TAGGING CO_2 TO ENABLE QUANTITATIVE INVENTORIES OF GEOLOGICAL CARBON STORAGE

DOE AWARD #DE-FE0001535

Cantwell Carson

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 21-23, 2012

Lenfest Center for Sustainable Energy
Earth Institute | Columbia University

Presentation Outline

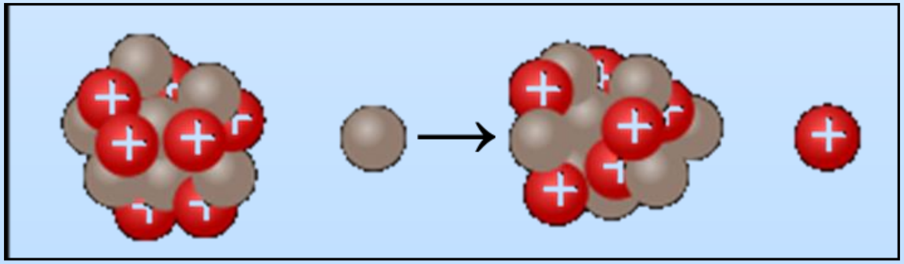
- Benefit to the program
- Project overview: Why ^{14}C for MVA?
- Technical status: Cartridges, injections, lasers
- Summary
- Organizational chart
- Collaborators

Benefit to the Program

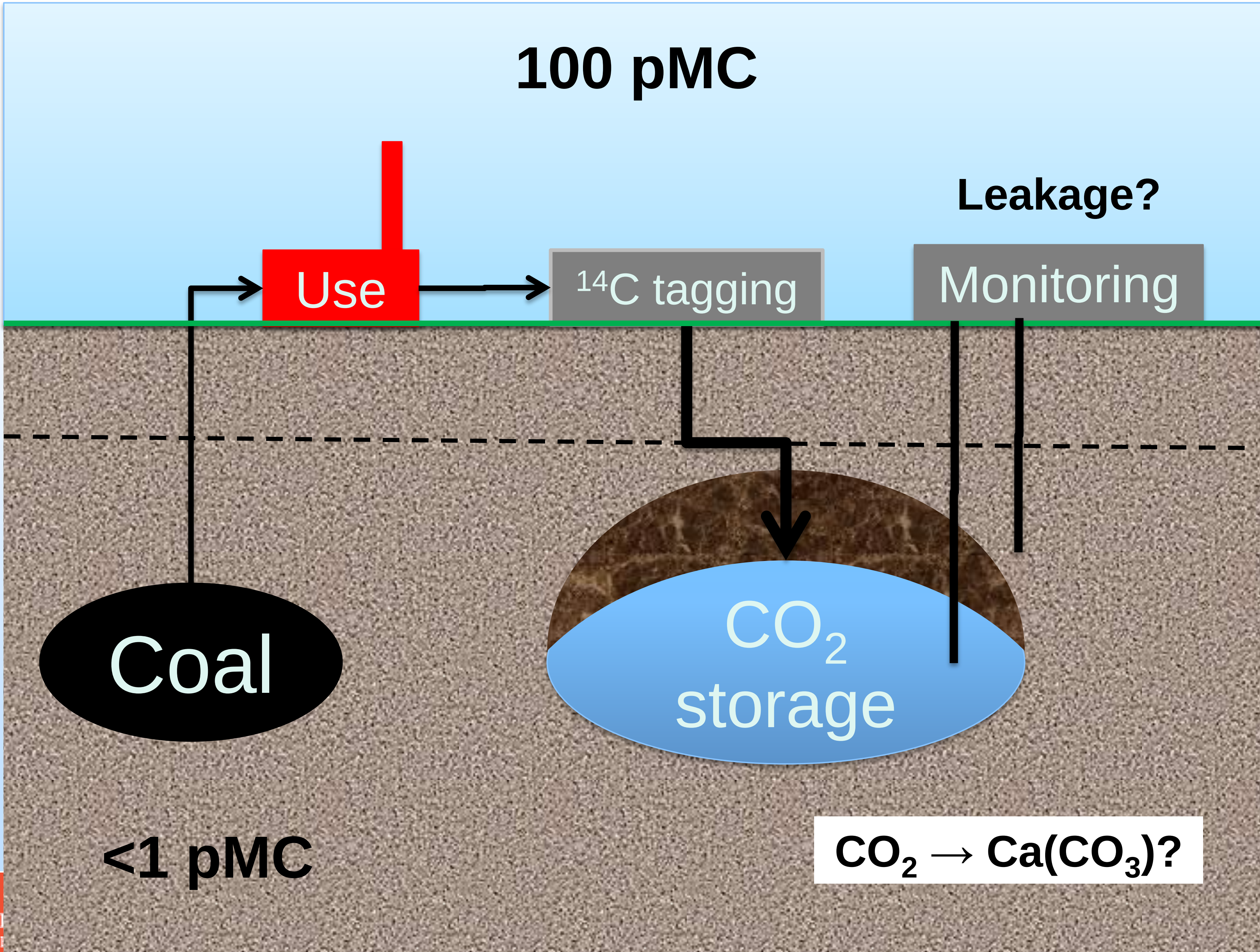
- Develop technologies to demonstrate that 99 percent of injected CO_2 remains in the injection zones.

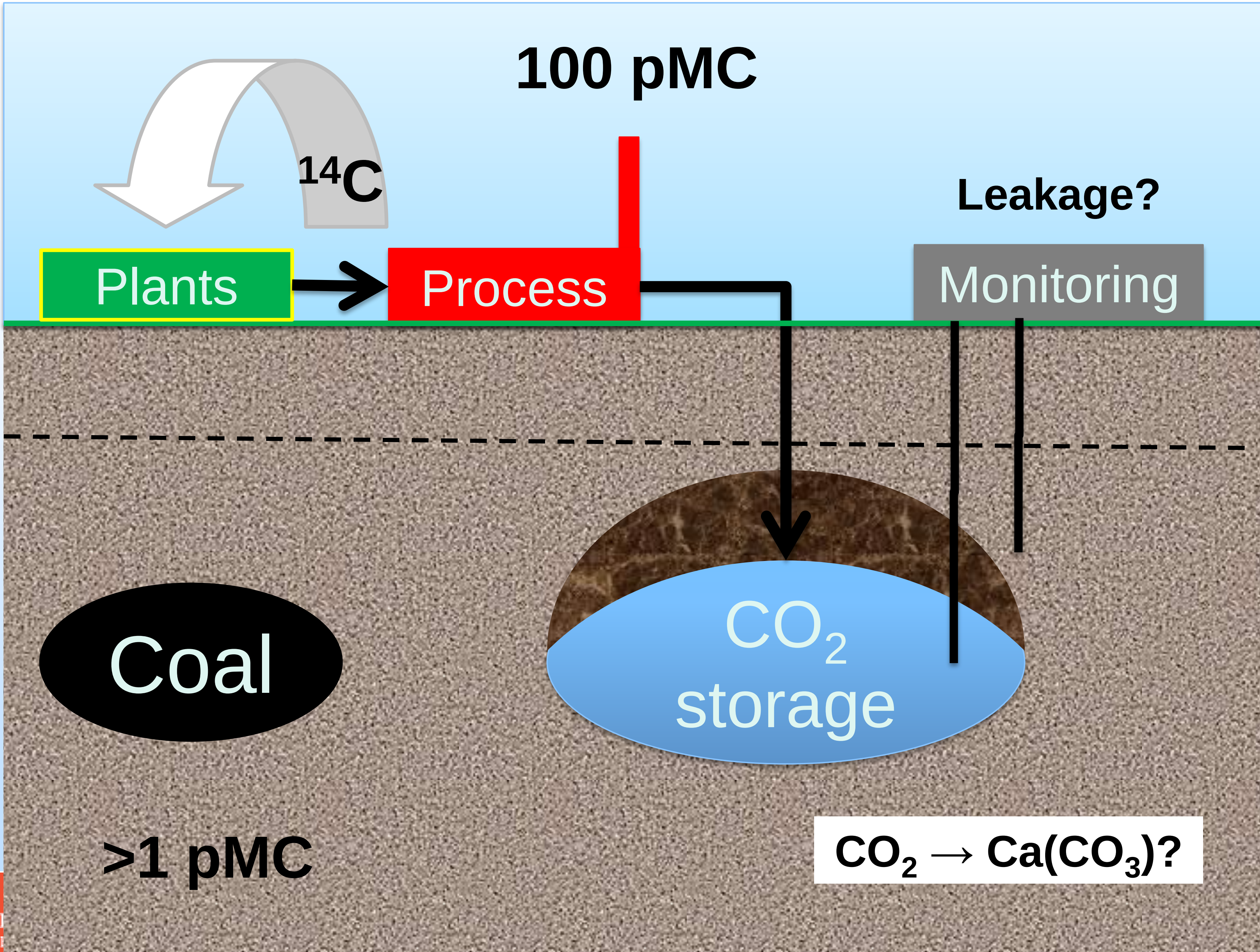
Permanent storage of CO_2 can be demonstrated by adding carbon-14 (^{14}C) prior to injection. This research project aims to demonstrate this by tagging fossil CO_2 with ^{14}C at a field site. When completed, this system will show that ^{14}C can be a safe and effective tracer for sequestered CO_2. 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
14C tagging
Leakage?
Monitoring
Coal
CO2
storage
<1 pMC
CO2 → Ca(CO3)?

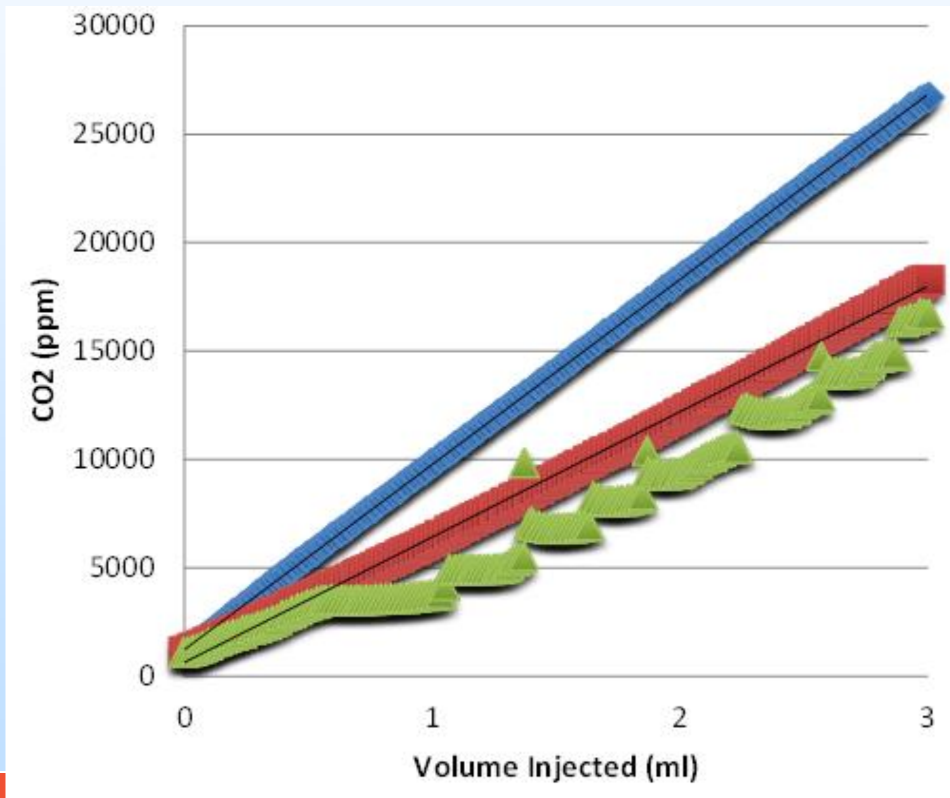

100 pMC
^{14}C
Leakage?
Plants
Process
Monitoring
Coal
CO_2 storage
>1 pMC
$CO_2 \rightarrow Ca(CO_3)$?

^{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
  - Membrane-based gas/water solution apparatus
  - Produced CO_2-water solutions
  - Produced calibrated SF_6-CO_2-water tag cartridges



Pure CO_2, CO_2-H_2O

^{14}C tagging

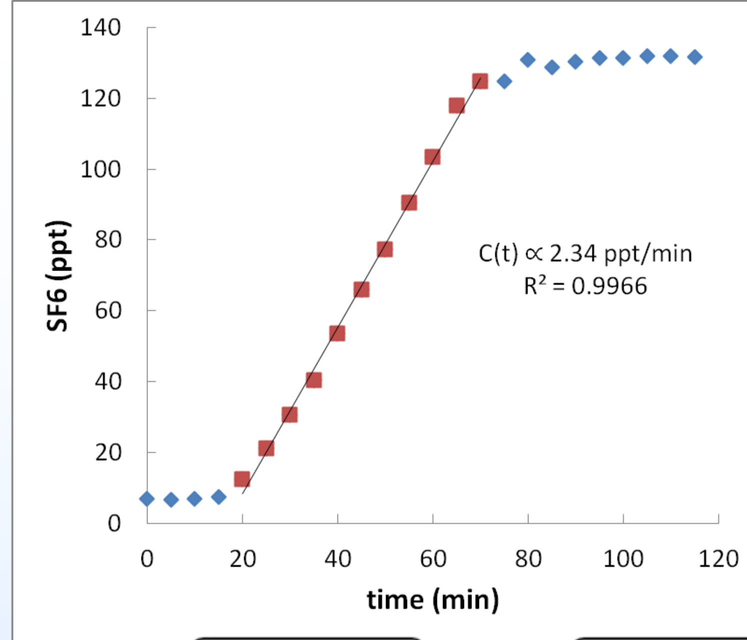
1-day ^{14}C tag cartridge filling

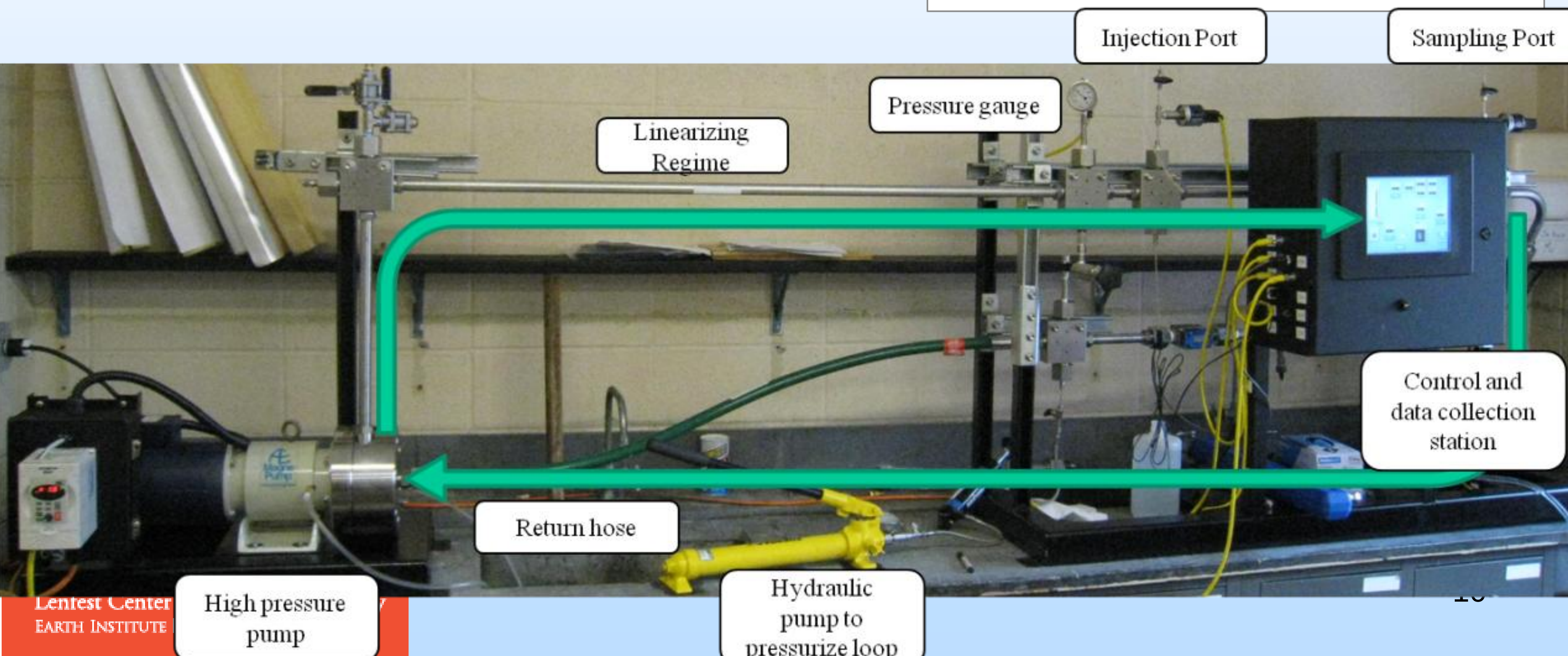
^{14}C tag injection

^{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
  - Injected SF_6 solution into super critical CO_2 at the 100 part-per-trillion level
  - Test bed for future weathering experiments





^{14}C tagging

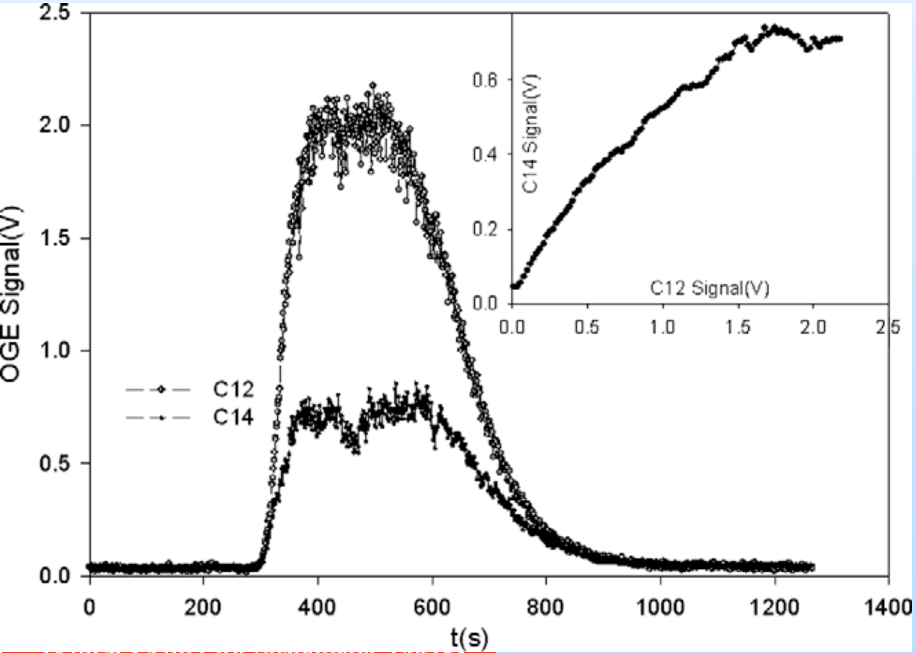
1-day ^{14}C tag cartridge filling

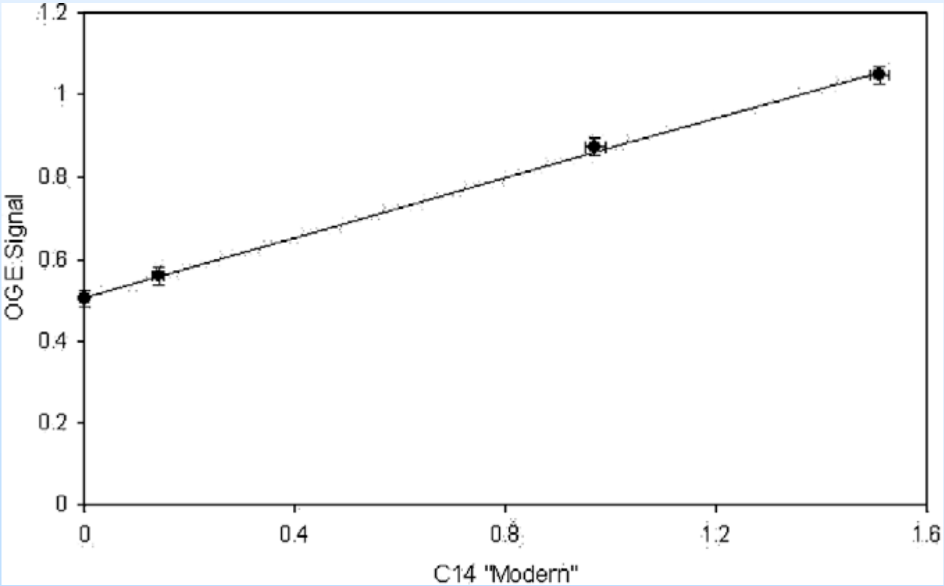
^{14}C tag injection

^{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 methods is required

- Development of $^{14}CO_2$ Detector
- IntraCavity OptoGalvanic Spectroscopy (ICOGS) can
  - Detect ^{14}C at the part-per-trillion level
  - Be carried out on-line in real time
  - Be built for >$100k
- We formed a partnership with researchers at Rutgers University to build and develop this detector



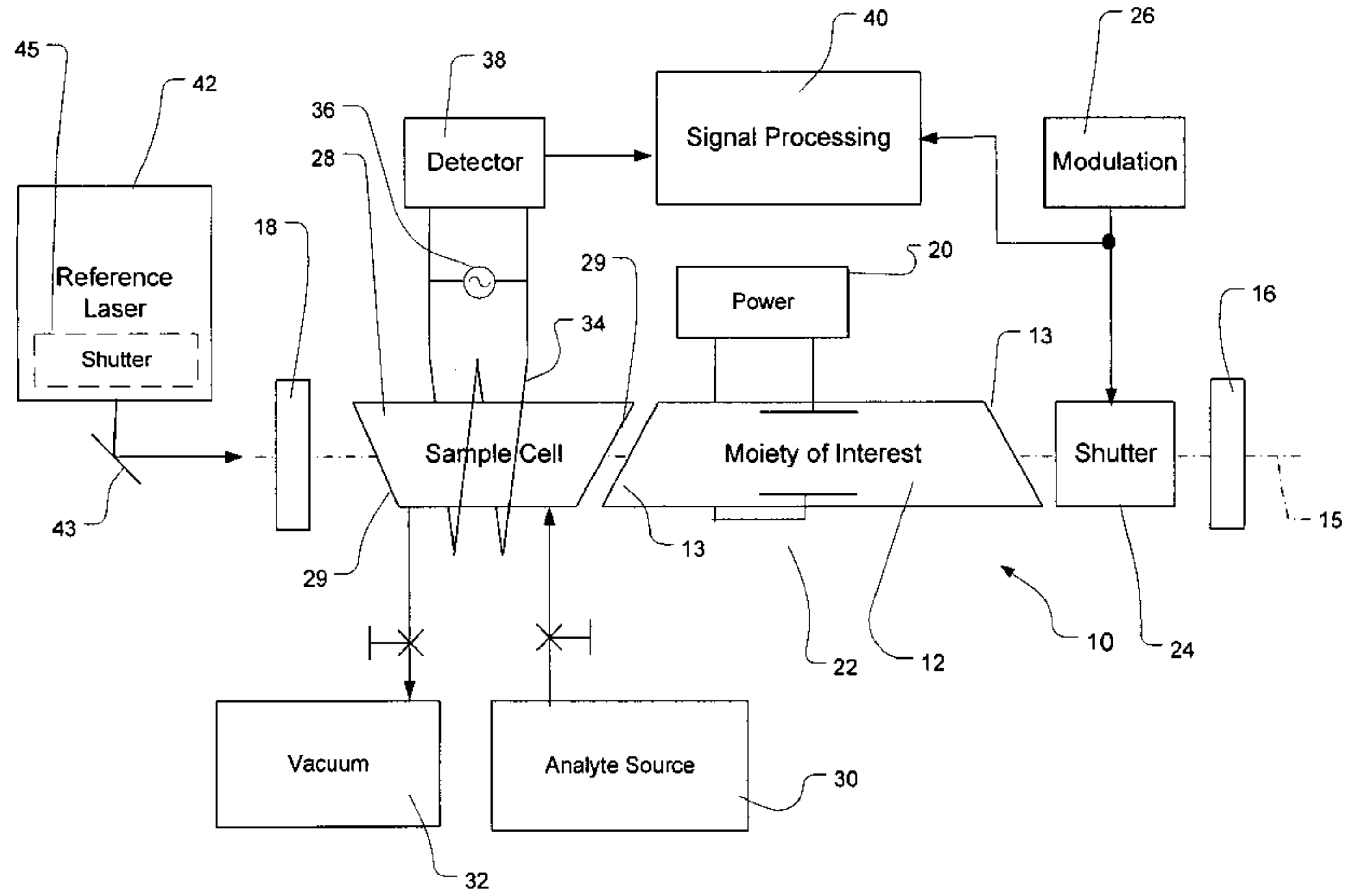


Murnick et al., Analyt. Chem. 2008

- Development of $^{14}CO_2$ Detector

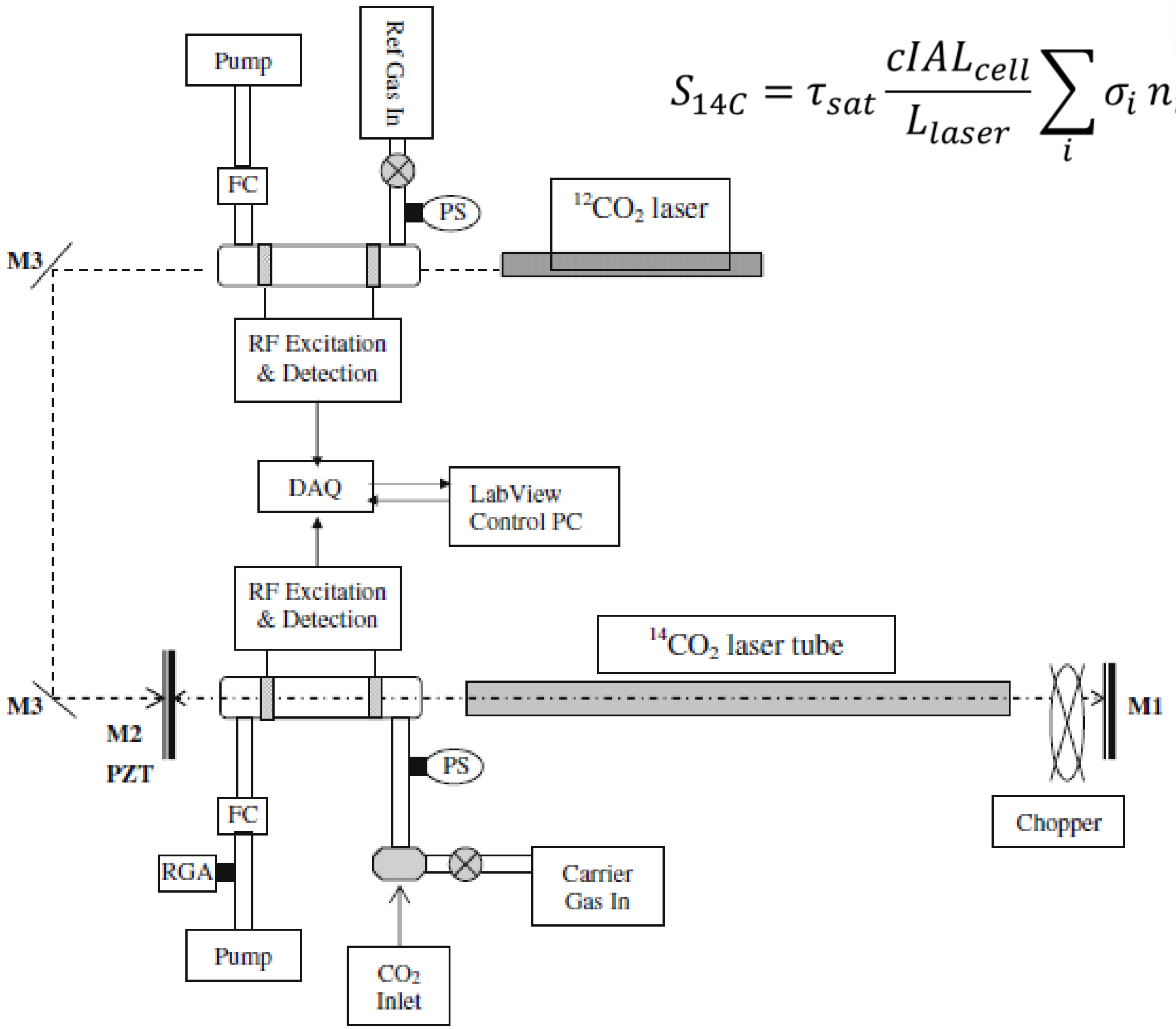
(12) **United States Patent**
Murnick

(10) **Patent No.: US 7,616,305 B2**
(45) **Date of Patent: Nov. 10, 2009**



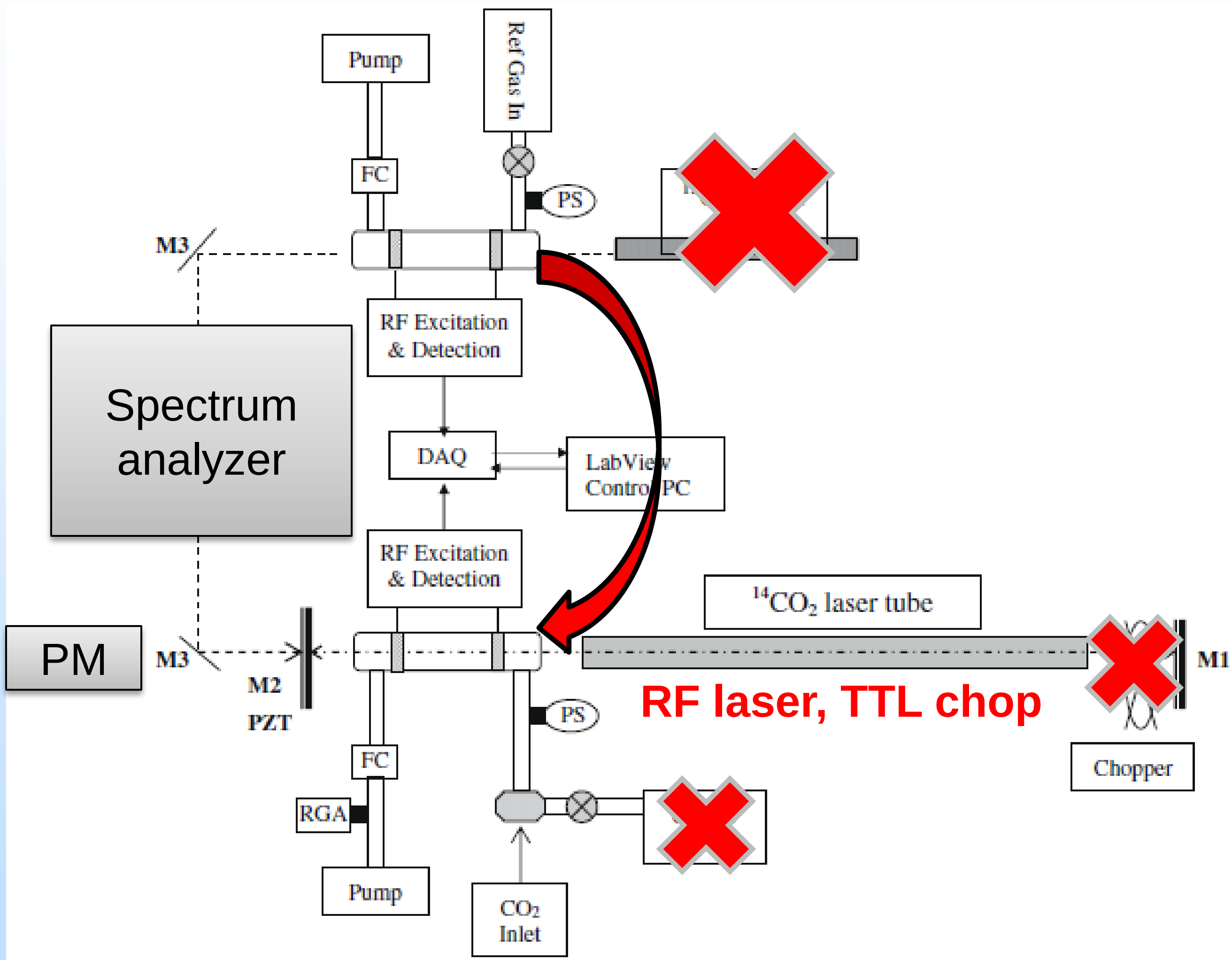
- Development of $^{14}CO_2$ Detector

$$S_{14C} = \tau_{sat} \frac{cIAL_{cell}}{L_{laser}} \sum_i \sigma_i n_i$$

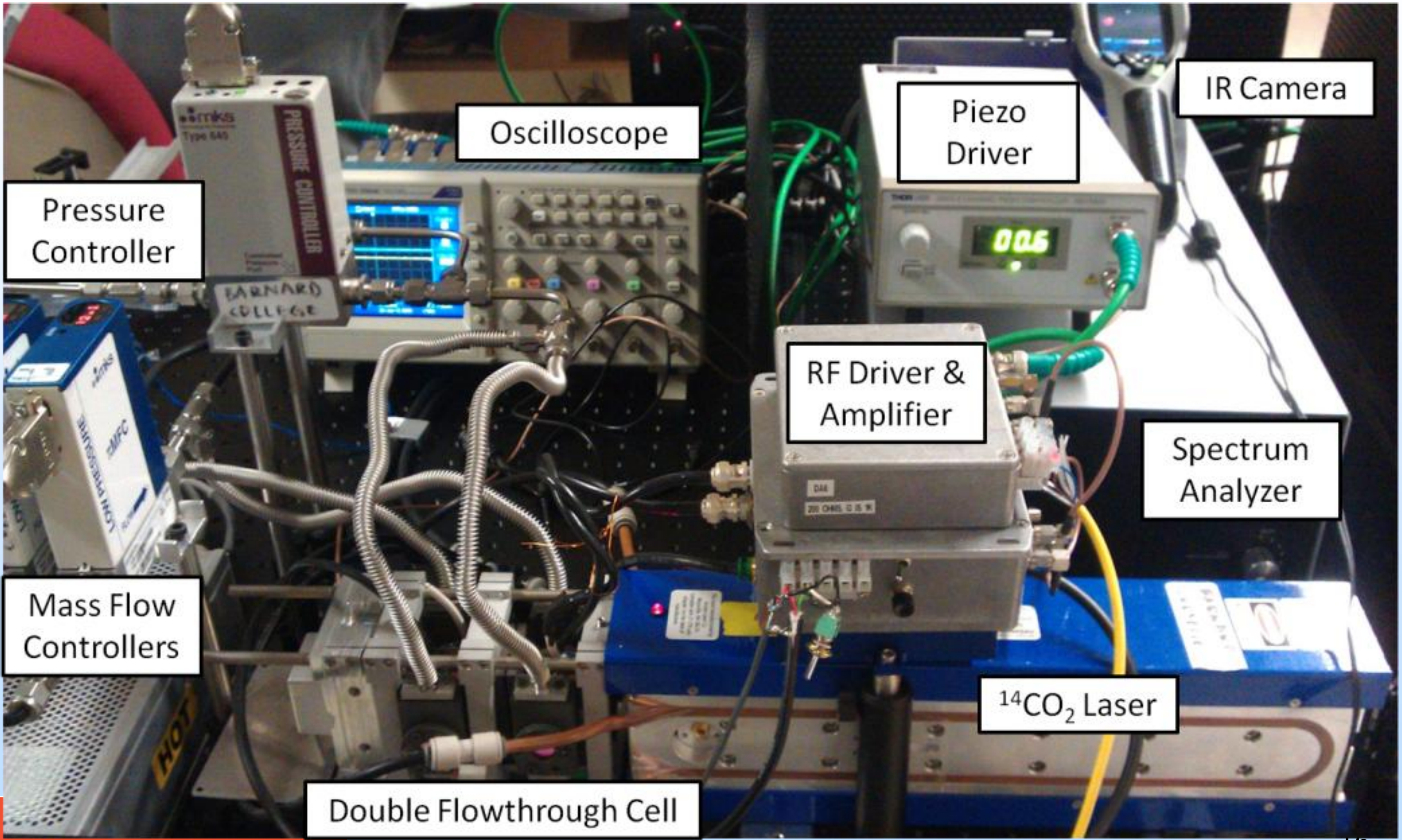


Murnick et al., Analyt. Chem. 2008

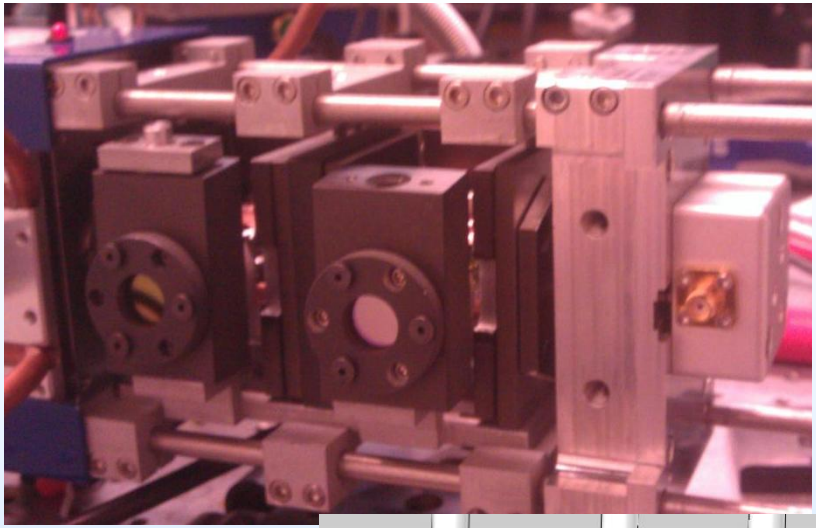
• Development of $^{14}CO_2$ Detector

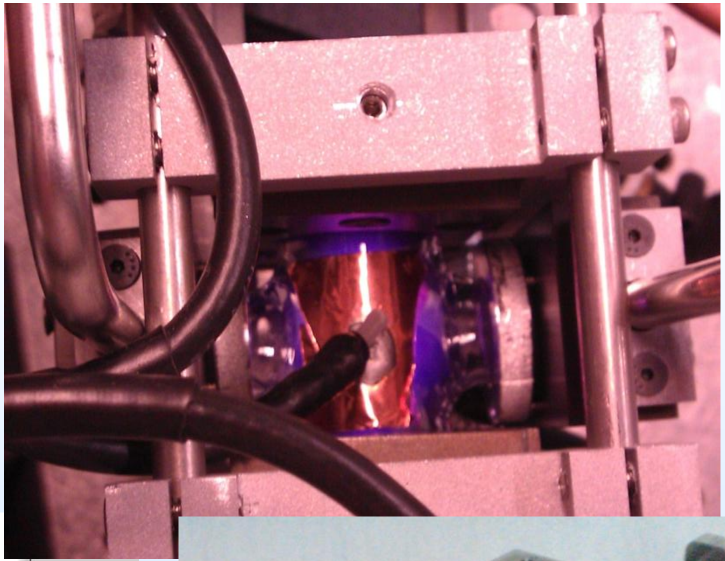


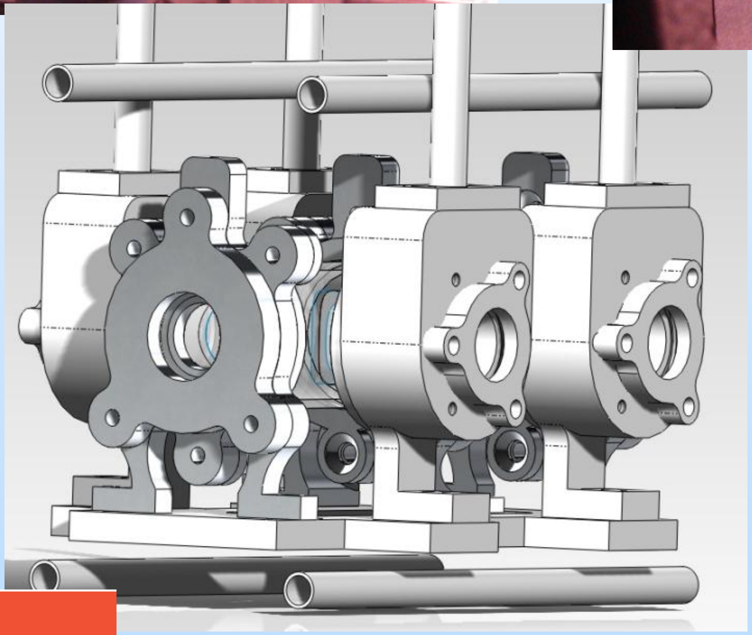
- Laser-based $^{14}CO_2$ detector
  - Assembled Intra-Cavity Opto-Galvanic Spectrometer (ICOGS) Redesigned glow discharge and detection circuit

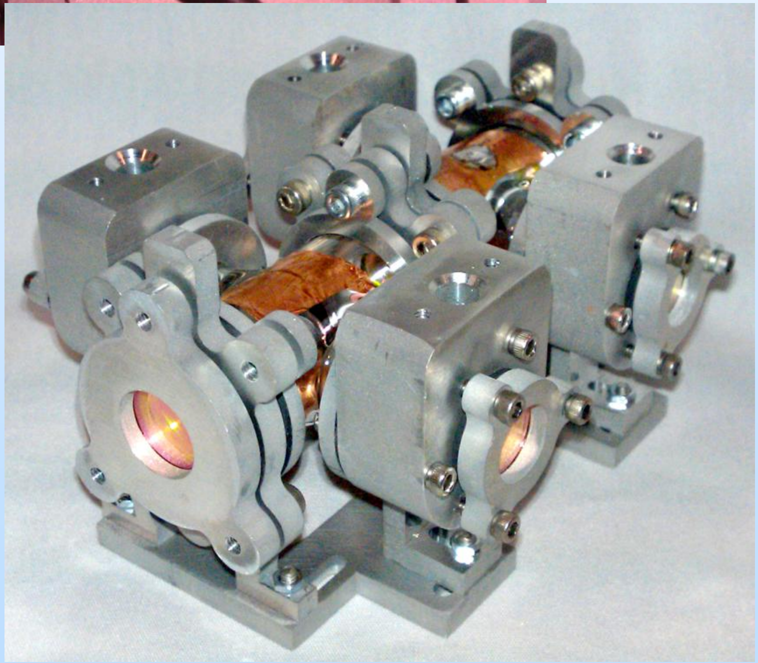


- Laser-based $^{14}CO_2$ detector
  - Constructed new double flow-through cell





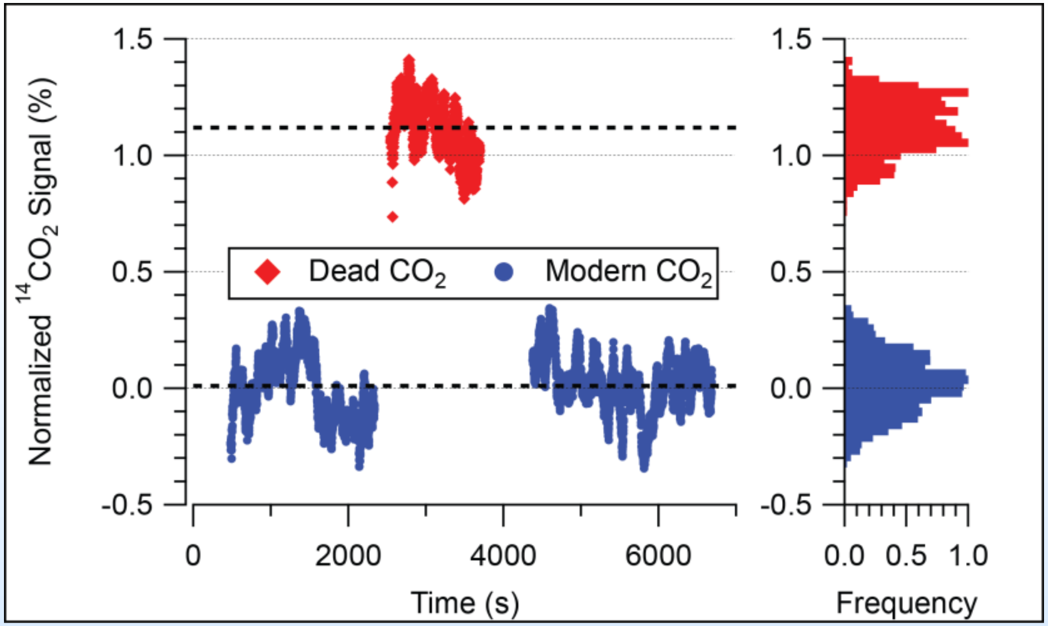


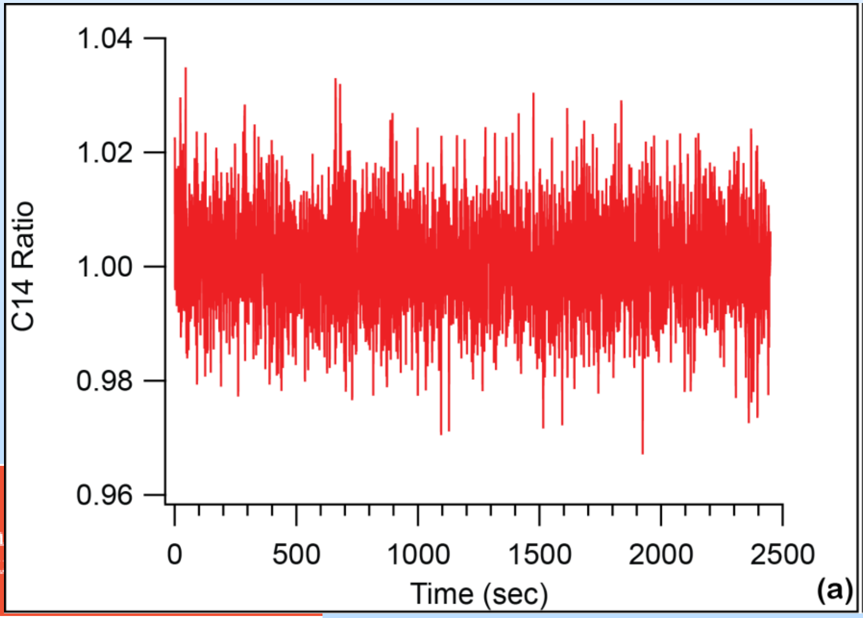


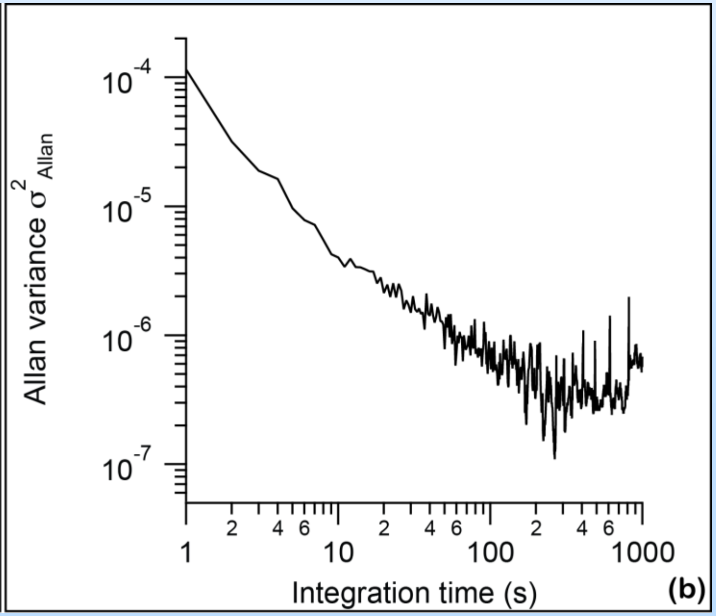
- Laser-based $^{14}CO_2$ detector
  - Measured separation of 100 pMC versus >0.1 pMC

$$\sqrt{\sigma^2_{Allan}\left\langle\frac{S_{sam}}{S_{ref}}\right\rangle^{-1}} \approx 5.5\times10^{-4}$$

$$\frac{5.5\times10^{-4}}{1.12\times10^{-2}} \approx 5\%$$







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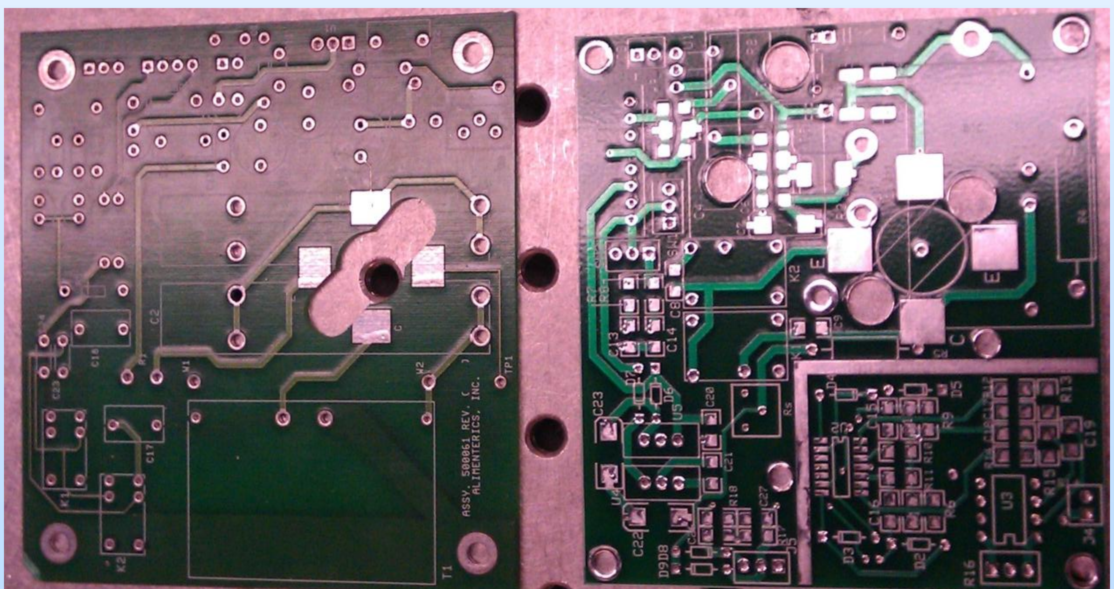
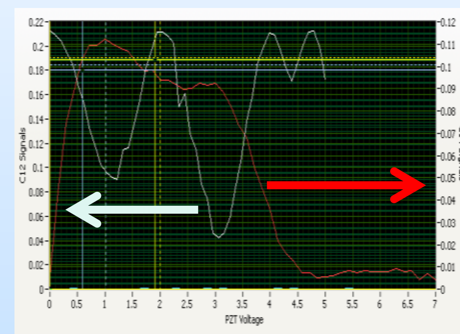
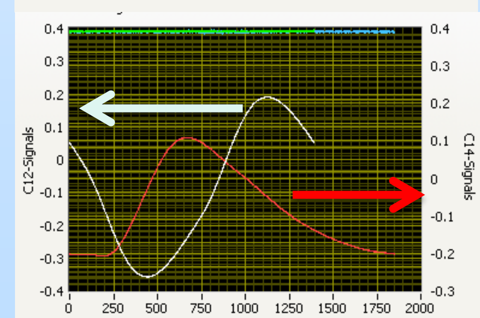
- Key Findings
  - Gas-water solutions can be produced in µL volumes with high precision
  - SF_6-CO_2-water solutions are suitable for tagging high-pressure CO_2
  - ^{14}C can be detected in CO_2 by the ICOGS system
- Lessons Learned
  - ICOGS circuitry, sample handling, signal analysis still require substantial development to achieve full potential

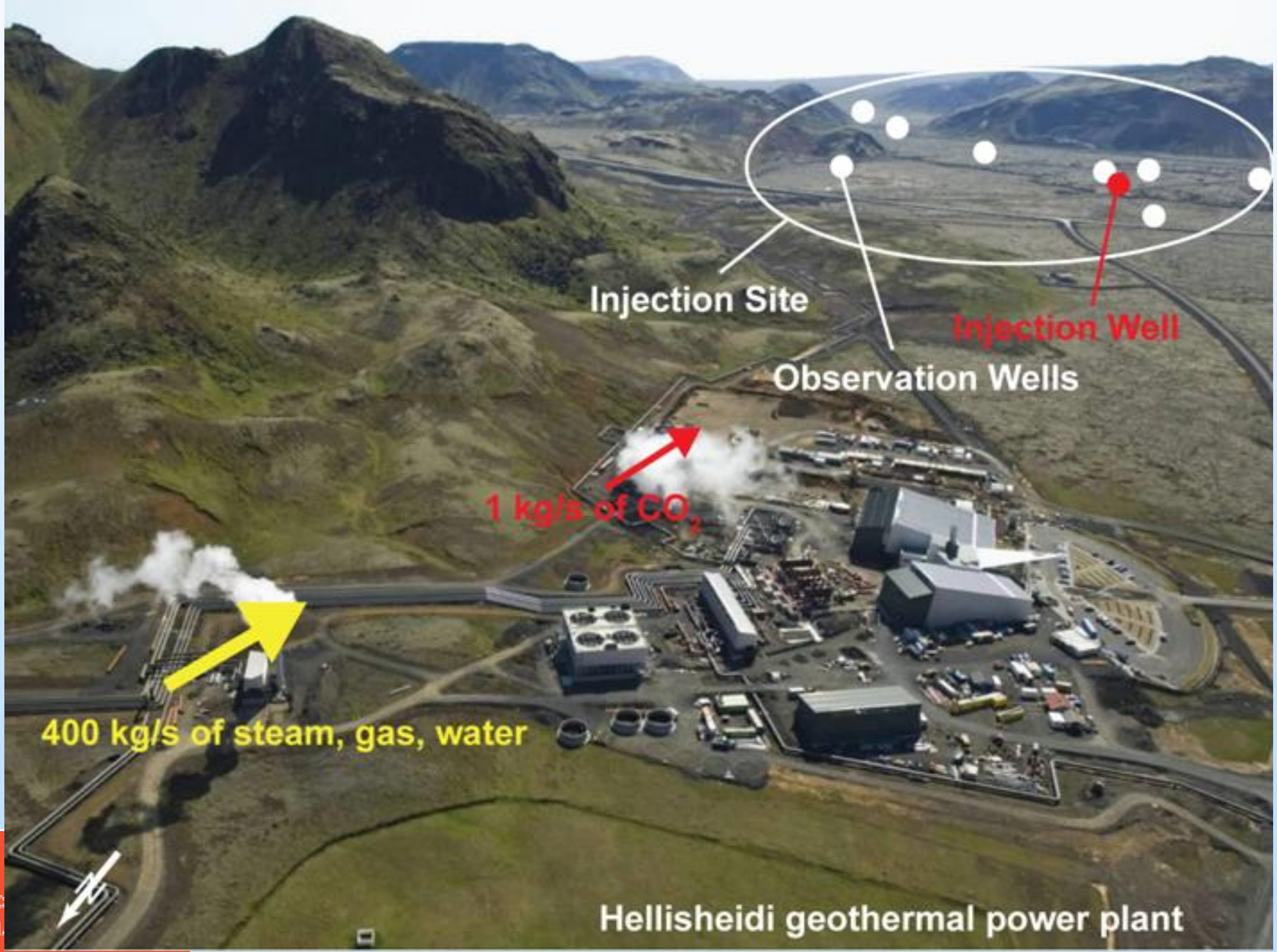


Previous circuit board and one of the new layouts





- Future Plans
  - Improve ICOGS detector
  - Inject $^{14}CO_2$ into high-pressure flow loop
  - Inject $^{14}CO_2$ at CarbFix pilot injection site in Iceland
  - Demonstrate detection of $^{14}CO_2$ from samples taken at field site



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:

- Rutgers University:
  - Daniel Murnick
  - Mark DeGuzman
  - Tulu Bacha
  - Bill Thomas

- University of Groningen
  - Harro Meijer
  - Dipayan Paul

- Access Laser
  - Yong Zhang

Thank you!

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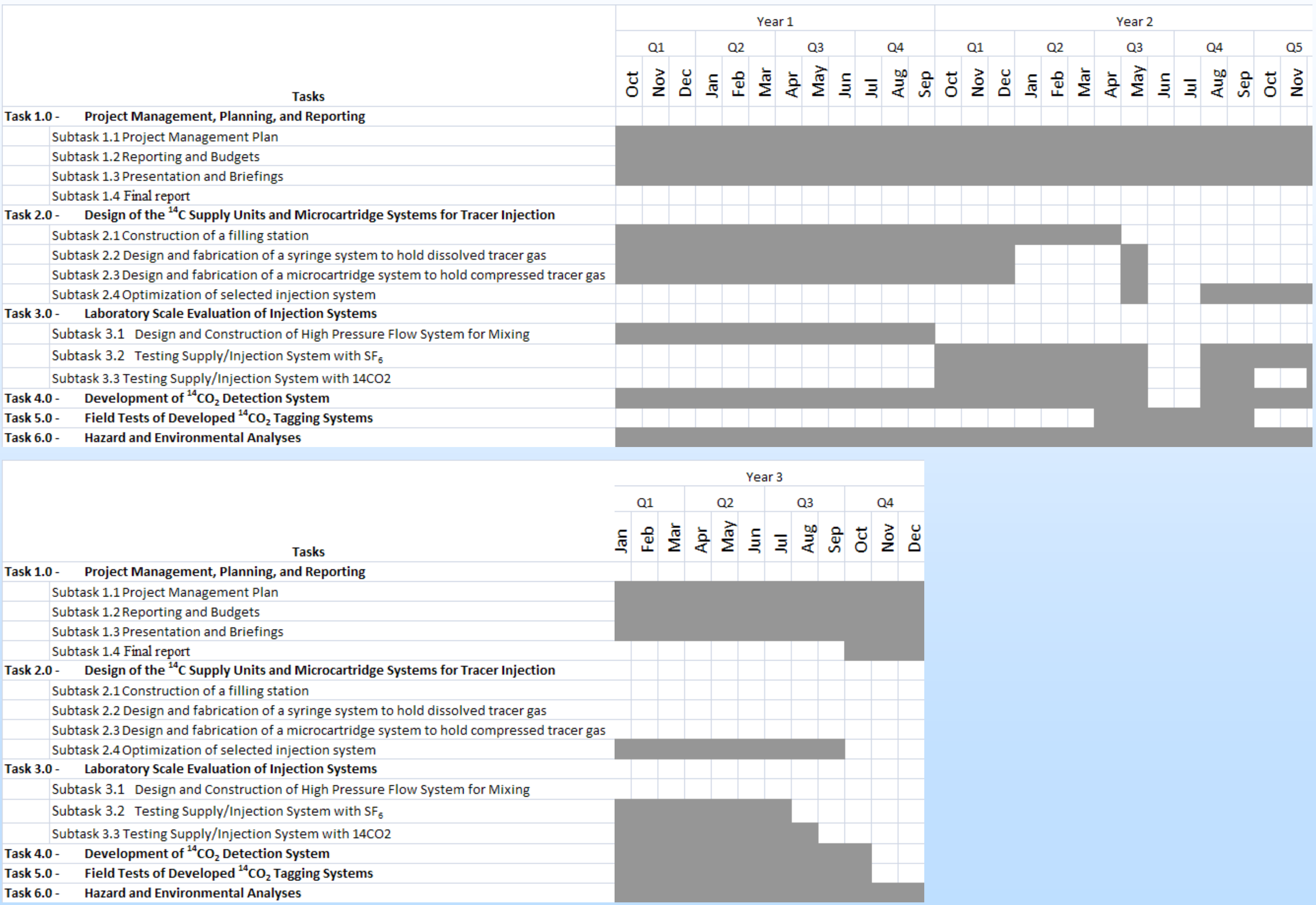
Appendix

– Gantt Chart
– Bibliography

Gantt Chart


Year 1
Year 2
Q1
Q2
Q3
Q4
Q5
Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov
Tasks
Task 1.0 - Project Management, Planning, and Reporting
Subtask 1.1 Project Management Plan
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 SF6
Subtask 3.3 Testing Supply/Injection System with 14CO2
Task 4.0 - Development of 14CO2 Detection System
Task 5.0 - Field Tests of Developed 14CO2 Tagging Systems
Task 6.0 - Hazard and Environmental Analyses
Year 3
Q1
Q2
Q3
Q4
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
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Bibliography

- Journal articles:
  - 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, *in preparation*
  - 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.*
- Patents
  - Carson, C. G., DeGuzman, M., Murnick, D., Linear multi-chamber gas analysis device, in preparation.