Miniature subsurface LIBS probe

Advanced Sensors Task 71

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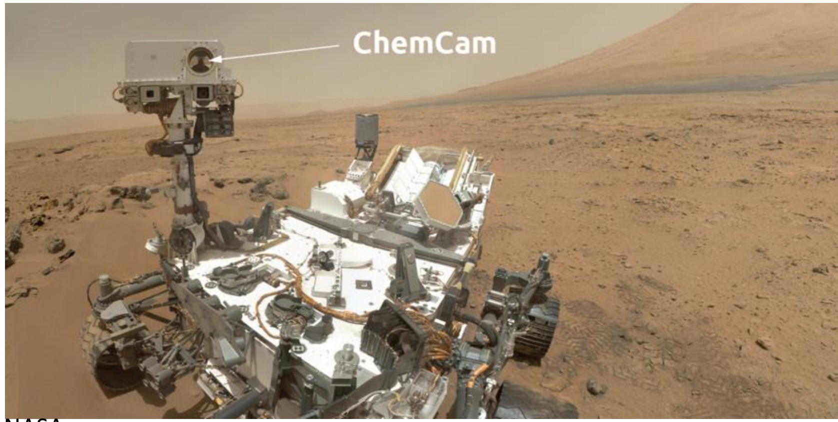
Project Description and Objectives

- Validate complex subsurface LIBS measurements with lab based system
- Improved online high resolution subsurface and/or process sensor based on underwater LIBS
- Show system can rapidly take large complex data sets
- Show system can produce concentration information of multiple elements in-situ
- Determine pinch-points in deployment and document
- Determine best practices for construction, deployment, and calibrations
- Prove system works as described in a relevant environment
- Show that system has potential for subsurface and process applications
  - Critical materials “Securing the domestic supply chain”
  - Environmental Justice

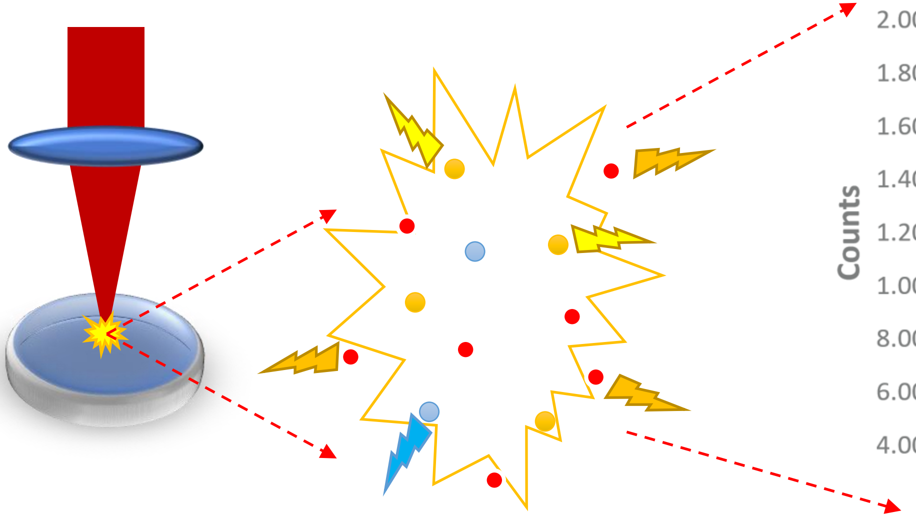
Project Update

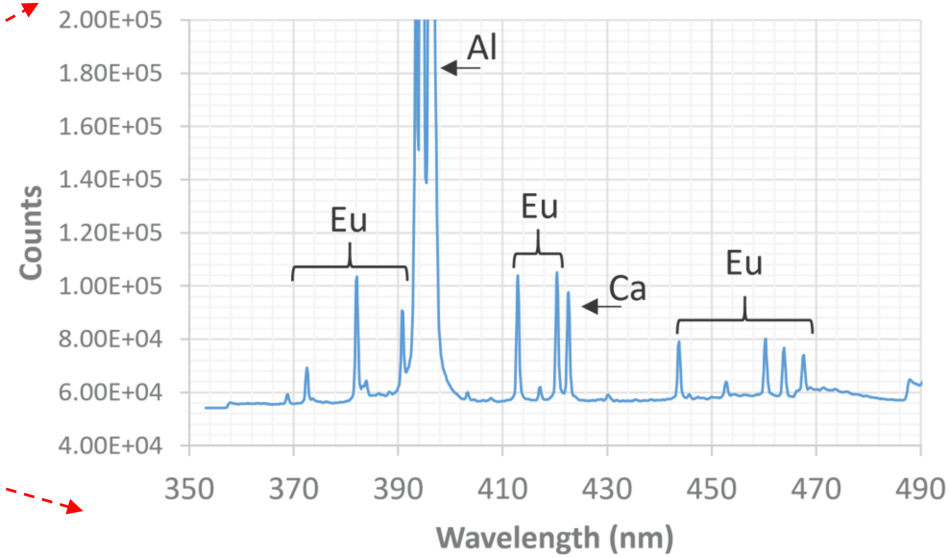
What is LIBS?

- **Laser Induced Breakdown Spectroscopy (LIBS)**
  - Elemental analysis
  - Rapid
  - Minimal sample preparation
  - Hostile environments
    - Ex: ChemCam (Mars)



NASA





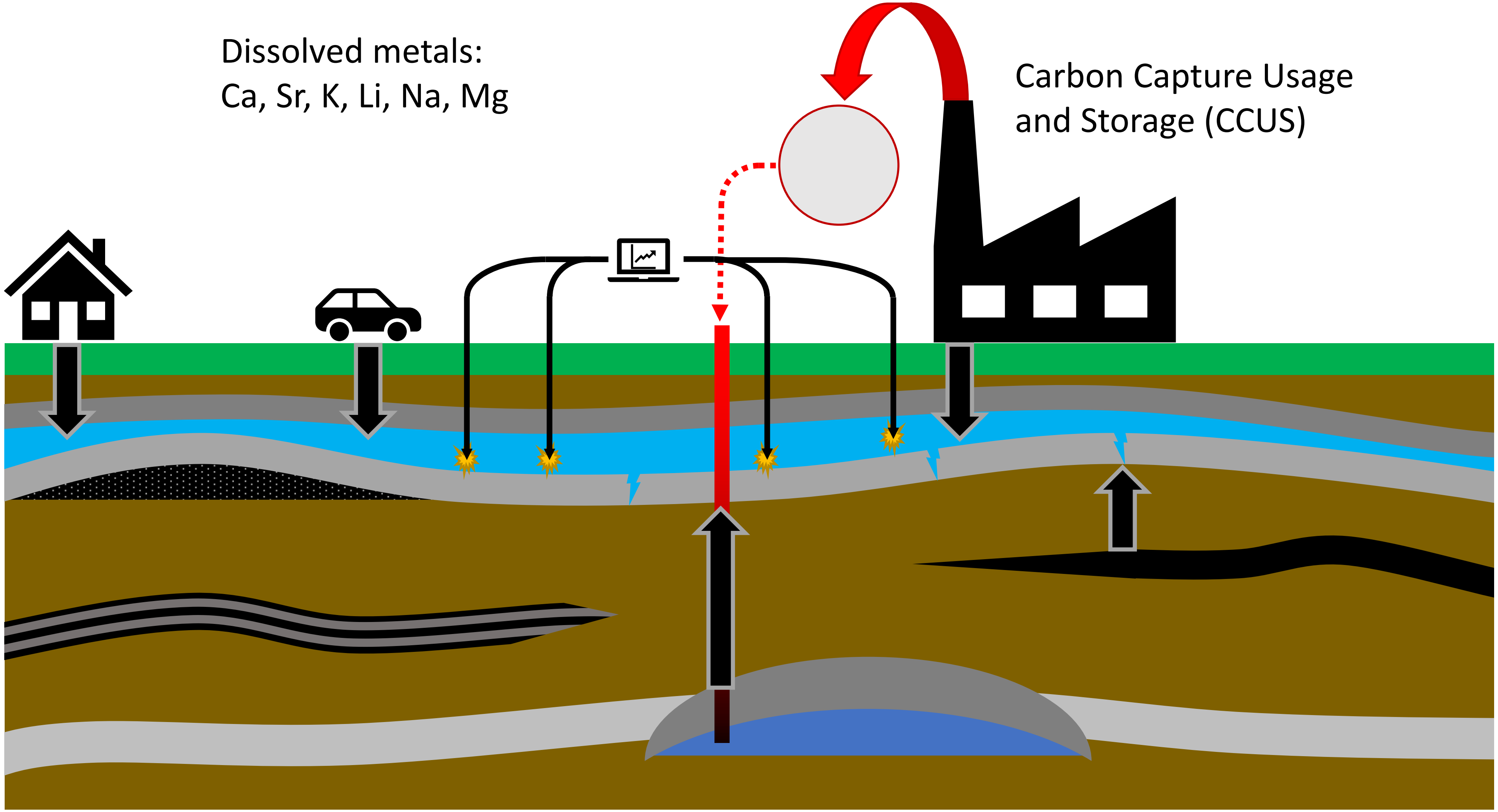
Springer

Project Update

Miniaturized LIBS Probe

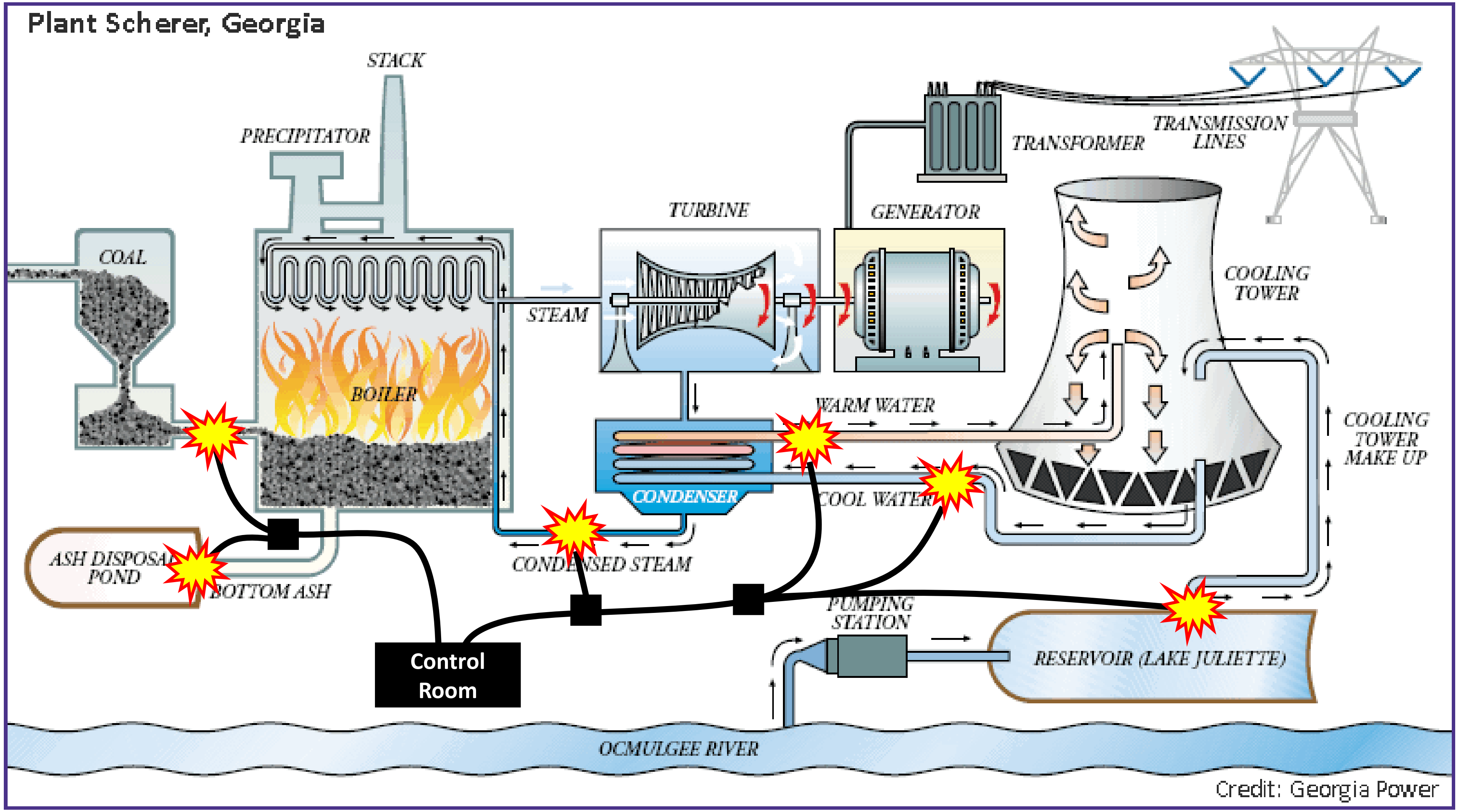
Dissolved metals:
Ca, Sr, K, Li, Na, Mg

Carbon Capture Usage
and Storage (CCUS)



Project Update

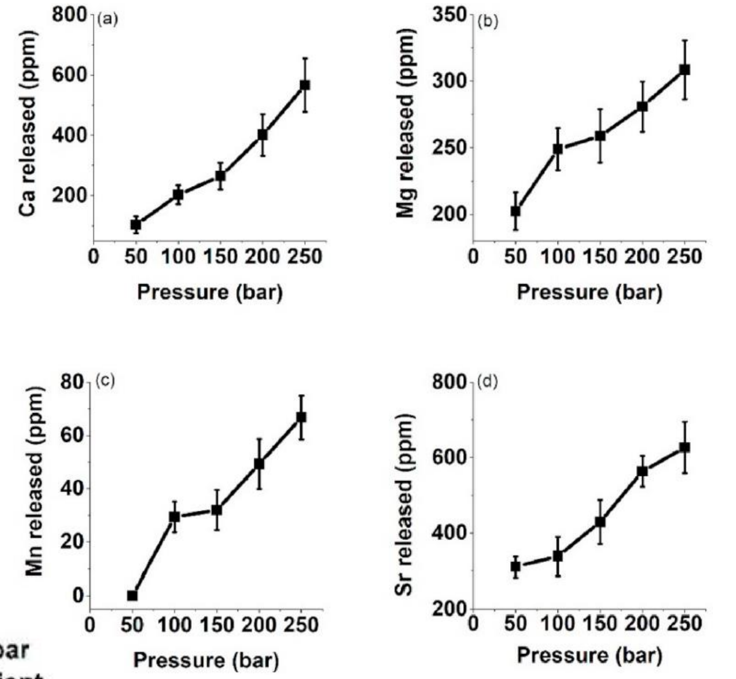
Miniaturized LIBS Probe



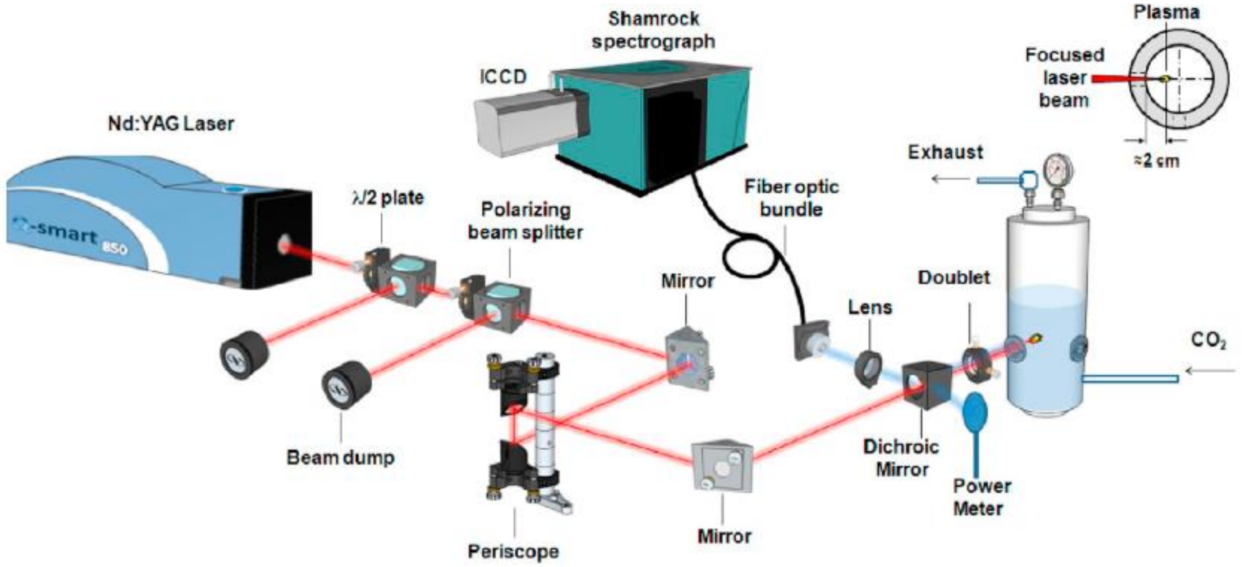
Project Update

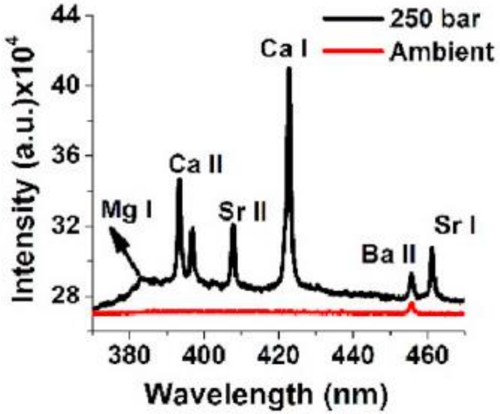
Carbonate Dissolution

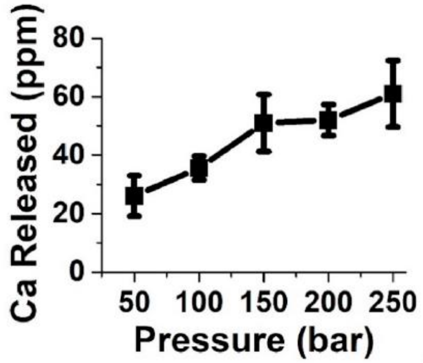
- Simulation of fluids under Carbon Storage Pressure Conditions
- Validation that LIBS can measure multiple components noninvasively
- Validation that LIBS can measure over a wide range of pressures and pH
- Common Carbonates of Ca, Mg, Mn, Sr were measured for dissolution
- Mt Simon Sandstone sample was measured for dissolution
- All elements go into solution a different pH and different rate and conc.



Bhatt, C.R., Jain, J.C., Edenborn, H., McIntyre, D.L., "Mineral carbonate dissolution withincreasing CO2 pressure measured by underwater laser induced breakdown spectroscopy and its application in carbon sequestration," Talanta, 205 (2019) 120170, https://doi.org/10.1016/j.talanta.2019.120170







Project Update

Miniaturized LIBS Probe

Split laser system

<u>Benefits</u>

All Optical downhole

Minimize component count and processes downhole

Lower unit cost for deployable component.

<u>Surface</u>

Expensive/Delicate components on surface

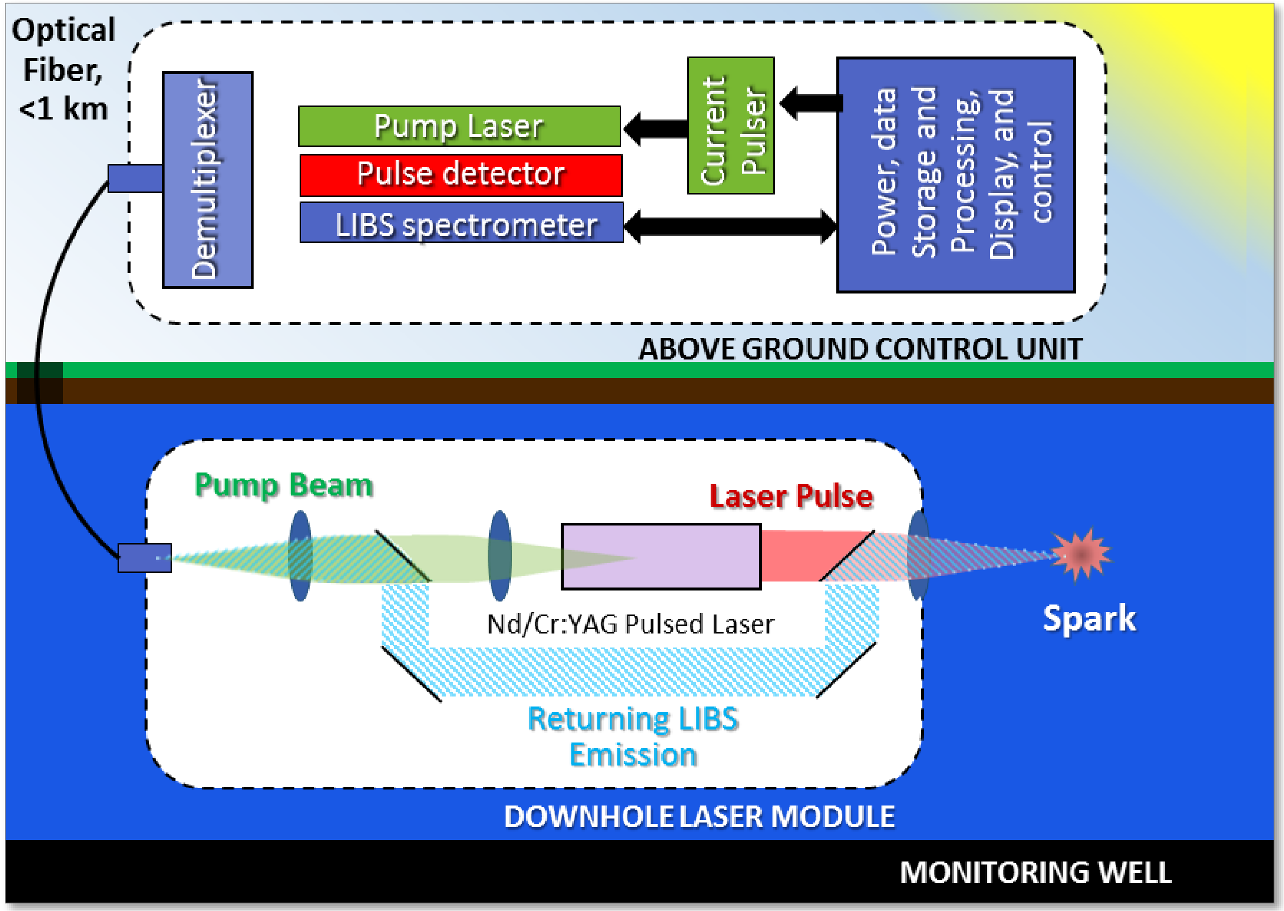
Analytical measurement and control

<u>Subsurface</u>

All control and data through optical fiber

All optical rugged components in subsurface

Detachable, can be left in place or continuously interrogated



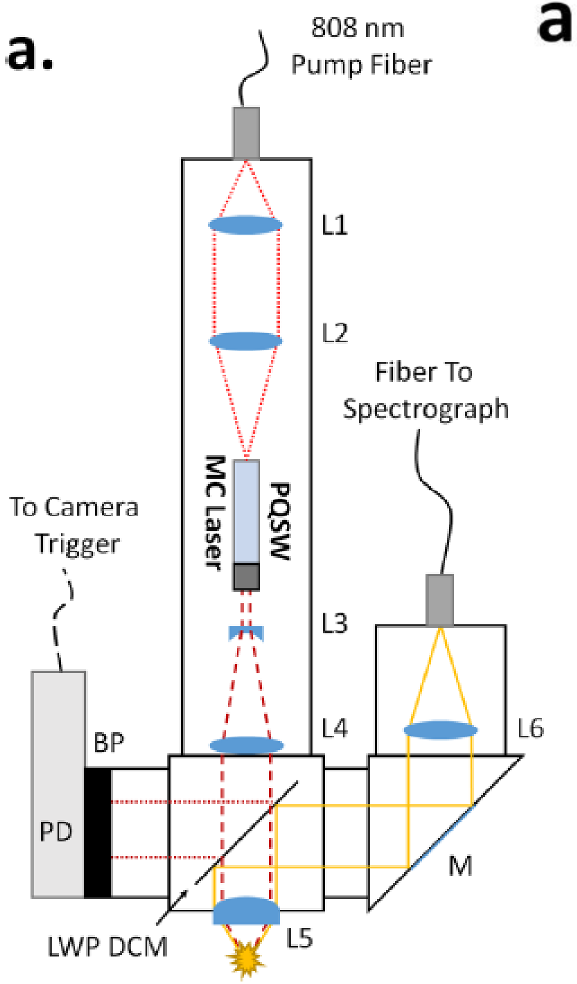
- SD Woodruff, DL McIntyre, JC Jain, U.S. Patent US 8,786,840 (2012)
- SD Woodruff, DL McIntyre, U.S. Patent US 9,297,696 (2013)
- DL McIntyre, U.S. Patent US 10,145,737 (2017)
- JC Jain, DL McIntyre, and CL Goueguel, National Innovation Summit & Showcase (2017)
- CG. Carson., CL Goueguel, JC Jain, DL McIntyre., Proc. SPIE 9467, Micro- and Nanotechnology Sensors, Systems, and Applications VII, 94671K (2015)

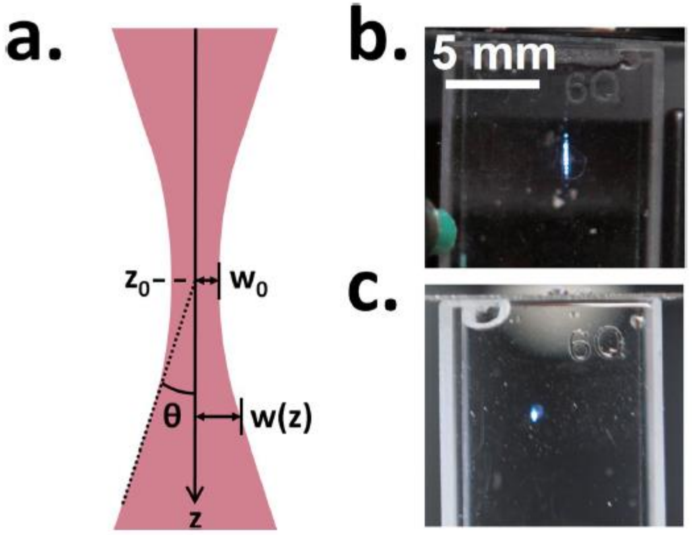
Project Update

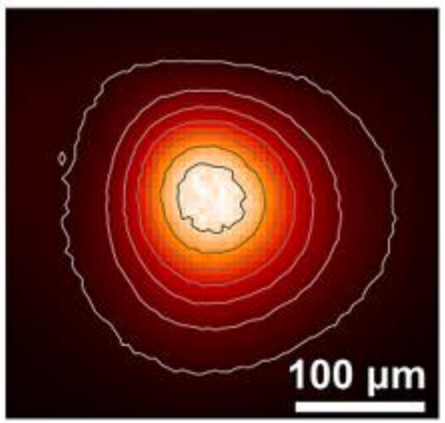
Prototype validation

- Miniature prototype constructed and validated
- Laser optical parameters were validated
  - Beam Quality (M^2)
  - Reproducibility (SNR reduction)
  - Noise Characteristics (Allen Deviation)
- Laser beam shaping to improve performance
- Adjustments for more efficient use of available pump
  - 2 fibers instead of 1

Laser System Characteristics
Pump wavelength: 808 nm
Pump pulse width: 300 microseconds
Pump pulse power: 500 watts
Output wavelength: 1064nm
Output Energy: 4.5 mJ
Pulse width (FWHM): 3.3 ns
Beam Quality (M^2): 1.04x and 1.55y





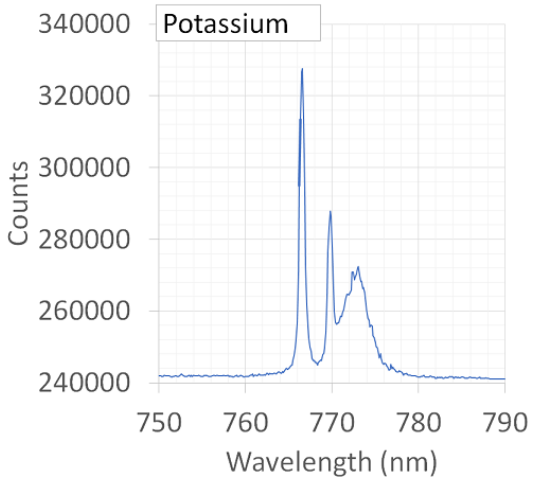


Project Update

Prototype Validation

Element	Line (nm)	LOD (ppm)	LOD (literature) (ppm)		
Calcium	422.7	0.10[A]	0.94[B,†]	0.047[E]	0.13[G]
	393.4[‡]			0.01[E,Δ]	0.6[G]
Strontium	460.7	0.04[A]	2.89[B,†]		
	421.5[‡]		0.34[C,#]		
	407.8[‡]		0.025[D]		
Potassium	766.6	0.009[A]	0.03[B,†]	0.006[E,Δ]	1.2[H]
	769.9	0.069[A]			

Table. Room temperature and pressure limits of detection for Ca, Sr, and K. **A** – This study, **B** – Goueguel et. al. 2015 [22], **C** – Fichet et. al. 2006 [24], **D** – Popov et. al. 2016 [26], **E** – Pearman et. al. 2003 [23], **F** – Golik et. al. 2012 [47],**G** – Knopp et. al. 1996 [25], **H** – Cremers et. al. 1984 [21], **‡** – Lines showed self-absorption over the concentration ranges used in this study, **†** – NaCl solution matrix, # – LIP on liquid surface, **Δ** – fs LIBS + LIP on liquid surface



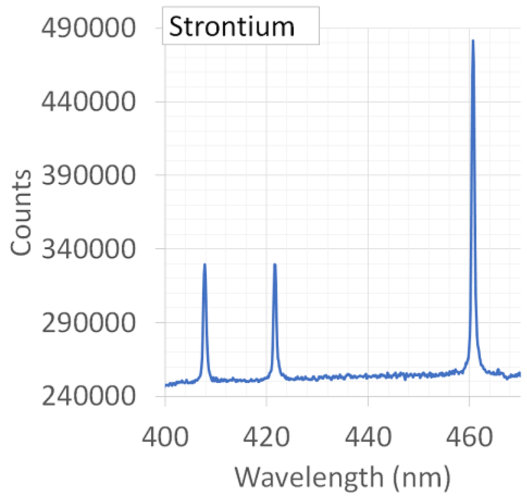
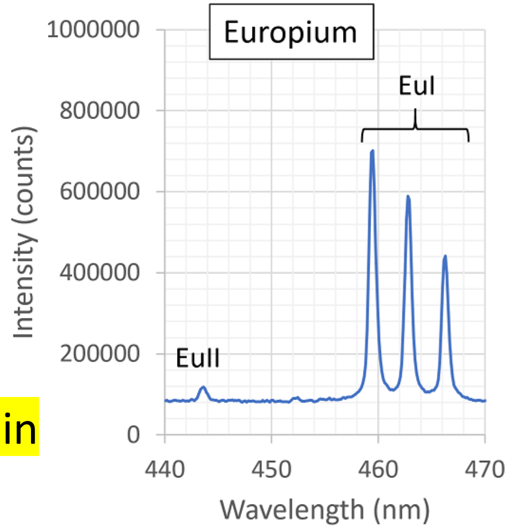


Table 2 **Liquid solutions limits of detection for Eu and Yb emission lines**

Element	Line (nm)	Calibration curve R^2	LOD (ppm) aqueous solution			Preconcentrate solution
Eu	466.19	0.9984	1.54[a]		5.0[b,c,d]	
	462.72	0.9988	1.05[a]		5.0[b,c,d]	1.9[e,f]
	459.40	0.9988	0.85[a]	256[g]	5.0[b,c,d]	
Yb	398.80	0.9987	1.15[a]	156[g]		

a – this study, **b –** Yun et. al. 2001 [24], **c –** Integrated area of all three emission lines used for calibration, **d –** Eu^{3+} aqueous solution, **e –** Alamelu et. al. 2008 [25], **f –**evaporation onto filter paper prior to measurement, **g -** Bhatt et. al. 2017 [23]

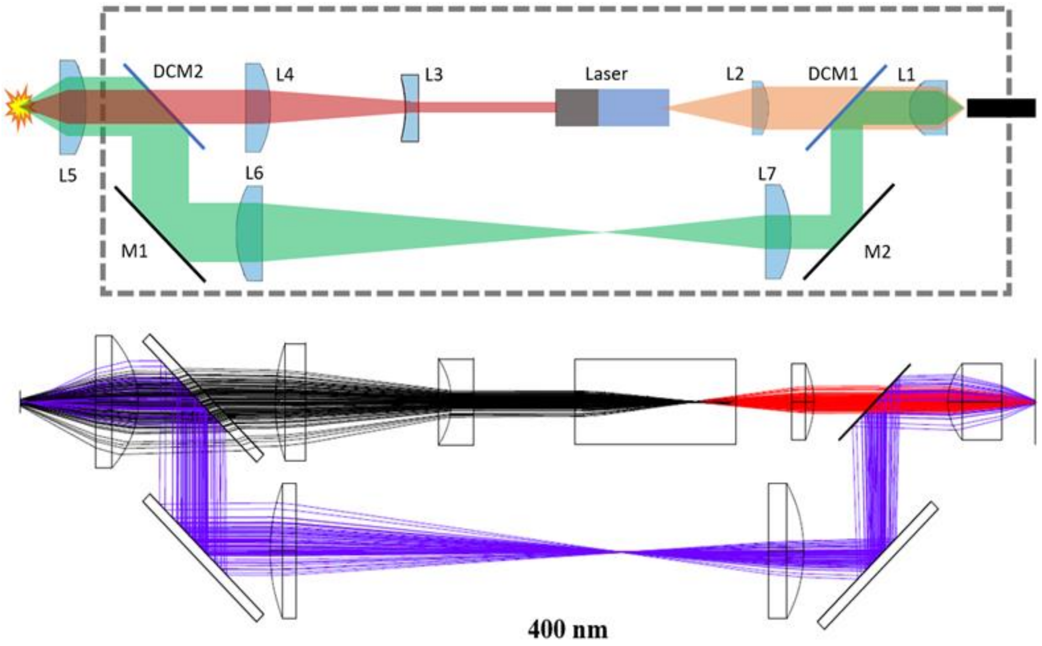
Securing the domestic supply chain
Environmental Justice

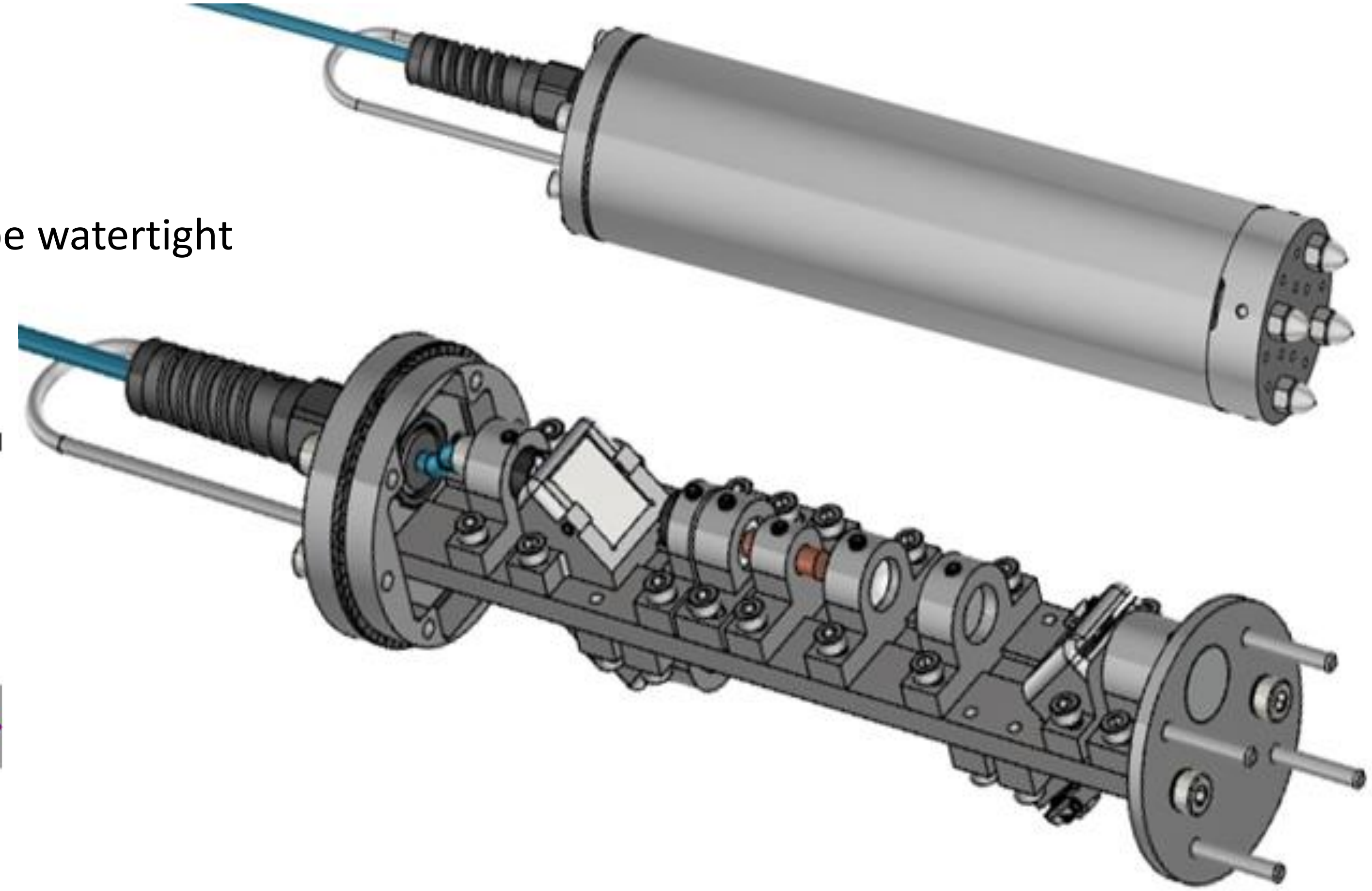


Project Update

Submersible Prototype

- System Optical modeling
  - Pump laser at 808nm
  - Atomic Spectra Data 300-900nm
- System physical modeling
  - Must fit inside 2in diameter wellbore and be watertight





Project Update

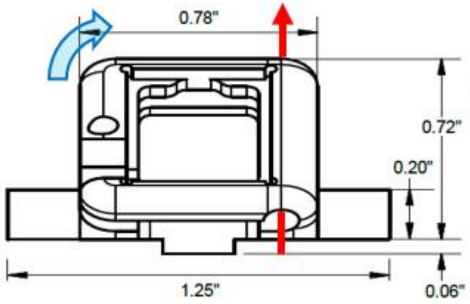
Additive Manufacturing for complex geometry

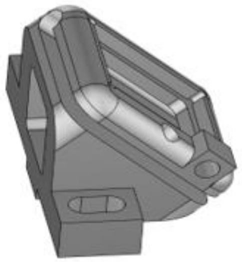
Mocking up prototype

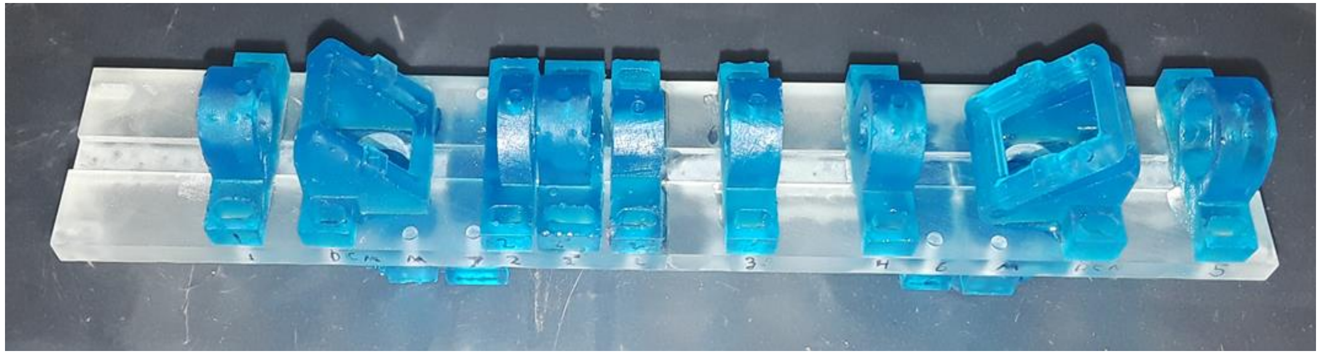
- Do all of the parts fit together
- Does the system work as a whole

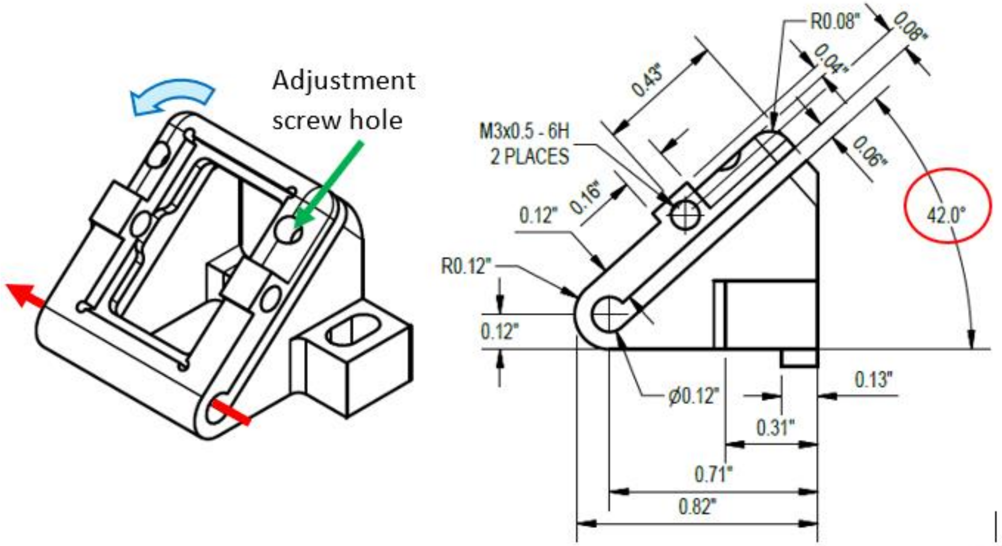
3D printing of flexible mirror mounts

- **Complicated geometry**
- Time consuming to machine traditionally







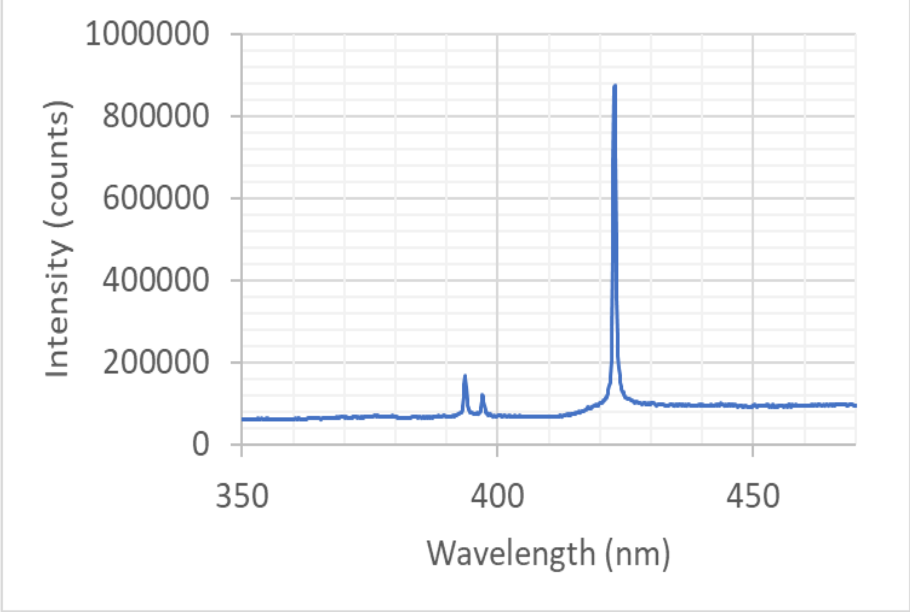


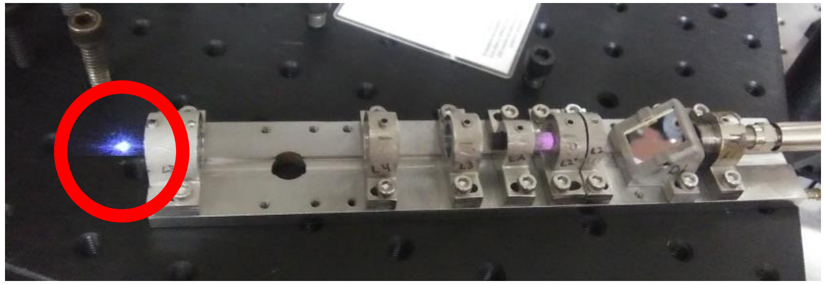
Project Update

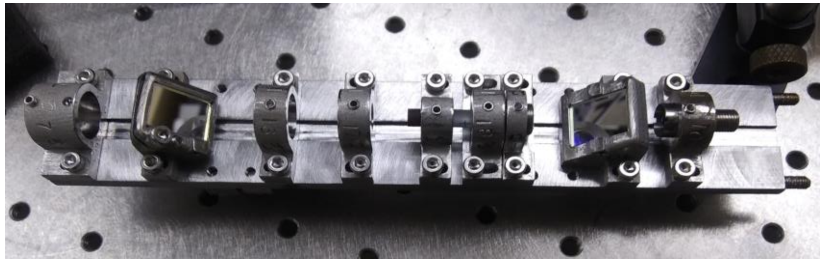
Submersible Prototype

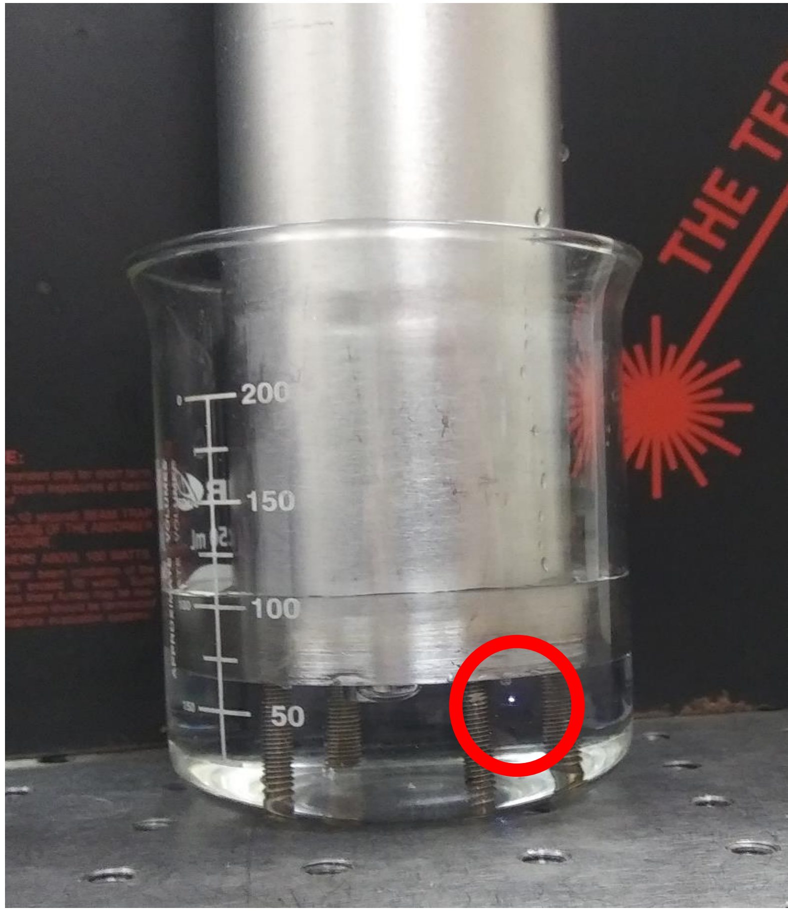
- Construction: <2in diameter
- <8in long, watertight
- Operation in Air
- Validation in water

Calcium spectra in water









Preparing Project for Next Steps

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Market Benefits/Assessment

- Rapid online measurement of trace elements in liquids or solids. Identification and/or quantification of toxic elements or significant changes due to subsurface activities.
- Does not use X-ray, Isotopic, or high-power radio waves. Laser can be easily shielded and interlocked.
- Deployable device can significantly reduce trips required to collect data over extended periods. [Reduces repeat fluid collection travel and lab delays]

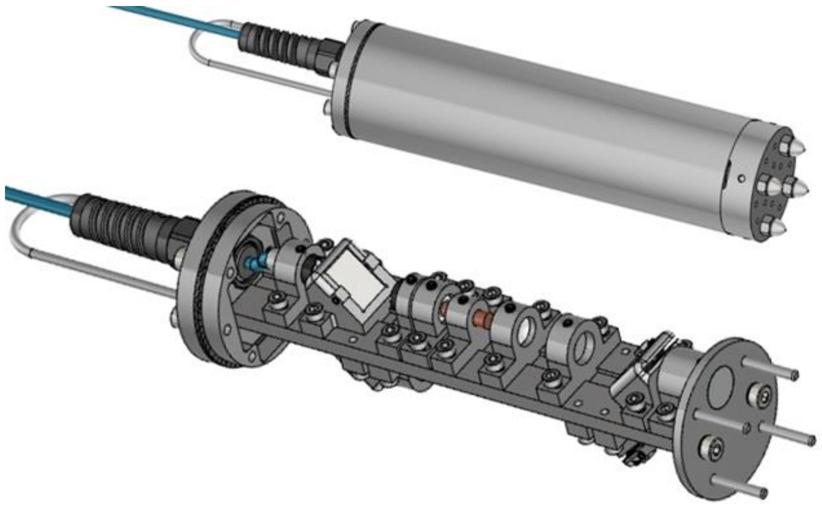
Technology-to-Market Path

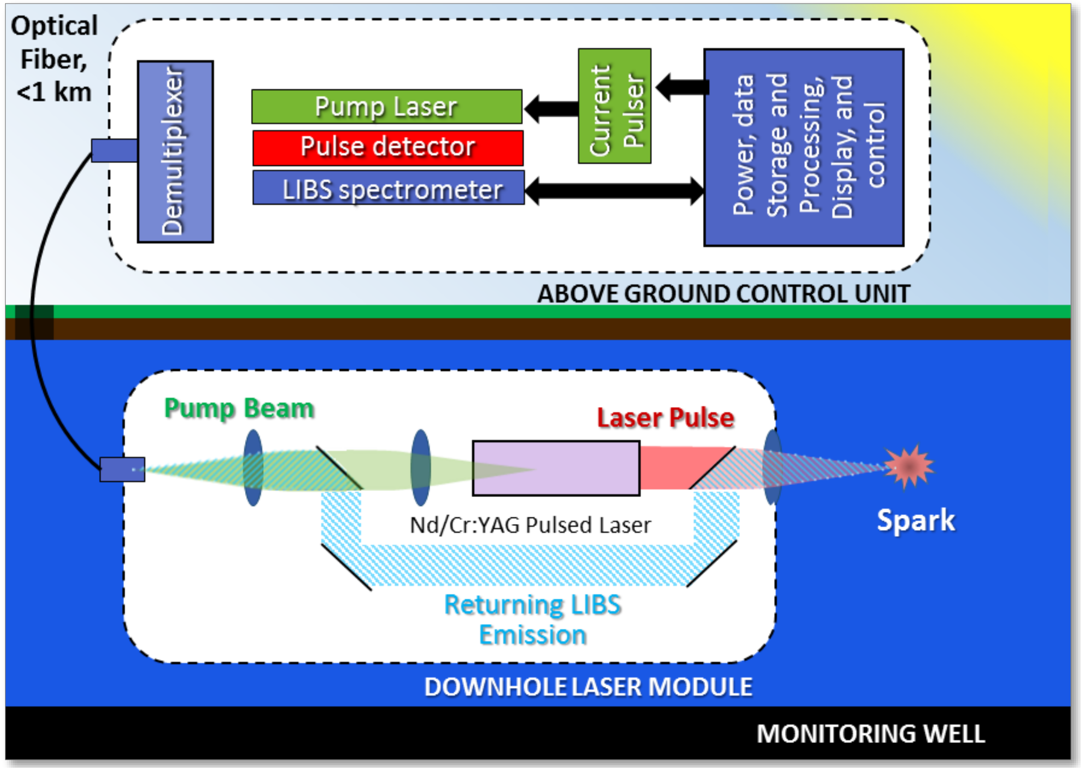
- Current industry partners include Applied Spectra Inc (benchtop LIBS) and Tronix3D (additive manufacturing and productization)
- Engineering challenges remain in reduction of size and cost of key equipment. Narrowing device scope and operational characteristics can overcome these challenges in the short term.
- New research includes the addition of Raman spectroscopy the LIBS measurements

Preparing for next steps

Field validation

- Next Steps
  - Project will be field validated in the subsurface at NETL-MGN
    - Sampling well near B23
    - Planned for later this year
  - Plans are being made to validate the device in the subsurface off-site
    - Legacy management sites





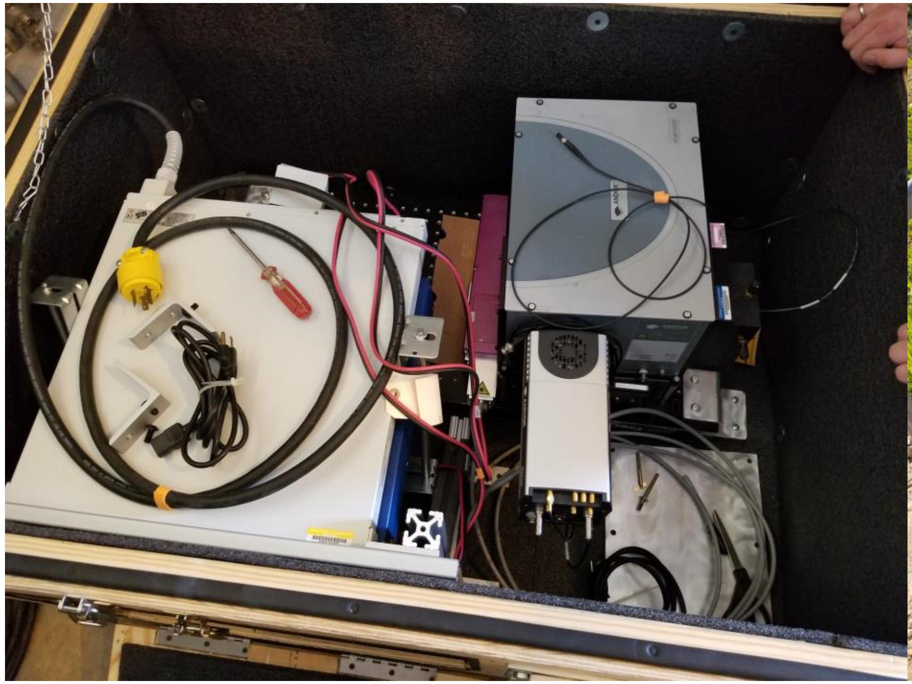
Initial Leak Testing

Completed probe assembled and connected to optical fibers

Initial leak testing in the lab

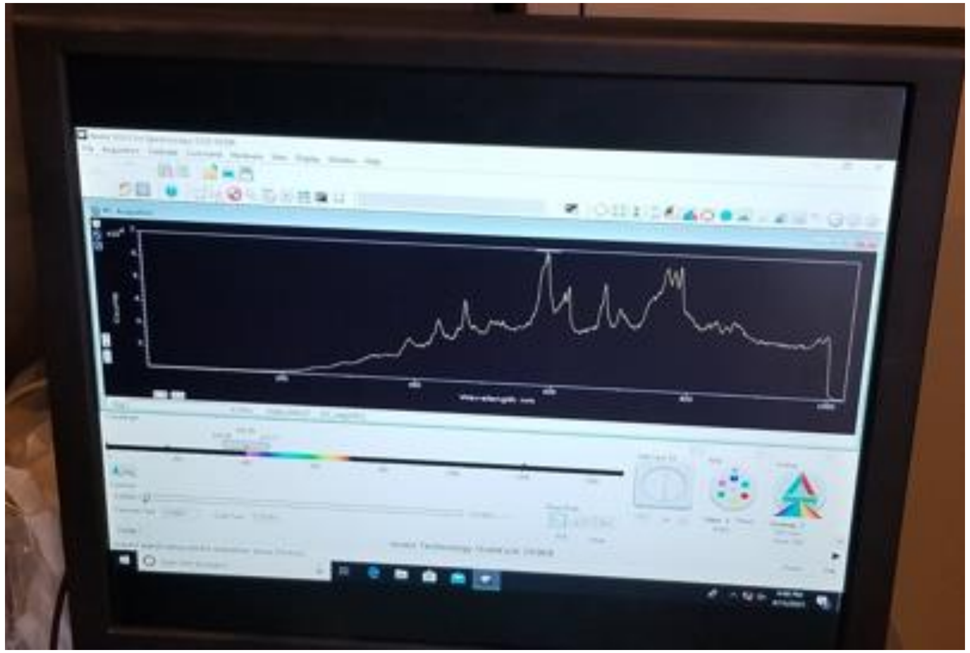
Initial deployment

- Existing water test well at Morgantown campus, near B23
- Laser tight box for sensitive components, laser safe deployment
- 30 meters of fiber pulled though conduit and available for deployment
- Multipoint calibrations performed prior to deployment
- Multiple electrical issues addressed and surmounted

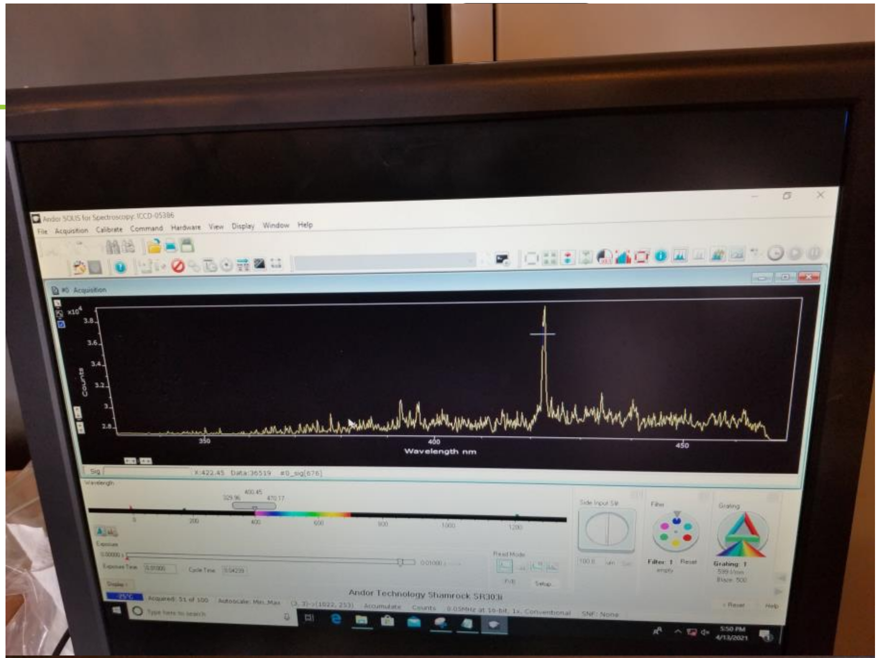


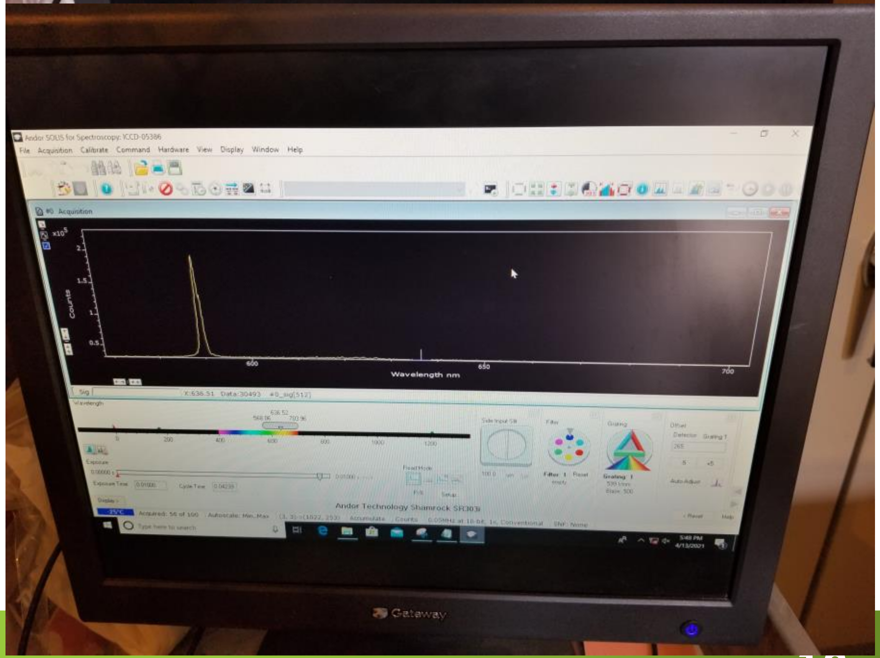
First Downhole Data

Initial Issues with trapped bubbles provided spectra of air



Readjustment of the probe provided sharp atomic spectra of Na, K, Ca, and Mg





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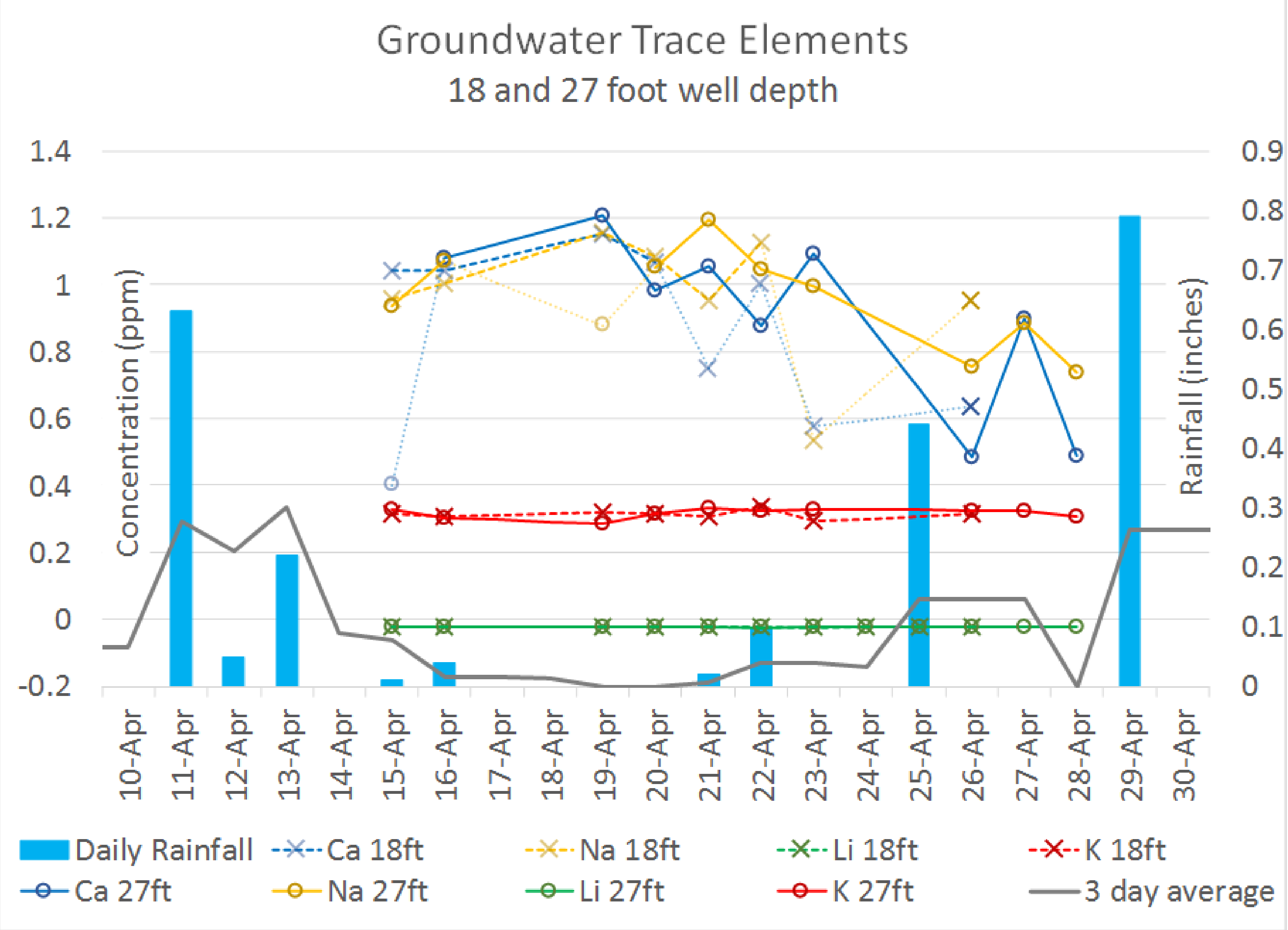

Element calibrations performed prior

Multiple depths interrogated

Each data point is a few hundred spectra

Rainfall dilution indicated for Na and Ca

K appears unaffected

Li too low to measure (LOD = 8ppb in lab)

Concluding Remarks

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- Next Steps
  - Continue seeking intellectual property
  - Continue publishing high quality journal papers
  - Continue attending international scientific conferences
  - Reducing lab scale equipment to more appropriately size and cost components.
  - Continue arranging beneficial CRADA’s and applying for TCF and other funding that can help lead to commercialization.

nature

SCIENTIFIC REPORTS