous carbon

Han, 2020. https://doi.org/10.1016/j.powtec.2020.12.052
Kimber, 1994. *Electrode coke from coal via solvent extraction.*

Structural materials

Structural applications have the potential for the largest volume of utilized material, and could be a secondary use for tailings after critical mineral extraction

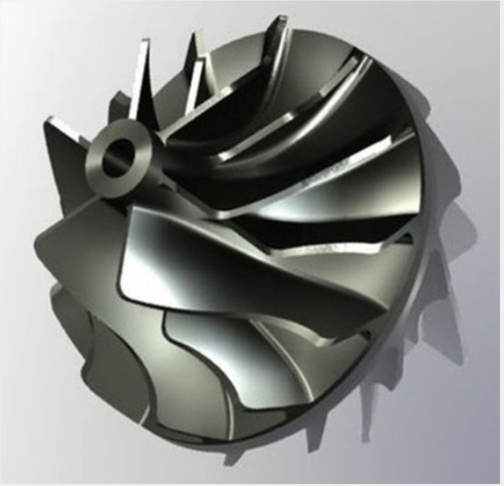
Bricks produced from coal or coal mine waste rocks reduce waste and immobilize contained heavy metals



Taha, 2017. https://doi.org/10.1016/j.mineng.2016.09.001

Carbon-carbon composites

Compositing carbon fiber in an amorphous or graphitic carbon matrix



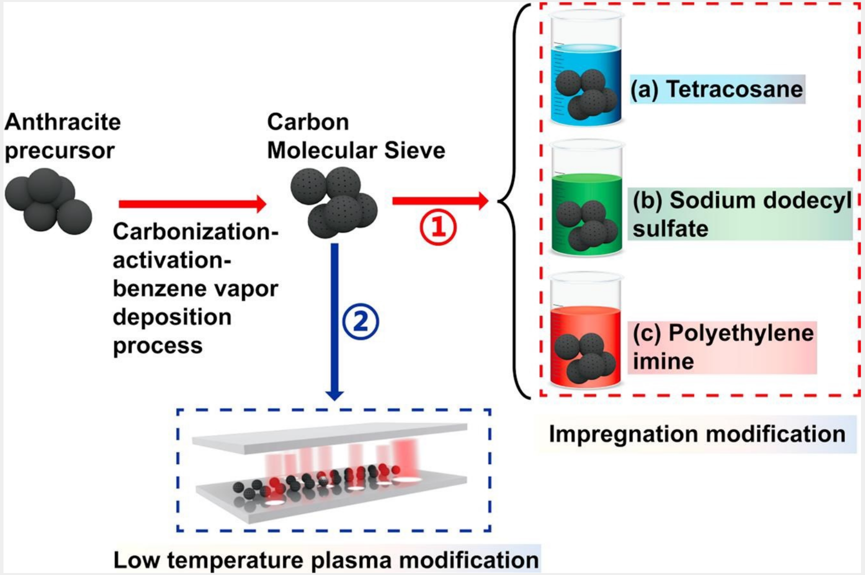
Large degree of control of properties by adjusting fiber density, direction, weave, and dimensionality within the material

Can be derived from coal pitch

Sharma, 2017. Chapter DOI: 10.1007/978-3-662-49514-8_10

Molecular sieves

Carbon molecular sieves can be made by grinding and washing followed by high temperature carbonization. Benzene vapor deposition is used to create uniform pores



Yang, 2019. https://doi.org/10.1016/j.seppur.2019.02.048

Nanomaterials and coal as a chemical precursor

Carbon nanotubes, carbon fibers, fullerenes, graphite, diamond-like thin films, and graphene quantum dots can be made from coal solids or pitch derived from coal

Chemical processing of coal for a precursor to value added organics

Song, 2005. ISBN 92-9029-413-2
Hoang, 2018. https://doi.org/10.1016/j.apmt.2018.06.007

Resource, Technology, and Infrastructure

Brent Goehring, Earth and Environmental Sciences

November 2, 2023

LA-UR-20-21659

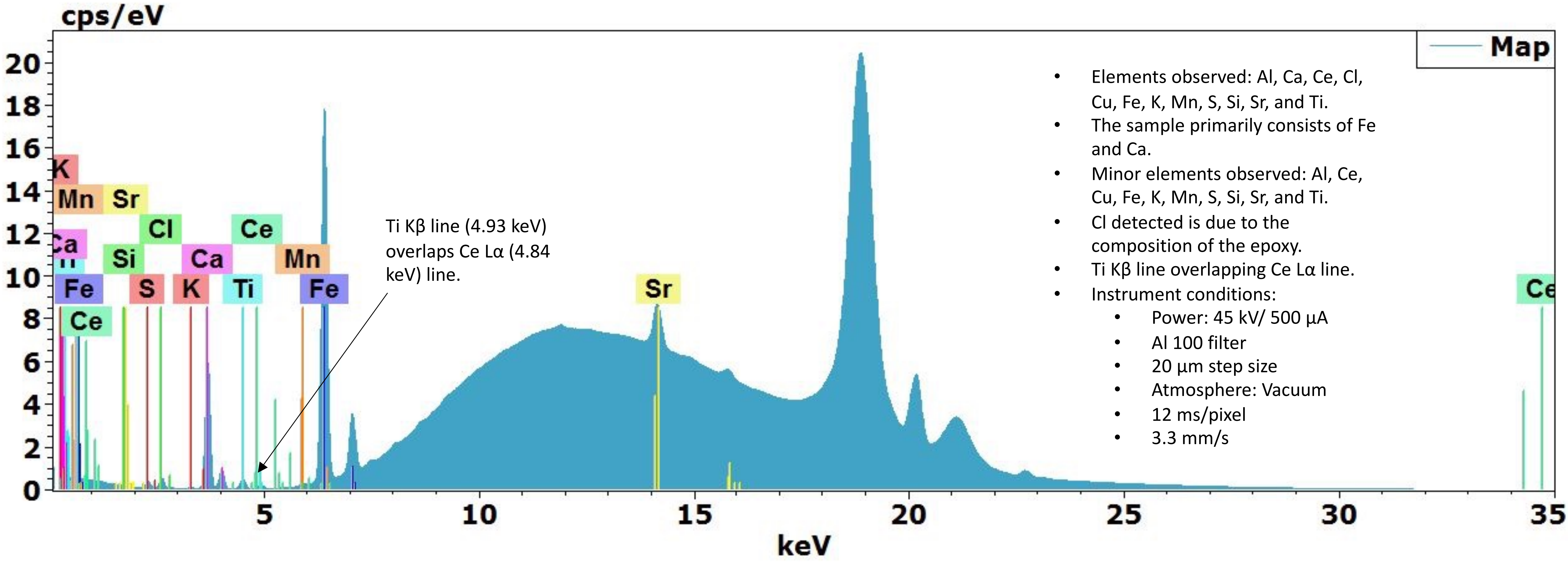
Characterization Methods

Samples Received (to be)

- Coal
- Black sands
- Trona
- Phosphate wastes

Analyses Performed/Planned

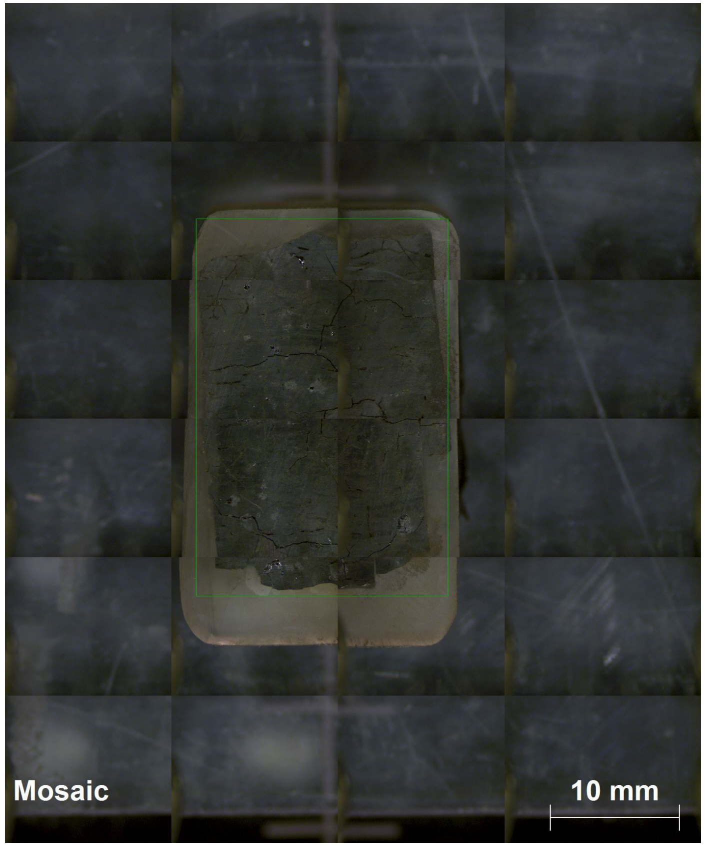
- XRD
- ICP-MS
- Portable XRF
- Micro XRF
- Raman Spectroscopy

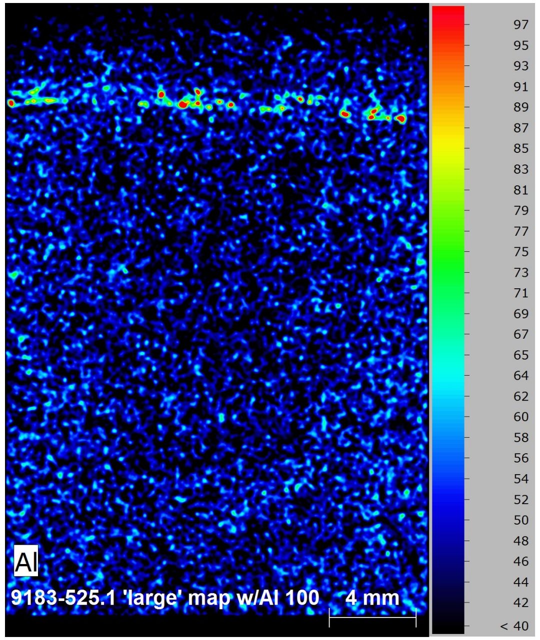


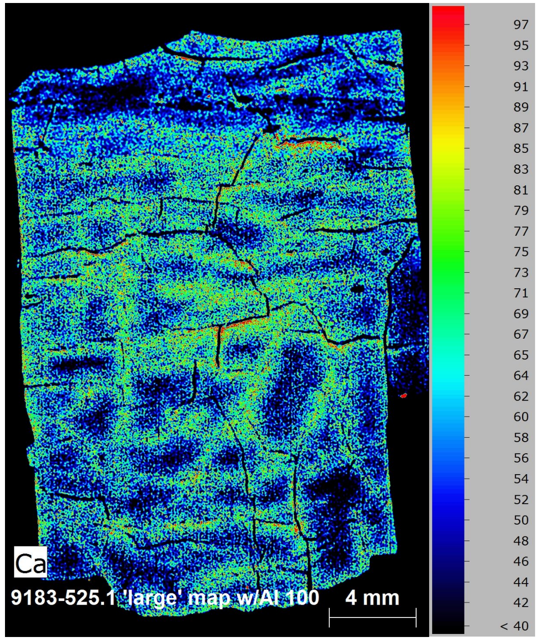
- Elements observed: Al, Ca, Ce, Cl, Cu, Fe, K, Mn, S, Si, Sr, and Ti.
- The sample primarily consists of Fe and Ca.
- Minor elements observed: Al, Ce, Cu, Fe, K, Mn, S, Si, Sr, and Ti.
- Cl detected is due to the composition of the epoxy.
- Ti Kβ line overlapping Ce Lα line.
- Instrument conditions:
  - Power: 45 kV/ 500 µA
  - Al 100 filter
  - 20 µm step size
  - Atmosphere: Vacuum
  - 12 ms/pixel
  - 3.3 mm/s

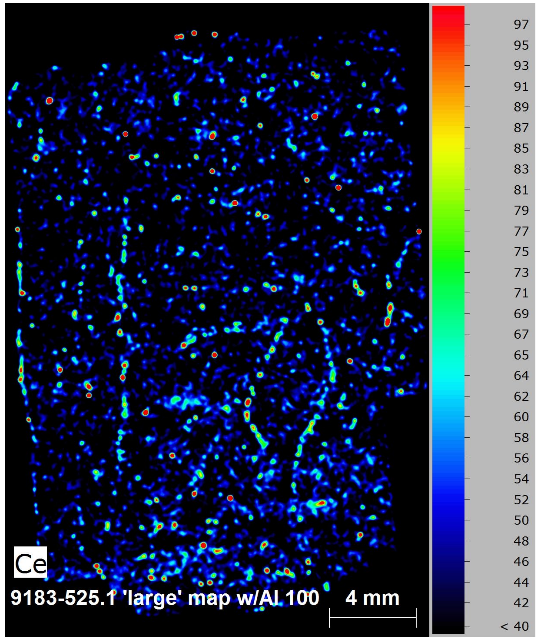
Preliminary Results 3/16/23
Kate McIntosh
Oscar Duarte

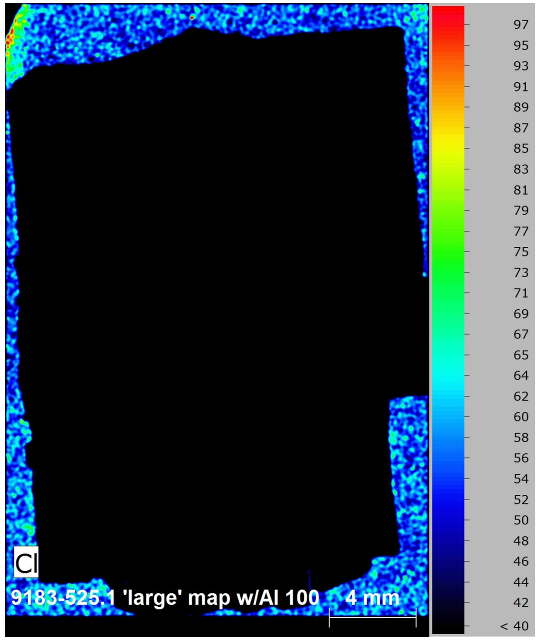
Last ~1 mm of map is missing due to the instrument computer running out of RAM

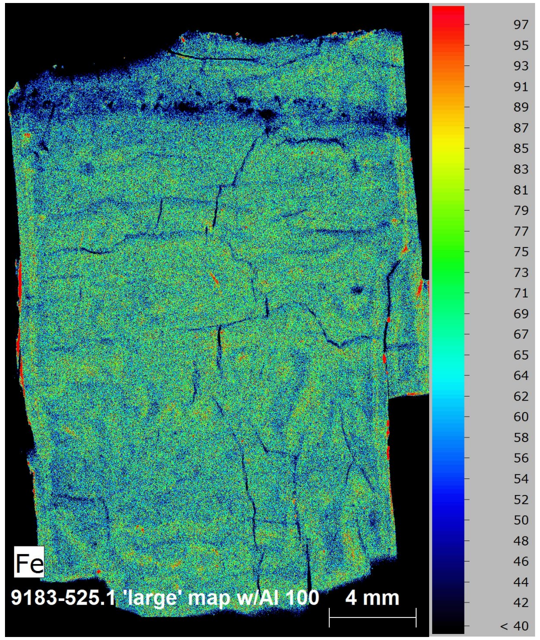


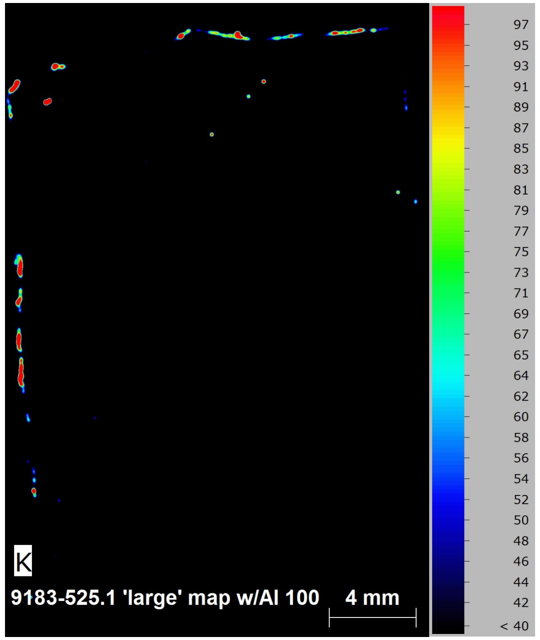




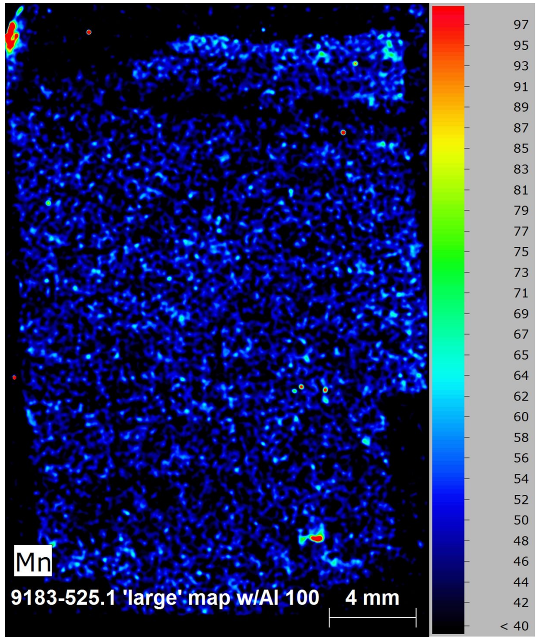


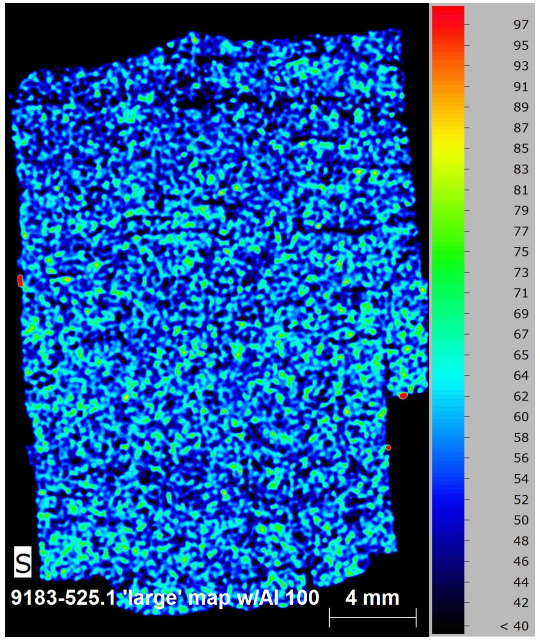


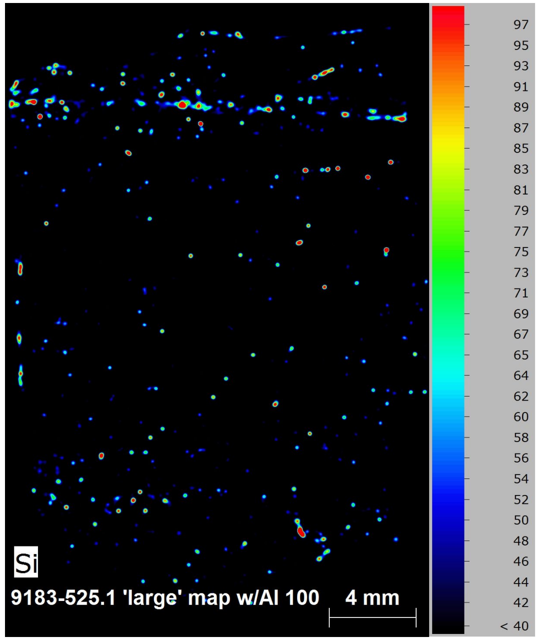


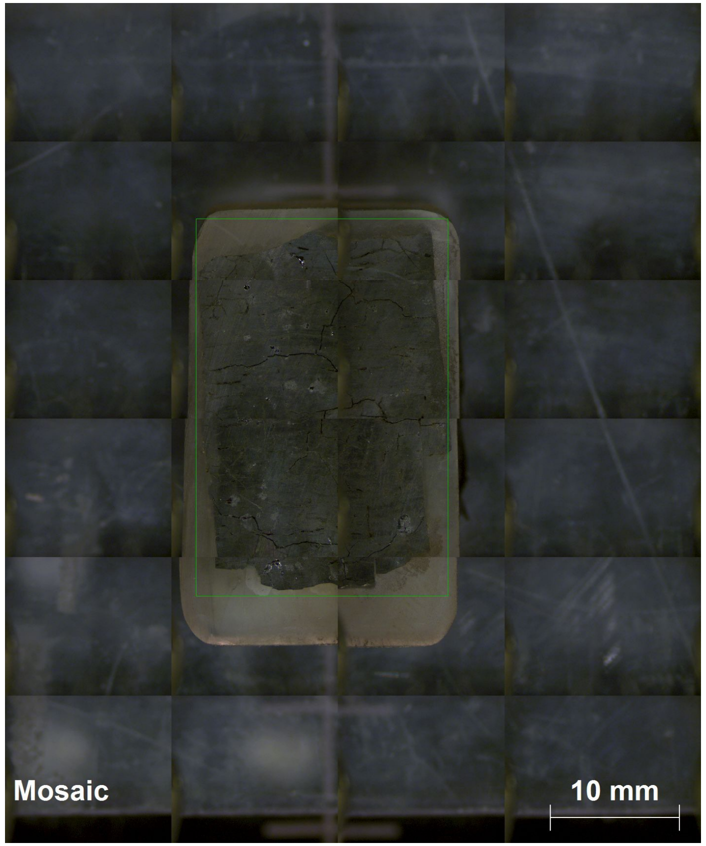


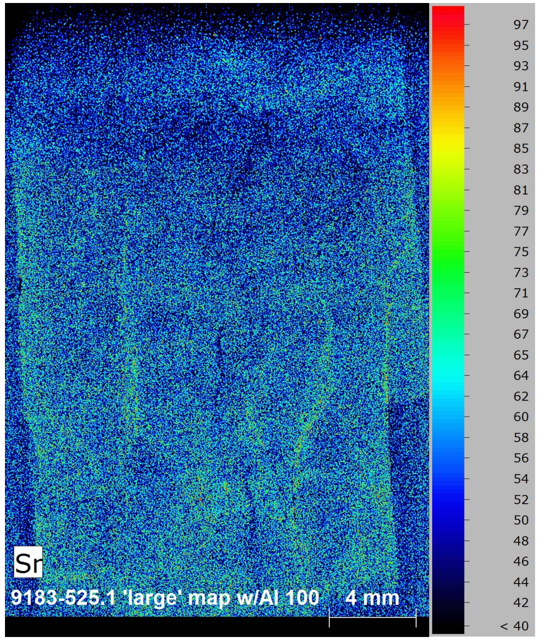
Sr was observed in the sample spectrum, but backscatter is contributing to artificial signal on map.

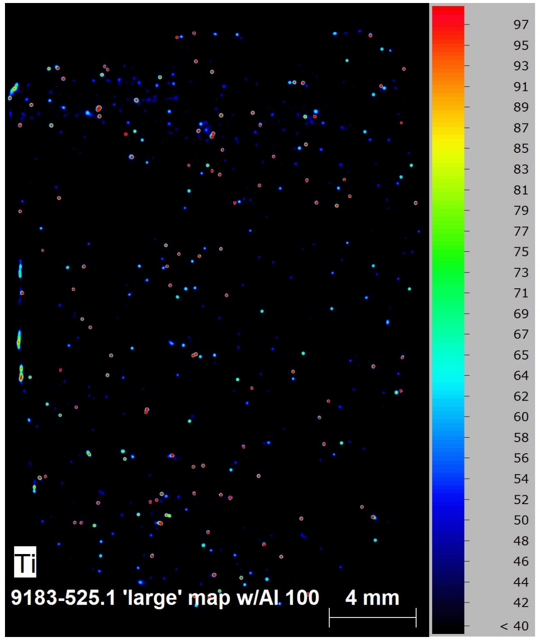












Extraction vs separation vs liberation

- Beneficiation of feed stocks is key
- Solubility (or lack thereof) means REE and many CM require acidic solutions to liberate elements from host mineral phase
  - Options: bioleaching, acidic leaching/digestion, alkali treatment
- For LANL approach, which yields mixed REE Fluorides (of industrial interest)
  - Require acidic feedstock
  - Potential for bioleaching of pyrite to generate sulfuric acid

- Ideals
  - Bioleaching of coal with elevated REE, refinement of LANL method to yield partial separation of REE as fluorides

Hints from nature

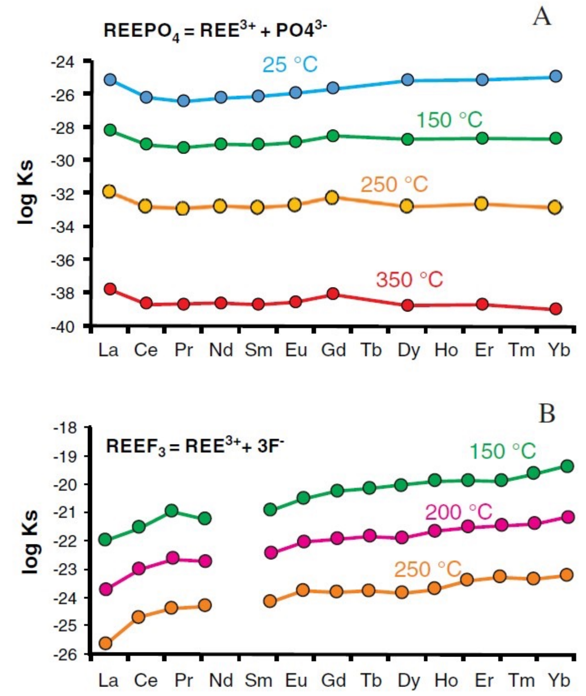
Nature does not use expensive reagents or strong acids to extract and concentrate REE to ore bodies– not much more than hot water and abundant ligands!

Known natural depositional (concentration) mechanisms:

Extremely low solubility of REE phosphates and fluorides. Just traces of F or PO_4 lead to REE precipitation

Solubilities are so low that REE precipitation is preferential against other elements (selective)

Solubilities are retrograde (decrease with increasing temperature): most efficient at higher T



Migdisov et al. *Chem. Geol.* **439**, 13–42 (2016).

Method

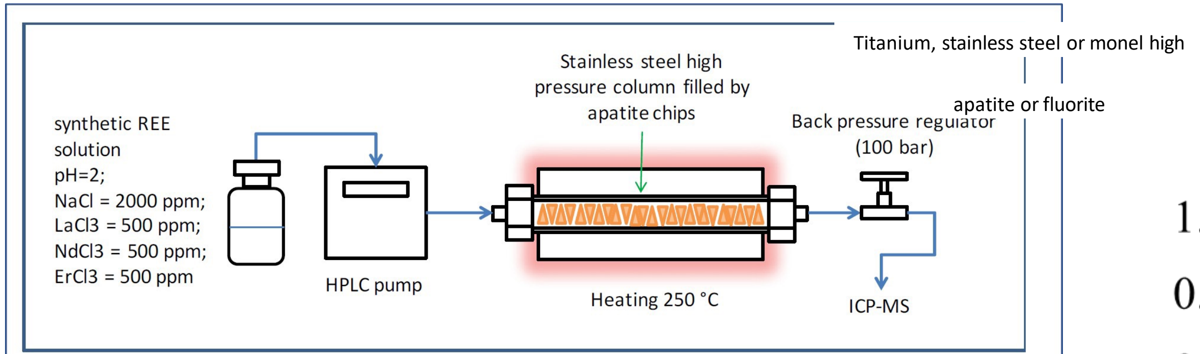
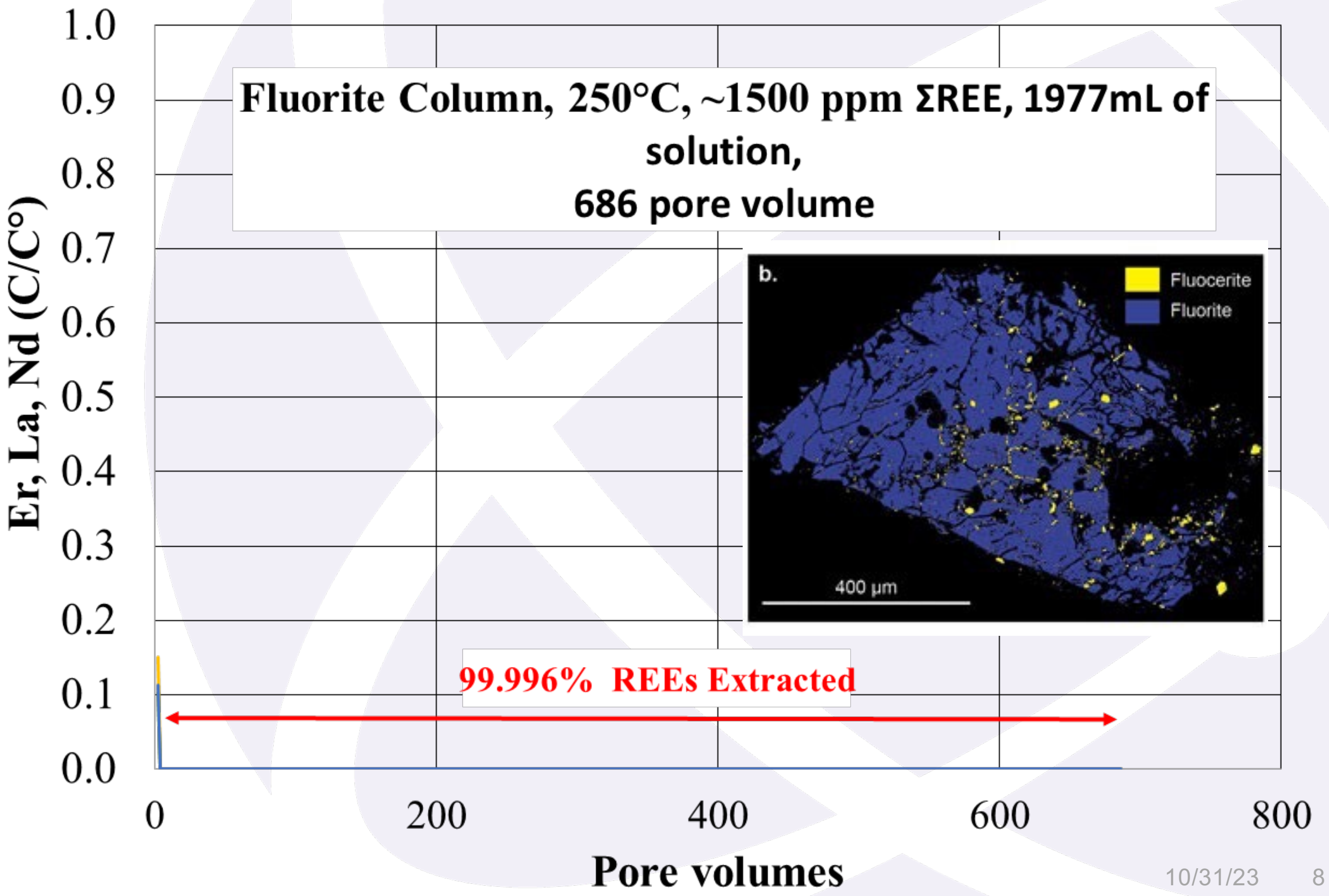
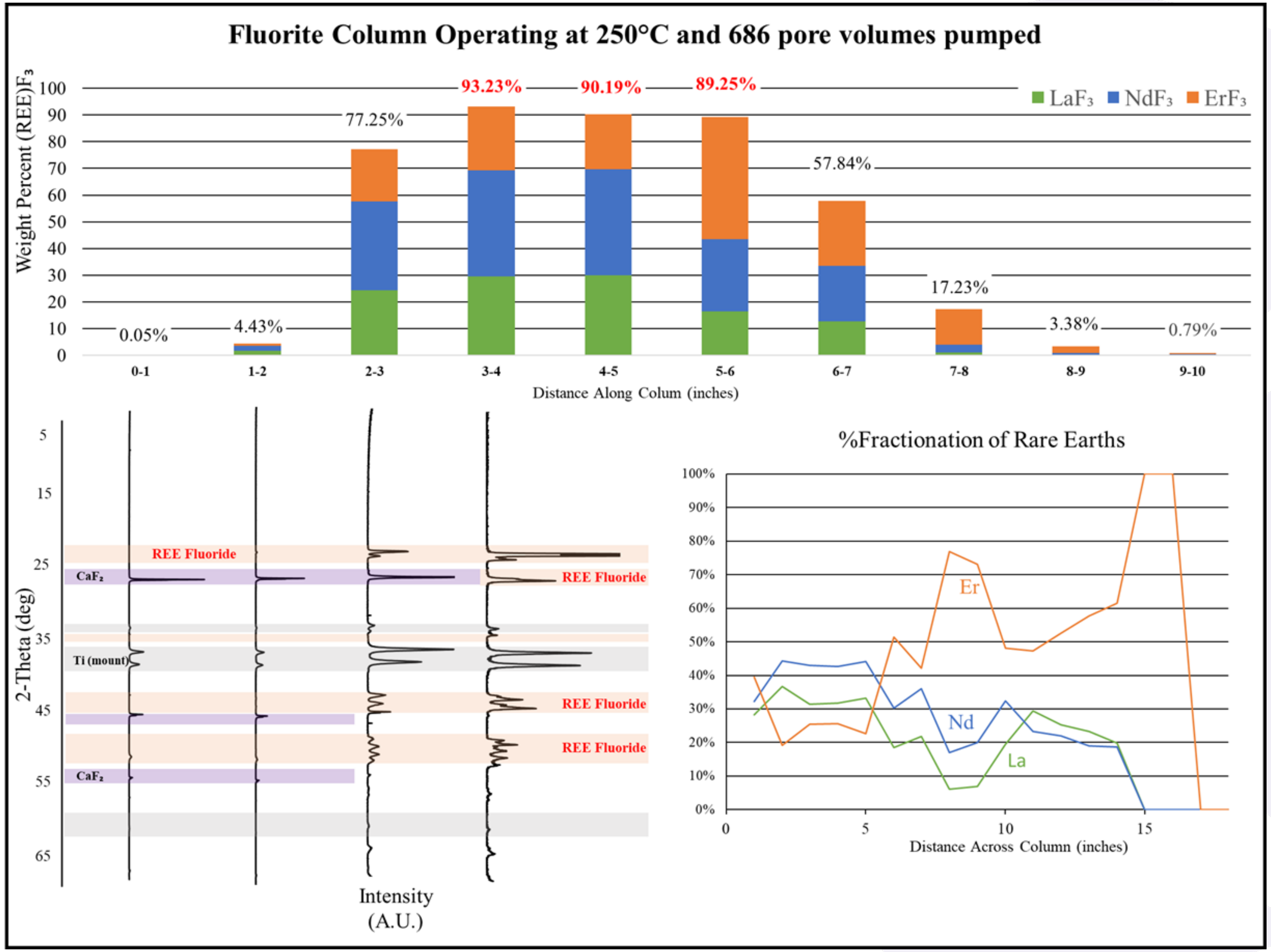


Figure 2. Design of the proof-of-concept experiments mimicking extraction and separation mechanisms illustrated in Figure 1.

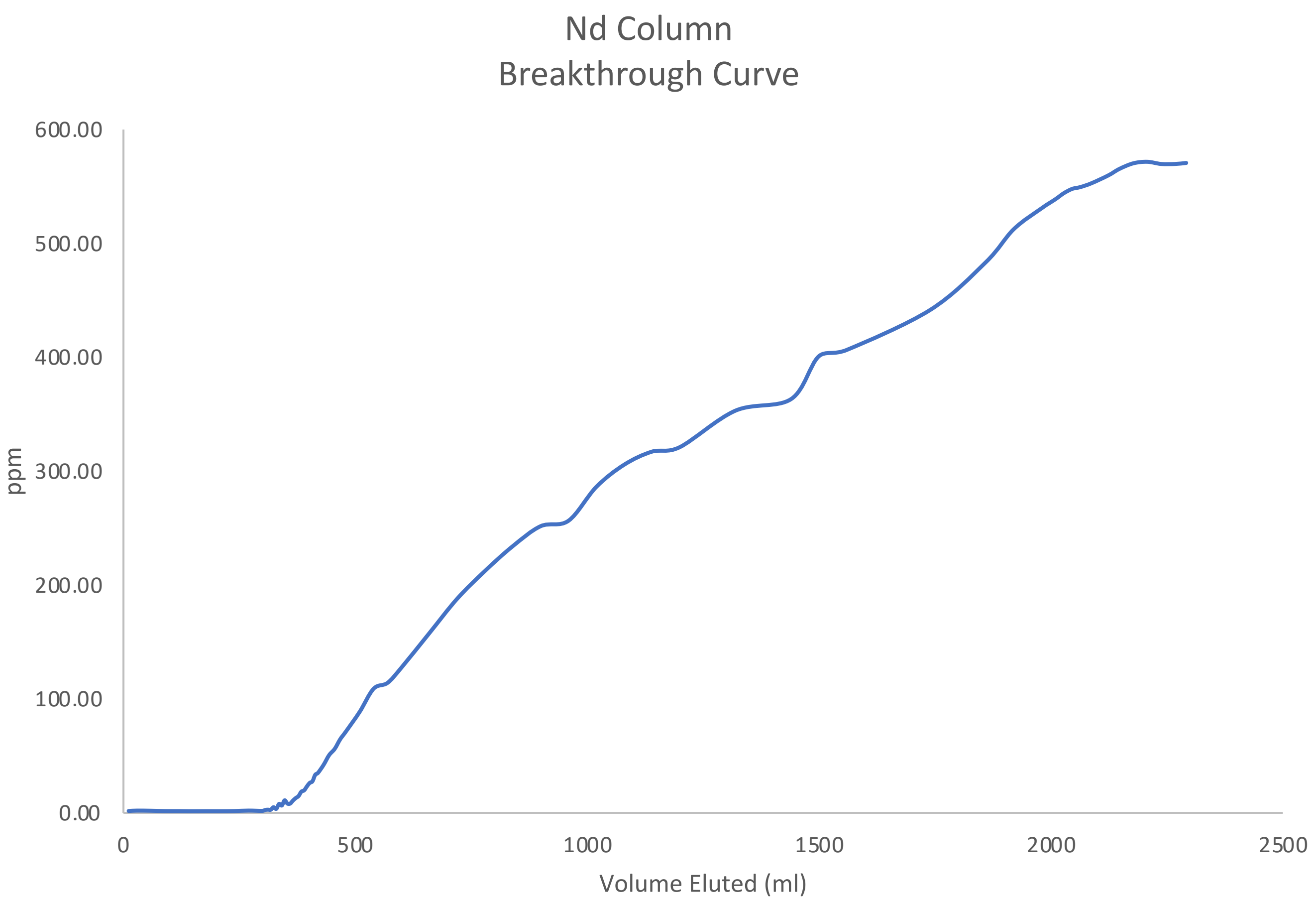


Fluorite (CaF_2) - filled columns



Breakthrough Experiments with Nd

- 22.5 cm length, 0.318 cm ID
- 3 cm quartz chips, 16.5 cm 1:1 mix quartz/fluorite, 3 cm quartz
- 900 psi at 200 °C, 12 ml/hr
- Purposefully difficult conditions – low fluorite volumes and high concentrations



Challenges and next experiments

- Multiple pressure failures. Feared:
  - Clogging of column due to volumetric expansion of fluorite during cracking and reprecipitation.
  - Had also feared linked to use of sulfate solution, but appears to not be cause.
  - Root cause was multiple failures of pressure controllers. Trying new brands.
- Similar test to Nd-breakthrough test to check for REE mass dependence

REE Fluoride Uses

- Solid powder lubricants in high temperature environments
- Nanocrystals and nanocoatings
- Anhydrous fluorides are precursor to oxide preparation
- Extraction of metals from molten RRE-fluorides
- Fiber optics
- Polishing

GGRB Value Added Products/Exploration

- Low-cost solar panels from pyrite due to its semiconductor properties and data storage
  - Jeff Walter et al.,Voltage-induced ferromagnetism in a diamagnet.Sci. Adv.6, eabb7721(2020).DOI:10.1126/sciadv.abb7721
- Pyrite as anode in lithium batteries
  - Harneet Kaur, Ruiyuan Tian, Ahin Roy, Mark McCrystall, Dominik Valter Horvath, Guillermo Lozano Onrubia, Ross Smith, Manuel Ruether, Aideen Griffin, Claudia Backes, Valeria Nicolosi, and Jonathan N. Coleman ACS Nano 2020 14 (10), 13418-13432 DOI: 10.1021/acsnano.0c05292
- U and Th byproducts from REE separation
- Nuclear grade fuels and other extractants from monazite sands
- REE and U/Th from phsosphate deposits (slrry and phospogyrosum)
- Coal to carbon fibers from coal tar pitch (important for potential Wyoming nuclear future)
- Resins from carbon fines
  - Miller, D., Hupka, J., Halbe, D., Nalaskowski, J., & Liu, N. (1997). Recovery of fossil resin from coal fines. Fizykochemiczne Problemy Mineralurgii, 211-220.
- REE and other CM from waste streams from phosphate production
- REE and other CM from U ISR solutions

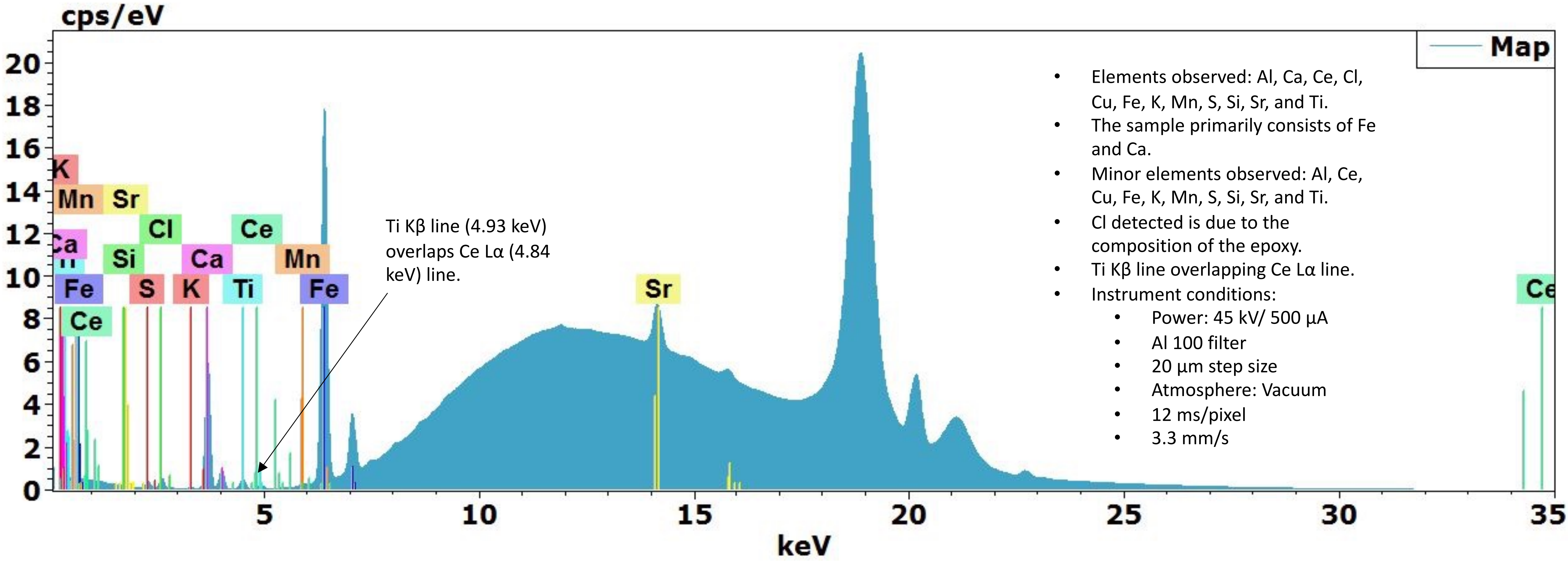
Characterization Methods

Samples Received (to be)

- Coal
- Black sands
- Trona
- Phosphate wastes

Analyses Performed/Planned

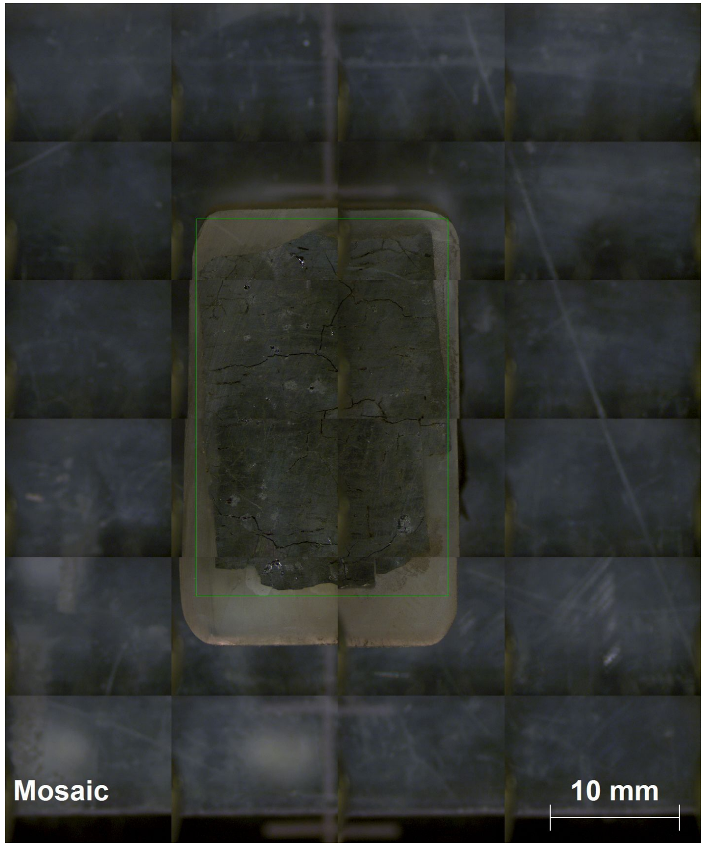
- XRD
- ICP-MS
- Portable XRF
- Micro XRF
- Raman Spectroscopy

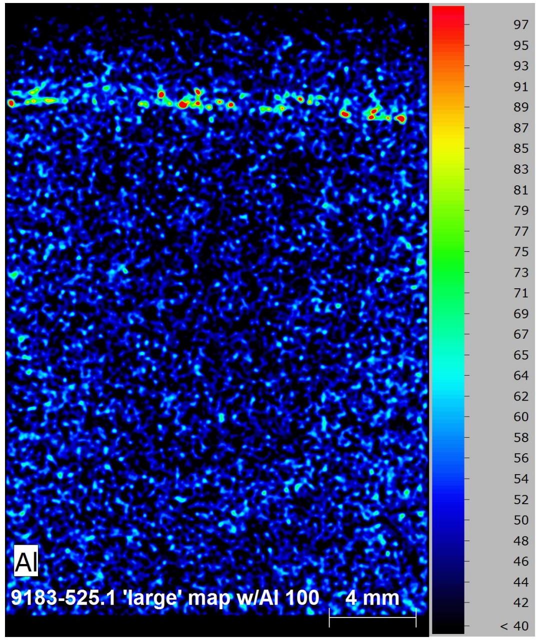


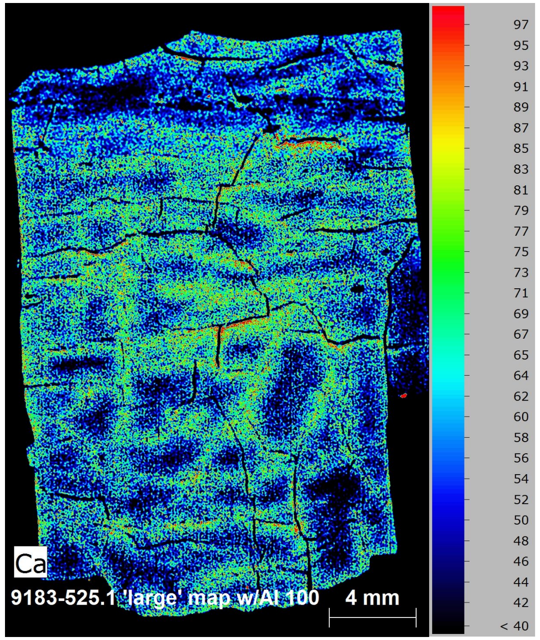
- Elements observed: Al, Ca, Ce, Cl, Cu, Fe, K, Mn, S, Si, Sr, and Ti.
- The sample primarily consists of Fe and Ca.
- Minor elements observed: Al, Ce, Cu, Fe, K, Mn, S, Si, Sr, and Ti.
- Cl detected is due to the composition of the epoxy.
- Ti Kβ line overlapping Ce Lα line.
- Instrument conditions:
  - Power: 45 kV/ 500 µA
  - Al 100 filter
  - 20 µm step size
  - Atmosphere: Vacuum
  - 12 ms/pixel
  - 3.3 mm/s

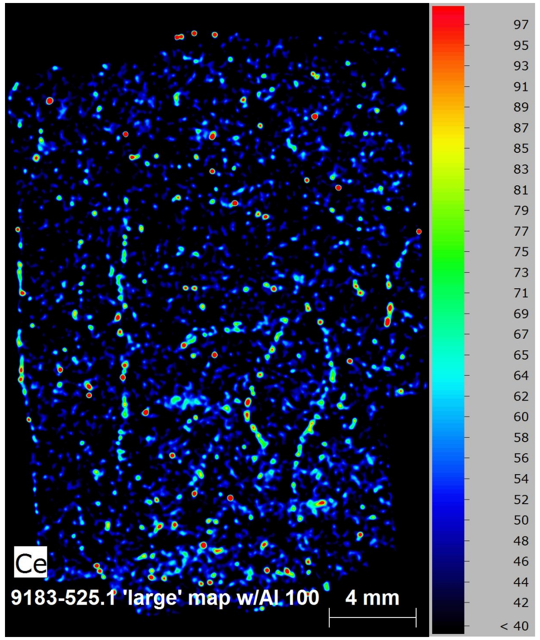
Preliminary Results 3/16/23
Kate McIntosh
Oscar Duarte

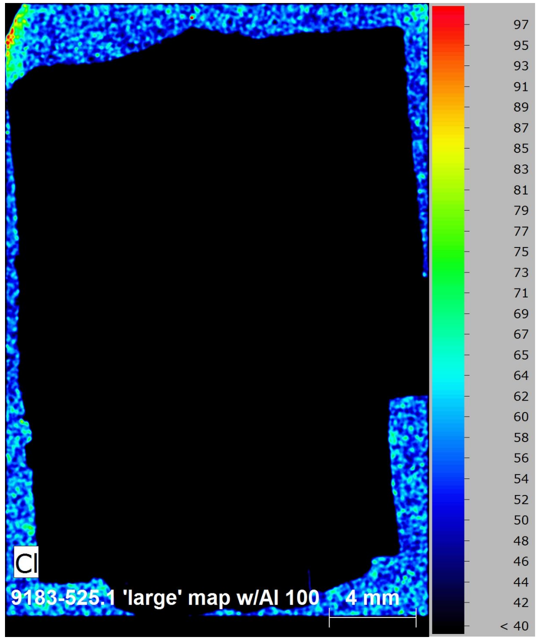
Last ~1 mm of map is missing due to the instrument computer running out of RAM

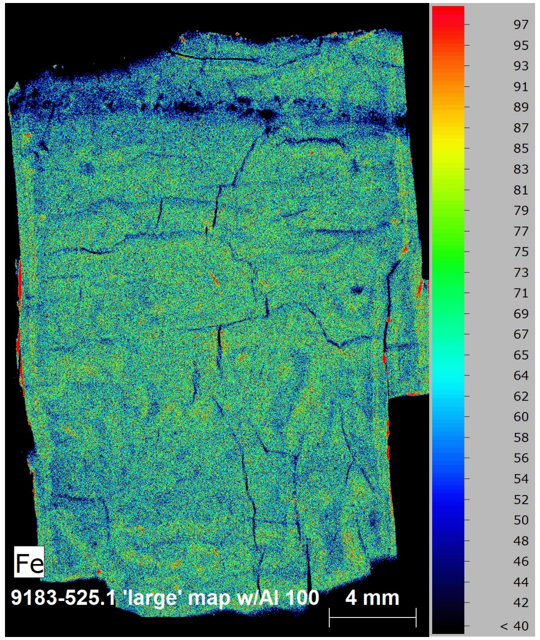


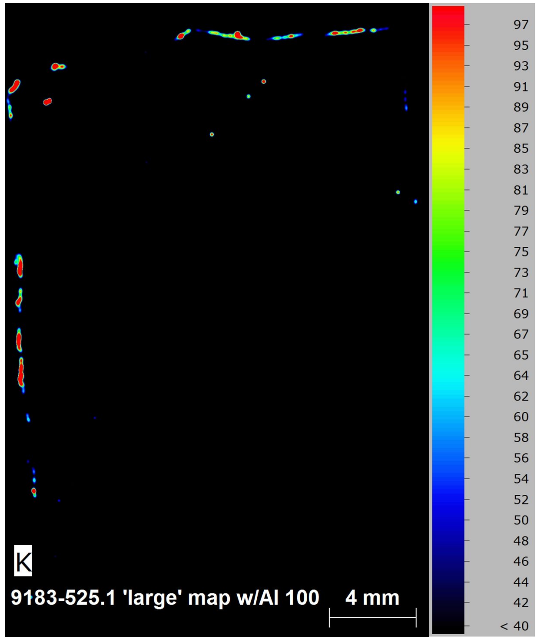






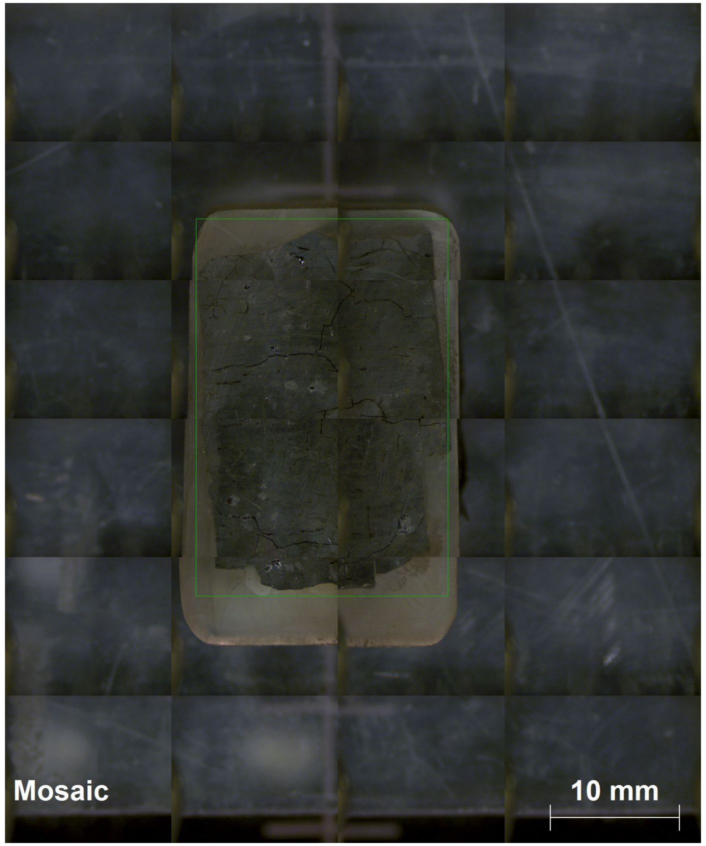


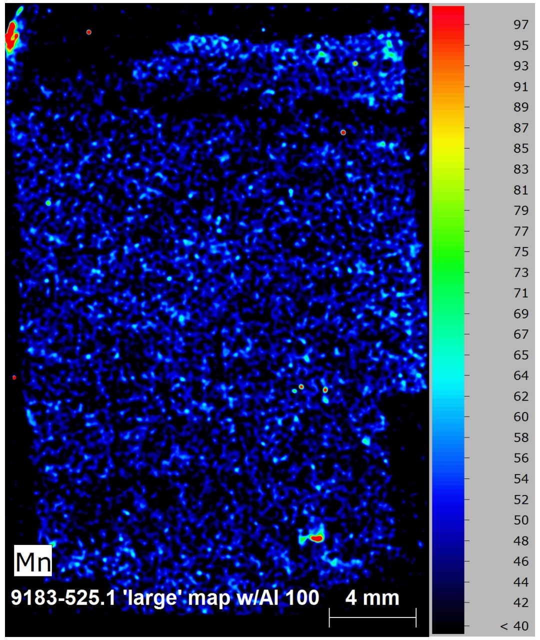


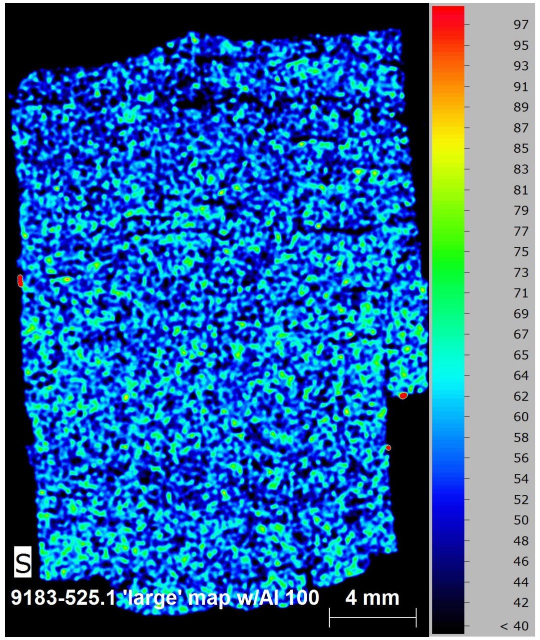


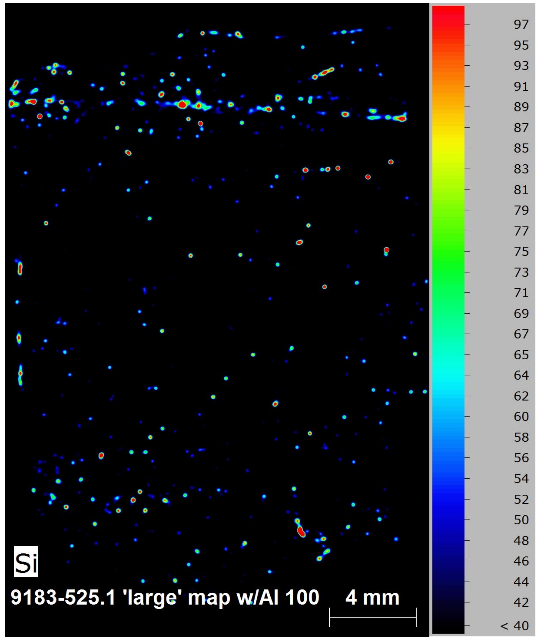
Kate McIntosh
Oscar Duarte

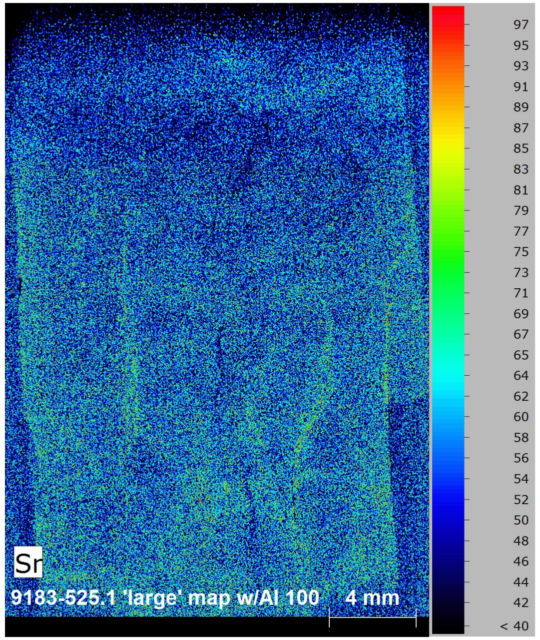
Sr was observed in the sample spectrum, but backscatter is contributing to artificial signal on map.

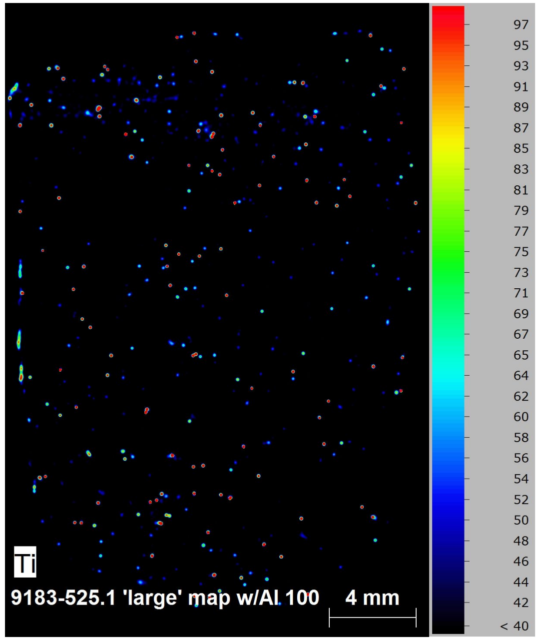












Extraction vs separation vs liberation

- Beneficiation of feed stocks is key
- Solubility (or lack thereof) means REE and many CM require acidic solutions to liberate elements from host mineral phase
  - Options: bioleaching, acidic leaching/digestion, alkali treatment
- For LANL approach, which yields mixed REE Fluorides (of industrial interest)
  - Require acidic feedstock
  - Potential for bioleaching of pyrite to generate sulfuric acid

- Ideals
  - Bioleaching of coal with elevated REE, refinement of LANL method to yield partial separation of REE as fluorides

Hints from nature

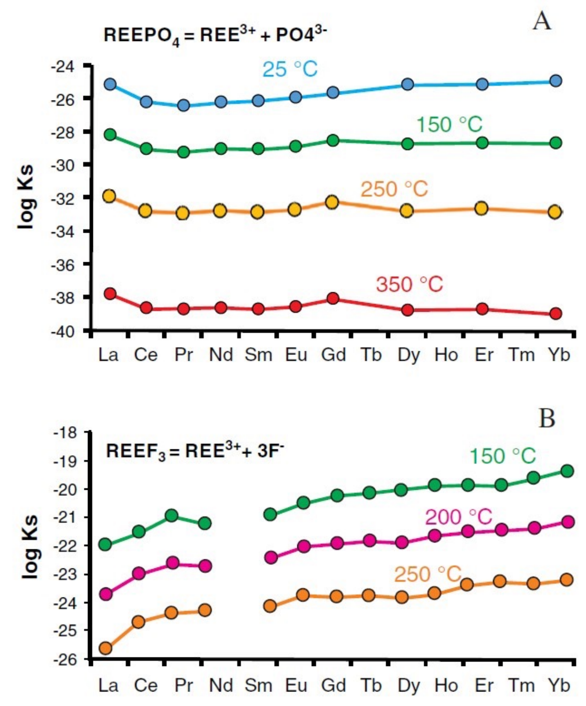
Nature does not use expensive reagents or strong acids to extract and concentrate REE to ore bodies– not much more than hot water and abundant ligands!

Known natural depositional (concentration) mechanisms:

Extremely low solubility of REE phosphates and fluorides. Just traces of F or PO_4 lead to REE precipitation

Solubilities are so low that REE precipitation is preferential against other elements (selective)

Solubilities are retrograde (decrease with increasing temperature): most efficient at higher T



Migdisov et al. *Chem. Geol.* **439**, 13–42 (2016).

Method

Titanium, stainless steel or monel high

apatite or fluorite

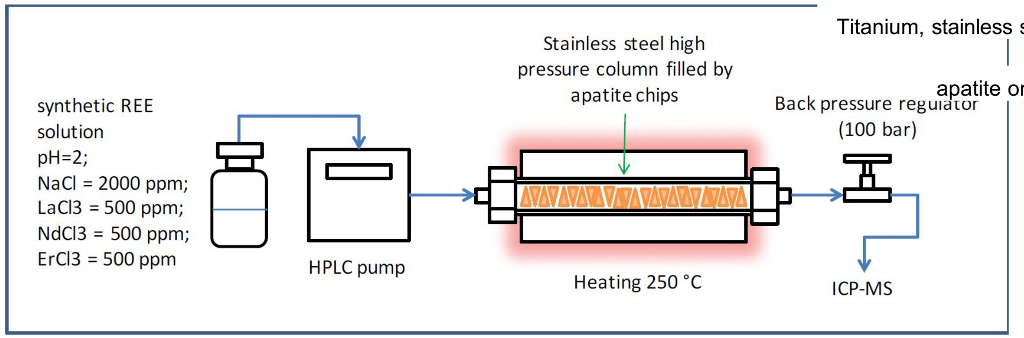
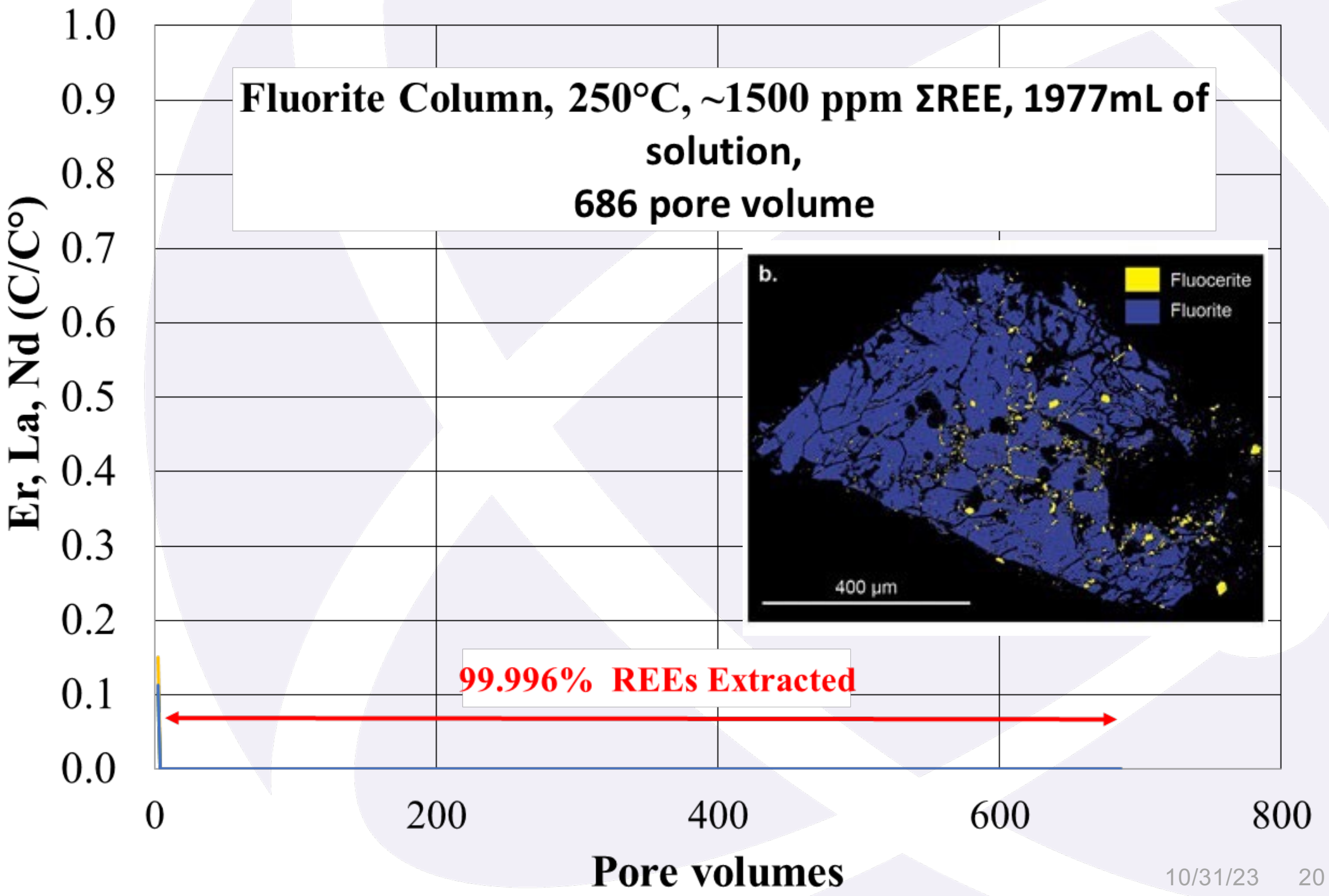
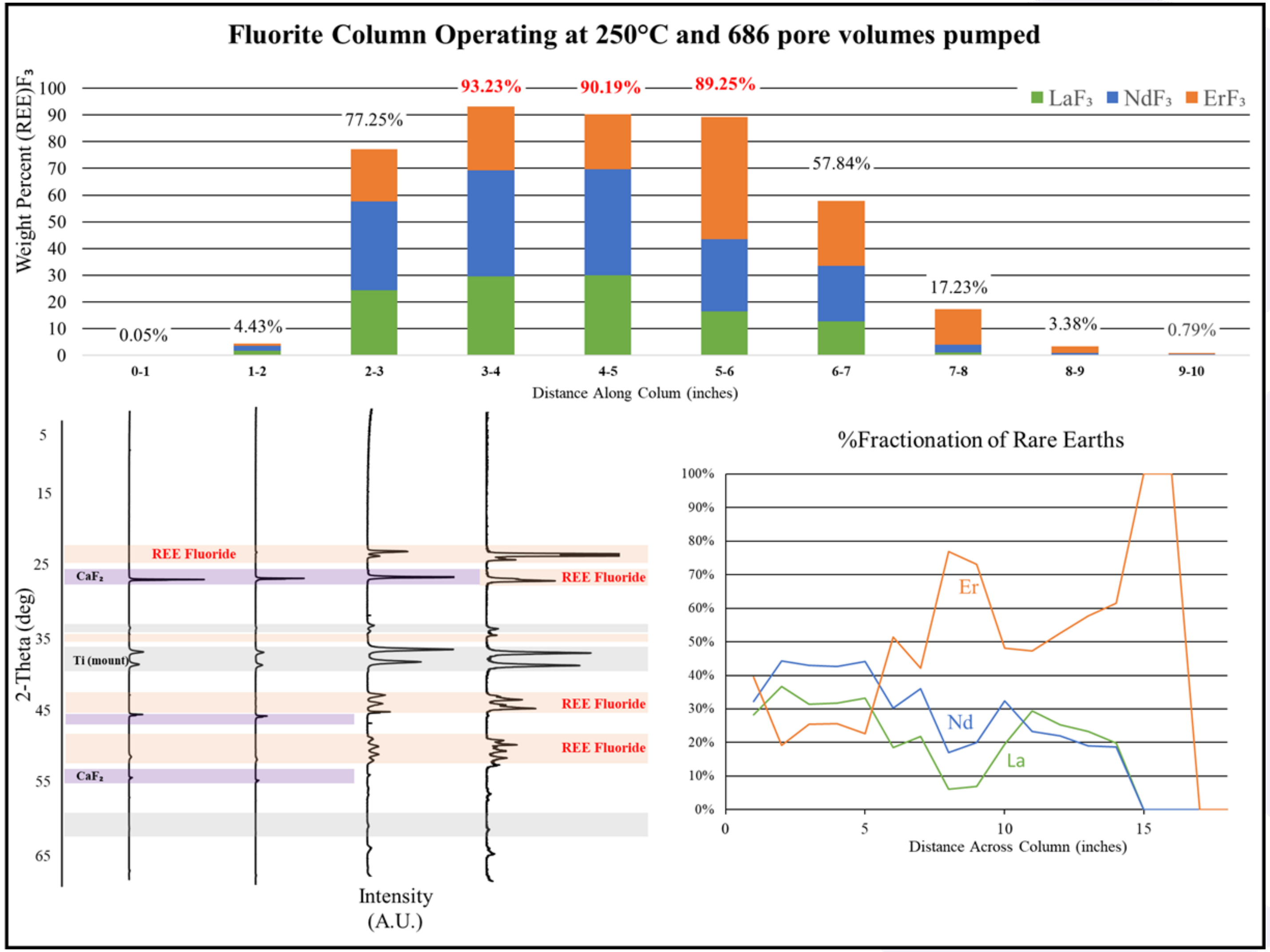


Figure 2. Design of the proof-of-concept experiments mimicking extraction and separation mechanisms illustrated in Figure 1.

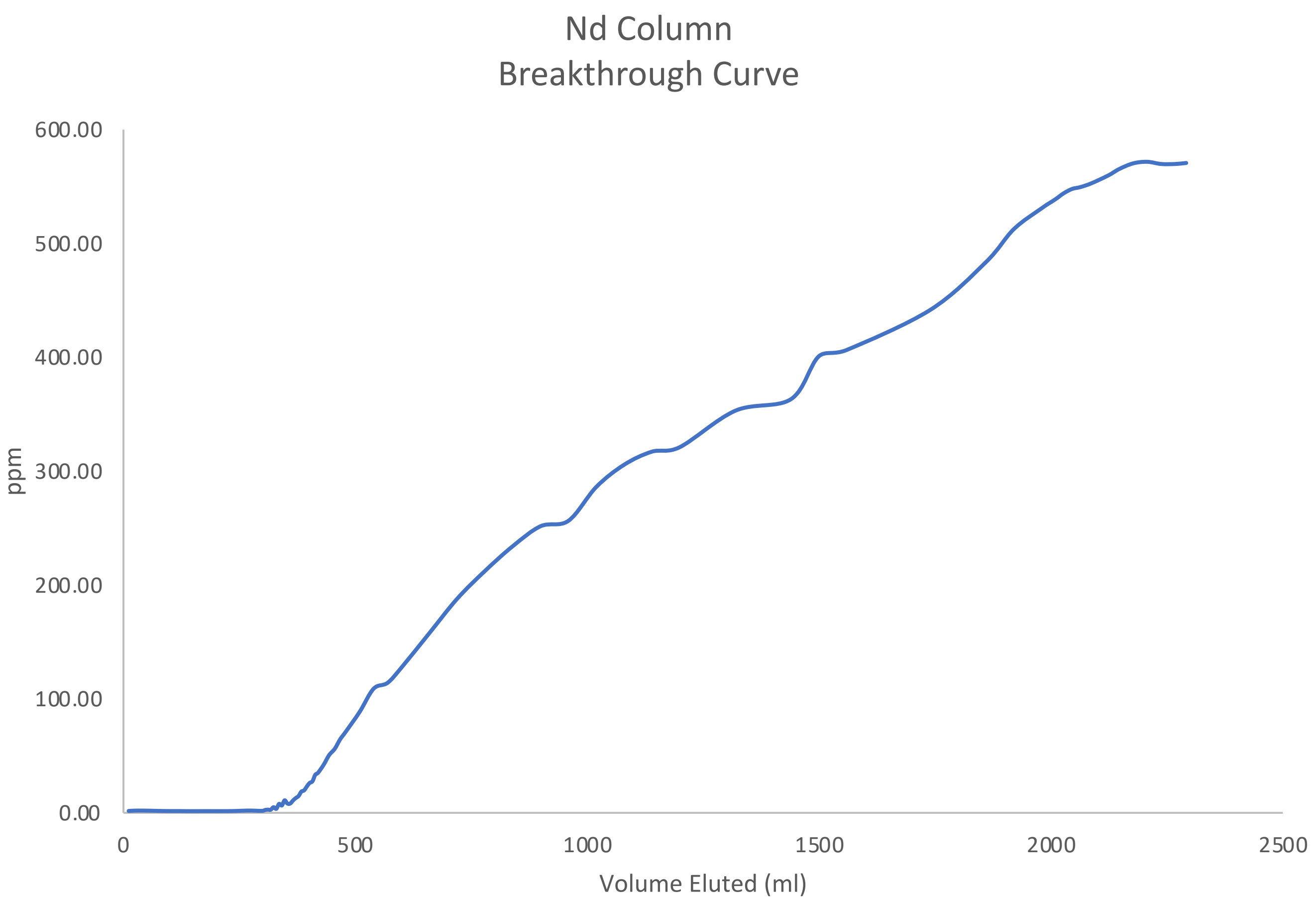


Fluorite (CaF_2) - filled columns



Breakthrough Experiments with Nd

- 22.5 cm length, 0.318 cm ID
- 3 cm quartz chips, 16.5 cm 1:1 mix quartz/fluorite, 3 cm quartz
- 900 psi at 200 °C, 12 ml/hr
- Purposefully difficult conditions – low fluorite volumes and high concentrations



Challenges and next experiments

- Multiple pressure failures. Feared:
  - Clogging of column due to volumetric expansion of fluorite during cracking and reprecipitation.
  - Had also feared linked to use of sulfate solution, but appears to not be cause.
  - Root cause was multiple failures of pressure controllers. Trying new brands.
- Similar test to Nd-breakthrough test to check for REE mass dependence

REE Fluoride Uses

- Solid powder lubricants in high temperature environments
- Nanocrystals and nanocoatings
- Anhydrous fluorides are precursor to oxide preparation
- Extraction of metals from molten RRE-fluorides
- Fiber optics
- Polishing

GGRB Value Added Products/Exploration

- Low-cost solar panels from pyrite due to its semiconductor properties and data storage
  - Jeff Walter et al.,Voltage-induced ferromagnetism in a diamagnet.Sci. Adv.6, eabb7721(2020).DOI:10.1126/sciadv.abb7721
- Pyrite as anode in lithium batteries
  - Harneet Kaur, Ruiyuan Tian, Ahin Roy, Mark McCrystall, Dominik Valter Horvath, Guillermo Lozano Onrubia, Ross Smith, Manuel Ruether, Aideen Griffin, Claudia Backes, Valeria Nicolosi, and Jonathan N. Coleman ACS Nano 2020 14 (10), 13418-13432 DOI: 10.1021/acsnano.0c05292
- U and Th byproducts from REE separation
- Nuclear grade fuels and other extractants from monazite sands
- REE and U/Th from phsosphate deposits (slrry and phospogyrosum)
- Coal to carbon fibers from coal tar pitch (important for potential Wyoming nuclear future)
- Resins from carbon fines
  - Miller, D., Hupka, J., Halbe, D., Nalaskowski, J., & Liu, N. (1997). Recovery of fossil resin from coal fines. Fizykochemiczne Problemy Mineralurgii, 211-220.
- REE and other CM from waste streams from phosphate production
- REE and other CM from U ISR solutions