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

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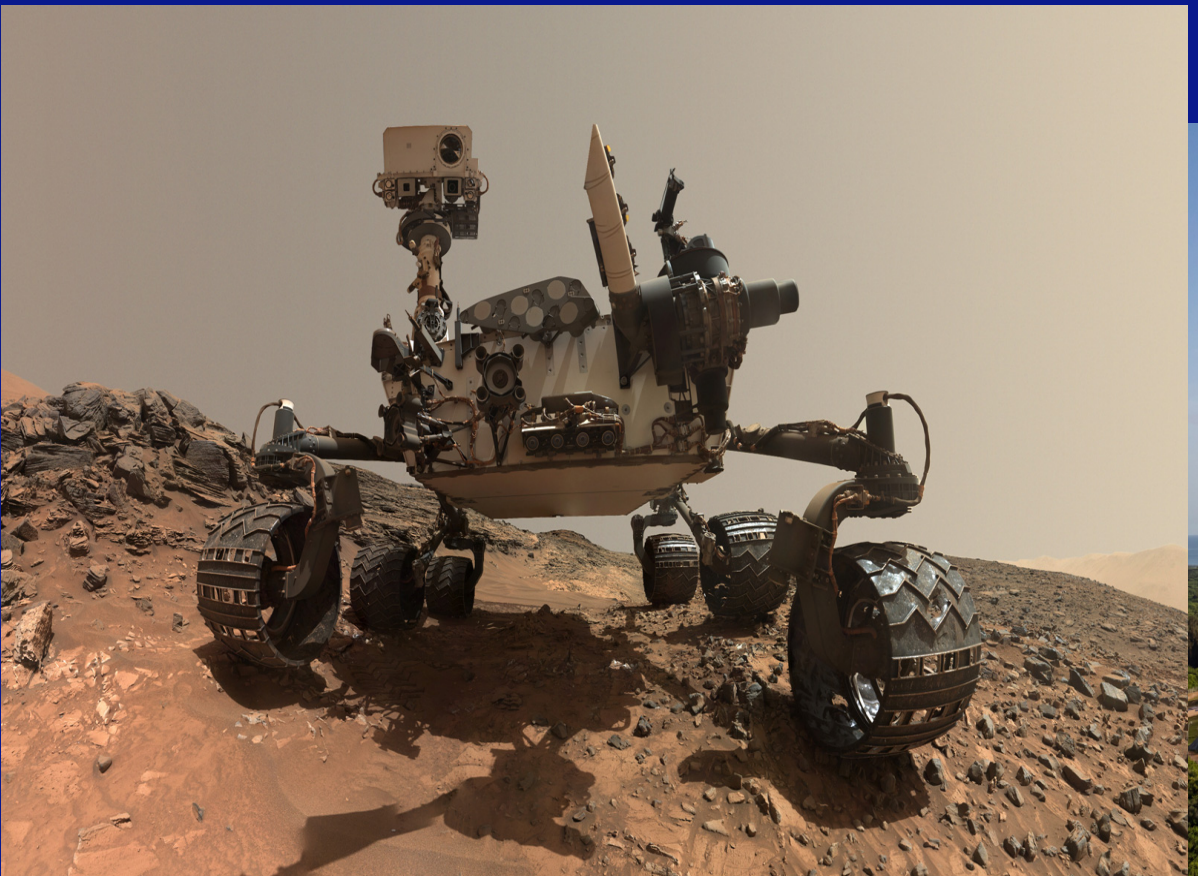
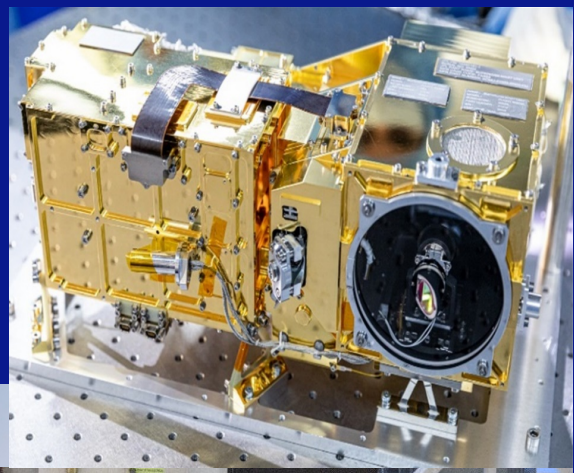
Project Description and Objectives

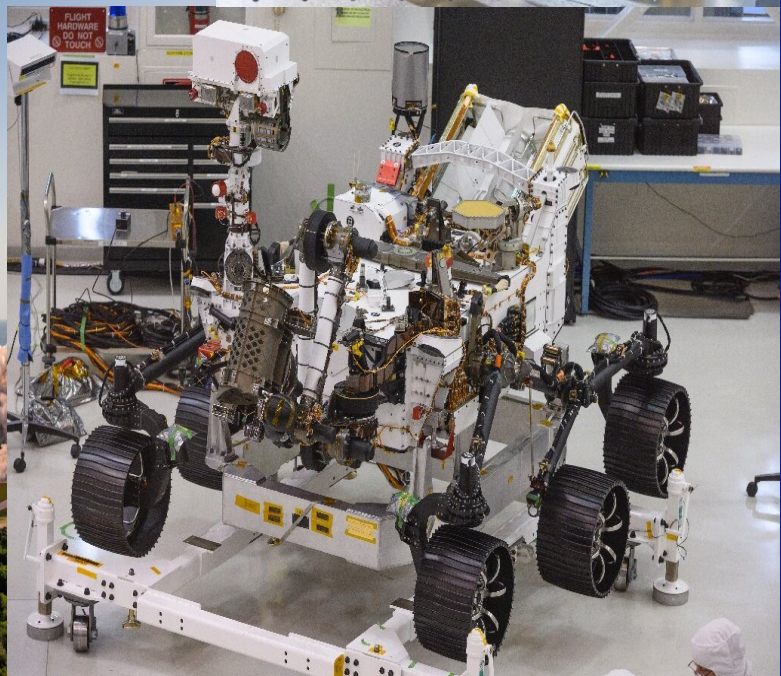
- Previous Work

ChemCam on the Curiosity Rover
Remote LIBS
Remote Micro-Imager
8 years on Mars, ~800,000 laser shots



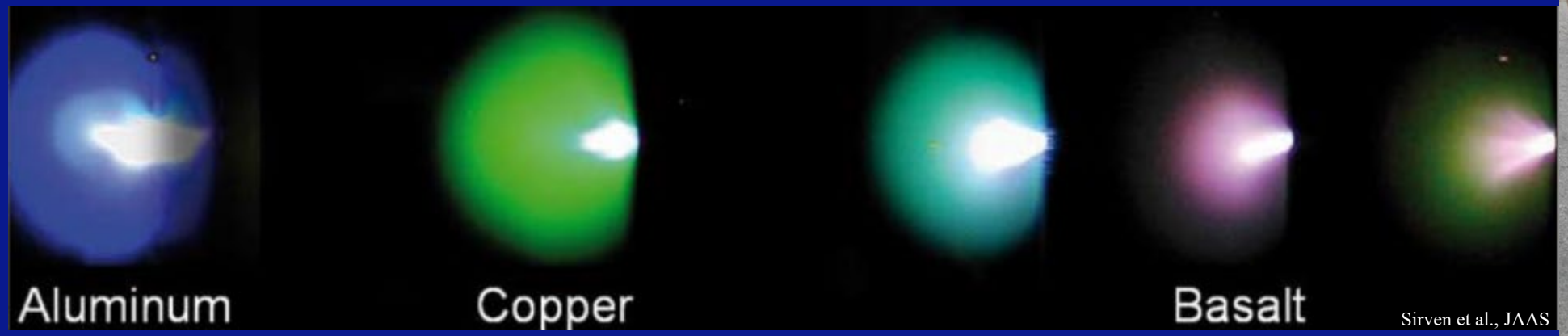
SuperCam on the Perseverance Rover
Remote LIBS, Raman, Visible and Near Infrared, Luminescence, and Remote Micro-Imager
Landed on February 18, 2021





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
  - in situ analysis
  - Integrated interlock for eye-safe operation



Sirven et al., JAAS

Project Description and Objectives

Progress and status (1/2)

- Status at beginning of project → driving question
  - Some literature regarding REE qualitative analysis
    - No published LIBS spectral library, critical first step
  - No literature on REE quantitative analysis
  - Driving questions
    - Accuracy, precision, detection limits
    - Define sampling methodology

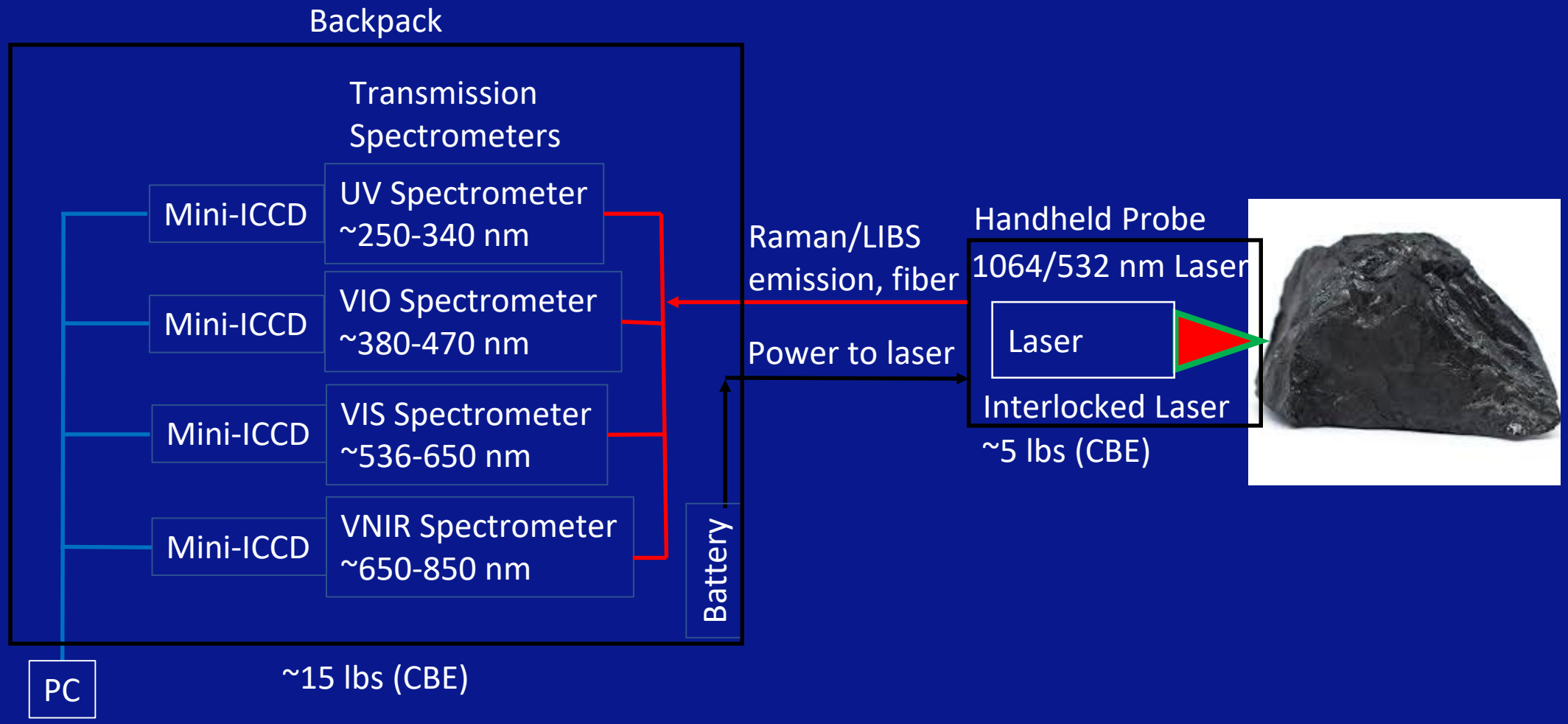
Project Description and Objectives

Progress and status (2/2)

- **Technology benchmarking** – provide comparative analysis to current state-of-the art technology alternatives.
- Current Status of project
  - x-ray fluorescence (XRF) for elemental analysis
  - x-ray diffraction (XRD) for mineralogical analysis
  - Refer to Lin et al. 2018 "Evaluation of trace elements in U.S. coals using the USGS COALQUAL database version 3.0. Part I: Rare earth elements and yttrium (REY)
    - *"Assessment of data quality indicates that some of the REY data are **semi-quantitative and should be used with caution**.*
    - ***Different analytical instruments and methods** with varying accuracies and precisions are thought to be the main sources of errors."*
  - **Industry/input or validation**
    - Engage industry when field demonstration completed.

Project Update

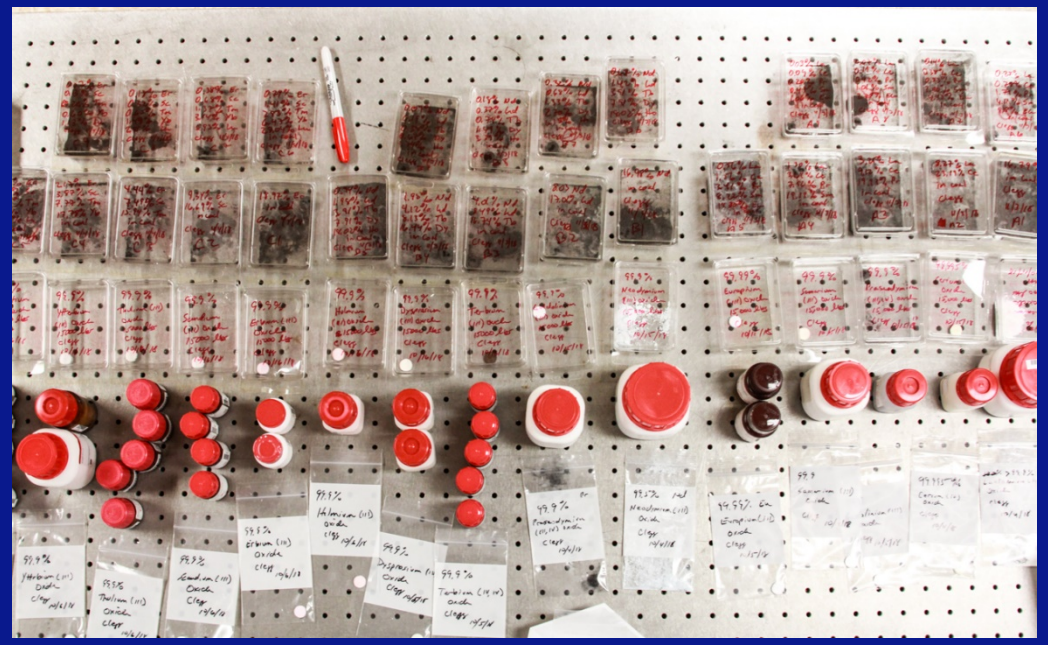
Raman-LIBS Backpack Instrument – Block Diagram



Project Update

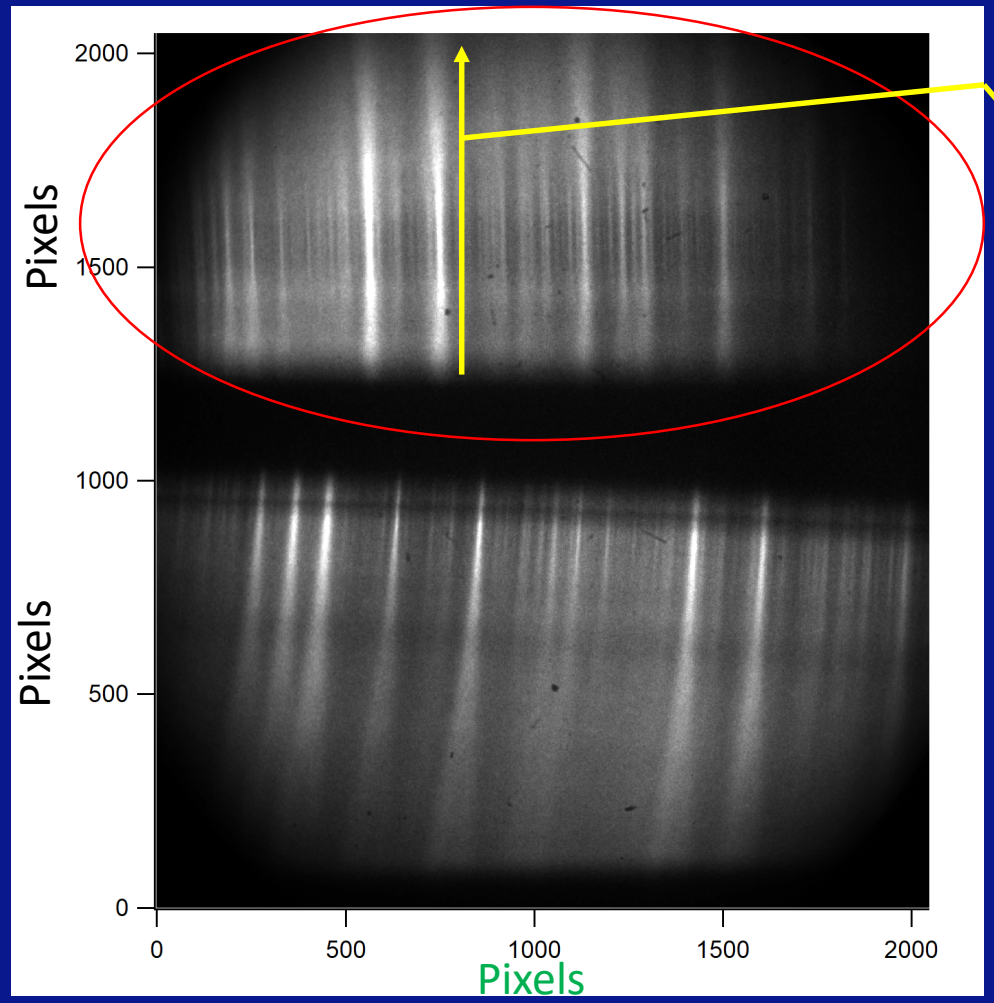
Field Instrument

- Complete construction of the backpack instrument
- Calibrate the Backpack LIBS Raman Instrument
  - Collect LIBS spectral library
  - Recalibrate LIBS elemental analysis
  - Collect Raman spectral library
- Test the instrument in the field
  - San Juan, NM region
  - Perhaps other regions as time permits
  - Complete field tests when COVID-safe

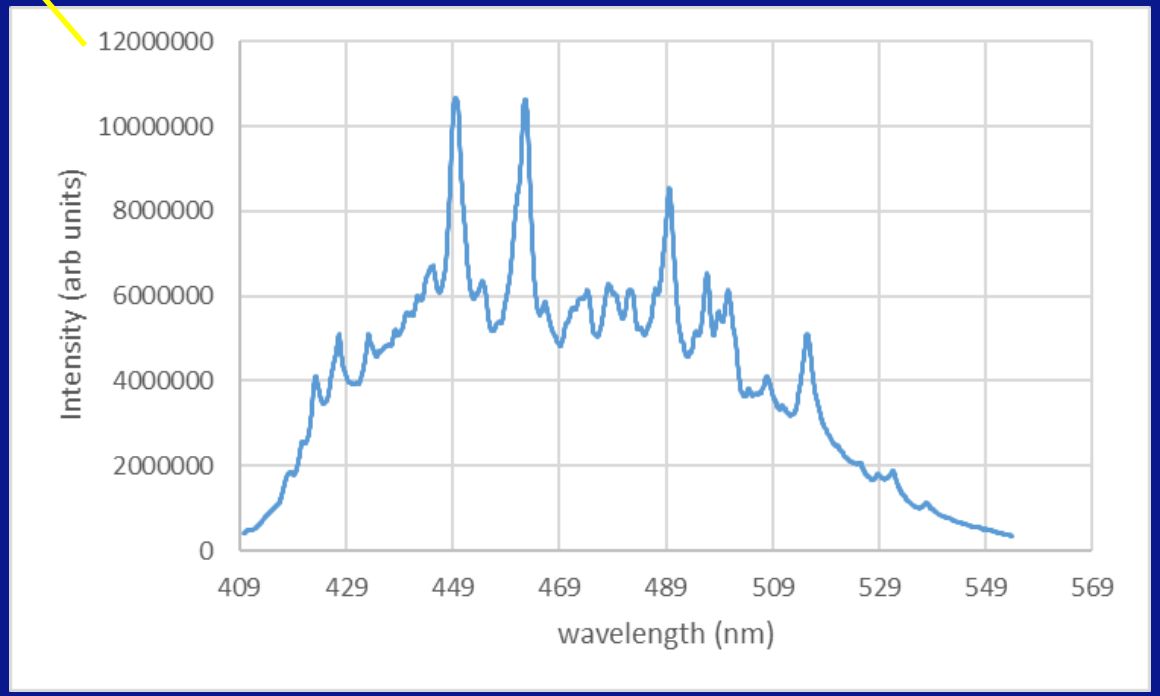


Project Update

Data from Backpack Spectrometers



Sum up intensities in each column into a single intensity



Convert Pixels to Wavelength (nm)

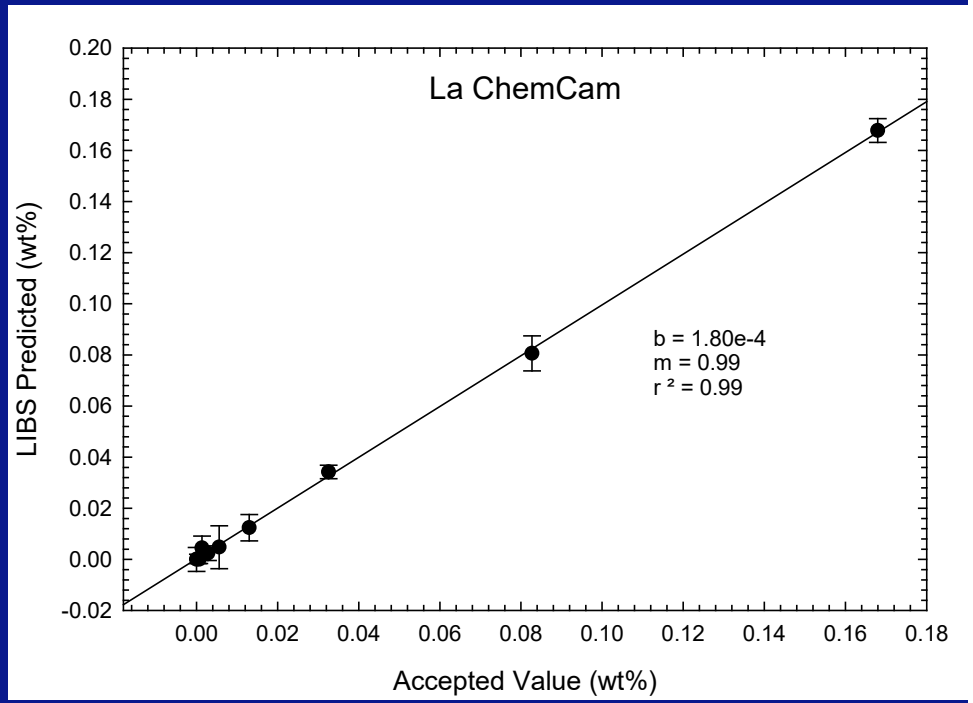
Project Update

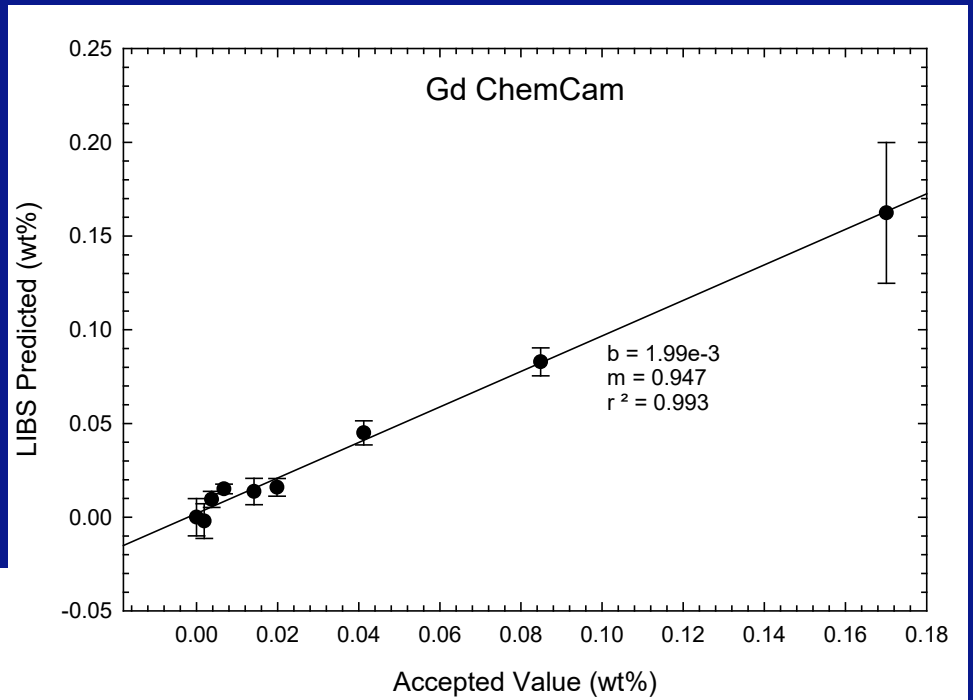
Calibration Analysis

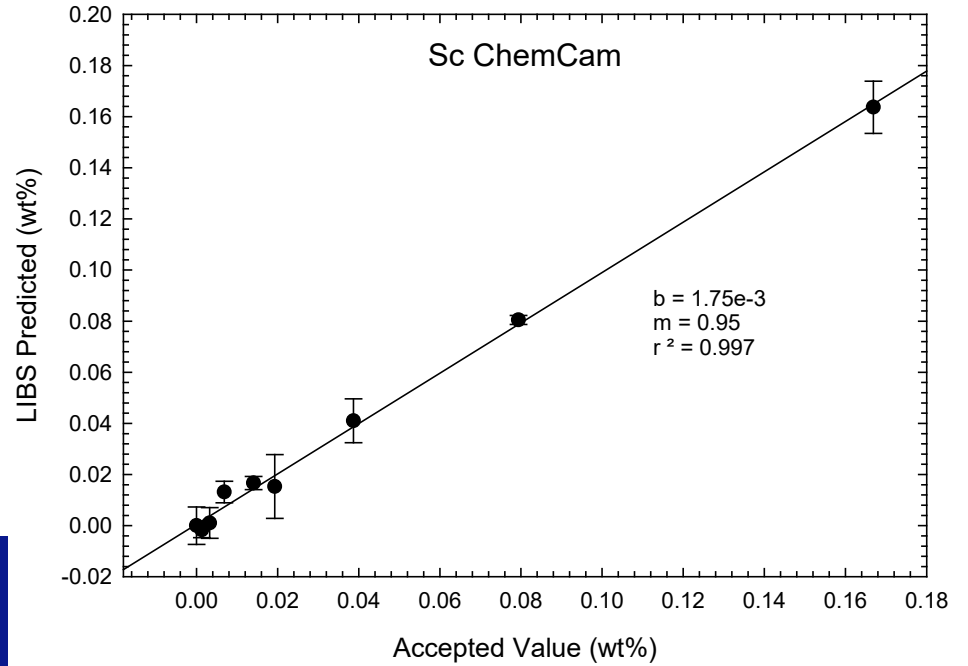
- Partial Least Squares (PLS)
  - PyHAT Program developed by Anderson (USGS) and Clegg (LANL)
  - Used to develop calibrations for ChemCam and SuperCam
  - Leave one target out analysis
    - One target is treated as an unknown
    - Repeated for all targets
- Variables
  - X: LIBS Spectra, all wavelength channels
  - Y: Concentrations
- Developed 15 separate PLS models
- Uncertainty Analysis
  - 3 replica measurements per sample
- Estimate detection limits (conservative and likely)

Project Update

Original ChemCam Calibration Curves







Project Update

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

Project Update

Conservative Estimated Detection Limits – Backpack Instrument

	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)
- In situ analysis, not remote like ChemCam
- Obtain more certified calibration standards
  - Requires correct matrix
- Sampling protocol

Preparing Project for Next Steps

Path to market

Market Benefits/Assessment

- Handheld Raman instruments have been available.
- Handheld LIBS instruments are only now becoming available
  - Quantitative analysis by univariate analysis
  - LANL instrument employs more accurate multivariate analysis techniques.
- No integrated LIBS and Raman instruments commercially available
  - Higher resolution than commercial units.

Technology-to-Market Path

- File a provisional patent on the backpack instrument.

Concluding Remarks

- Remaining Tasks
  - Backpack instrument under construction
    - Spectrometers assembled
    - Handheld laser assembly being assembled, need to integrate the laser safety interlock
    - Software under development
  - LIBS and Raman calibration in the lab
  - Field test and demonstration
- Define project's next steps and current technical challenges.
  - COVID has delayed the field tests, this should not be as much of a problem at this time.

Acknowledgements

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