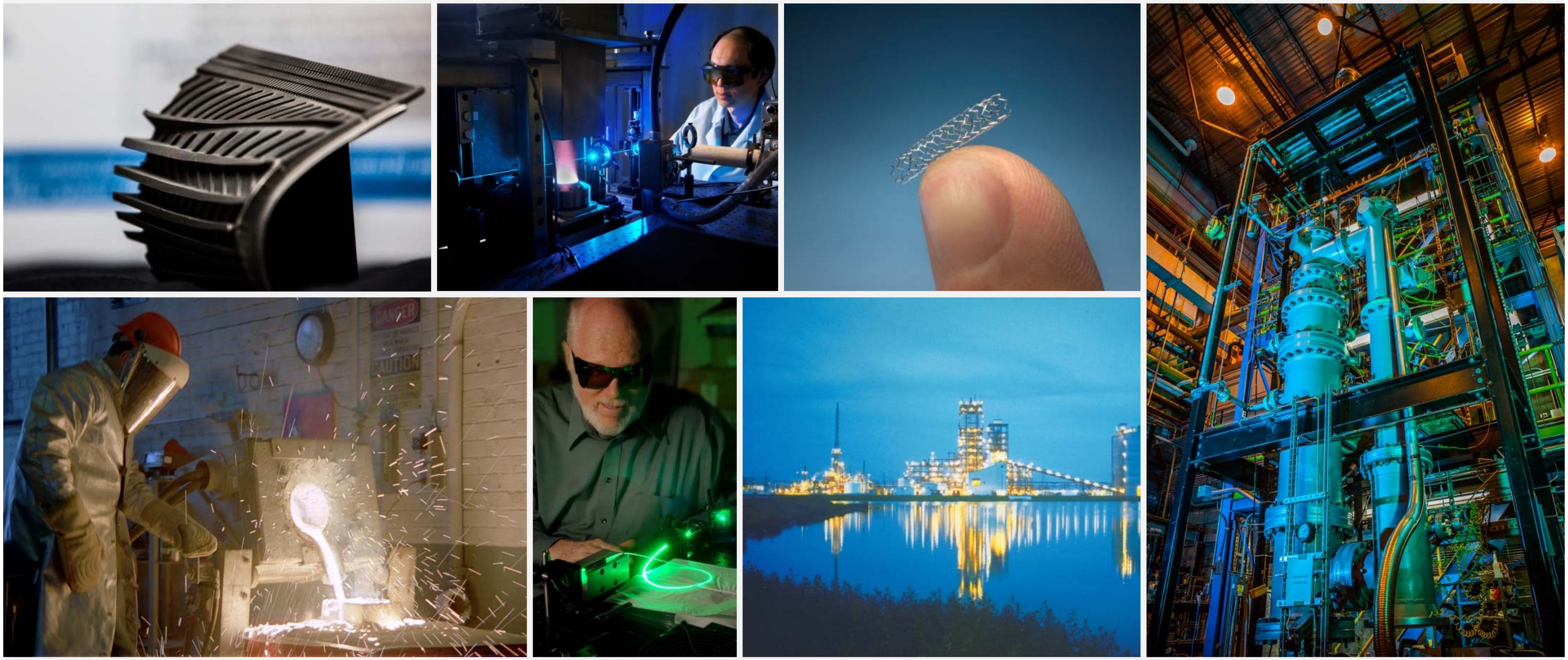
Driving Innovation ♦ Delivering Results



Crosscutting Research and REE Review
Innovative Process Technologies

Dustin McIntyre, PhD, PE

NETL's Research and Innovation Center

April 18^{th}, 2016

Presentation Overview

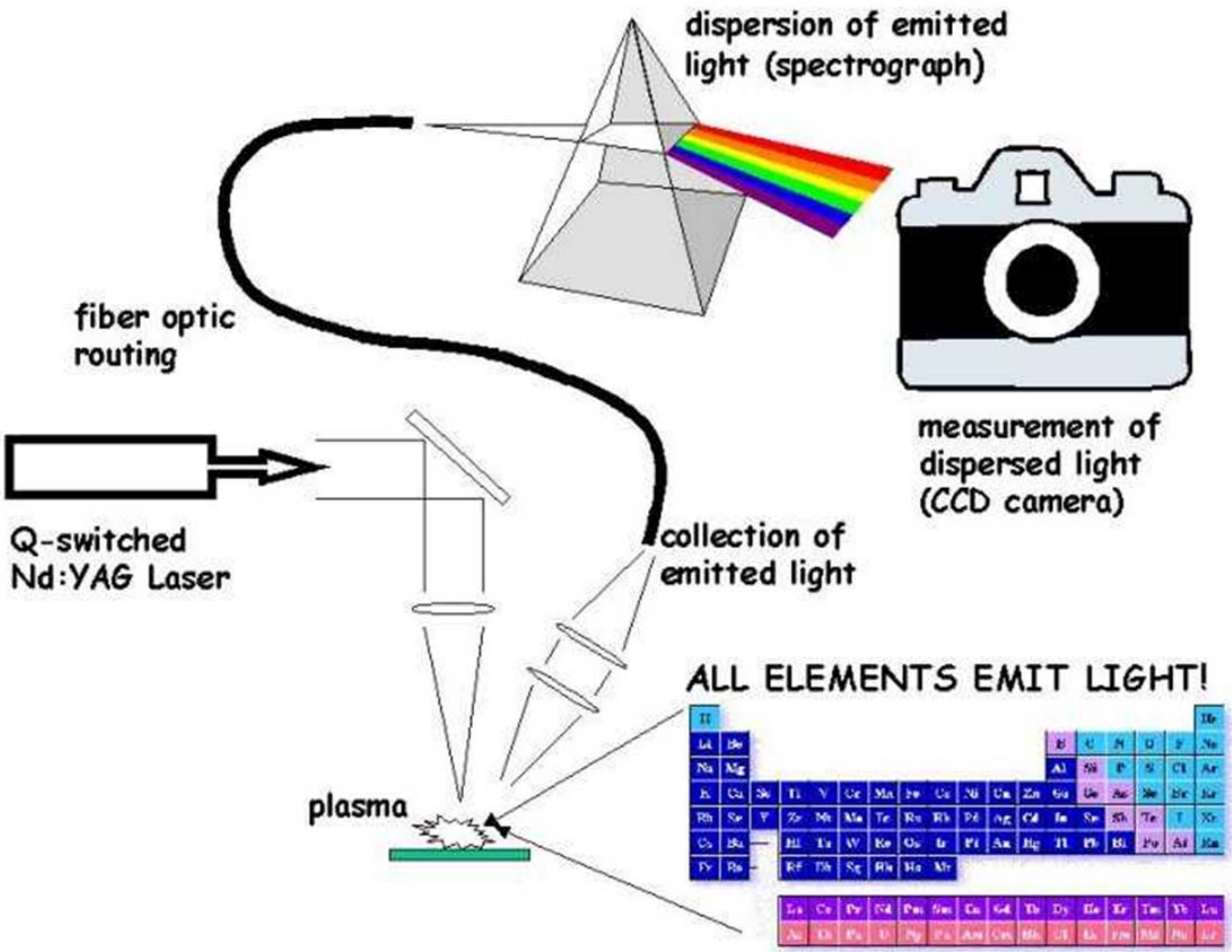
- Concept overview
- Experimental work
- Prototype development and miniaturization
- Intellectual property work
- Proposal development

Downhole Laser Induced Breakdown Spectroscopy (LIBS) Update

Concept Overview:

- No technology available that measures a range of ions in solution under in-situ conditions.
  - Samples have to be brought to the surface and transported to lab
  - Solubility of the constituents may have changed due to P,T differences or by interaction with the atmosphere.
- Miniaturization of a laser system that can be deployed downhole as part of an in place constant monitoring tool is being developed.
- Use of LIBS is projected as a potential downhole method of dissolved metal analysis and could be coupled with metal carbonate dissolution as an effective monitoring tool.

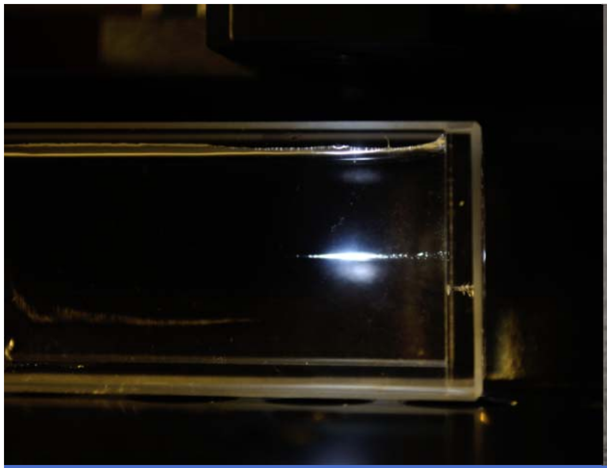
What is LIBS?

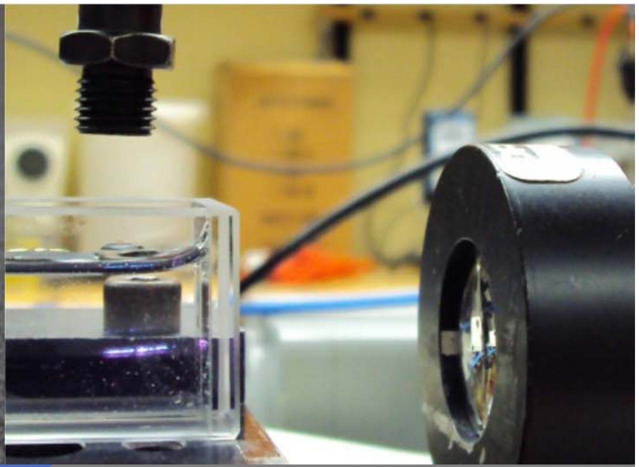


Wikipedia

Groundwater Monitoring Application

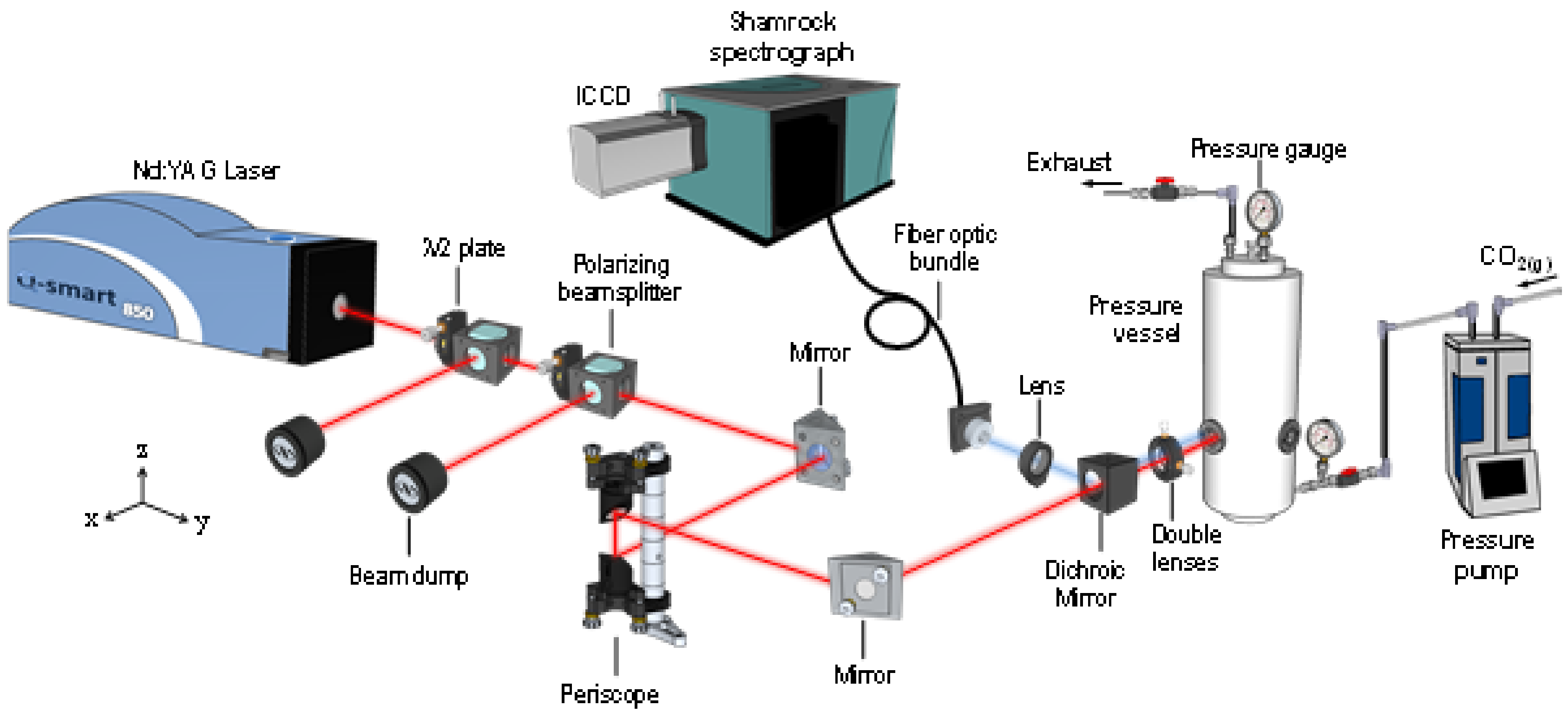
- Miniaturized laser technology produces sparks underwater; resulting atomic emission from sparks can be used to measure concentrations (via Inductively Coupled Plasma Mass Spectrometry).
- Probe can be placed down-hole for in-situ measurements of groundwater chemistry.
- Qualitative and quantitative analysis of brine (Na, Li, Mg, Ca, K, Sr). Concentrations measured from the ppb and ppm range to the % range using synthetic brines in the lab.



Experimental Work

- **Elevated temperature and pressure**
- **Investigated effect on atomic emission**
- **Investigated measurement capability**



Experimental Work

- **Elevated temperature and pressure**
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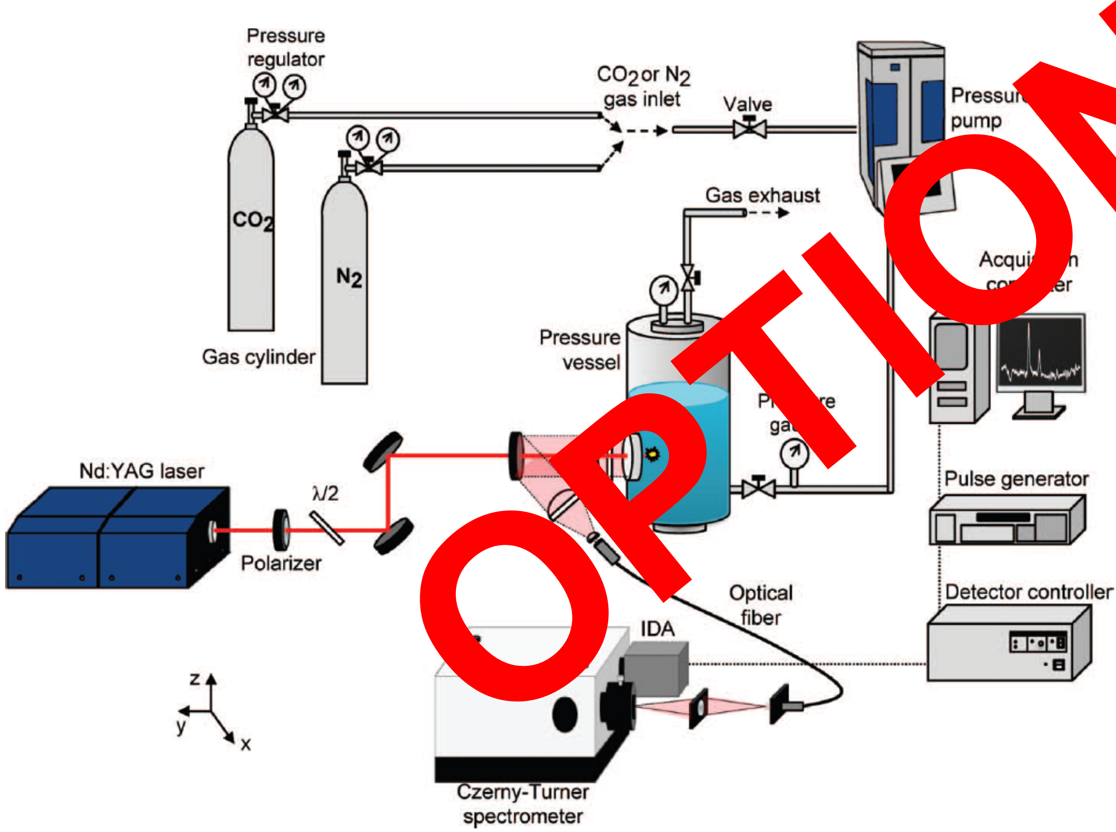
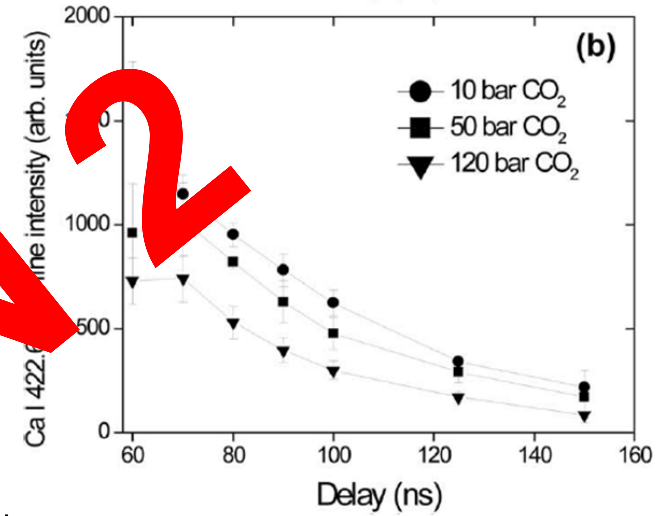
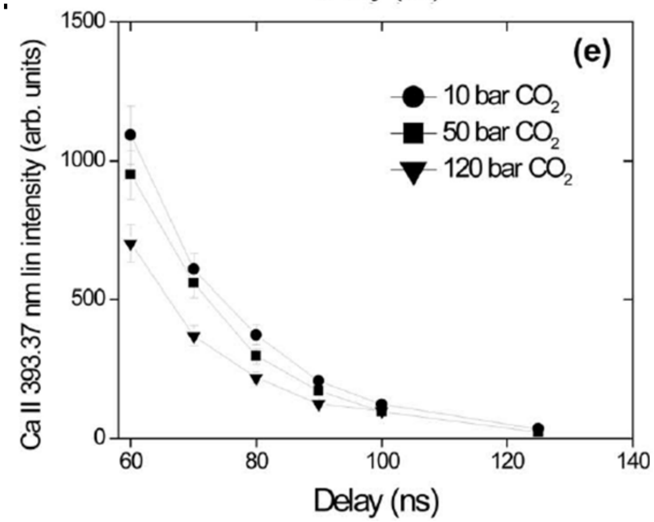




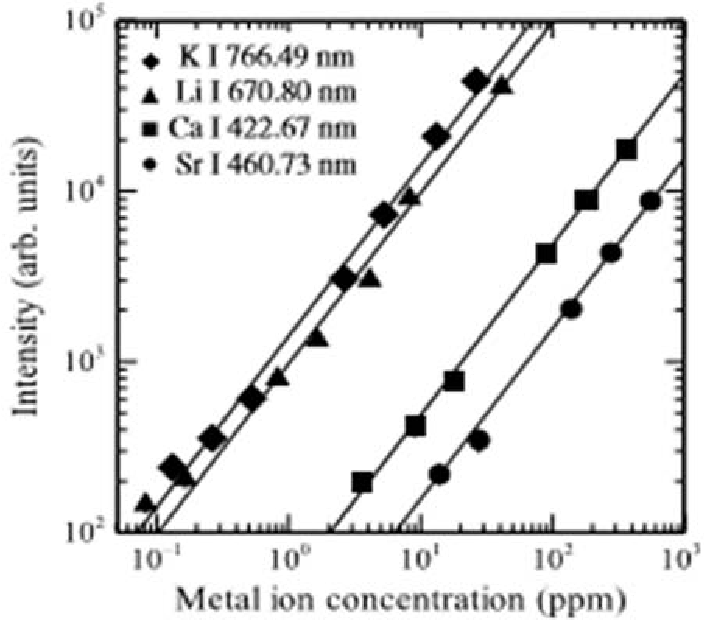


OPTION 2

Experimental Work (STP)

STEP 1

- Ability to make measurement across relevant concentration ranges
- Determine linearity

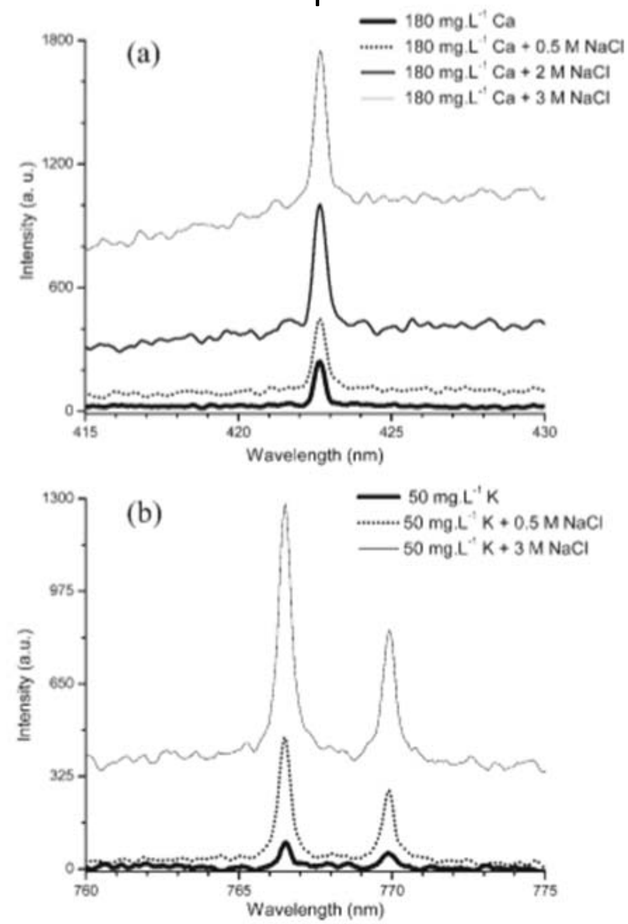


	R^2	LOD	LOQ
Sr	0.9990	2.89 ± 0.11 ppm	9.63 ± 0.39 ppm
Ca	0.9997	0.94 ± 0.14 ppm	3.11 ± 0.07 ppm
Li	0.9988	60 ± 2 ppb	0.19 ± 0.01 ppm
K	0.9977	30 ± 1 ppb	80 ± 4 ppb

[a]The coefficient of correlation (R^2) is indicated.

STEP 2

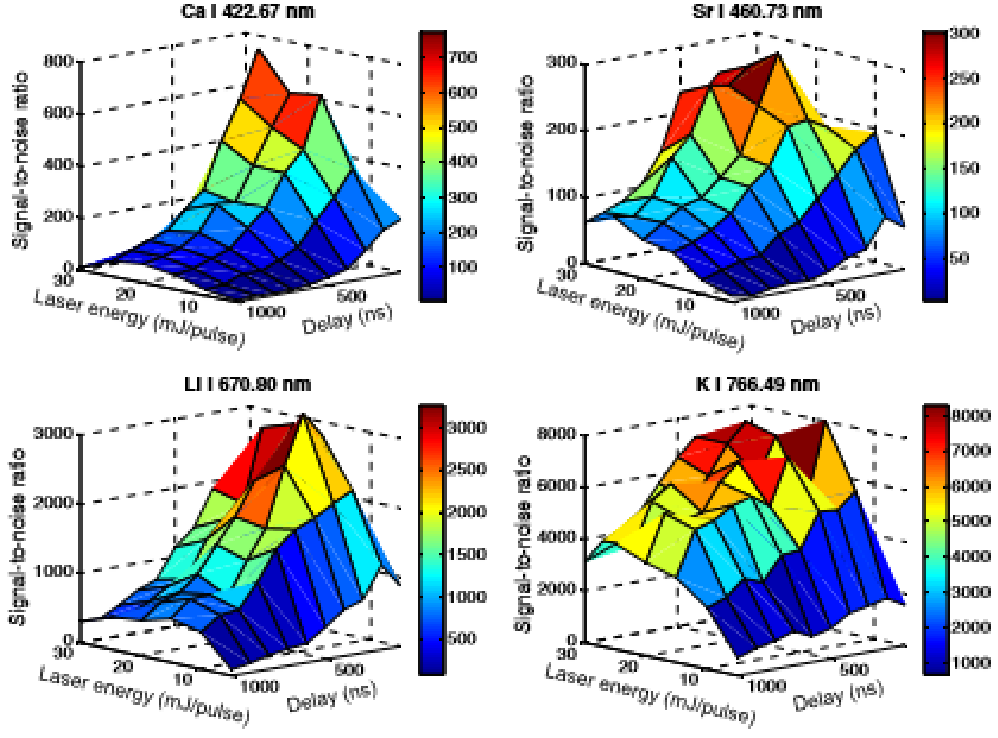
- Study interference from other high concentration species



Experimental Work (Elevated T&P)

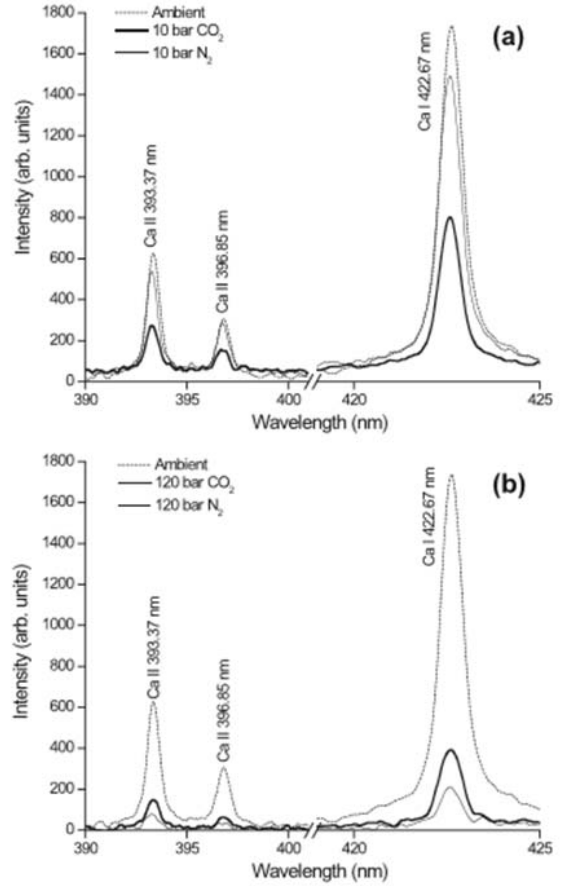
STEP 3

- Develop response surfaces for analytes (laser pulse energy and gate delay)

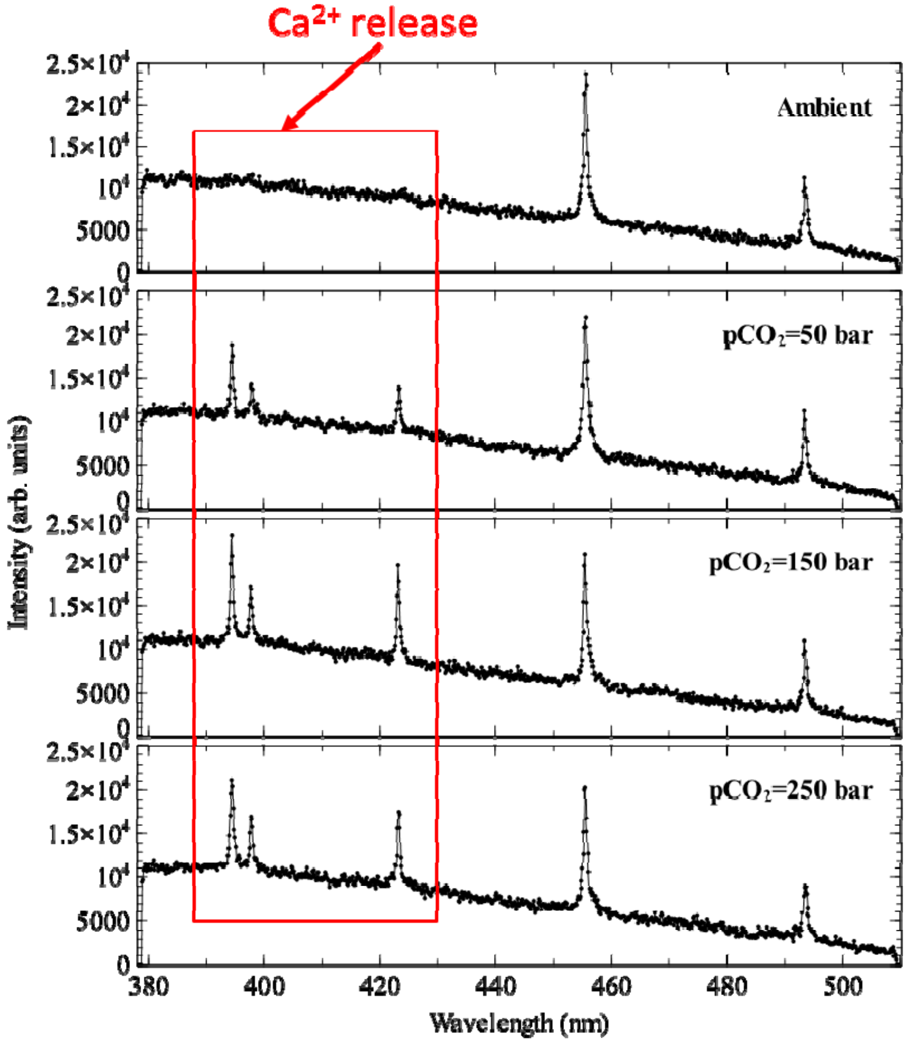


STEP 4

- Determine effects of pressure on measurement

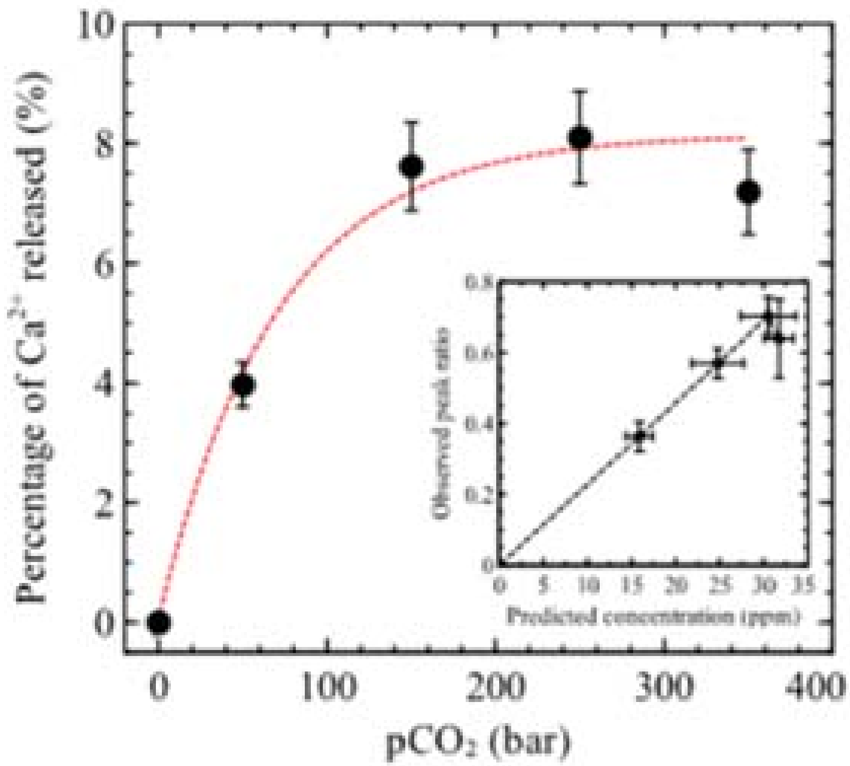


Experimental Work (Elevated T&P)



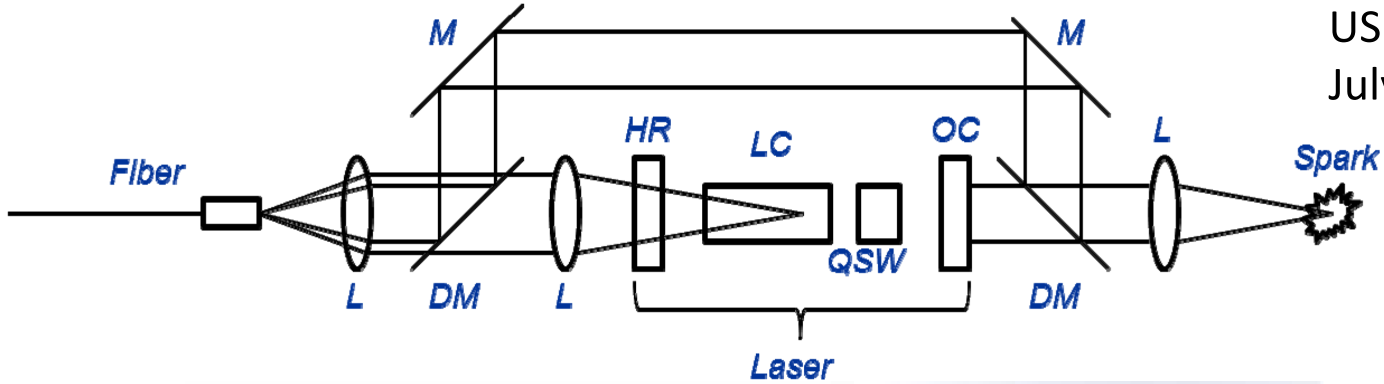
STEP 5

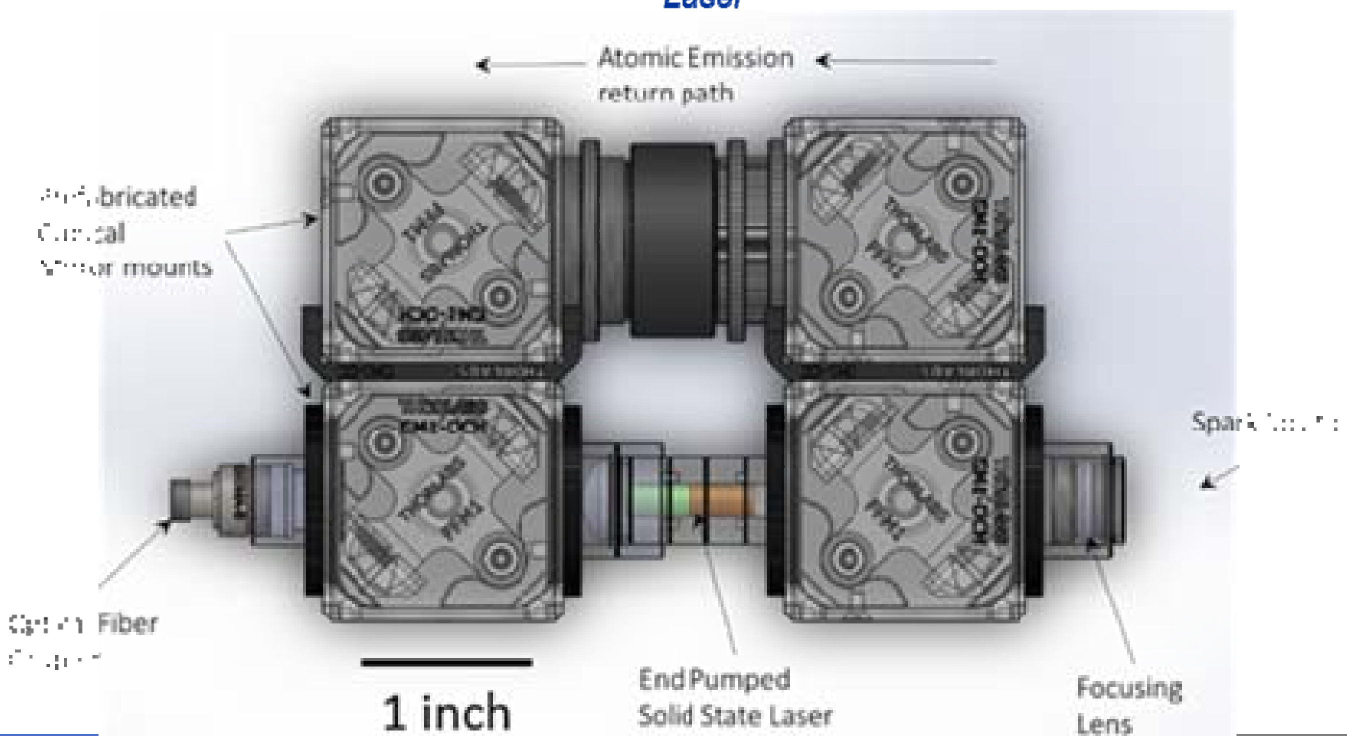
- Study Ca dissolution as a function of CO2 pressure



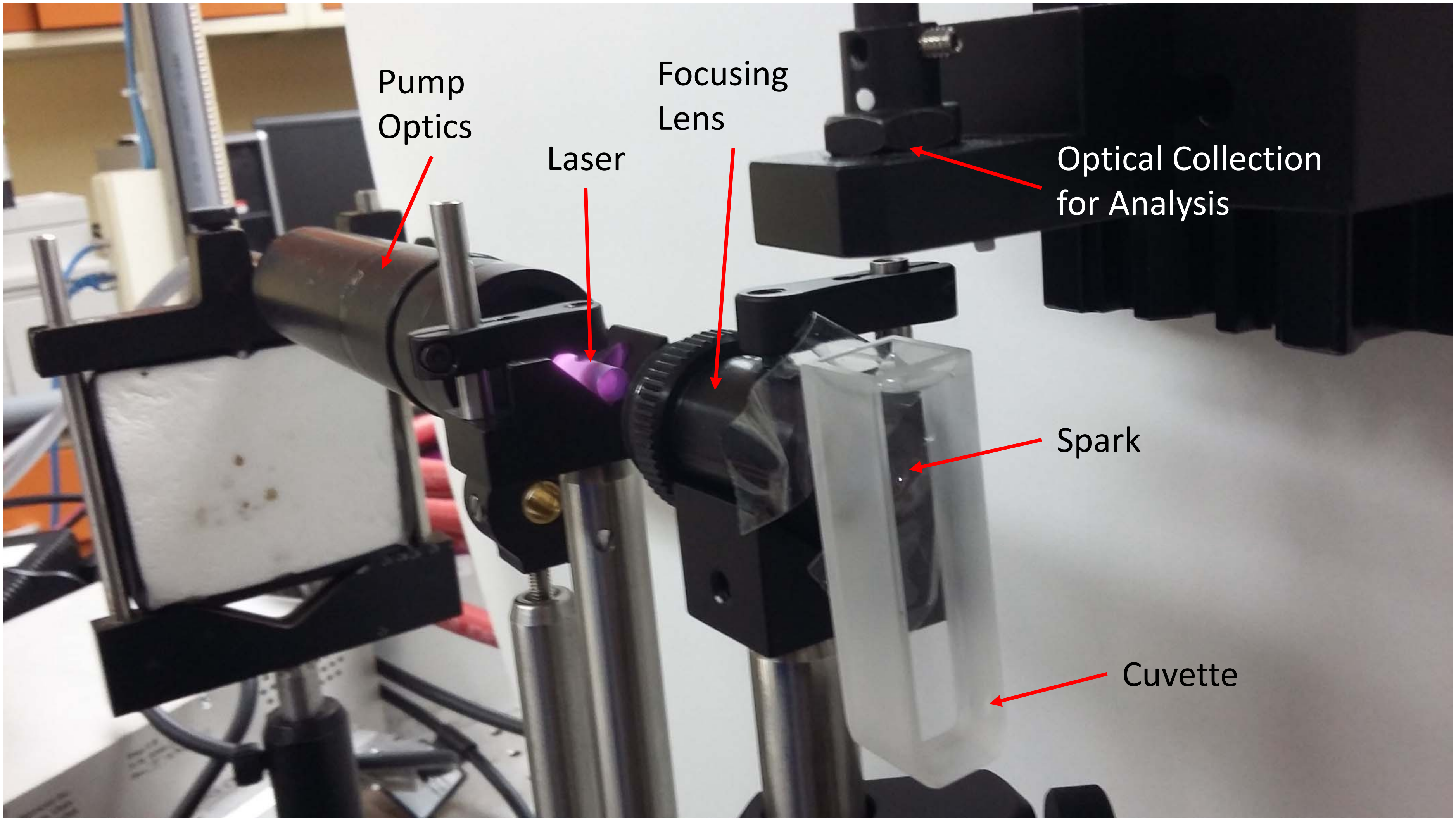
Prototype Development

US Patent 8,786,840
July 2014

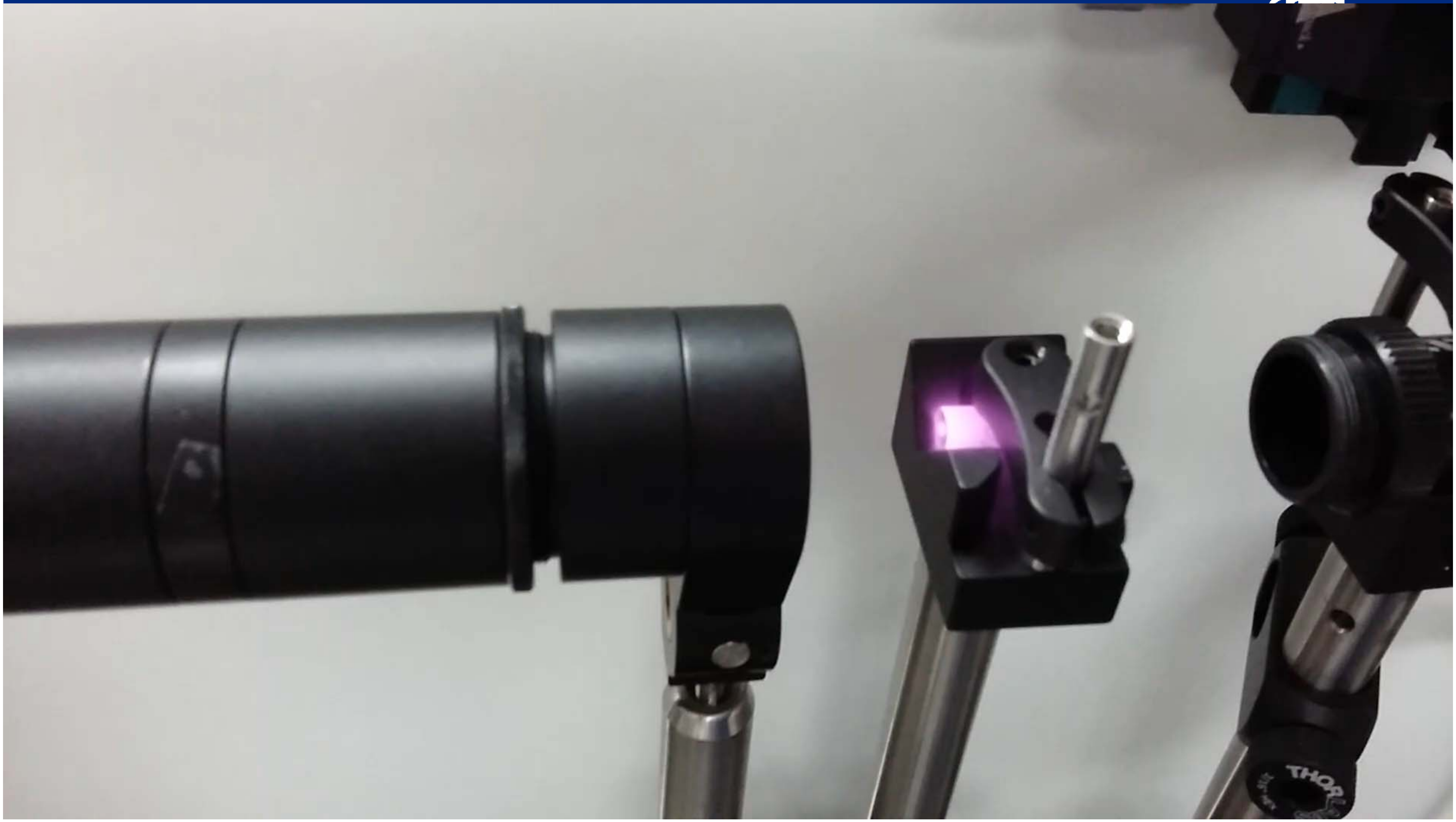




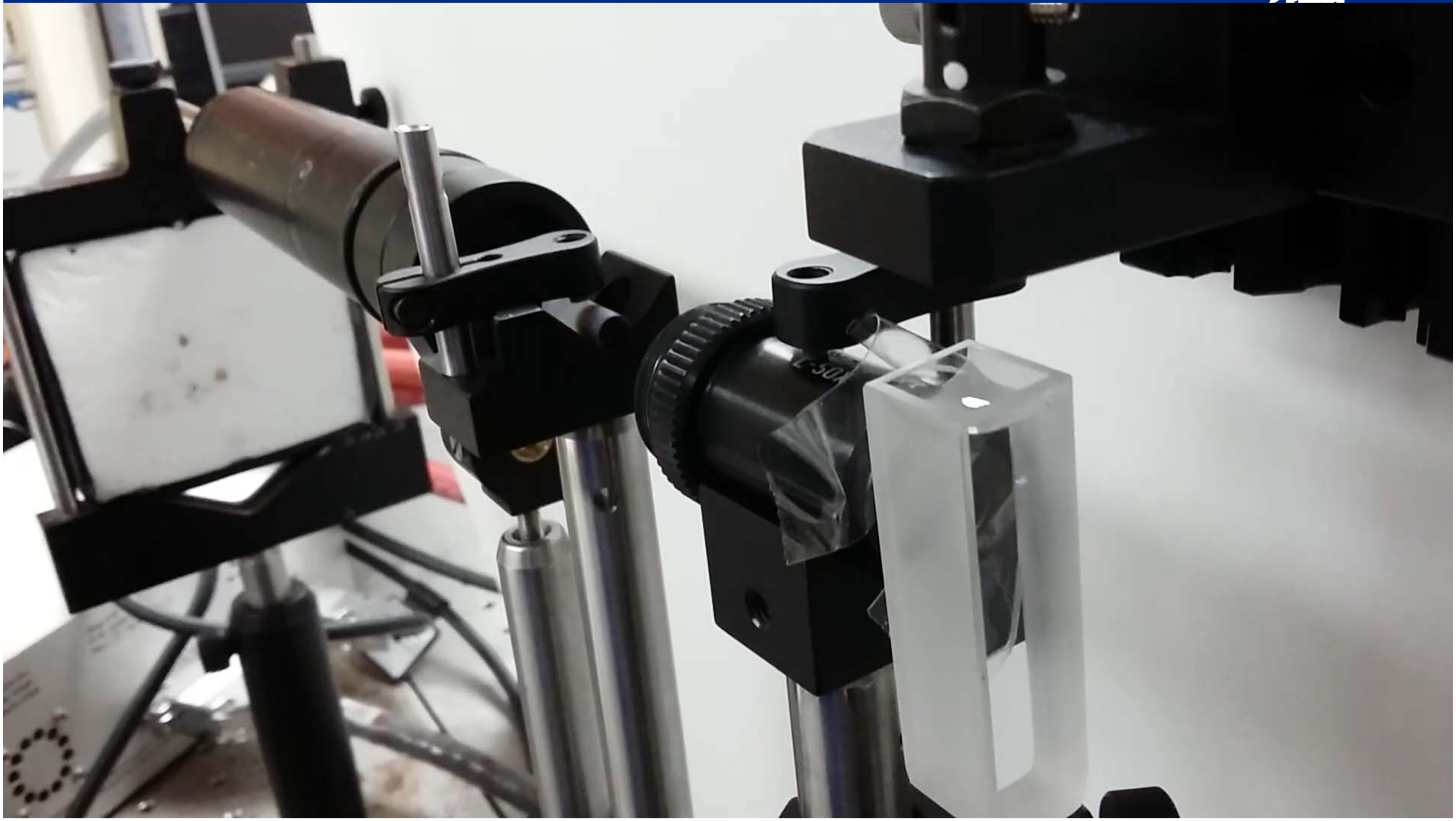
Prototype Development



Prototype Development

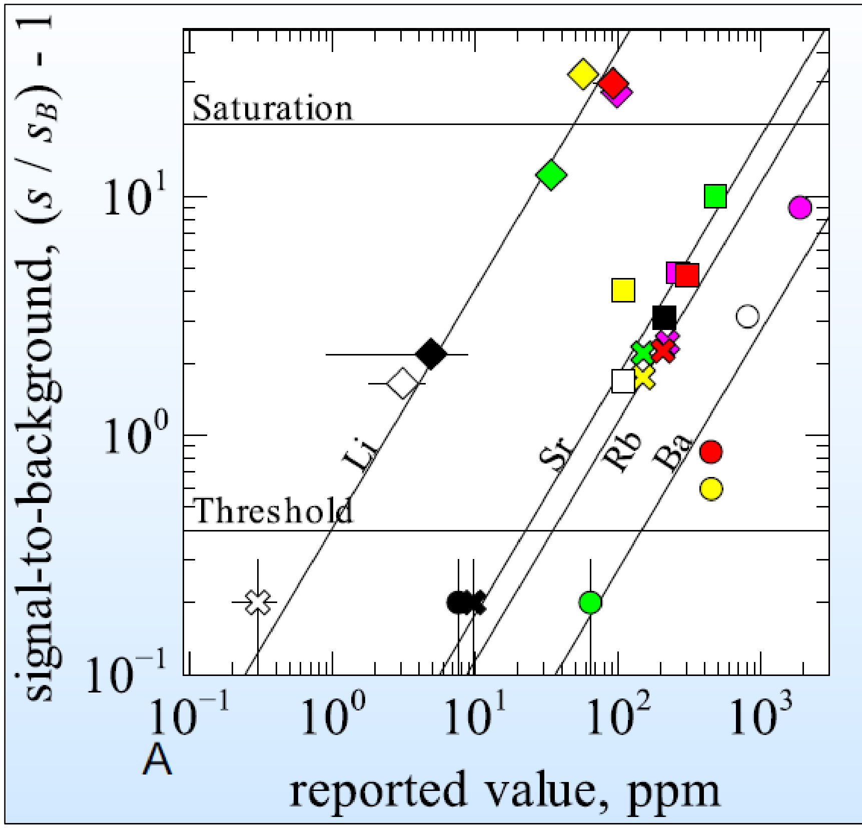


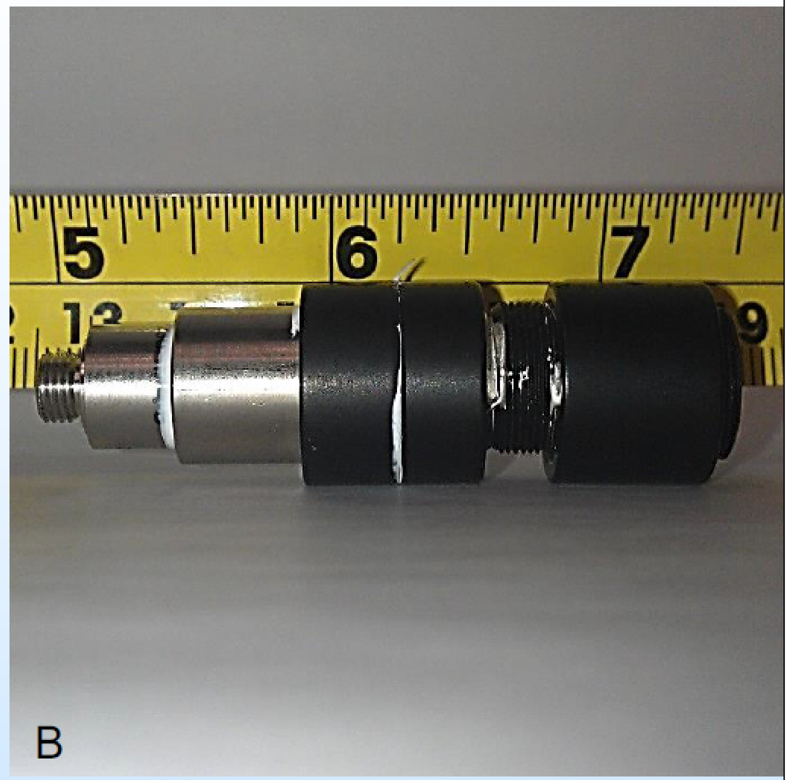
Prototype Development



LIBS Sensor Miniaturization

Enabling downhole deployment of measurement optics



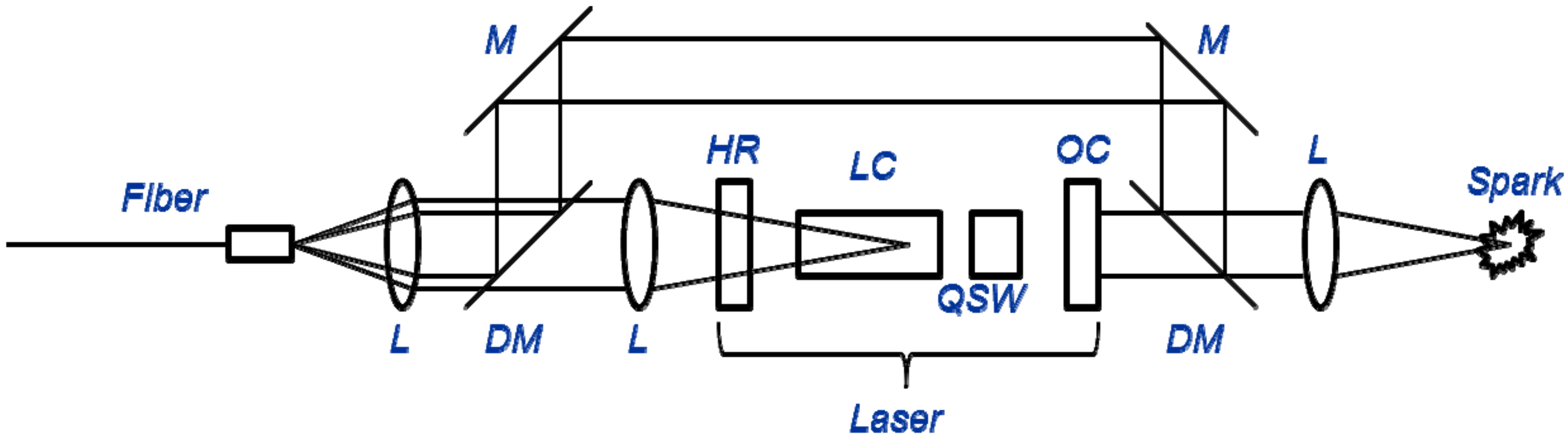


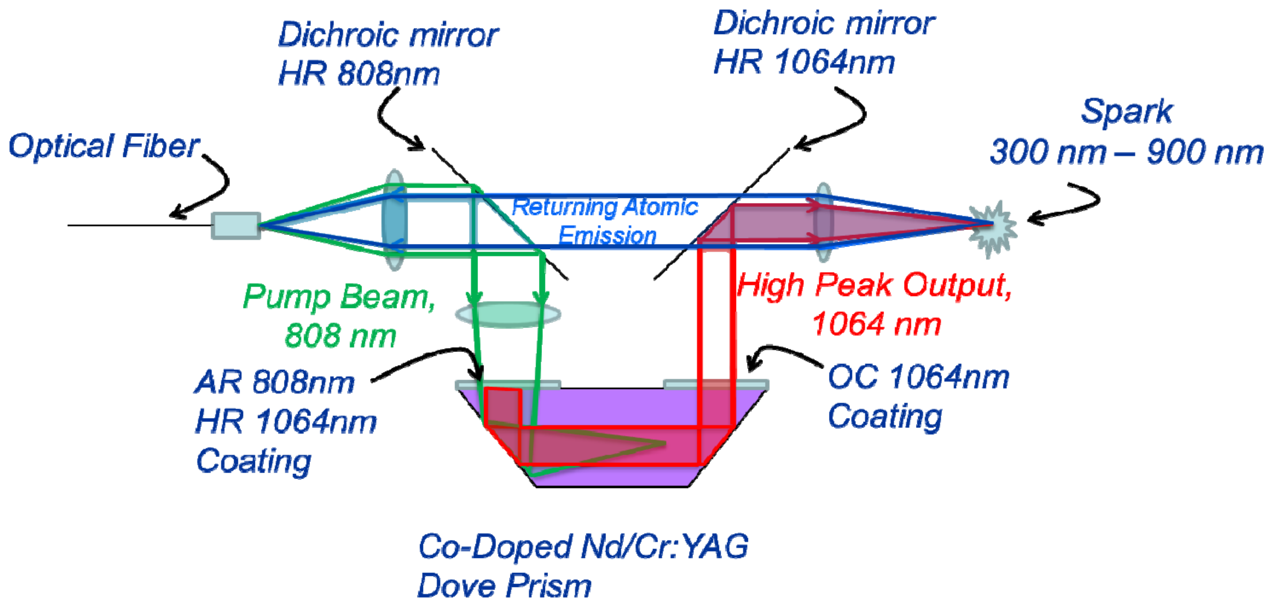
Calibration curves for Li, Sr, Rb, and Ba for a series of calibrated rock glasses using LIBS from a passively q-switched laser.

Prototype downhole passively q-switched laser

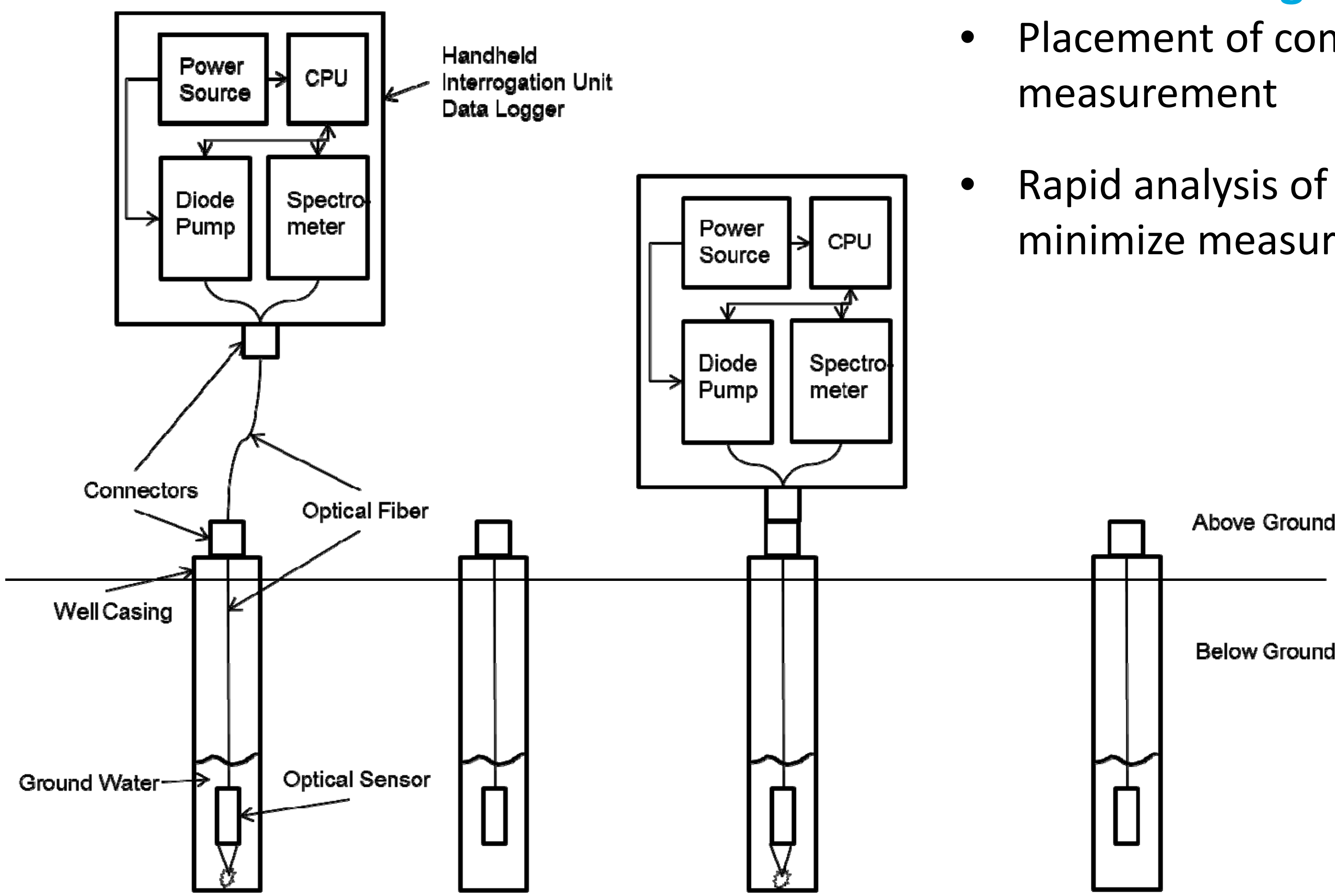
1 Patent, 4 Pending

Intellectual Property





Intellectual Property



Other IP moving forward

- Placement of components to optimize measurement
- Rapid analysis of laser output to minimize measurement variation

On-going Work

Research Status

- **Mark 1 prototype development completed.**
- **Atomic interferences and enhancements currently being studied.**
- **Studying Alkali and Alkaline dissolution vs. pH**

Patent Status

- **US Patent 8,786,840 Granted July 2014**
  - Overall distributed down hole system with miniaturized laser and optical distributor
- **US Patent 9,297,696 Granted March 2016**
  - Method for using passively Q-switched laser for quantitative measurements
- **Patent application (2015) describing a laser arrangement that allows:**
  - Longer LIBS spark residence times
  - Improved signal to noise ratios
  - Application of multiple laser beams to one location at the same time and/or at different times
  - Enhance plasma emission and plasma lifetime.

Proposal Development

- **Lab Call "Technology Commercialization Fund" Applied Spectra (Fremont, CA)**
- **NASA Roses "Instrument Incubator" WVU**

Related Publications

- Goueguel, C., Singh, J.P., McIntyre, D.L., Jain, J., Karamalidis, A.K., "Effect of NaCl concentration on elemental analysis of brines by laser-induced breakdown spectroscopy," Applied Spectroscopy, Volume 68, Issue 2, Pages 34A-44A and 133-262 (February 2014), pp. 213-221(9).
- McIntyre, D.L., Jain, J.C., Goueguel, C.L., Singh, J.P., "Application of Laser Induced Breakdown Spectroscopy (LIBS) to Carbon Sequestration Research and Development," Spectroscopic Techniques for Security, Forensic, and Environmental Applications, pp. 25-51, Nova Science Publishers, 2014, ISBN: 978-1-63117-404-9
- Goueguel, C., McIntyre, D., Singh, J., Jain, J., Karamalidis, A., "Laser-Induced Breakdown Spectroscopy of High-Pressure CO_2-Water Mixture: Application to Carbon Sequestration," Applied Spectroscopy, Vol. 68, No. 9, pp. 997-1003, 2014.
- Woodruff, S.D., McIntyre, D.L., Jain, J.C., "A method and device for remotely monitoring an area using a low peak power optical pump," U.S. Patent 8,786,840 July 22, 2014.
- Goueguel, C., McIntyre, D.L., Jain, J., Karamalidis, A.K., Carson, C., "Matrix effect of sodium compounds on the determination of metal ions in aqueous solutions by underwater-laser induced breakdown spectroscopy," Applied Optics, Vol. 54, No. 19, pp. 6071-6079, July 1 2015.
- Goueguel, C., Jain, J., McIntyre, D., Sanghapi, H., Carson, C., Edenborn, H., "In-situ measurements of calcium carbonate dissolution under rising CO2 pressure using underwater laser-induced breakdown spectroscopy," Journal of the Royal Society of Chemistry, Manuscript Submitted March 2016.
- Woodruff, S.D., McIntyre, D.L., "Laser based analysis using a passively Q-switched laser" U.S. Patent Application 2014/0209794 A1, July 31, 2014.

Thank You!

Team Members

Dustin McIntyre
Jinesh Jain
Christian Goueguel
Cantwell Carson

Downhole Laser Induced Breakdown Spectroscopy (LIBS)

Agreement Type: Field Work Proposal	**Program Element:** MVA
Award No. FWP-2012.02.00 - Subtask 4.1 (FY2015) RIC Storage FY2016-2020 FWP – Subtask 8.0 (FY2016)	**Focus Area**: Geochemical/Geophysical
Recipient: National Energy Technology Laboratory	
PI: Dustin McIntyre	

Year 1 Scope: Miniaturization and laboratory signal testing under different CO_2 storage conditions for the development of LIBS will commence in FY16, getting NETL closer to the ultimate goal of developing in situ methods for sensing geochemical changes in the subsurface.

Years 2 – 5: Begin field testing.

Project Budget

	FWP Total	Task 8.0
FY2016	$6,525,000	$1,045,000
FY2017	$6,525,000	$1,045,000
FY2018	$6,525,000	$1,045,000
FY2019	$6,525,000	$1,045,000
FY2020	$6,525,000	$1,045,000
Total	**$32,625,000**	**$5,225,000**