TAGGING CO_2 TO ENABLE QUANTITATIVE INVENTORIES OF GEOLOGICAL CARBON STORAGE

DOE AWARD #DE-FE0001535

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The Earth Institute
Columbia University

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the Infrastructure for CO_2 Storage
August 20-22, 2013

Lenfest Center for Sustainable Energy
EARTH INSTITUTE | COLUMBIA UNIVERSITY

Presentation Outline

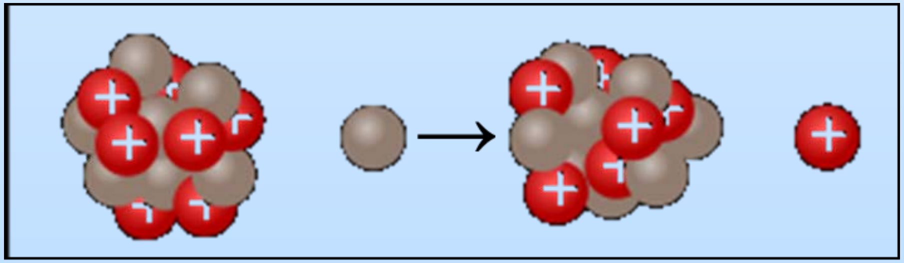
- Benefit to the program
- Project overview: Why ^{14}C for MVA?
- Technical status: Cartridges, injections, lasers
- Summary
- Organizational chart
- Collaborators

Benefit to the Program

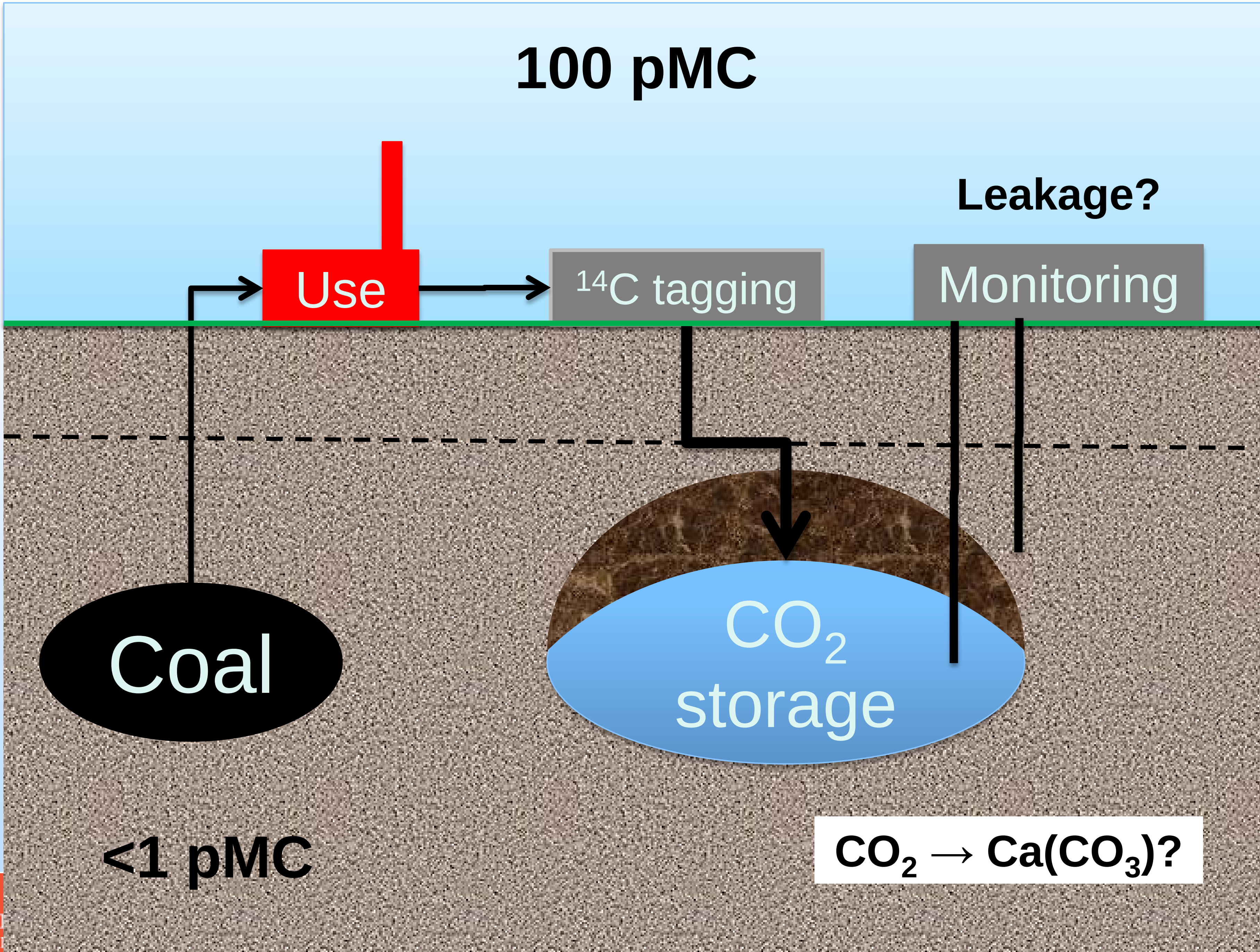
- Develop technologies to demonstrate that 99 percent of injected CO_2 remains in the injection zones.

Permanent storage of CO_2 can be demonstrated by adding carbon-14 (^{14}C) prior to injection. This research project aims to demonstrate this by tagging fossil CO_2 with ^{14}C at a field site. When completed, this system will show that ^{14}C can be a safe and effective tracer for sequestered CO_2. A laser-based ^{14}C measurement method is being adapted for continuous monitoring. This technology contributes to the Carbon Storage Program's effort of ensuring 99 percent CO_2 storage permanence in the injection zone(s) (Goal).

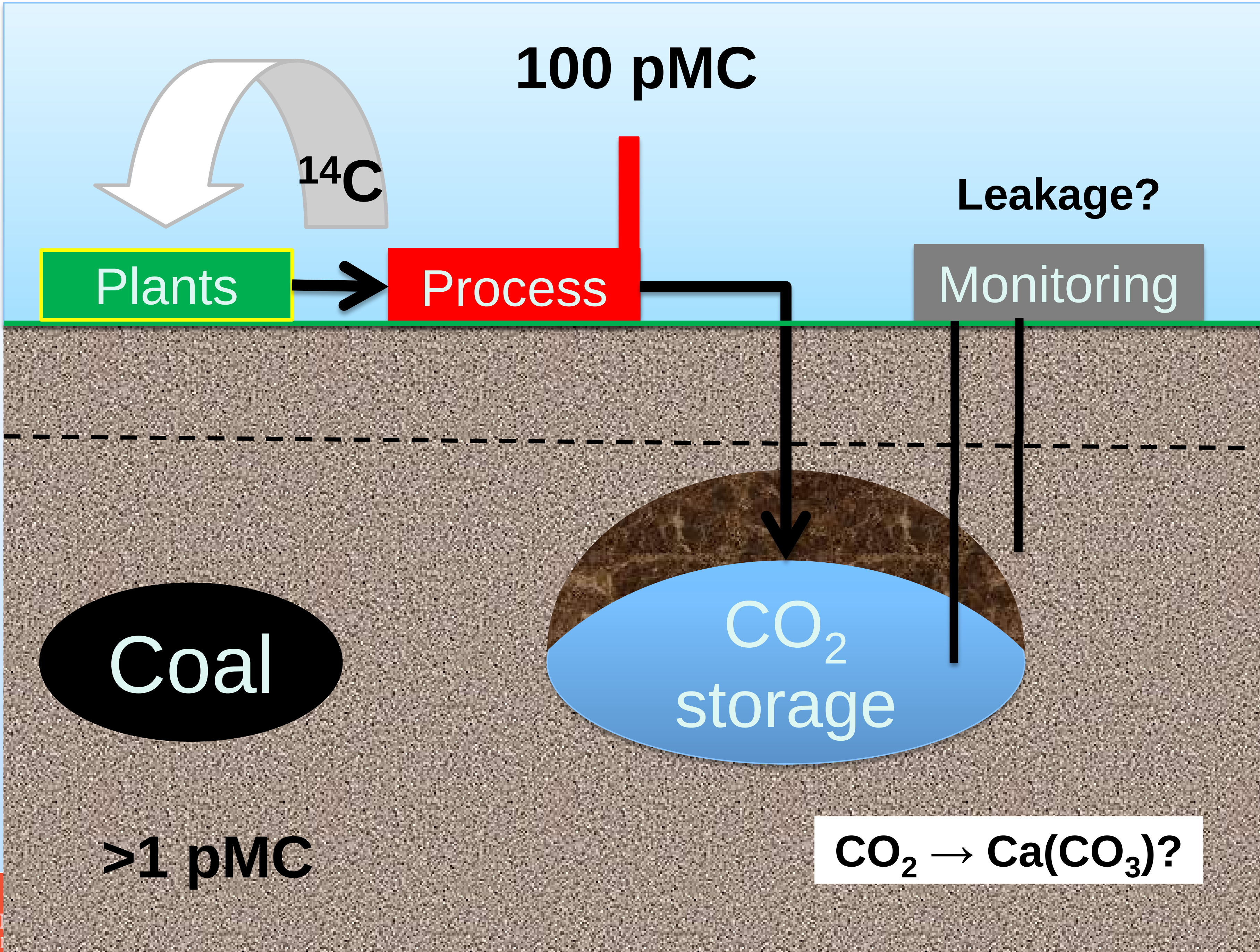
- **Project Overview: Why use ^{14}C in MVA?**
- Radiocarbon, or ^{14}C :
  - Long half-life radio isotope: $\tau_{1/2}$=5730 years
    - Produced naturally by cosmic radiation
    - Made artificially by neutron capture
  - Ambient concentration: $^{14}C/^{12}C \approx 10^{-12}$
  - Concentration in fossil fuels: $^{14}C/^{12}C < 10^{-14}$
- Fossil-based CO_2 has ~100x less ^{14}C than natural (biogenic) CO_2
- $^{14}CO_2$ is chemically identical to $^{12}CO_2$ and can indicate fixation



$$^{14}N + n \rightarrow {}^{14}C + p$$



100 pMC
Use
^{14}C tagging
Leakage?
Monitoring
Coal
CO_2 storage
<1 pMC
$CO_2 \rightarrow Ca(CO_3)$?

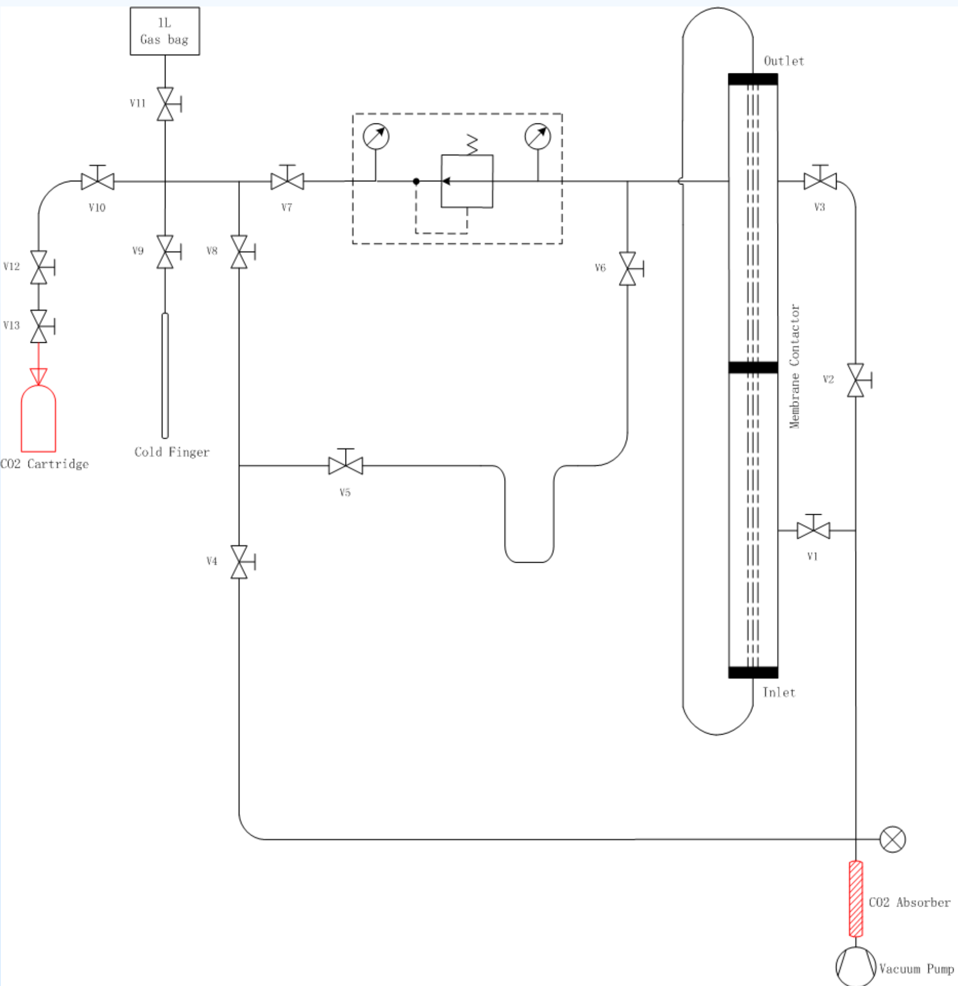

100 pMC
^{14}C
Leakage?
Plants
Process
Monitoring
Coal
CO_2 storage
>1 pMC
$CO_2 \rightarrow Ca(CO_3)$?

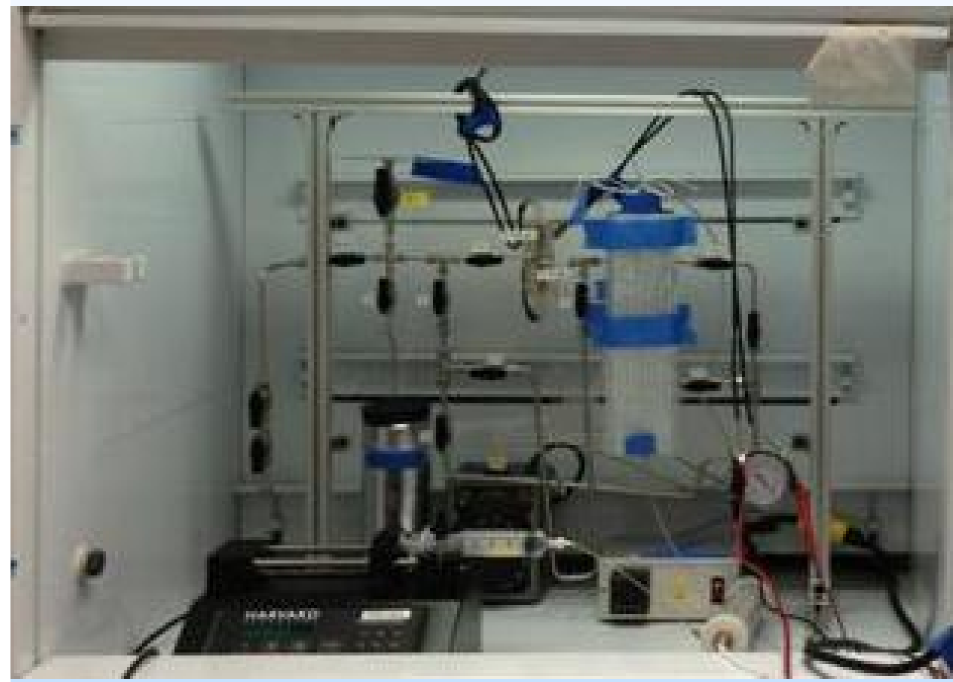
^{14}C tagging

1-day ^{14}C tag cartridge filling | ^{14}C tag injection | ^{14}C concentration monitoring

- Tag intended at ≈ 1 part per trillion
  - This limits subsurface concentration to ambient levels
  - Makes fossil based CO_2 look like bio-based CO_2
  - Requires 1 g $^{14}CO_2$ per million ton CO_2
- 1-day tag limits liability in the event of accidental release

- ^{14}C filling station
  - Produced calibrated SF_6-CO_2-water tag cartridges
  - Produced $^{14}CO_2$-water solutions with 190 pCi, 9.3 nCi and 37 nCi $^{14}CO_2$



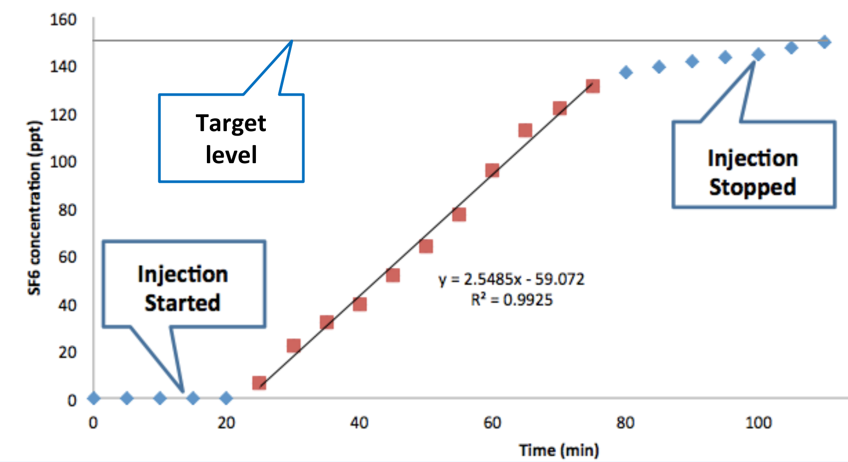


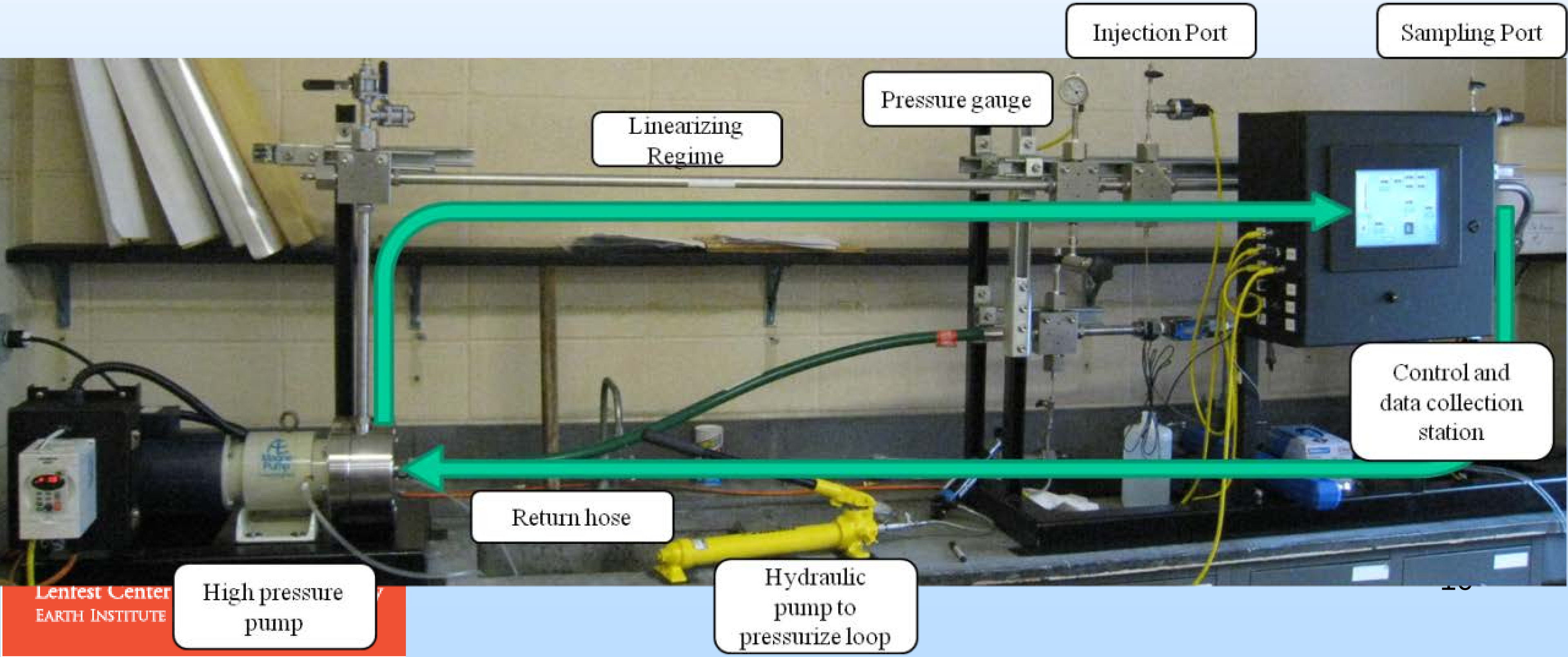
^{14}C tagging

1-day ^{14}C tag cartridge filling | ^{14}C tag injection | ^{14}C concentration monitoring

- Tagging very large stream with very small tag (1 in 10^{12})
  - 1 g $^{14}CO_2$ for 1 M ton CO2
- Needs to demonstrate accuracy and precision
- Potential injection into super critical or liquid CO_2
- Needs to be demonstrated at lab scale and in field test

- Bench-scale high-pressure flow loop
  - Turbulent flow regime
  - Pressurized CO_2 flow loop to 1457 psi CO_2, 33 ºC, supercritical regime
  - Injected SF_6 solution into super critical CO_2 at the 100 part-per-trillion level with error of <5%





^{14}C tagging

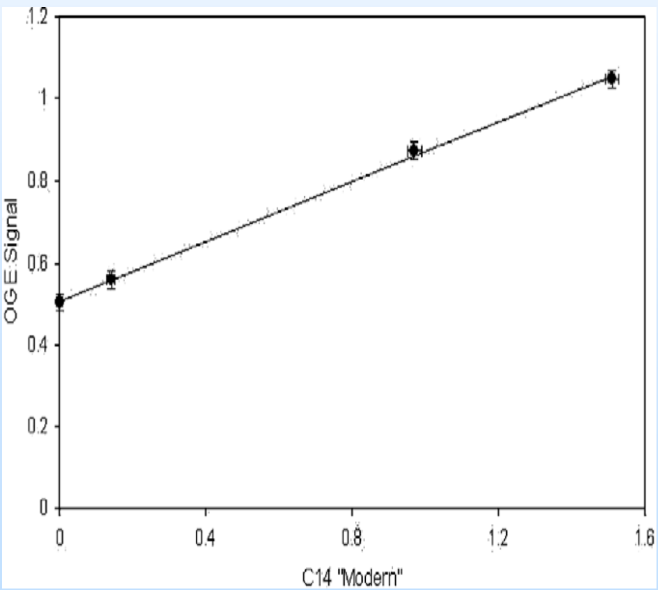
1-day ^{14}C tag cartridge filling

^{14}C tag injection

^{14}C concentration monitoring

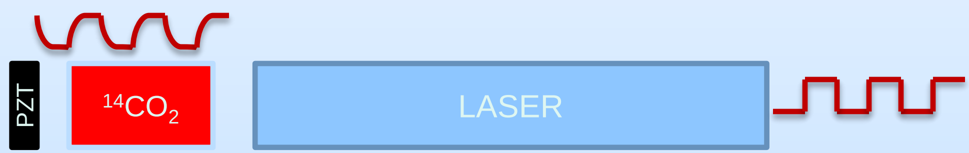
- We need a method to monitor, record, and control injection on-line and in real time
- Verification and accounting necessary at injection
- Standard methods are not viable for this application:
  - Accelerator Mass Spectrometry is a batch method
  - Liquid Scintillation Counting is too slow
- Development of laser-based currently pursued

- Development of $^{14}CO_2$ Detector
- IntraCavity OptoGalvanic Spectroscopy (ICOGS)
  - Initial results were very promising
    - Potential for fast, inexpensive, online ^{14}C measurement at the part-per-trillion (Modern) level



Original positive results

Laser pulses repeatedly excite $^{14}CO_2$ molecules in a glow discharge

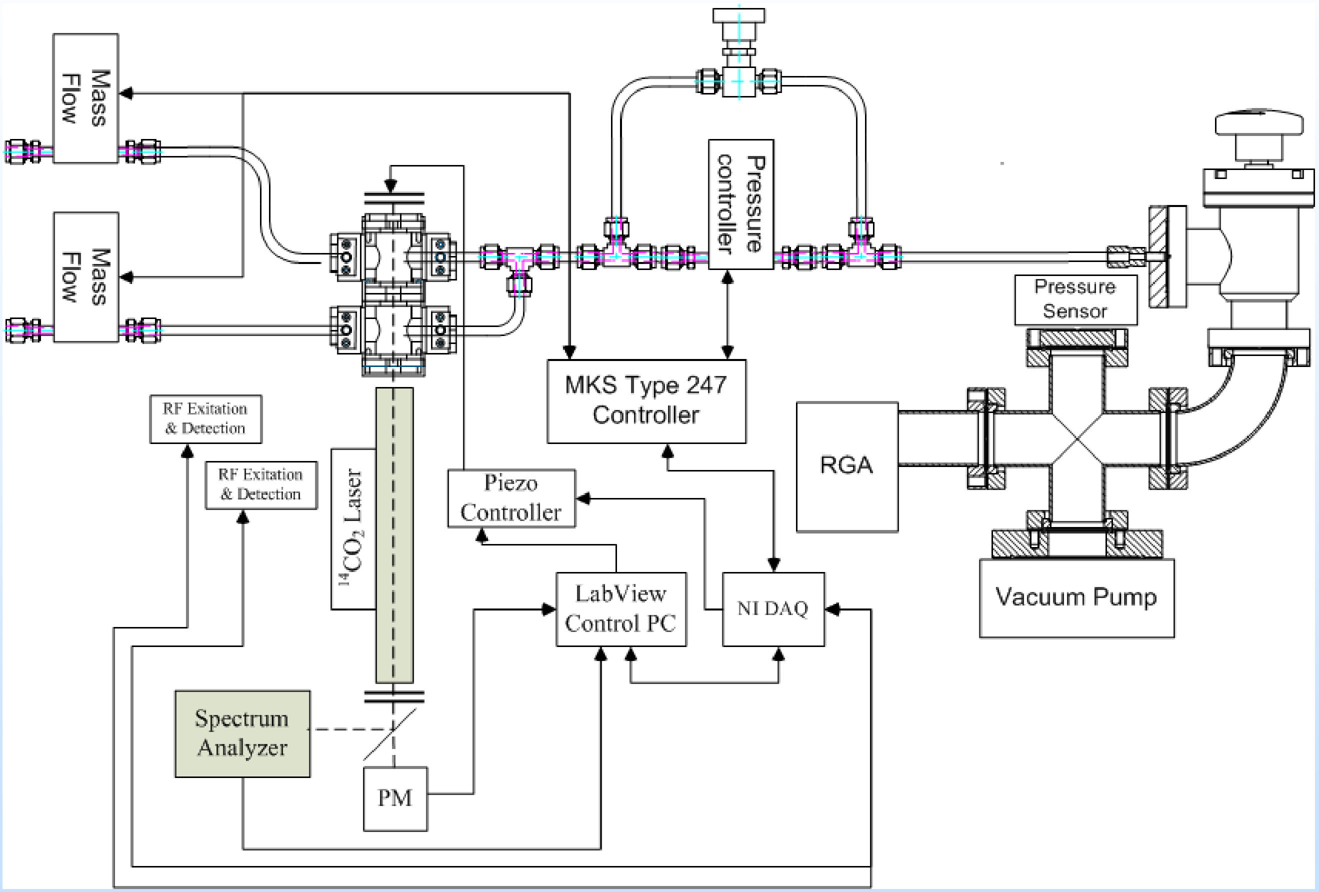


Which changes the discharge temperature

Which changes the discharge conductivity

Murnick et al., Analyt. Chem. 2008

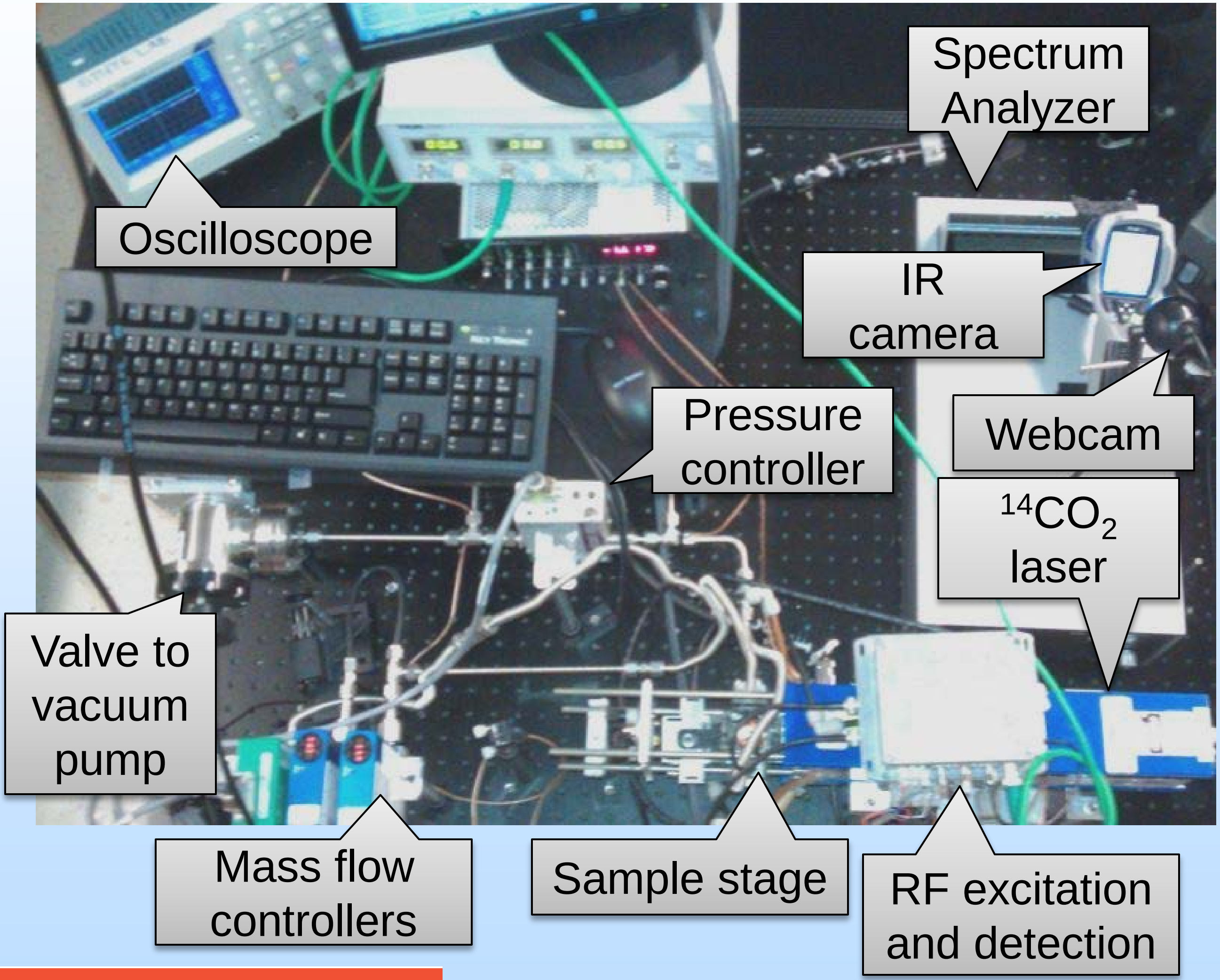
• Development of $^{14}CO_2$ Detector



We can measure:
Laser power
Laser wavelength
Cell pressure
Sample flow rate
OG voltage

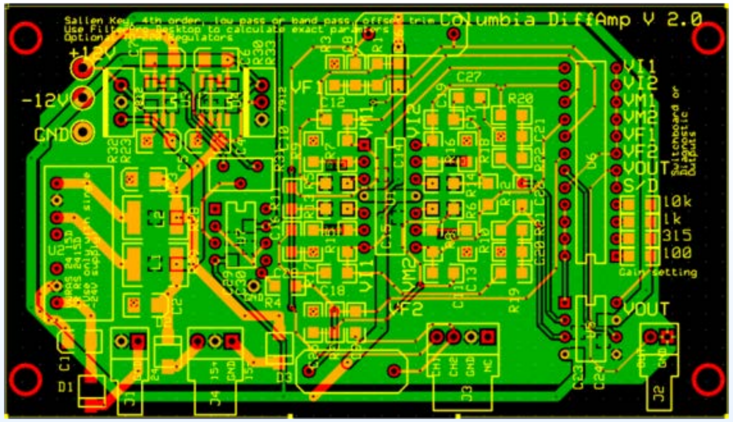
We can control:
Laser cavity position
Laser modulation mode
Cell pressure
Sample flow rate
Cell discharge power

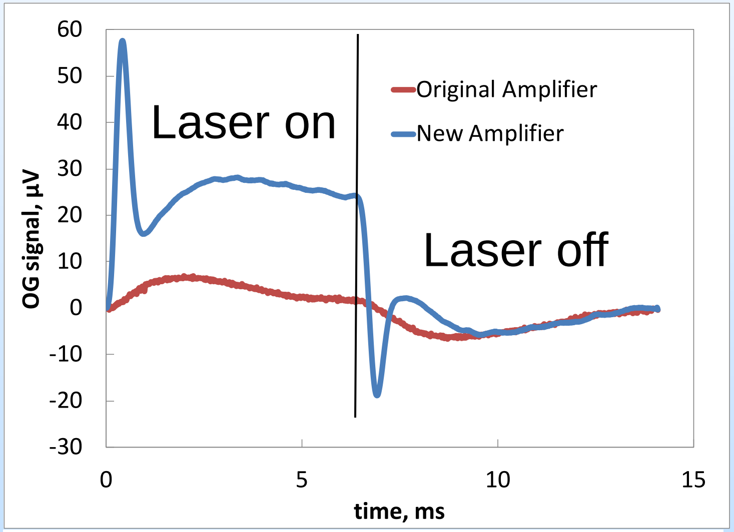
- Laser-based $^{14}CO_2$ detector
  - Assembled Intra-Cavity Opto-Galvanic Spectrometer (ICOGS)



- Not shown:
- Turbo pump
- NI CompactDAQ
- NI programmable power supplies

- Detection circuitry
  - Designed new filtering and amplifying circuitry for OG signal
  - Revealed a large transient at short times
  - Attributed to the response of the buffer gas to large changes in laser power (~40 W)
  - Appears to dominate signal when the laser is operated by generating a series of laser pulses (“Chopping mode”) at ~100Hz



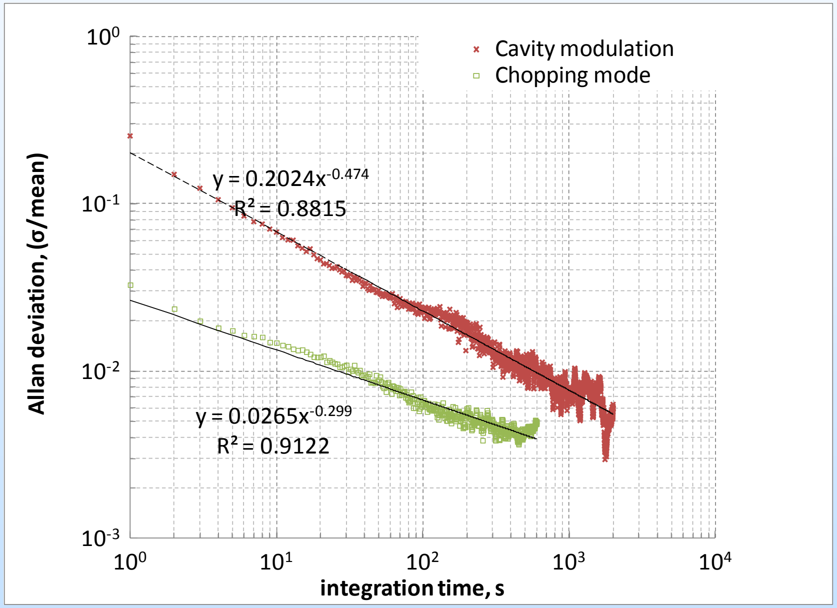


The new amplifier reveals a large transient response at short times

- Cavity Modulation
  - Developed new signal generation method: Cavity modulation
  - Generates a signal by changing the length of the laser at ~100 Hz
  - Produces a smoothly varying change in power and laser wavelength
  - Signal generation with cavity modulation was confirmed by external OG cell measurement on $^{12}CO_2$.
  - Similar signal to noise ratio when measuring CO_2 concentration.

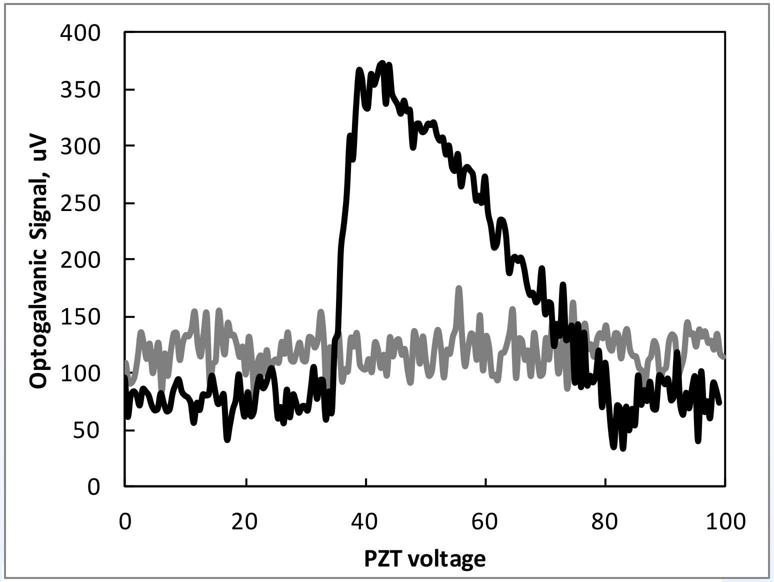
Voltage changes laser length

Which changes laser power

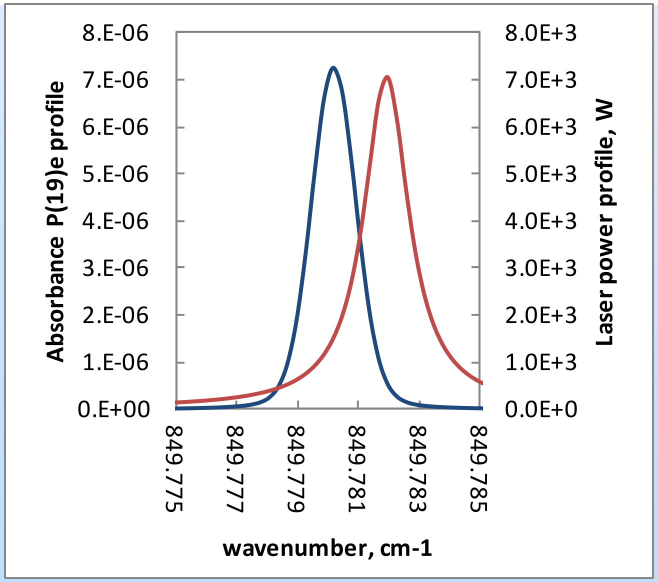


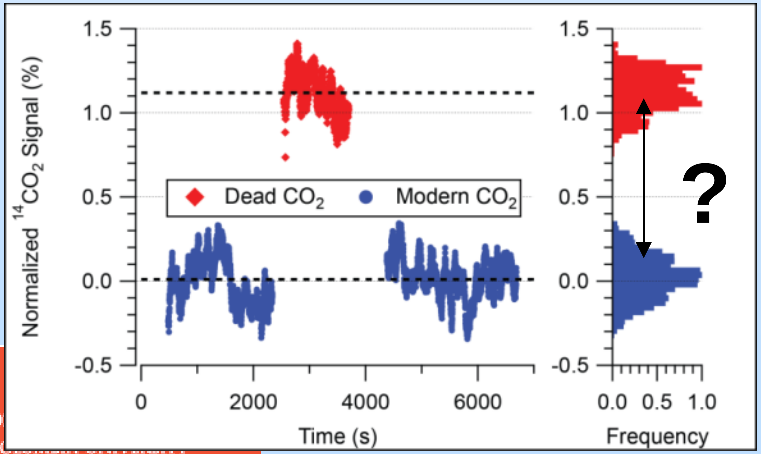
The deviation for cavity modulation (red) is shown against that of laser chopping (green) for $^{12}CO_2$.

- Development of $^{14}CO_2$ Detector
  - We were unable to see a signal in Cavity modulation
  - Indicates that most, possibly all, of the measured signals have been background fluctuations
  - Comparison with HITRAN data highlights an adjacent $^{12}CO_2$ absorbance line, 200 – 111, P(19)e
  - Work to explain role of P(19)e in ICOGS data is underway…



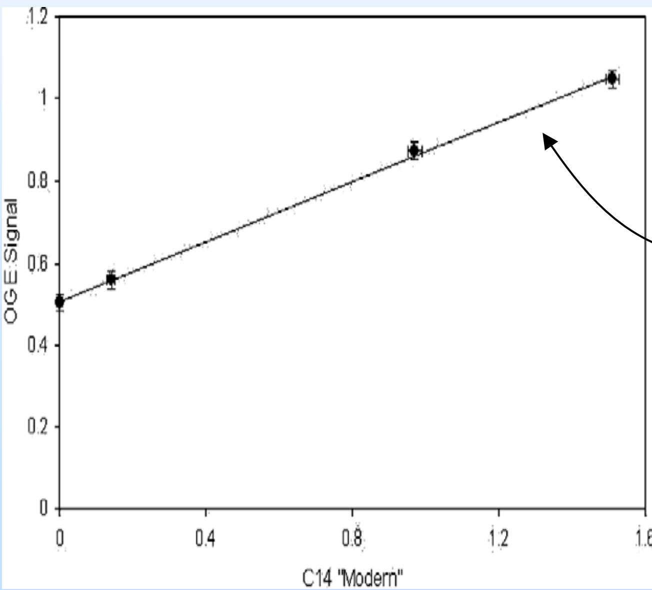
Scans do not reveal an intracavity response with cavity modulation





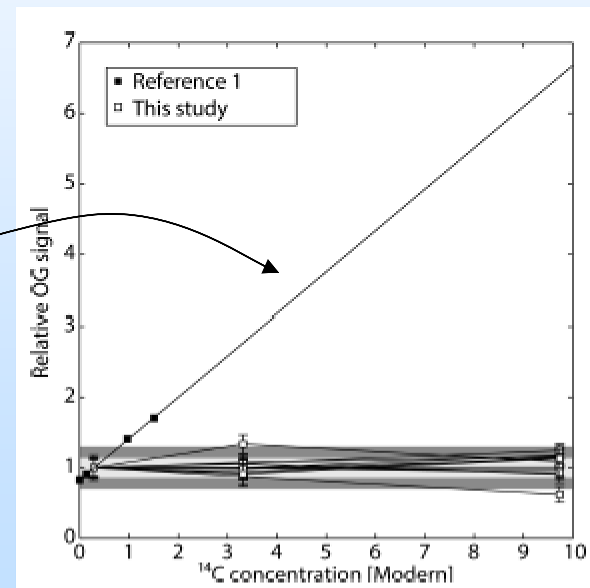
- Prospects for $^{14}CO_2$ Detector
  - Recent publications out of Uppsala University in Sweden have also highlighted this lack of reproducibility
  - Earlier results from Columbia are now attributed to small confounding pressure changes between samples
  - We are currently looking to use highly enriched samples to establish a quantitative lower limit of detection
  - Detection may be easier on other $^{14}CO_2$ laser lines away from $^{12}CO_2$ lines

Murnick et al., Analyt. Chem. 2008



Original, promising results

Persson et al., Analyt. Chem. 2013



Recent results highlighting irreproducibility of original results

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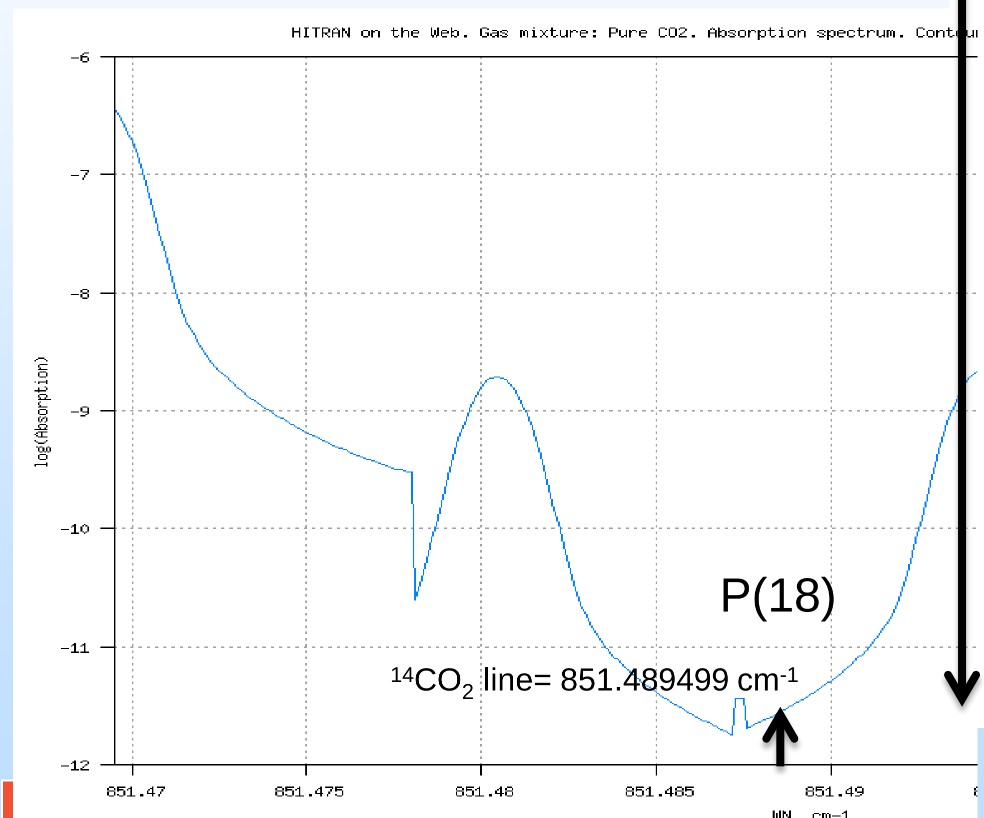
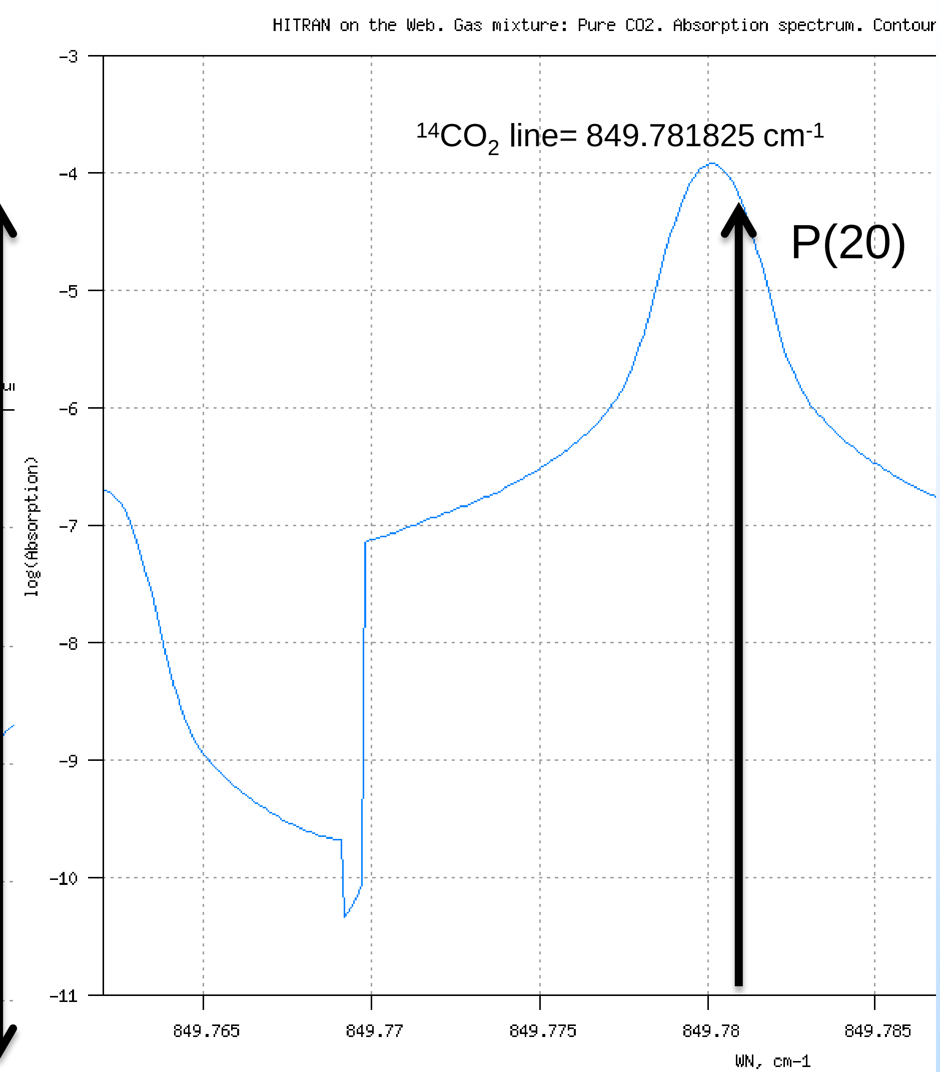
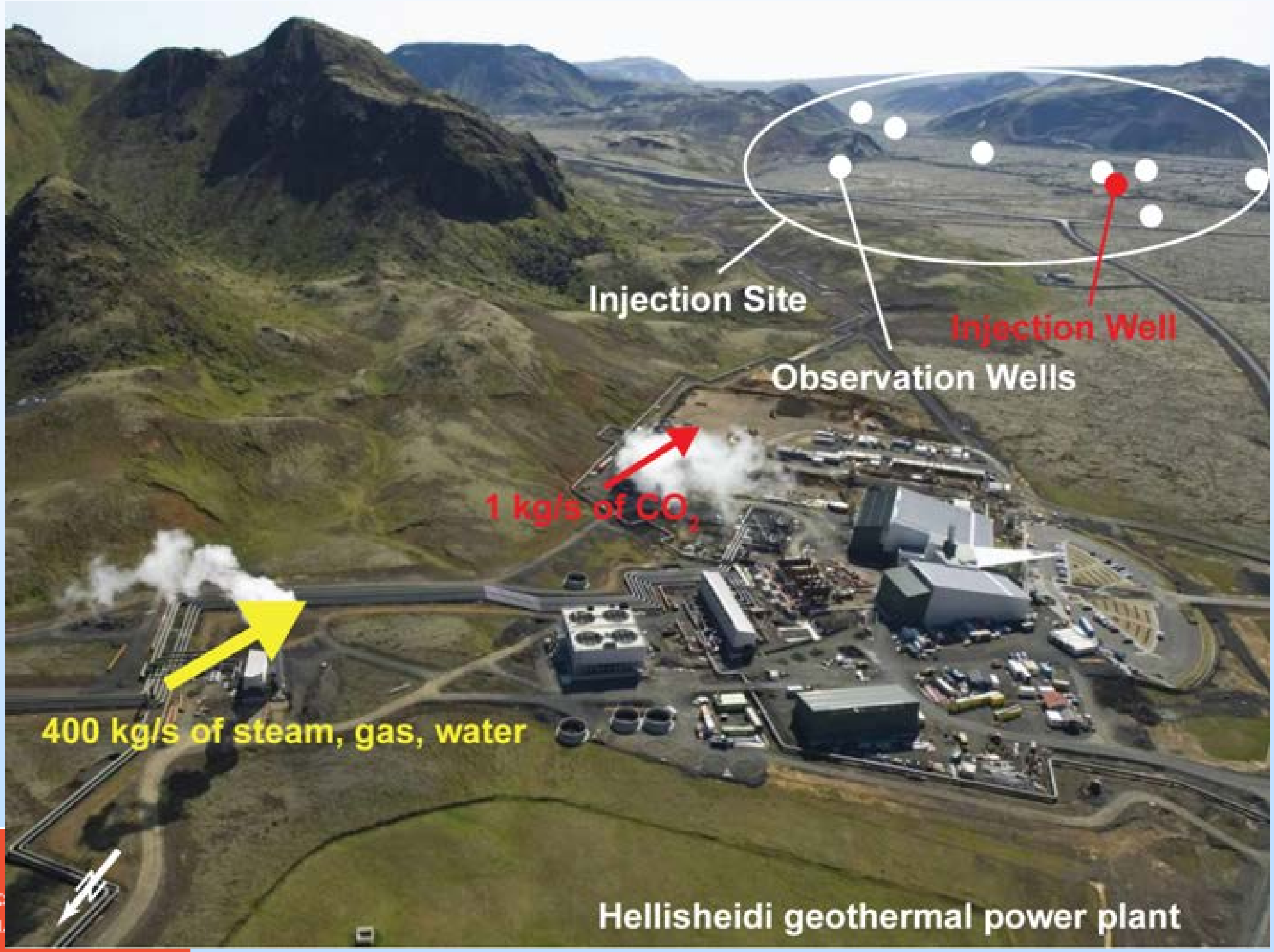
- Development of $^{14}CO_2$ Detector
  - $^{12}CO_2$ background lower at other $^{14}CO_2$ laser lines.





- Future Plans
  - Carry out ^{14}C detector experiments with highly enriched samples (>1k Modern)
  - Inject $^{14}CO_2$ into laboratory high-pressure flow loop
  - Inject $^{14}CO_2$ at CarbFix pilot injection site in Iceland



Organizational Chart

Columbia University

Klaus Lackner, PI: Oversight and development of 14C-detector

Alissa Ah-Hyung Park, co-PI: Construction of high-pressure flow loop

Juerg Matter, co-PI: Field tests at CarbFix site in Iceland

Barnard College

Martin Stute, co-PI: Construction of 14C detector and filling station design

Cantwell Carson, postdoc: Construction of 14C detector

Yinghuang Ji, student: Construction of filling station, testing flow loop

Collaborators:

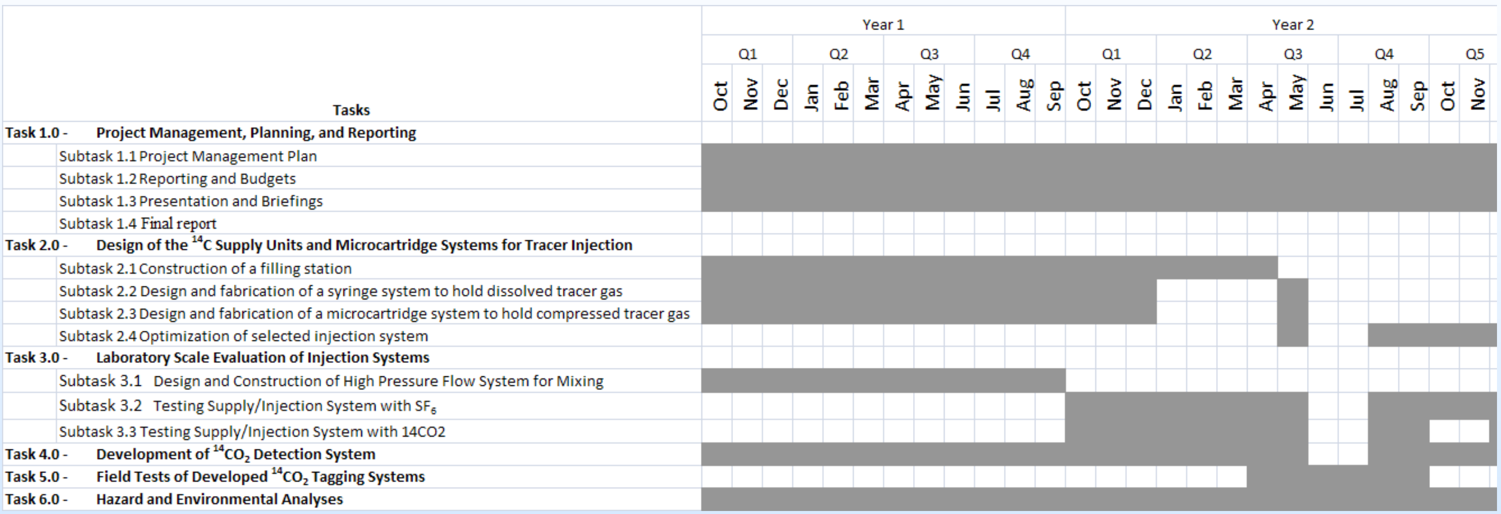
- University of Groningen
  - Harro Meijer
  - Dipayan Paul
- Access Laser
  - Yong Zhang

Thank you!

Appendix

– Gantt Chart
– Bibliography

Gantt Chart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Tasks
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Subtask 1.2 Reporting and Budgets
Subtask 1.3 Presentation and Briefings
Subtask 1.4 Final report
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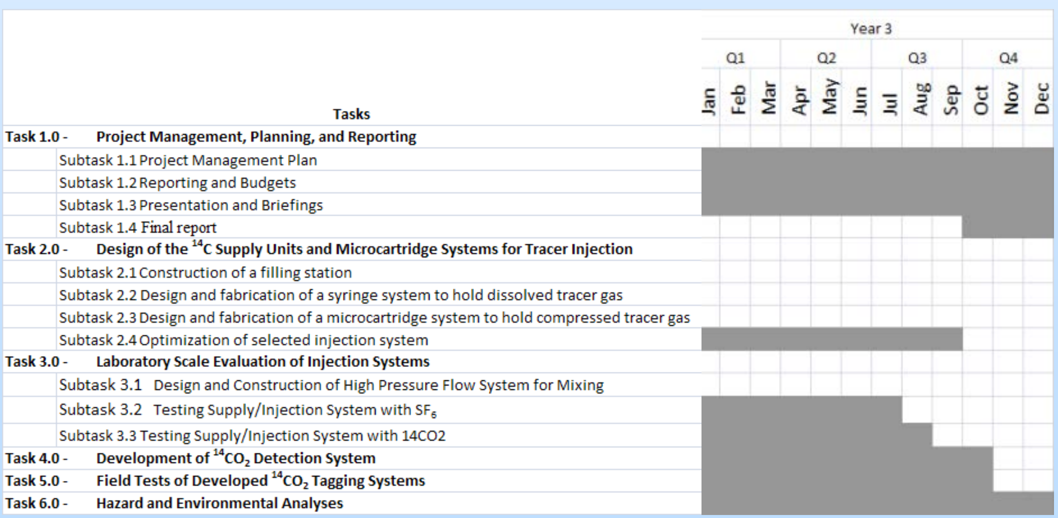
Subtask 2.2 Design and fabrication of a syringe system to hold dissolved tracer gas
Subtask 2.3 Design and fabrication of a microcartridge system to hold compressed tracer gas
Subtask 2.4 Optimization of selected injection system
Task 3.0 - Laboratory Scale Evaluation of Injection Systems
Subtask 3.1 Design and Construction of High Pressure Flow System for Mixing
Subtask 3.2 Testing Supply/Injection System with SF_6
Subtask 3.3 Testing Supply/Injection System with 14CO2
Task 4.0 - Development of $^{14}CO_2$ Detection System
Task 5.0 - Field Tests of Developed $^{14}CO_2$ Tagging Systems
Task 6.0 - Hazard and Environmental Analyses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Bibliography

- <u>Journal articles</u>:

  - Carson, C. G., Lackner, K. S., DeGuzman, M., Paul, D., Murnick, D., 2012, Double flow-though cell for intra-cavity opto-galvanic spectroscopy. Review of Scientific Instruments, *Submitted*
  - Ji, Y, Carson, C. G., Stute, M., Lackner, K. S., Hollow fiber membrane microvolume water-gas solution system for sub-surface tag production. Environmental Science & Technology, *in preparation.*