# Evaluation of Laser-Based Analysis of Rare Earth Elements in Coal-Related Materials

FWP-FE-781-16-FY17

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U.S. Department of Energy

National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
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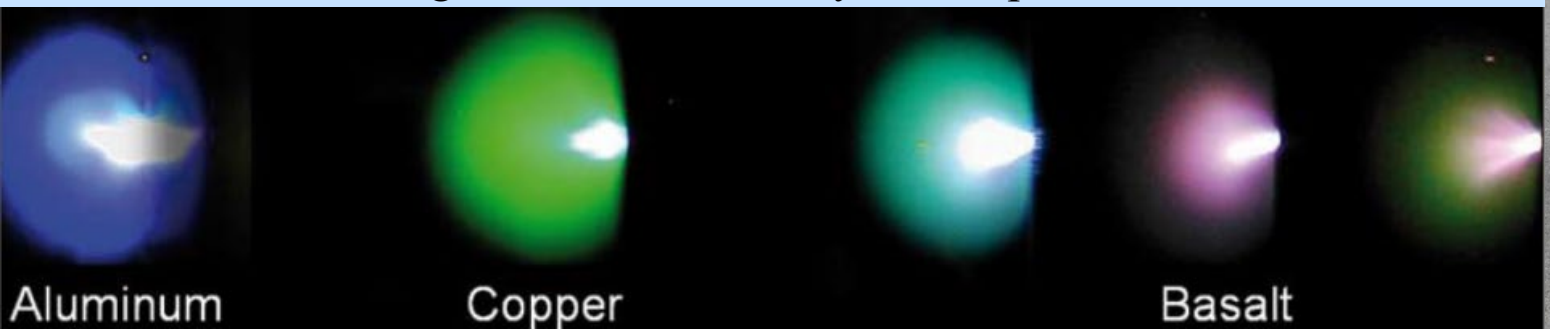
# Project Overview

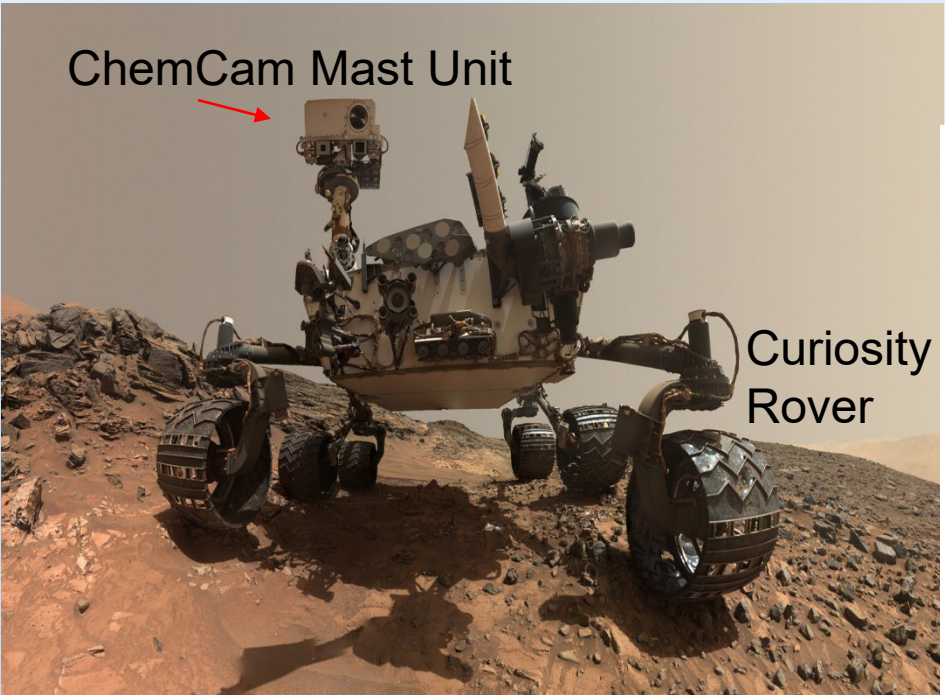
- Project Objectives
  - Demonstrate quantitative elemental analysis of REEs in coal sample in the lab.
    - Using Laser-Induced Breakdown Spectroscopy (LIBS)
  - Demonstrate molecular / mineralogical analysis of REEs in coal samples in the lab.
    - Using Raman Spectroscopy
  - Construct and Demonstrate a Backpack LIBS-Raman Spectroscopy Instrument
    - Lightweight Instrument
    - Capable of LIBS and Raman Spectroscopy
    - Integrated interlock for eye-safe operation



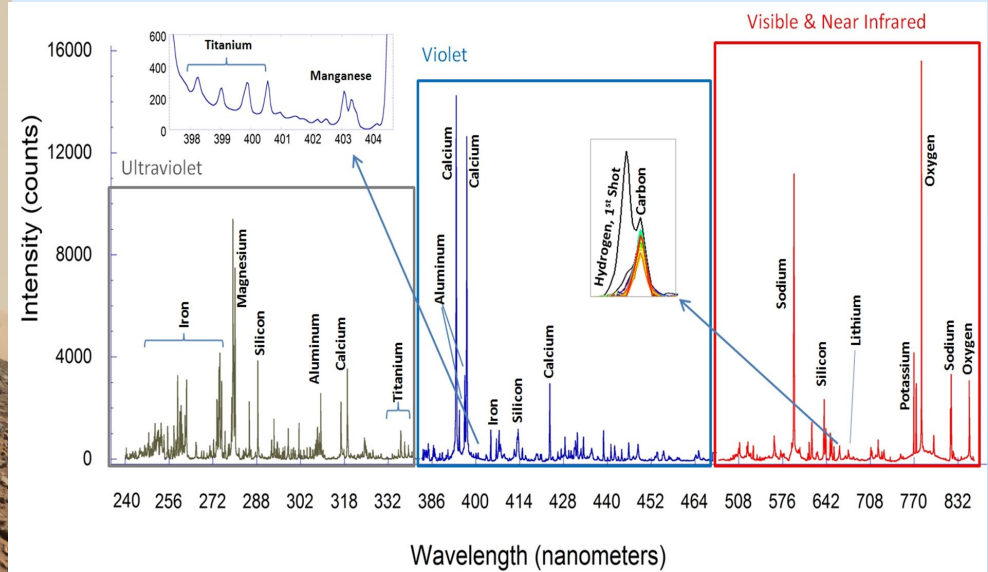

# Technology Background (1/3)

## ChemCam on the NASA Curiosity Mars Rover

- ChemCam
  - Remote Laser-Induced Breakdown Spectrometer
    - Elemental analysis from the mast of the rover to 7 m
    - >900,000 laser shots since landing on August 5, 2012
  - Grayscale Remote Micro-Imager (RMI)



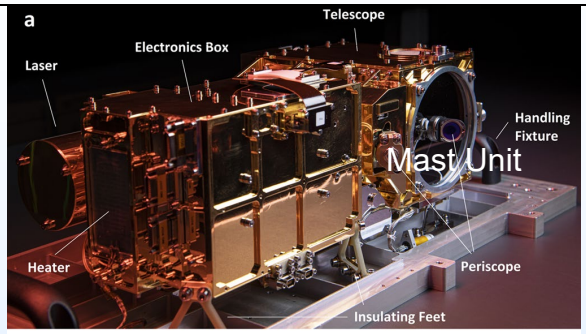

First LIBS Spectrum on Mars

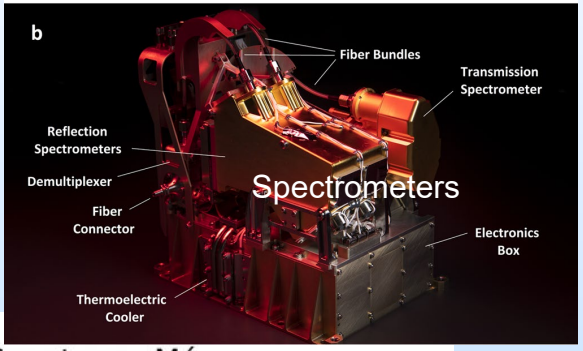


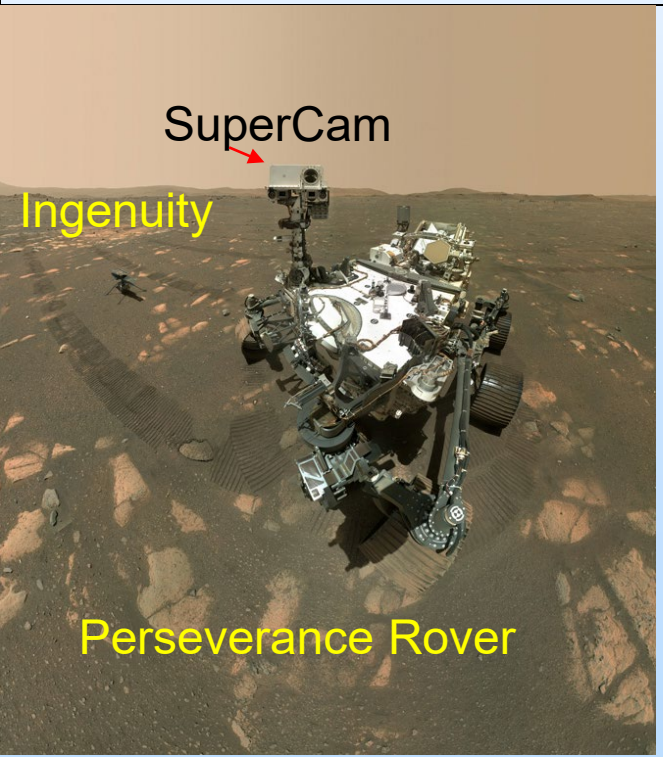
# Technology Background (2/3)

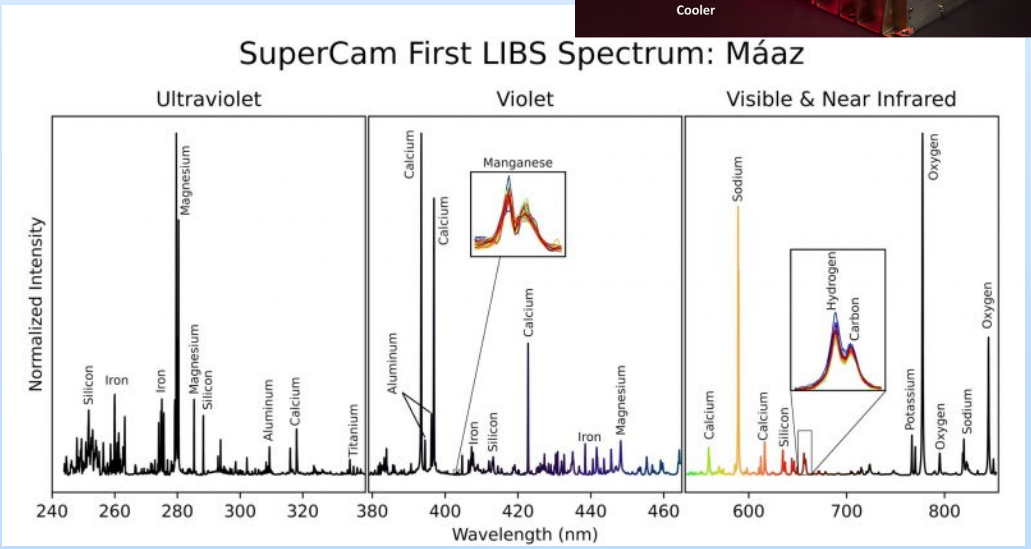
## SuperCam on the NASA Perseverance Mars Rover

**<u>SuperCam</u> – 6 remote analytical techniques, 1 instrument!**
Laser-Induced Breakdown Spectroscopy (LIBS): elemental
Raman Spectroscopy: molecular/mineralogy analysis
Time-Resolved Luminescence Spectroscopy (TRLS): elemental, molecular analysis
Visible and Near Infrared Spectroscopy (VisNIR): molecular/mineralogy analysis
Color Remote Micro-Imager
Microphone



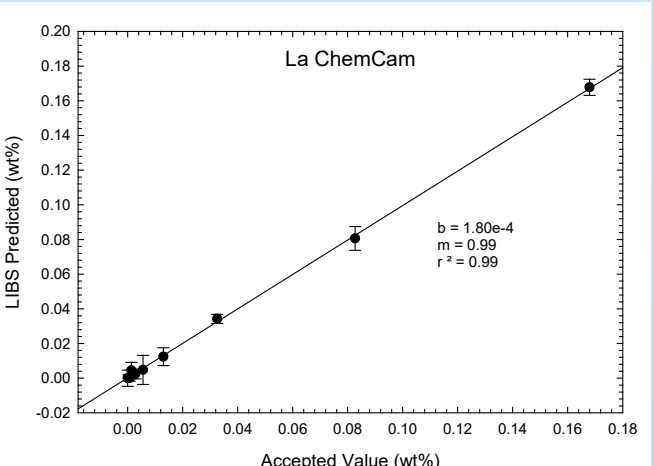



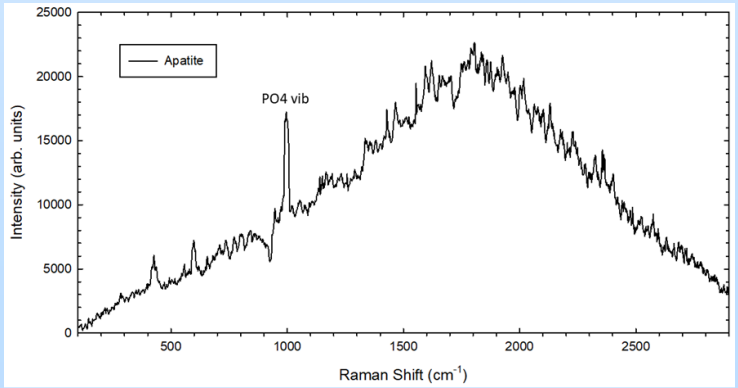



# Technology Background (3/3)

# Technical Approach/Project Scope

- Project Closeout
  - ✓ Demonstrated LIBS quantitative elemental analysis of REEs in coal sample in the lab.
  - ✓ Demonstrated Raman molecular / mineralogical analysis of samples containing REEs.
  - ✓ Constructed and Demonstrate a Backpack LIBS-Raman Spectroscopy Instrument
  - ✓ Field Tested the Instrument




# Progress and Current Status of Project

## Detection Requirements for Instrument Design

**Table 2**

A summary of REY data from the USGS COALQUAL V3.0 database (Concentrations in ppm on a moisture-free whole coal basis).

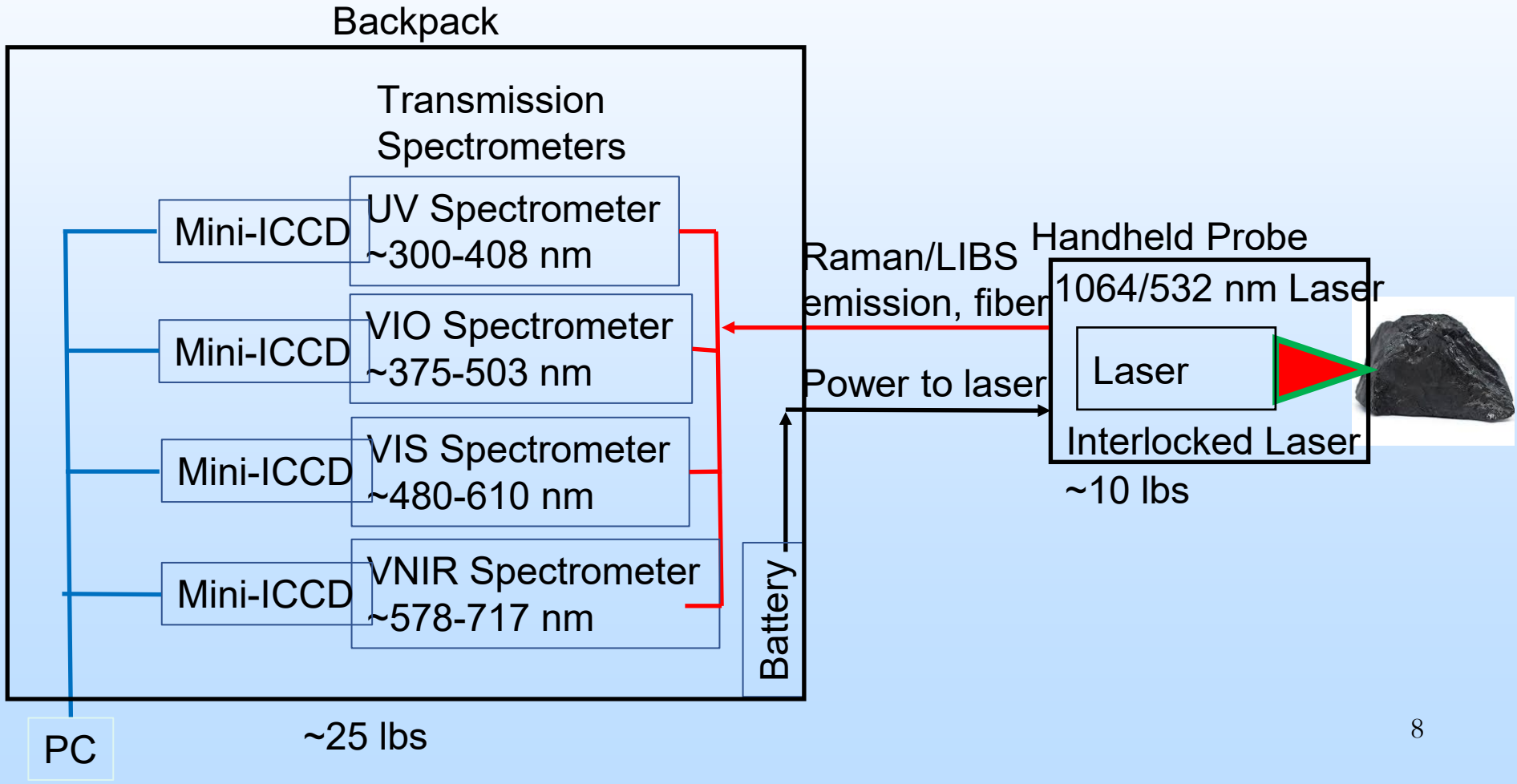
| Element | Include data with L qualifier | | | | Exclude data with L qualifier | | | | Data with L qualifier | | | From Finkelman (1993)[a] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No. of samples | Max | Mean[b] | SD[c] | No. of samples | Max | Mean | SD | No. of samples | %L[d] | Mean | No. of samples | Max | Mean | SD |
| Y | 7585 | 185 | 8.93 | 6.84 | 7560 | 185 | 8.94 | 6.83 | 25 | 0.3 | 4.92 | 7897 | 170 | 8.5 | 6.7 |
| La | 6652 | 236 | 11.70 | 9.42 | 6160 | 236 | 11.19 | 9.06 | 492 | 7 | 18.10 | 6235 | 300 | 12 | 16 |
| Ce | 6081 | 506 | 23.96 | 25.45 | 5557 | 506 | 20.69 | 17.42 | 524 | 9 | 58.68 | 5525 | 700 | 21 | 28 |
| Pr | 5601 | 110 | 10.21 | 8.33 | 948 | 67.5 | 6.48 | 7.32 | 4653 | 83 | 10.97 | 1533 | 65 | 2.4[e] | n/a[g] |
| Nd | 5946 | 236 | 12.32 | 11.09 | 4303 | 236 | 13.36 | 11.76 | 1643 | 28 | 9.60 | 4749 | 230 | 9.5[f] | n/a |
| Sm | 5588 | 68 | 2.54 | 3.78 | 5103 | 19.9 | 1.94 | 1.42 | 485 | 9 | 8.87 | 5151 | 18 | 1.7 | 1.4 |
| Eu | 5626 | 5.83 | 0.42 | 0.28 | 5270 | 5.83 | 0.43 | 0.28 | 356 | 6 | 0.32 | 5266 | 4.8 | 0.4 | 0.33 |
| Gd | 5602 | 39.7 | 2.91 | 2.39 | 1670 | 39.7 | 2.80 | 2.75 | 3932 | 70 | 2.96 | 2376 | 39 | 1.8[f] | n/a |
| Tb | 5619 | 47 | 1.16 | 3.76 | 4878 | 4.08 | 0.33 | 0.22 | 741 | 13 | 6.57 | 5024 | 3.9 | 0.3 | 0.23 |
| Dy | 5607 | 23 | 3.11 | 2.15 | 717 | 19.2 | 3.39 | 2.46 | 4890 | 87 | 3.07 | 1510 | 28 | 1.9 | 2.7 |
| Ho | 5598 | 19 | 1.03 | 1.06 | 351 | 4.59 | 0.75 | 0.56 | 5247 | 94 | 1.05 | 1130 | 4.5 | 0.35[f] | n/a |
| Er | 5603 | 16 | 1.24 | 0.95 | 1070 | 11.2 | 1.54 | 1.08 | 4533 | 81 | 1.17 | 1792 | 11 | 1 | 1.1 |
| Tm | 5603 | 7.7 | 0.63 | 0.48 | 42 | 1.99 | 0.44 | 0.41 | 5561 | 99 | 0.63 | 365 | 1.9 | 0.15[f] | n/a |
| Yb | 7269 | 9.27 | 1.01 | 0.68 | 7222 | 9.27 | 1.02 | 0.68 | 47 | 1 | 0.50 | 7522 | 20 | 0.95[f] | n/a |
| Lu | 5587 | 10.1 | 0.37 | 0.89 | 4945 | 10.1 | 0.16 | 0.24 | 642 | 11 | 1.99 | 5006 | 1.8 | 0.14 | 0.1 |

[a] Data obtained from the NCRDS before the release of the COALQUAL database.
[b] Mean: arithmetic mean.
[c] SD: standard deviation.
[d] Percent of data with L qualifier.
[e] Estimated based on NCRDS and literature data.
[f] Calculated from La and Ce data assuming a smooth chondrite-normalized REE distribution pattern with the exception of Eu.
[g] No data available.

Lin, Soong, and Granite, "Evaluation of trace elements in U.S. coals using the USGS COALQUAL database version 3.0. Part I: Rare earth elements and yttrium (REY)," International Journal of Coal Geology 192 (2018) 1–13

# Progress and Current Status of Project

## Raman-LIBS Backpack Instrument – Block Diagram

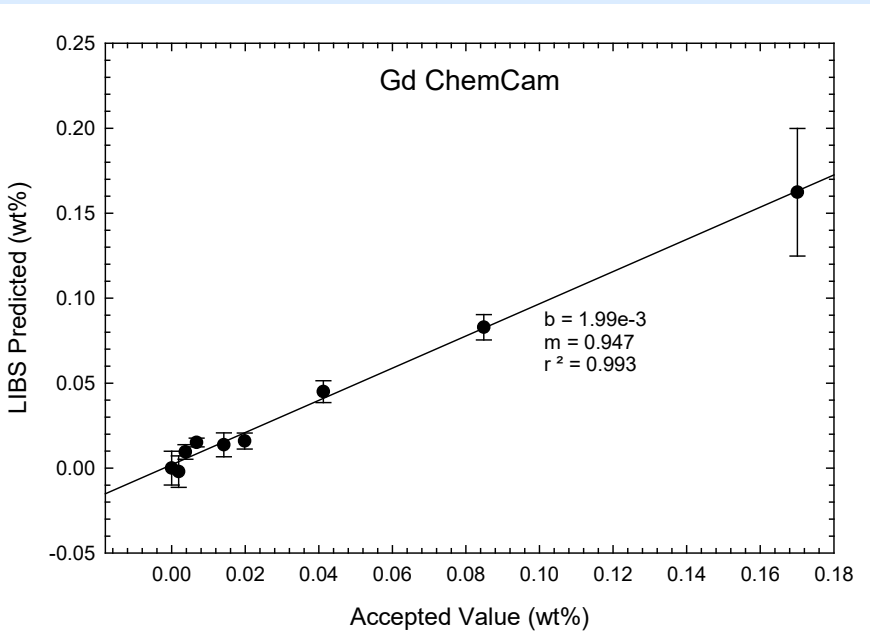


# Progress and Current Status of Project

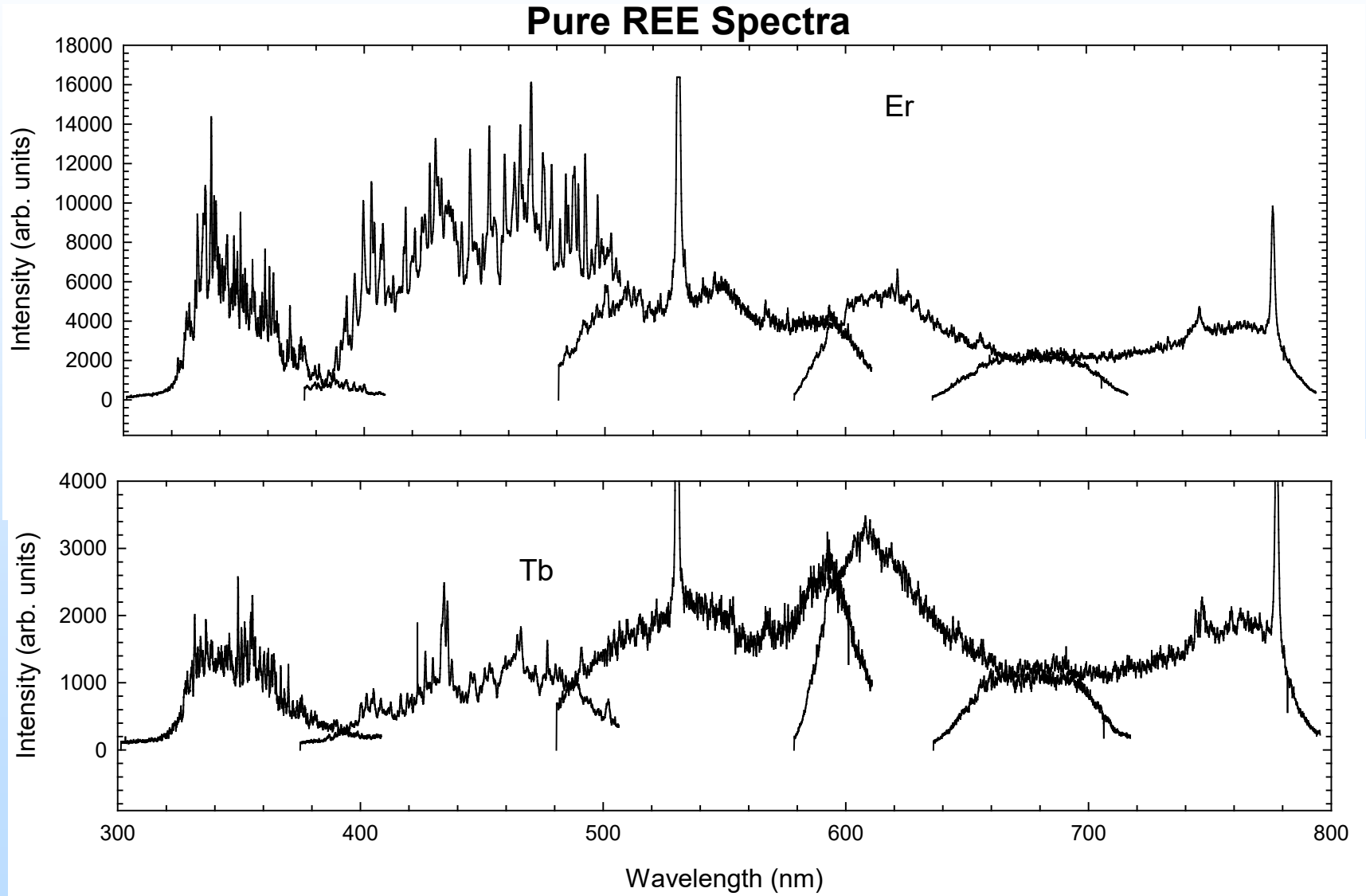
- Complete construction of the backpack instrument

# Progress and Current Status of Project

- Calibrate the Backpack LIBS Raman Instrument
  - Collect LIBS spectral library
  - Recalibrate LIBS elemental analysis
    - Partial Least Squares (PLS) model for each REE doped in a coal sample
    - PyHAT software developed at USGS Flagstaff



# Progress and Current Status of Project



# Progress and Current Status of Project

**REE Calibration Spectra – REEs Doped in Coal Sample**

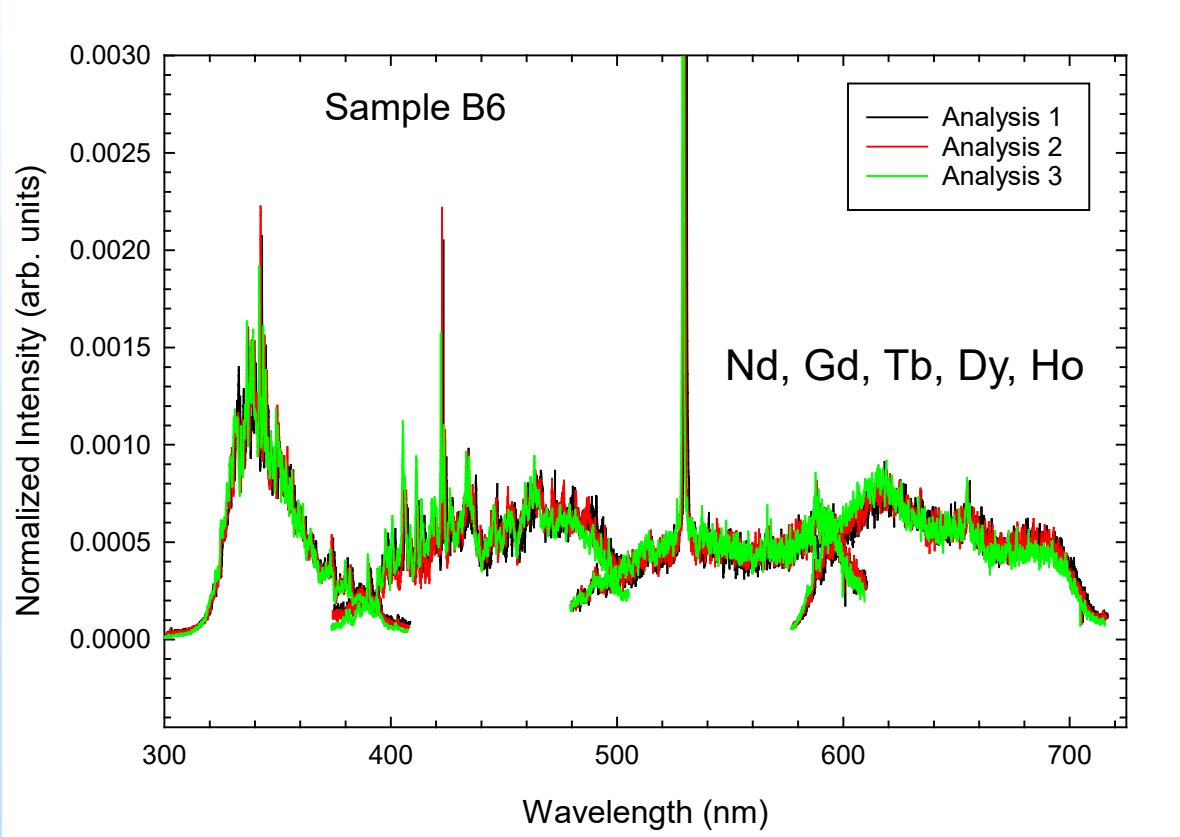
Calibration Procedure

- Sample X1 – add 1st REE
- Sample X2 – dilute X1 and add 2nd REE
- … Sample X5 – dilute X4 and add 5th REE
- Sample X6 to X9 – continue diluting

- Collected 3 sets, each with up to 5 REEs

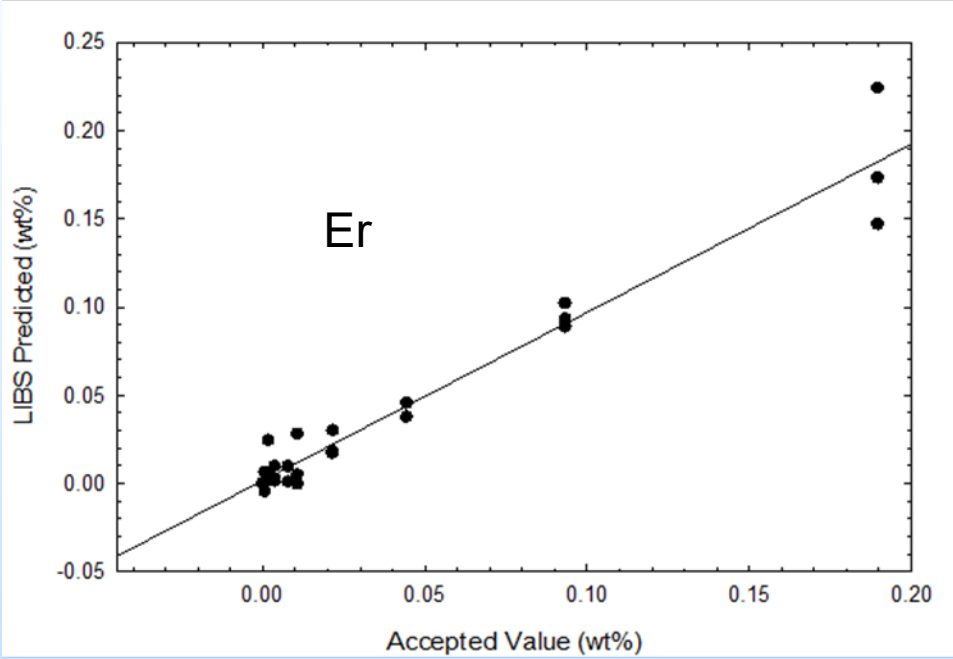
- Normalize the spectra to total emission intensity

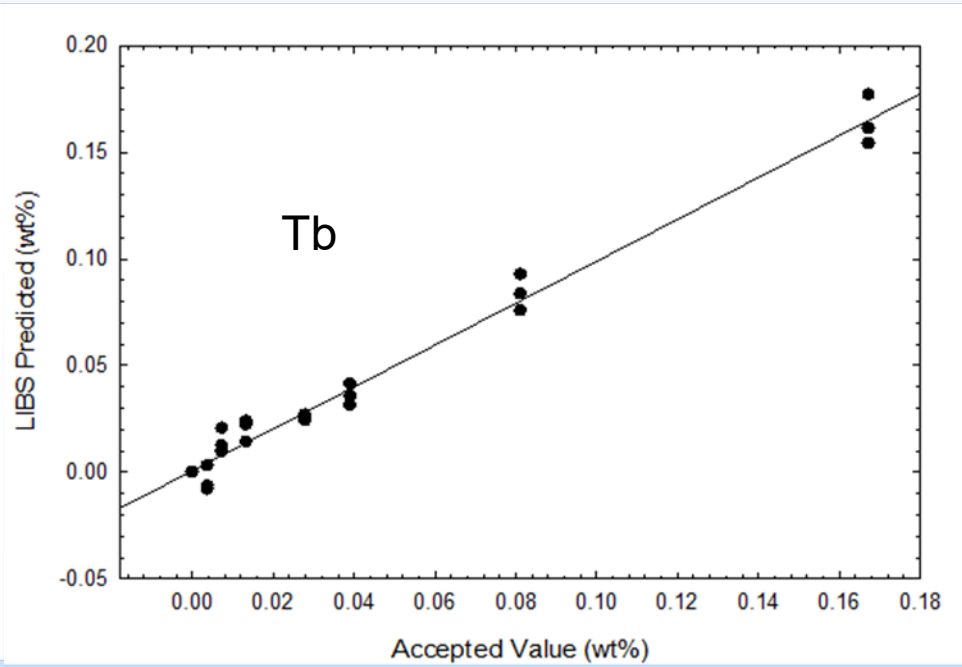
- Develop PLS model for Each REE.



# Progress and Current Status of Project

**Partial Least Squares Quantitative Analysis**



# Progress and Current Status of Project

## Conservative Estimated Detection Limits

| | Requirements (ppm) | | LIBS DL (ppm) | |
|---|---|---|---|---|
| Elements | Max | Mean | Conservative | Likely |
| Y | 185 | 8.94 | Not in study | |
| La | 236 | 11.19 | 100 | 10 |
| Ce | 506 | 20.69 | 150 | 15 |
| Pr | 67.5 | 6.48 | 70 | 5 |
| Nd | 236 | 13.36 | 200 | 10 |
| Sm | 19.9 | 1.94 | 60 | 4 |
| Eu | 5.83 | 0.43 | 50 | 5 |
| Gd | 39.7 | 2.8 | 60 | 5 |
| Tb | 4.08 | 0.33 | 50 | 4 |
| Dy | 19.2 | 3.39 | 20 | 3 |
| Ho | 4.59 | 0.75 | 40 | 1 |
| Er | 11.2 | 1.54 | 20 | 2 |
| Tm | 1.99 | 0.44 | 30 | 2 |
| Yb | 9.27 | 1.02 | 20 | 1 |
| Lu | 10.1 | 0.16 | 20 | 1 |

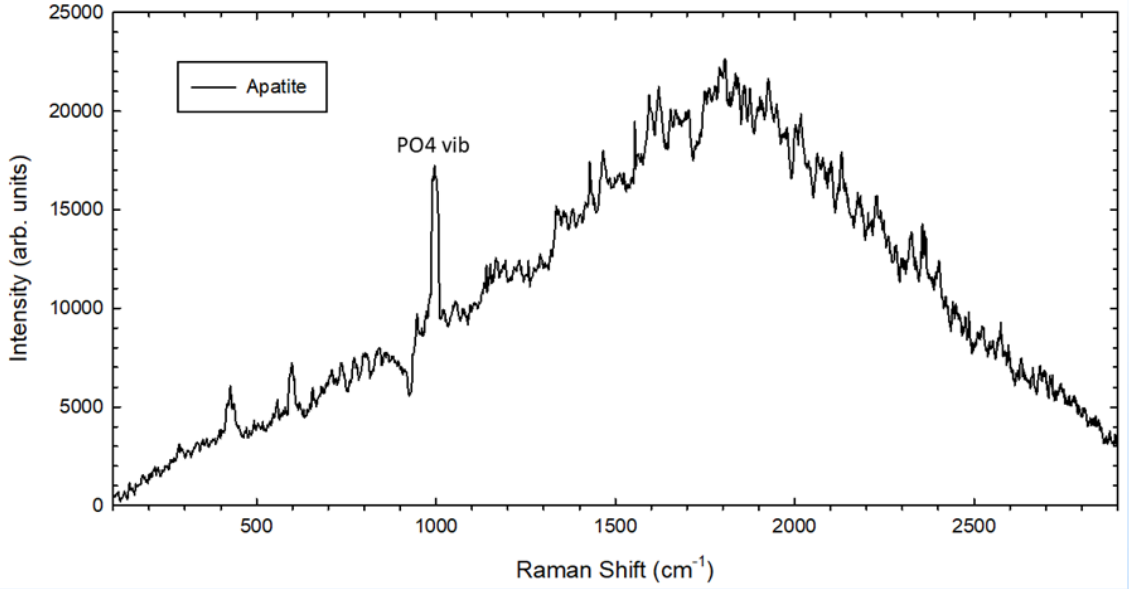
- Design instrument to meet requirements (Lin et al. International Journal of Coal Geology 192 (2018) 1–13)

# Progress and Current Status of Project

Raman Spectrum
- Sensitive to Molecular Vibrations
- Mineralogy determined by Raman Shift

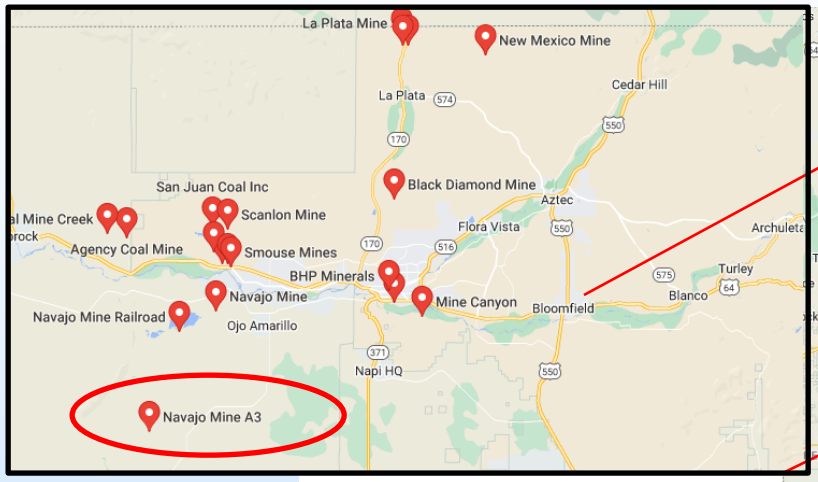
- Determine the molecular framework
  - Phosphates
  - Sulfates
  - Carbonates
  - Oxides
  - Etc…

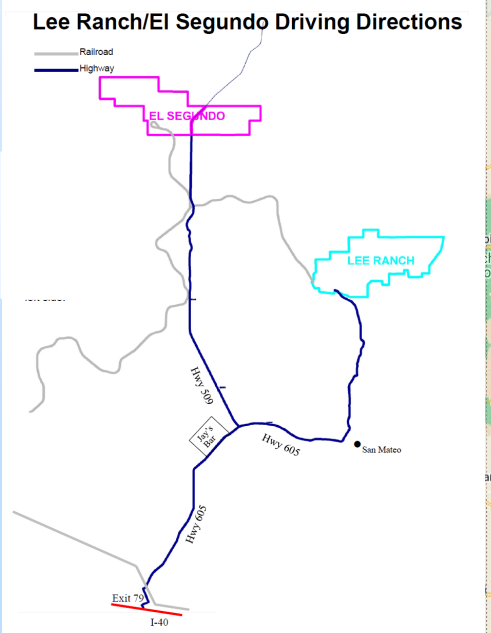
- Help inform on separation process decisions

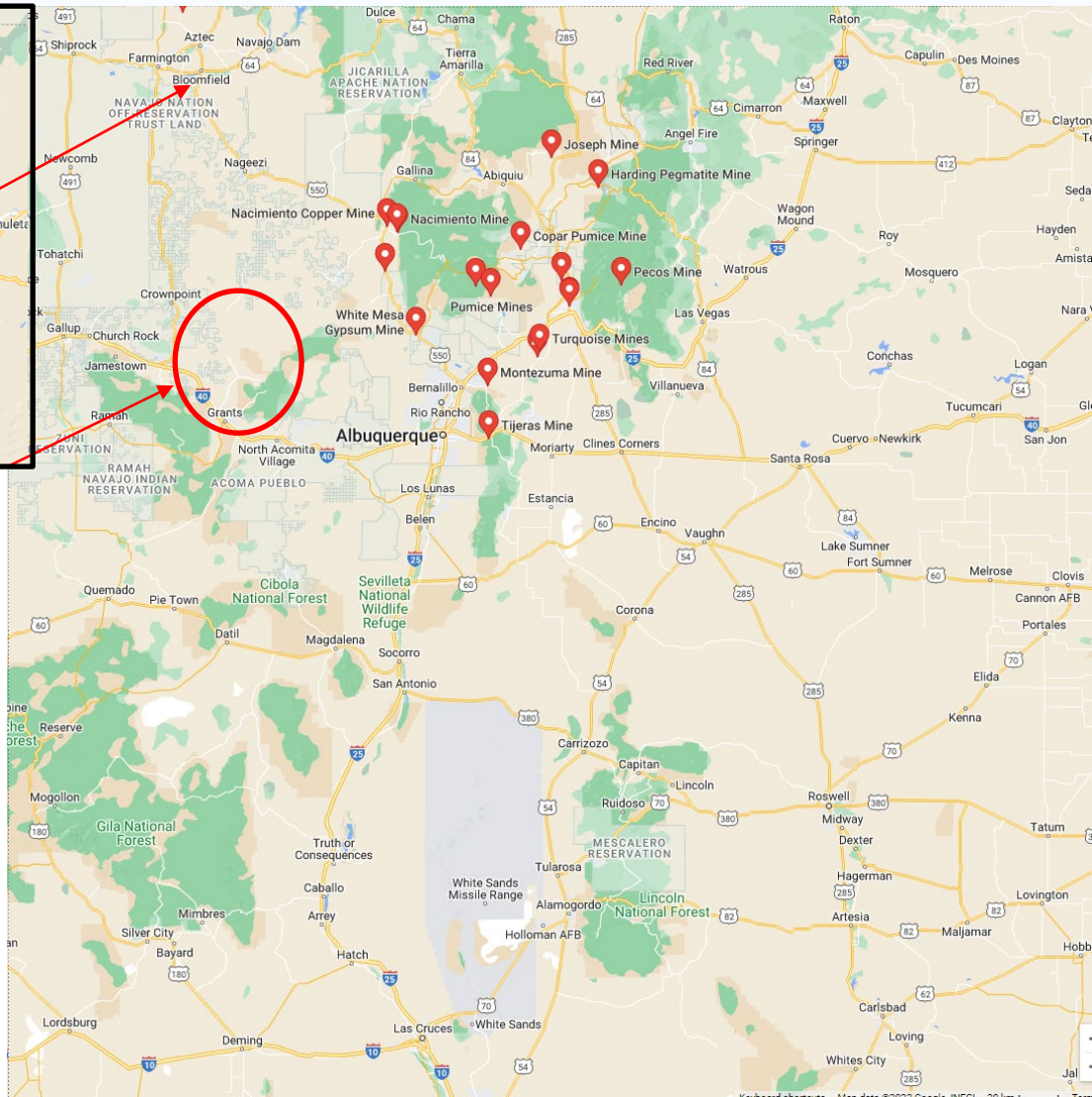



Complementary to LIBS
- LIBS determines REE concentration
- Raman only determines mineralogy/molecular characteristics

# Progress and Current Status of Project

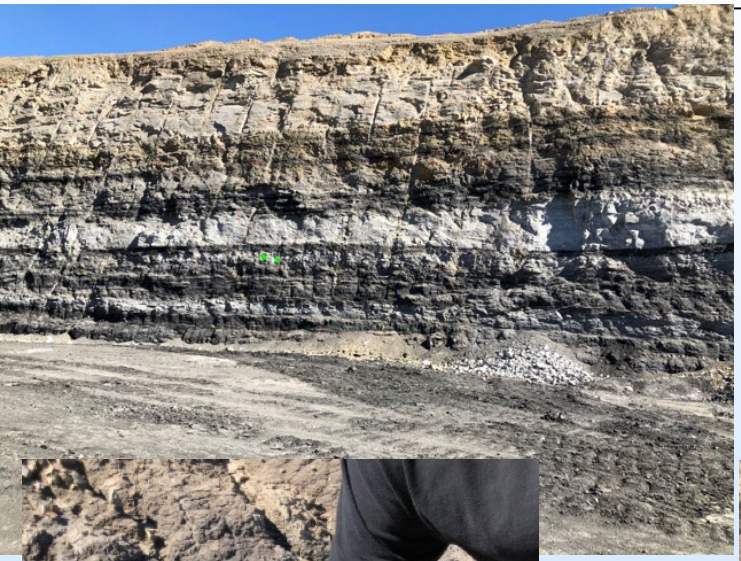


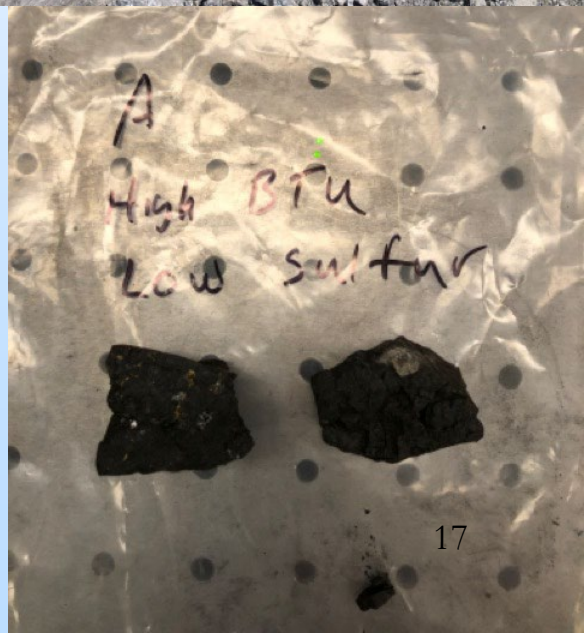



# Progress and Current Status of Project

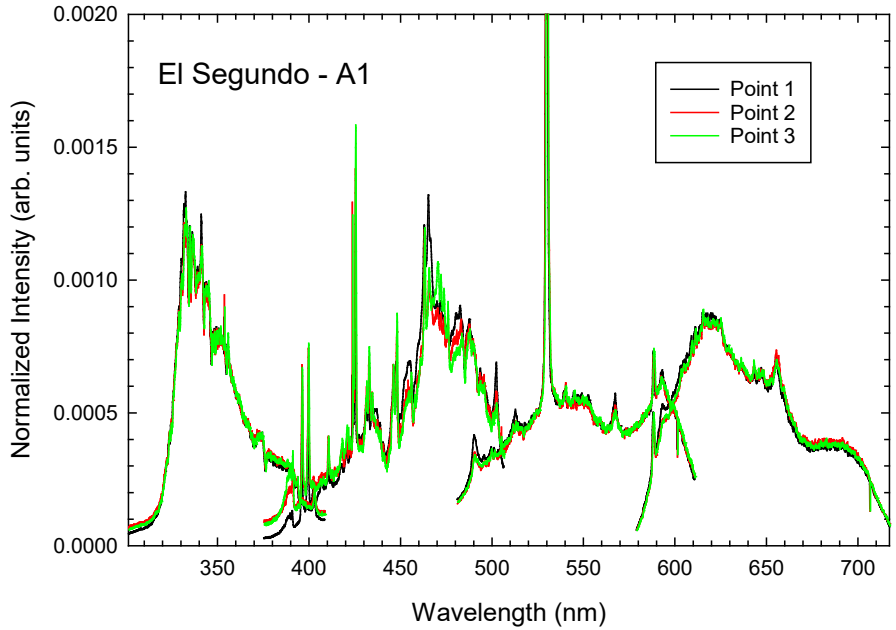
El Segundo Mine
Peabody Energy

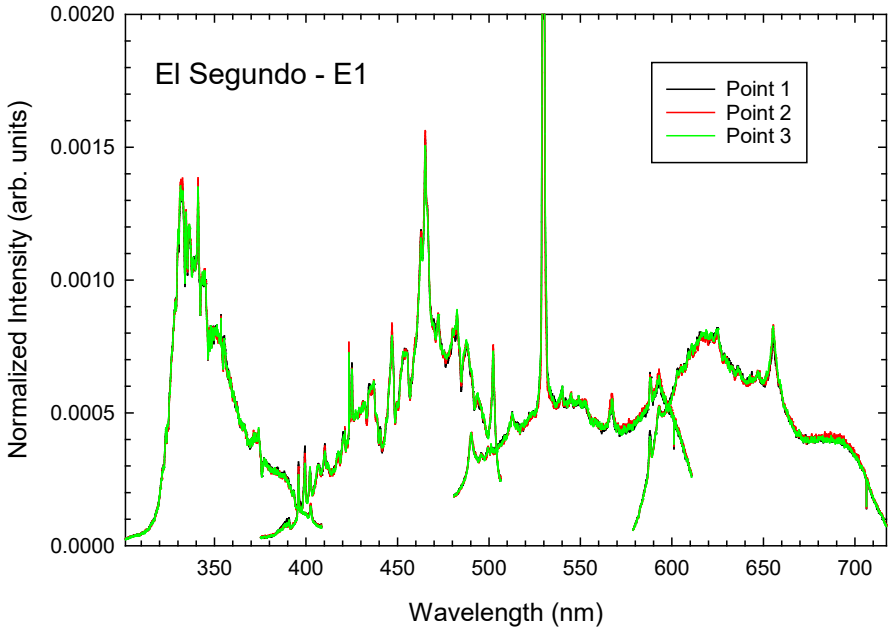


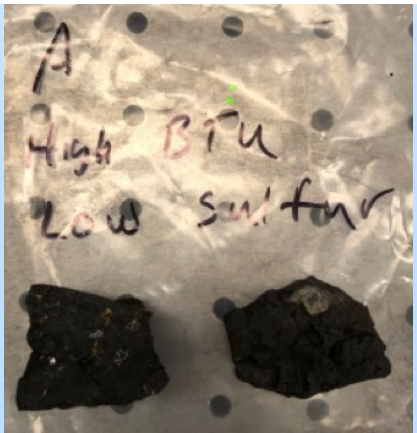


# Progress and Current Status of Project

Representative Spectra

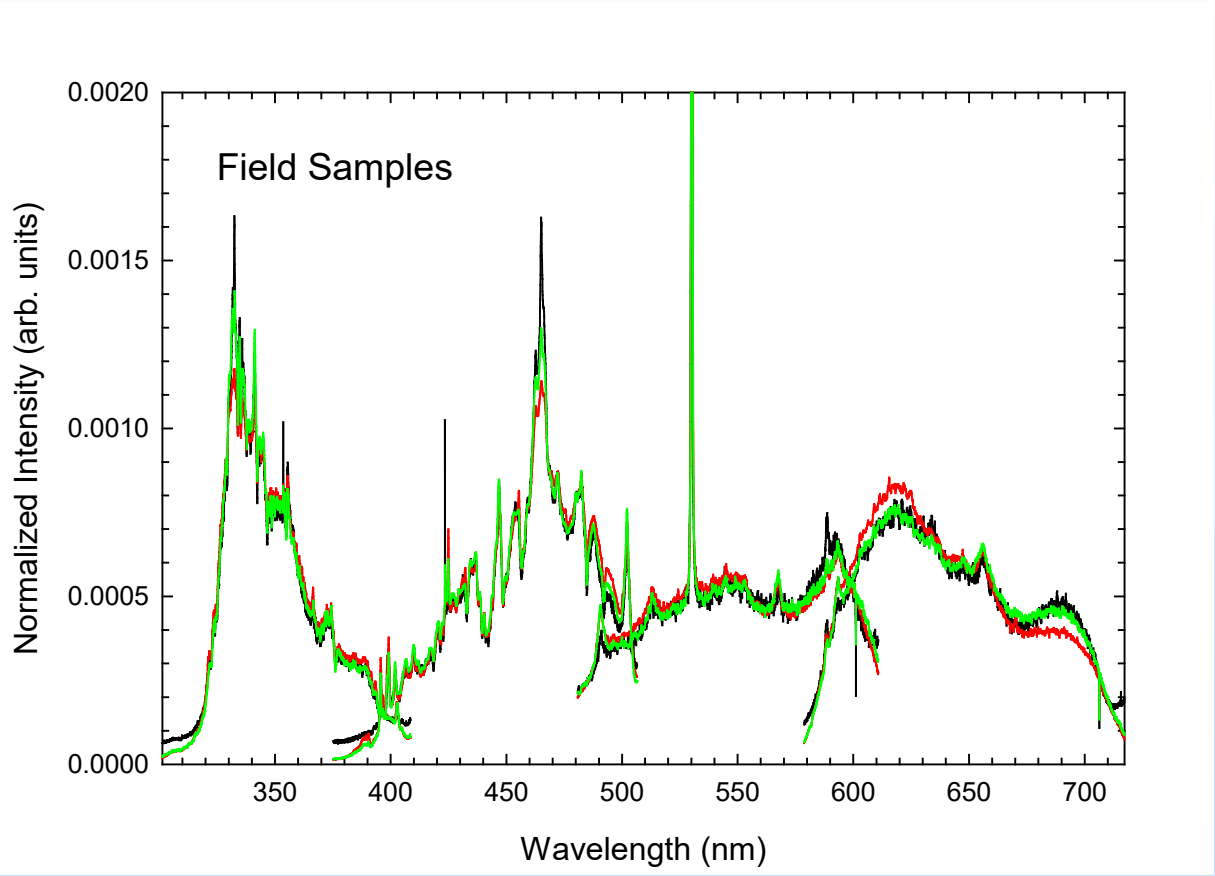



At this time, no REEs qualitatively detected in these coal samples.

# Progress and Current Status of Project



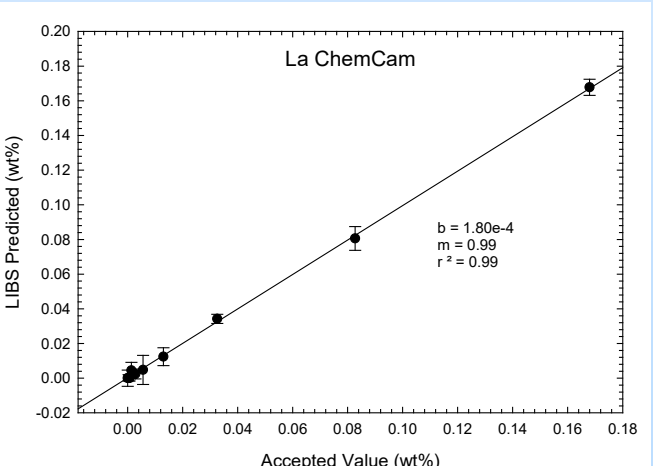

# Plans for future testing/development/ commercialization

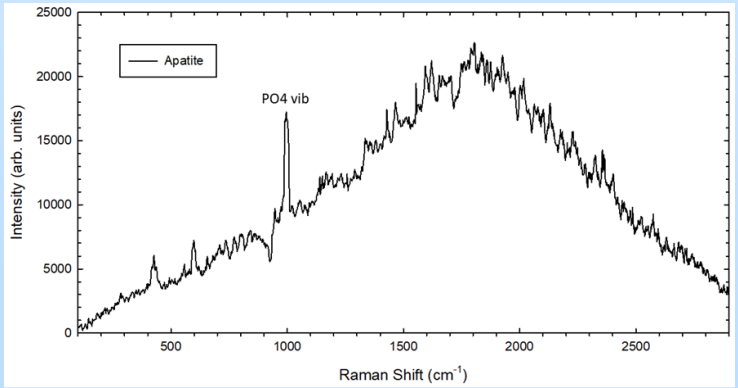
Plans for future testing/development/commercialization

a. In this project
    a. The project will be completed on November 18, 2022.
b. After this project
    a. No follow-on project currently planned.
c. Scale-up potential, if applicable
    a. IP application is in process at LANL.

# Summary Slide

- Project Closeout
  - ✓ Demonstrated LIBS quantitative elemental analysis of REEs in coal sample in the lab.
  - ✓ Demonstrated Raman molecular / mineralogical analysis of samples containing REEs.
  - ✓ Constructed and Demonstrate a Backpack LIBS-Raman Spectroscopy Instrument
  - ✓ Field Tested the Instrument




# Acknowledgements


- This material is based upon work supported by the Department of Energy Award Number FWP-FE-781-16-FY17
- Coal Mine Representatives
  - Christopher J. Schumacher, Sr. Engineer, El Segundo Mine, Peabody Energy
  - Joshua M. Johns, Senior Geologist, Navajo Mine, Navajo Transitional Energy Company

# Appendix

– These slides will not be discussed during the presentation but are mandatory.

# Organization Chart

- Describe project team, organization, and participants.
  - Sam Clegg (PI), LANL
  - Kristy Nowak-Lovato (Co-I) – now deputy group leader in Chemistry Division, LANL.
  - Ron Martinez (Co-I), LANL

# Gantt Chart

- The project will be completed on November 18, 2022.

# Outreach and Workforce Development Efforts or Achievements

- Outreach - Provide a bulleted list of community outreach efforts or achievements.
  - None
- Workforce Development – Provide a bulleted list of ways you have developed the current or future workforce including training/graduating students or postdocs, (re-)training tradespeople or professionals, etc.
  - Sam Clegg (Scientist 5) designed all transmission grating spectrometers and quantitative analysis.
  - Kristy Nowak-Lovato (Manager 3) designed the overall optical system
  - Ron Martinez (Research Technologist 2) completed the mechanical design, assembly, and characterization work.