# Measurements of $^{222}Rn$, $^{220}Rn$, and $CO_2$ Emissions in Natural $CO_2$ Fields in Wyoming: MVA Techniques for Determining Gas Transport and Caprock Integrity

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U.S. Department of Energy

National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and
Infrastructure for CCS

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# Presentation Outline

- Benefits to the Program
- Project Overview
- Technical Status
  - Field Work
  - Overview
  - Lab Work
- Accomplishments to Date
- Summary

# Benefit to the Program

- Carbon Storage Program goals being addressed.
  - Develop and validate technologies to ensure 99 percent storage performance.
- Project Benefits Statement.
  - The purpose of this project is to evaluate methods, already used for natural volcanic systems, for assessing the integrity of caprock formations. The methods use quantitative measurements of $CO_2$ flux and naturally occurring Radon (Rn) isotopes to determine the source of the $CO_2$ (escaped from a reservoir or degassed from shallow soil).

# **Project Overview**: Goals and Objectives

- To provide training opportunities for two graduate students and one undergraduate student in skills required for implementing and deploying CCS technologies.
- To perform fundamental research to advance the sciences of Monitoring, Verification, and Accounting (MVA).
- To take $^{222}Rn$, $^{220}Rn$, and $CO_2$ measurements at natural $CO_2$ analogues in Wyoming as well as in the laboratory to evaluate and calibrate the use of naturally occurring Rn isotopes for assessing the integrity of caprock formations.

# **Project Overview**:
## Goals and Objectives

- How the project goals and objectives relate to the program goals and objectives.
  - Measurements of Rn and $CO_2$ can constrain source and timescale of $CO_2$ fluxes. Supports the program goal of ensuring 99 percent storage performance.

# **Project Overview**:
## Goals and Objectives

- Success criteria for student training goals
  - Two graduate students complete advanced degrees
  - Three BS students perform undergraduate research.

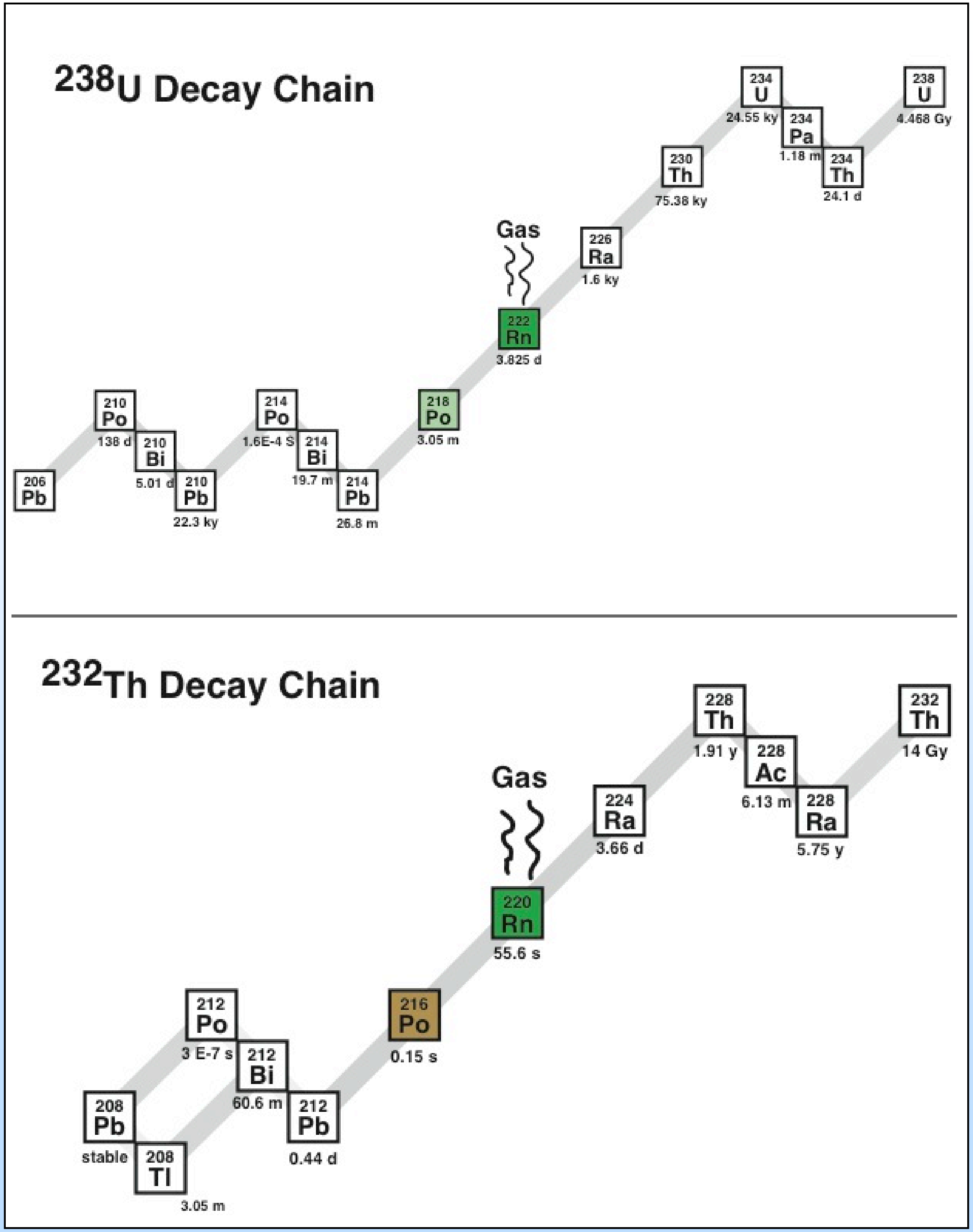
# **Project Overview**: Goals and Objectives

- Success criteria for MVA research
  - Perform integrated Rn and $CO_2$ measurements at natural $CO_2$ analogues in Wyoming
  - Replicate field conditions in the laboratory to evaluate effects of reactions at depth on Rn degassing.
  - Determine the suitability of using measurements as MVA techniques for CCS.

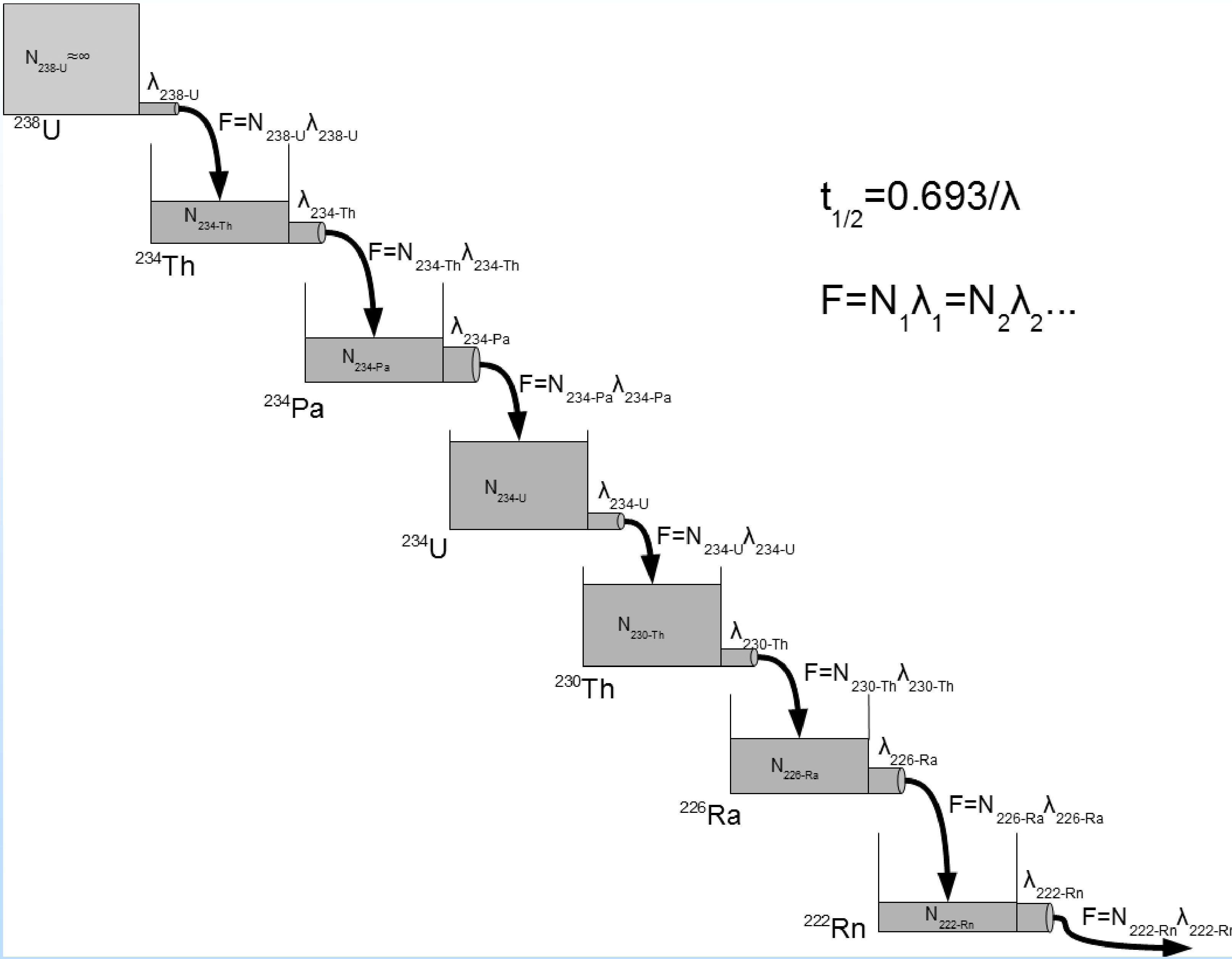
# Technical Status

- Field Measurements in Wyoming complete
  - La Barge $CO_2$ Field (SW Wyoming)
  - Yellowstone (high pH, high temperature, challenging)
  - Thermopolis (similar to Yellowstone but less extreme)
- Overview
  - U-Series Basics
  - Secular Equilibrium
  - $CO_2$ and Rn
- Lab work
  - Rad7 $CO_2$ corrections (Lane-Smith and Sims, 2013) (complete)
  - Evaluate grain size control on alpha recoil (complete)
  - Laboratory tests of effects of $CO_2$-$H_2O$-rock reaction

# U Series Decay Chains

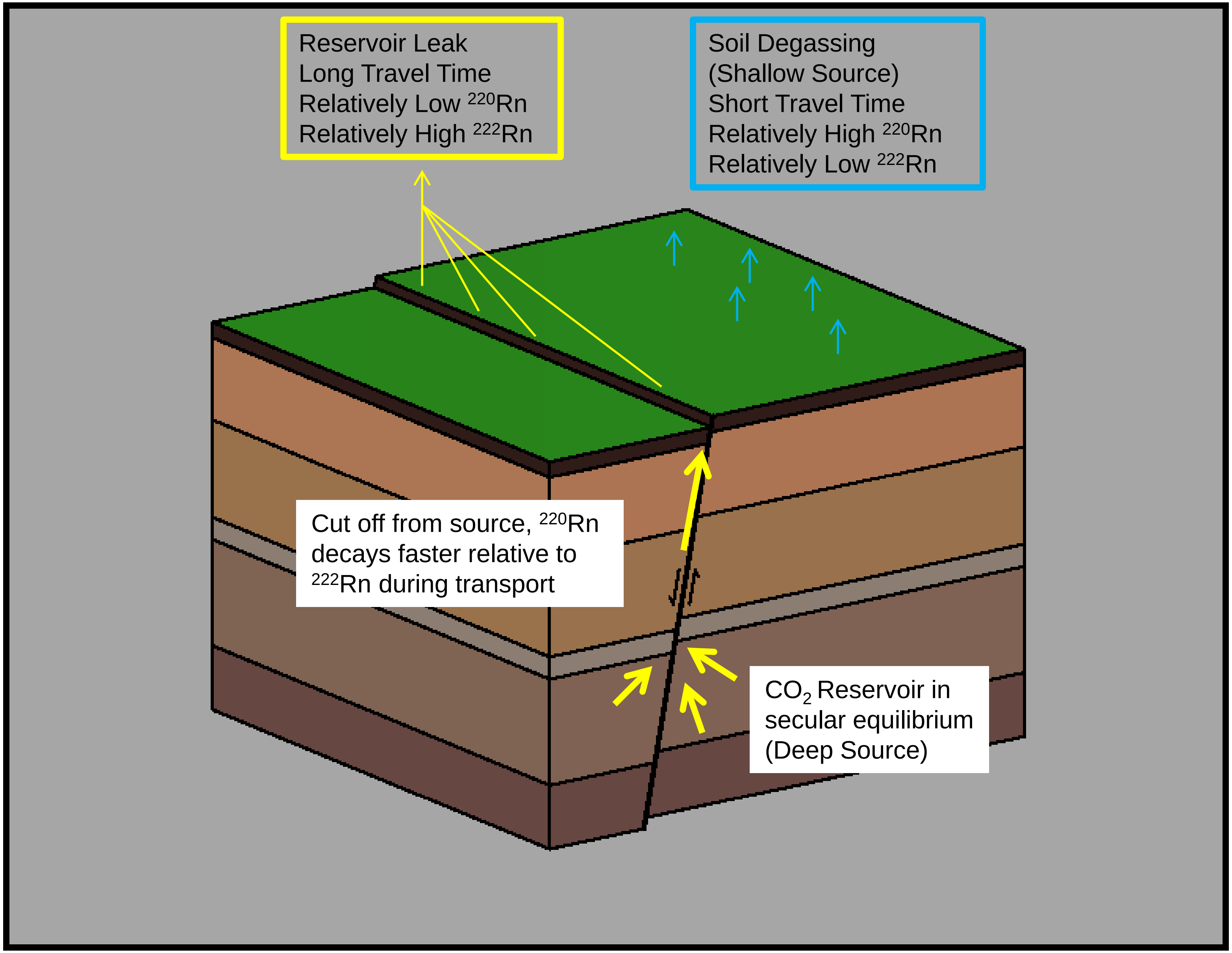


# Secular Equilibrium



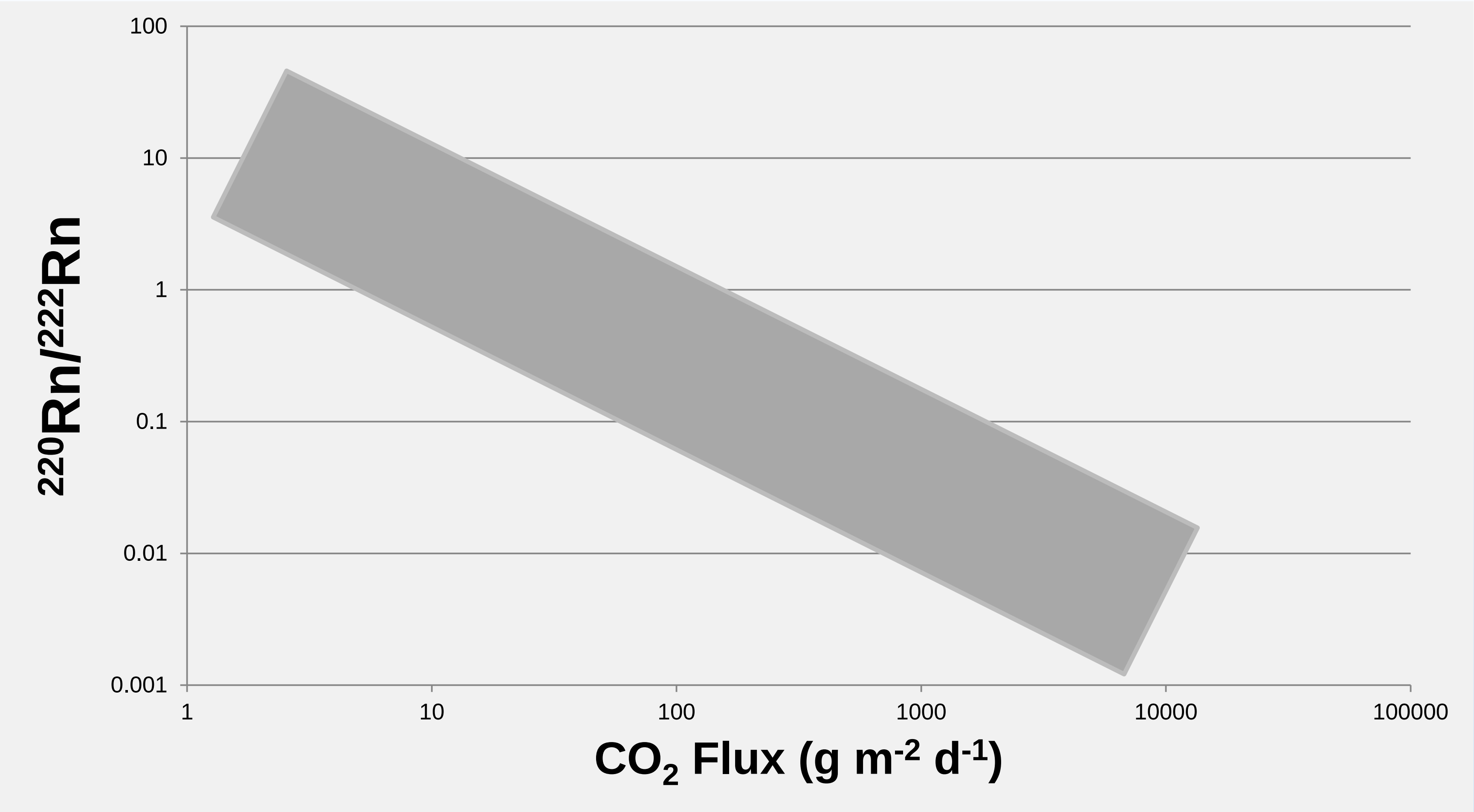

$t_{1/2}=0.693/\lambda$

$F=N_1\lambda_1=N_2\lambda_2\ldots$



Reservoir Leak
Long Travel Time
Relatively Low $^{220}Rn$
Relatively High $^{222}Rn$
Soil Degassing
(Shallow Source)
Short Travel Time
Relatively High $^{220}Rn$
Relatively Low $^{222}Rn$
Cut off from source, $^{220}Rn$ decays faster relative to $^{222}Rn$ during transport
$CO_2$ Reservoir in secular equilibrium (Deep Source)

# Schematic of Relationship Between Radon and $CO_2$ Flux observed by Giammanco et al., 2007

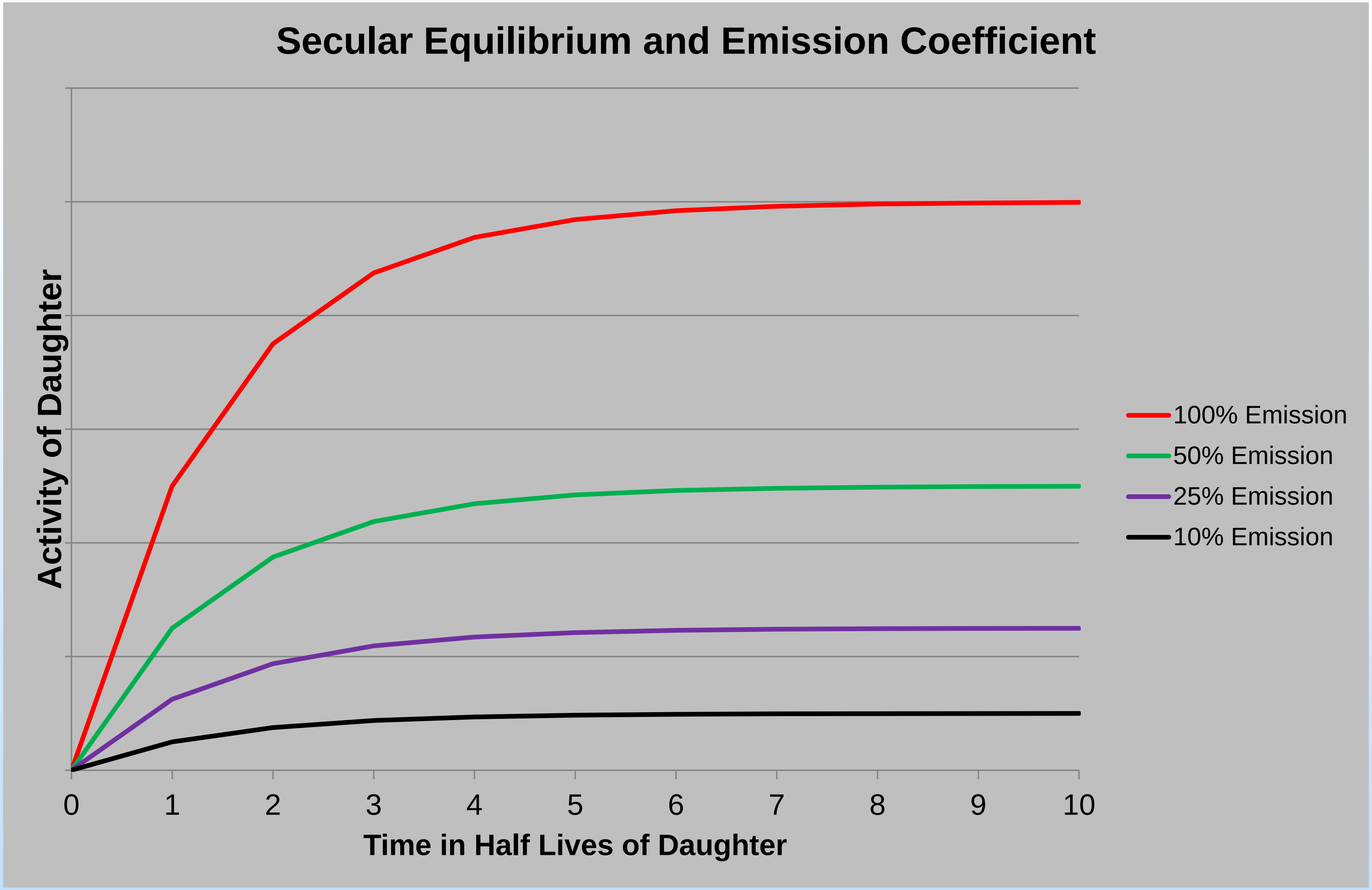


# Technical Status

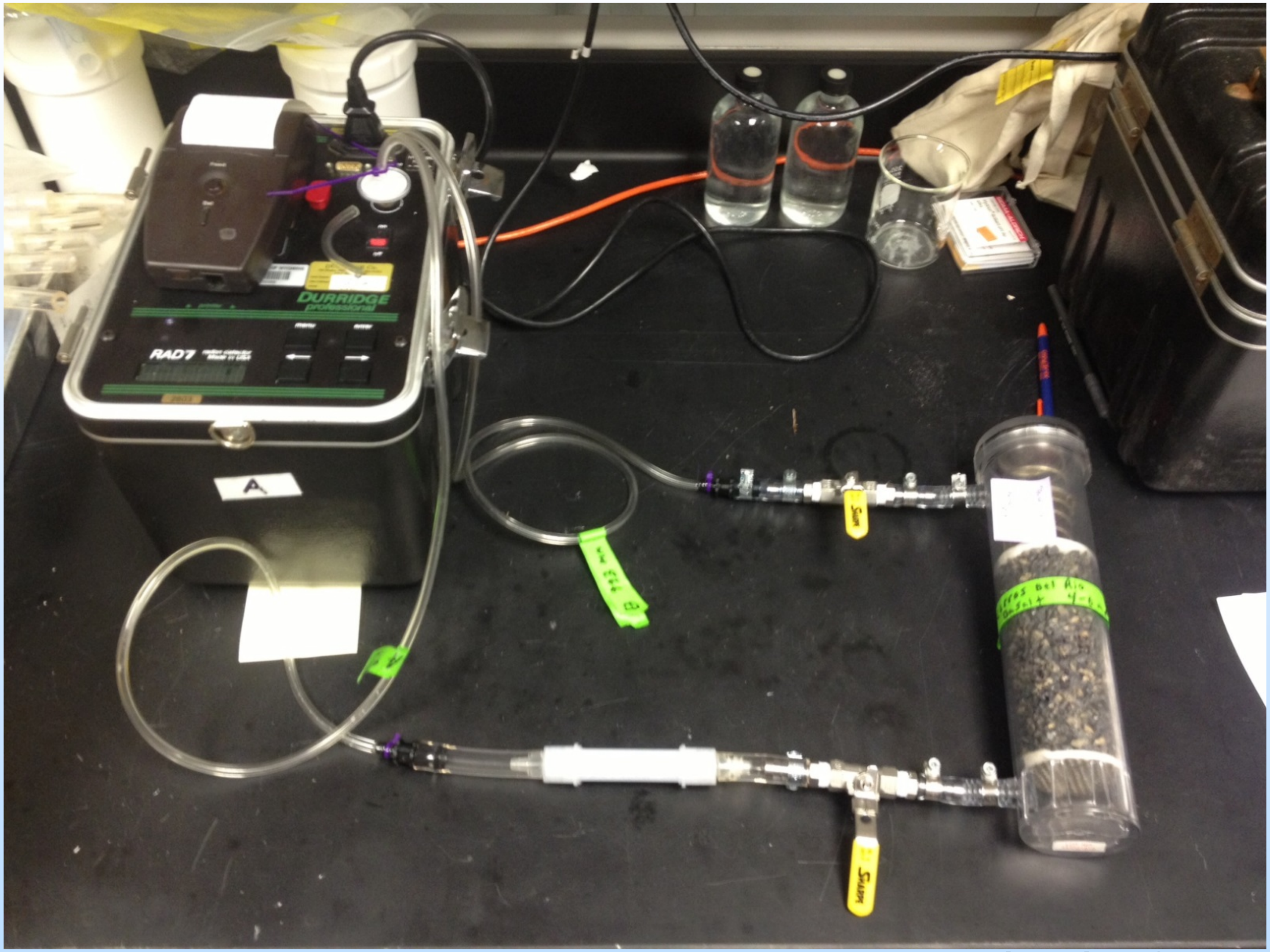
- Lab work grain size (previous year, Soderberg investigations)
  - Hypothesis: as grain size decreases, Radon Emissivity should increase due to an increase in specific surface area.
  - To understand Radon degassing we must understand what controls the degassing.
  - Alpha recoil might produce enough kinetic energy for the Rn to escape the grain.
  - More surface area on a grain should increase amount of Rn that can escape through recoil. This makes Surface area to volume ratio (specific surface area) an important metric.

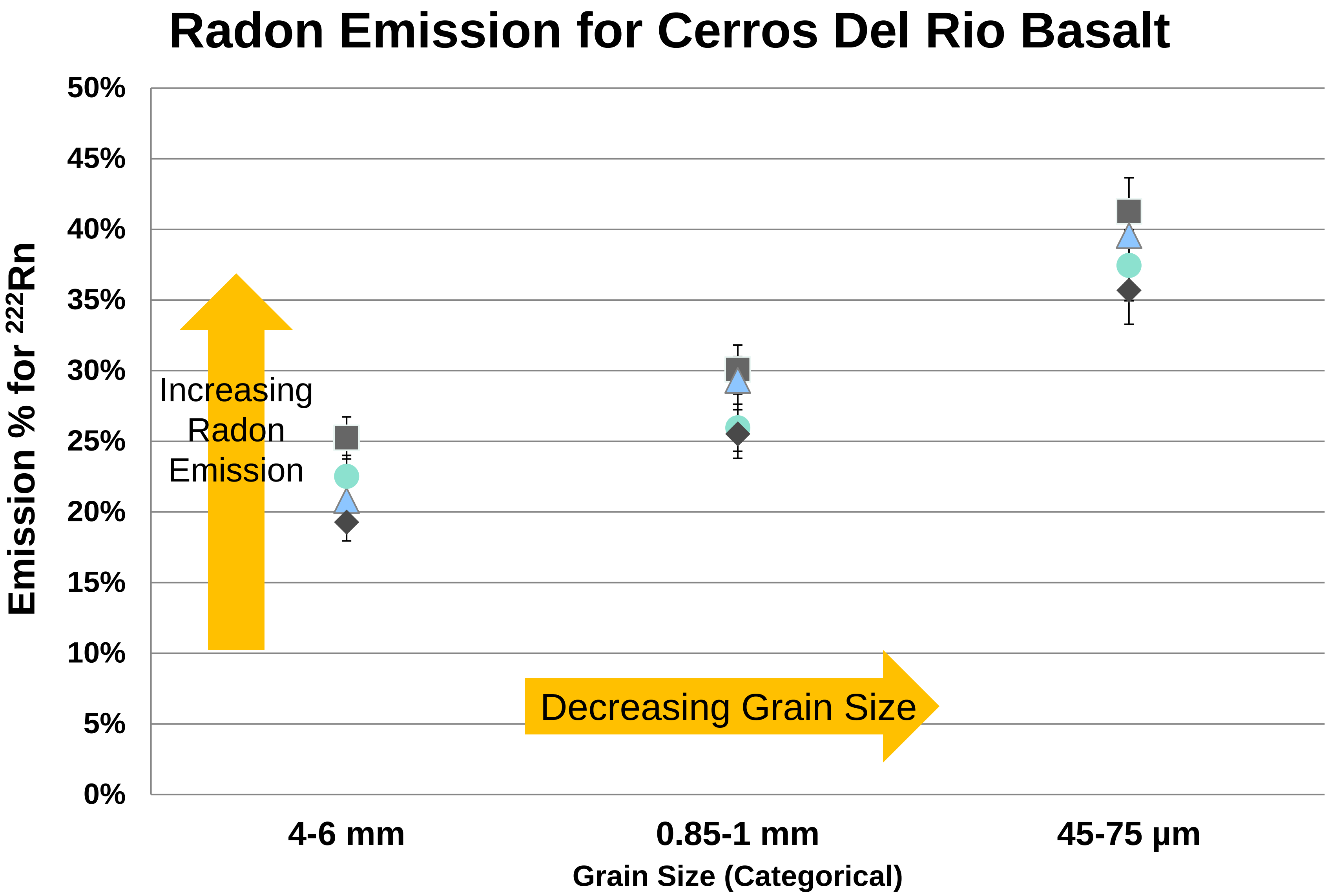
# Technical Status

- Design
  - 3 Grains Sizes
    - » 45-75 µm
    - » 0.85-1 mm
    - » 4-6 mm
  - 2 Lithologies
    - » Cerros Del Rio Basalt
      - » U=0.72 ppm Th=2 ppm
    - » Guaje Pumice
      - » U=11.8 ppm Th=40ppm

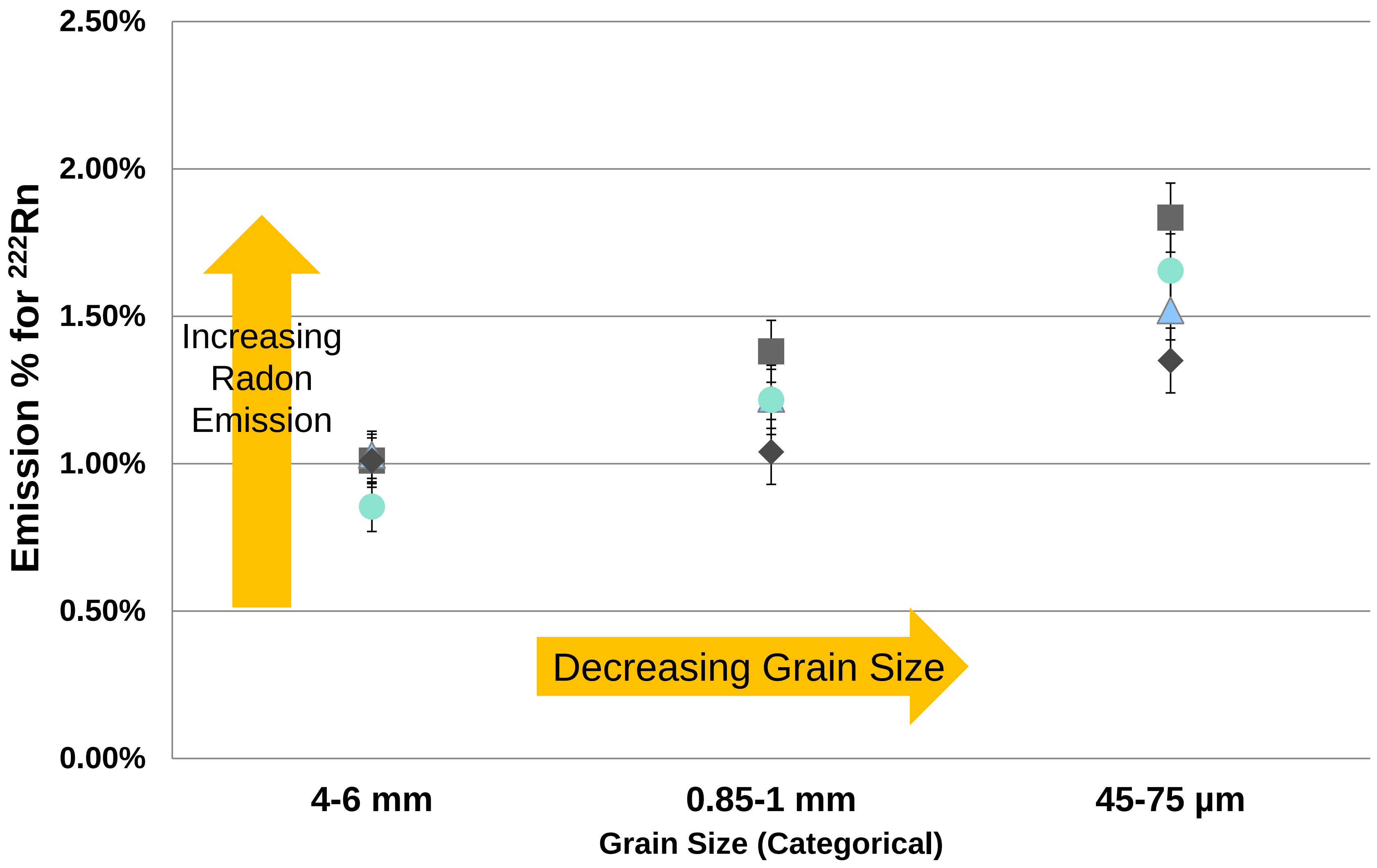

Secular Equilibrium and Emission Coefficient
Activity of Daughter
0
1
2
3
4
5
6
7
8
9
10
Time in Half Lives of Daughter
100% Emission
50% Emission
25% Emission
10% Emission

# Experiment Set-up




Radon Emission for Cerros Del Rio Basalt
50%
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
Emission % for $^{222}Rn$
Increasing Radon Emission
Decreasing Grain Size
4-6 mm
0.85-1 mm
45-75 µm
Grain Size (Categorical)

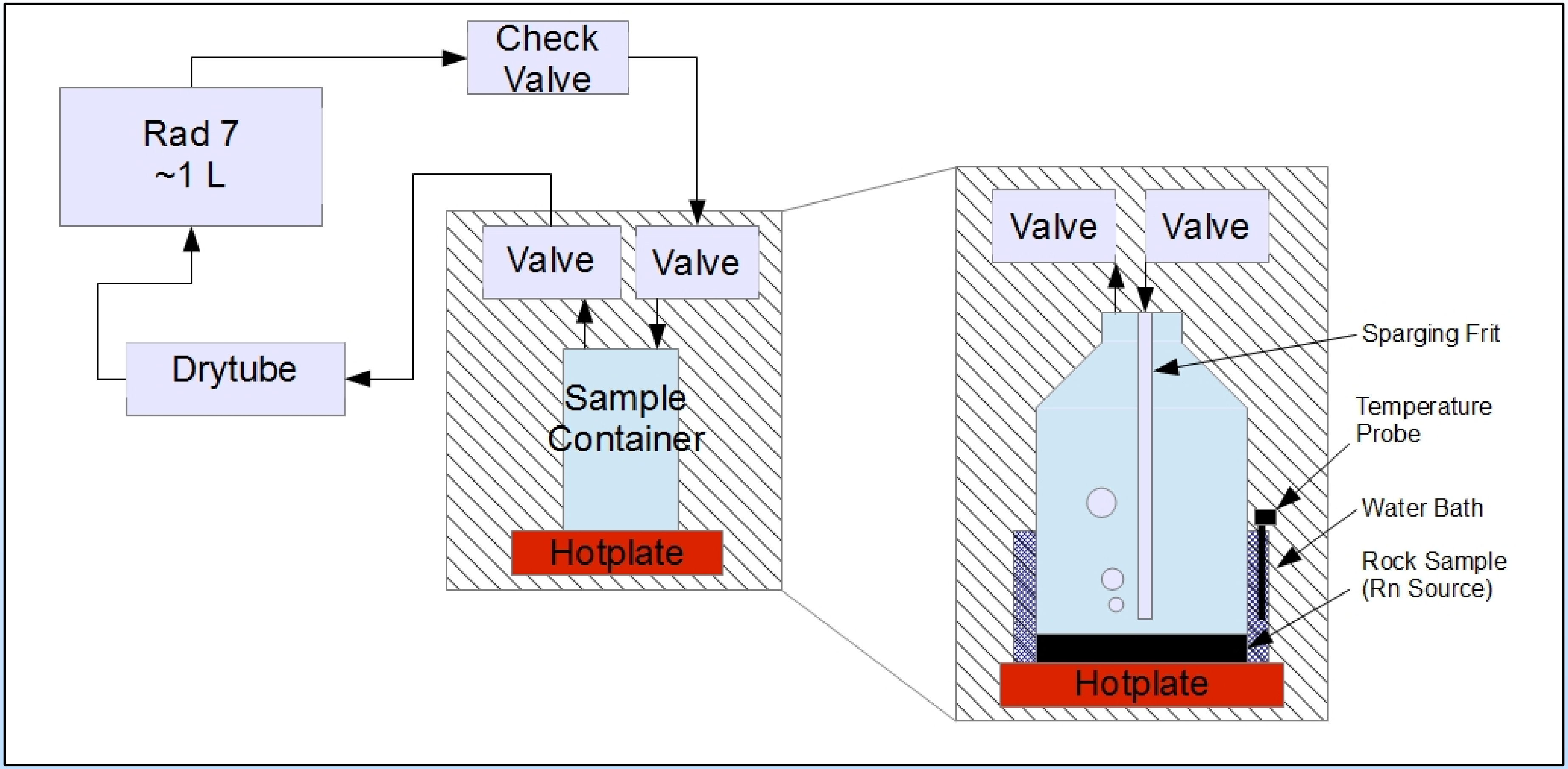
# Radon Emission for Guaje Pumice



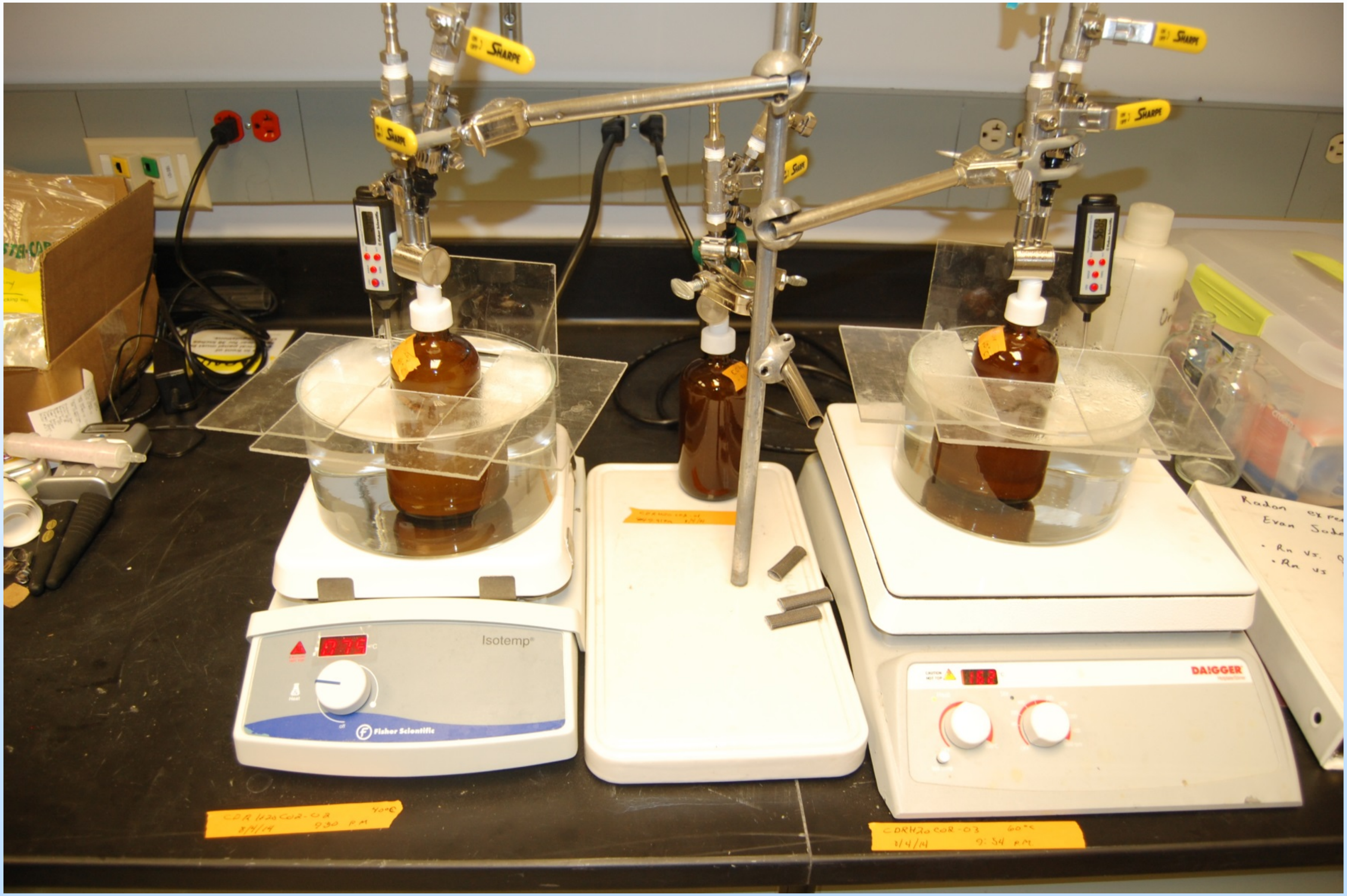
# Technical Status

- Lab Work Laboratory Tests of Effects of $CO_2$-$H_2O$-Rock Reaction (Soderberg investigations)
  - Hypothesis: as water temperature increases, Radon emissivity should increase.
  - Reacting with water can change surface area of grains through both armoring and dissolution (competing processes).
  - $CO_2$ in the water enhances reactions
  - Depending on temperature Radon may also begin diffusing out of grains.

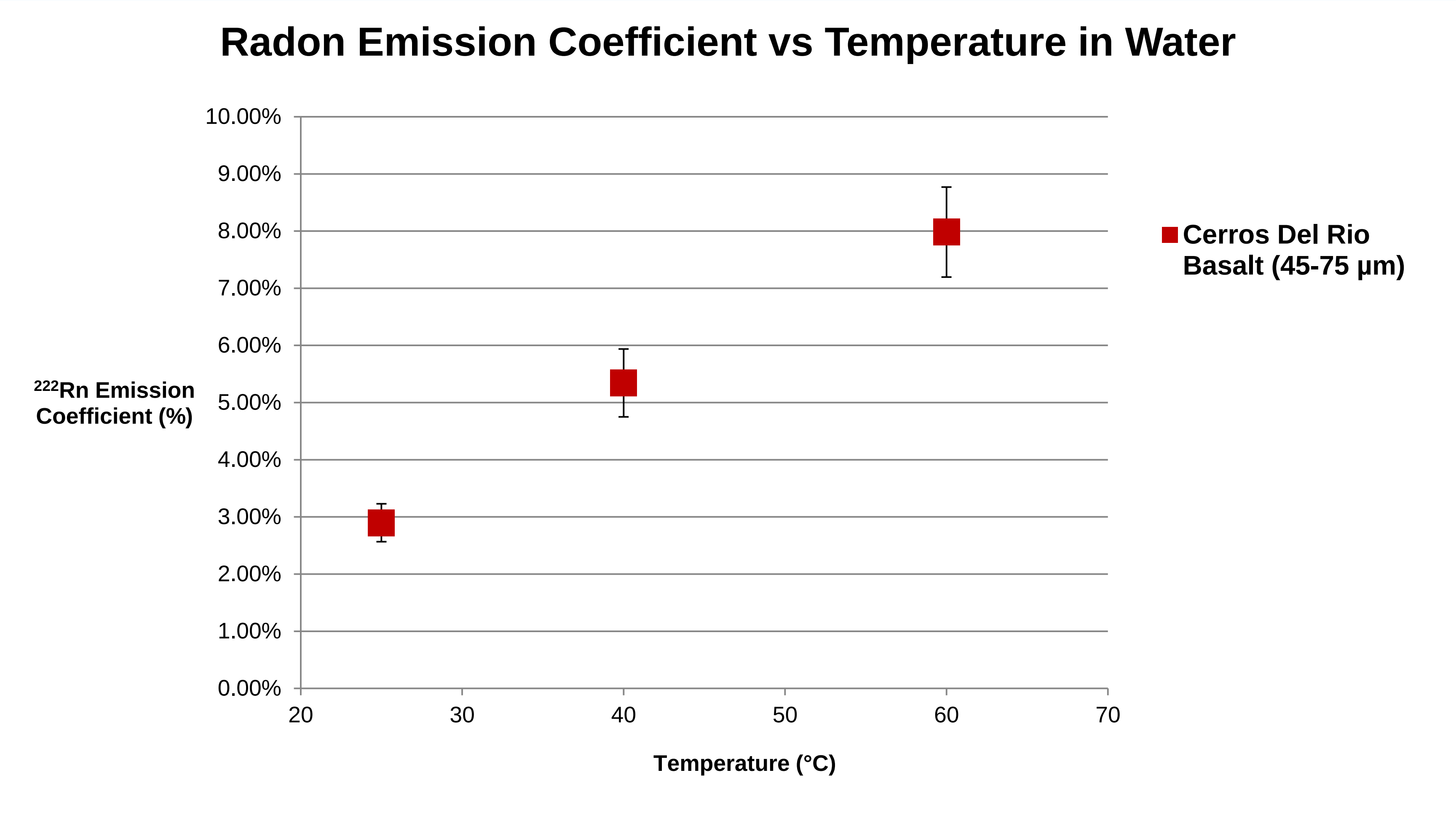
# Rn in water schematic



# Experiment Set-Up



# Preliminary Data



# Accomplishments to Date

- Two MS students performed research and successfully defended thesis
- Three BS students have performed undergraduate research
- Site characterization of natural analog (Moxa Arch, SW Wyoming; Thermopolis thermal area; Yellowstone) is complete

# Accomplishments to Date

- Determined that standard method for measuring Rn needs correction in high $CO_2$ environments
- Rn versus grain size alpha recoil experiments are complete
- Initial laboratory tests of effects of $CO_2$-$H_2O$-rock reaction complete
- Additional laboratory tests currently running (waiting to reach equilibrium)
  - One set with $H_2O$ and 10 mmol NaCl
  - One set with $CO_2$, $H_2O$ and 10 mmol NaCl

# Summary

– Key Findings
  - A measureable,semi-quantitative relationship exists between grain size and Radon
– Lessons Learned
  - In the presence of $CO_2$, Thoron and Radon must be corrected for the effect $CO_2$ has on the instrument
– Future Plans:
  - Finish Laboratory Tests of Effects of $CO_2$-$H_2O$-Rock Reaction
  - Write and submit final report

# Organization Chart

Dr. John Kaszuba
(co PI)

Dr. Ken Sims
(co PI)

**BS Students**
Virginia Marcon (graduated)
Matt Carberrry (graduated)
Evan Soderberg (graduated)
Mike Schedel

**MS Students**
Tim Moloney (defended)
Allison Pluda (defended)

**External Collaborators**
Dr. Salvatore Giammanco (Istituto Nazionale di Geofisica e Vulcanologia)
Dr. Matt Charette (WHOI)
Dr. Derek Lane-Smith (Durridge Company, Inc.)

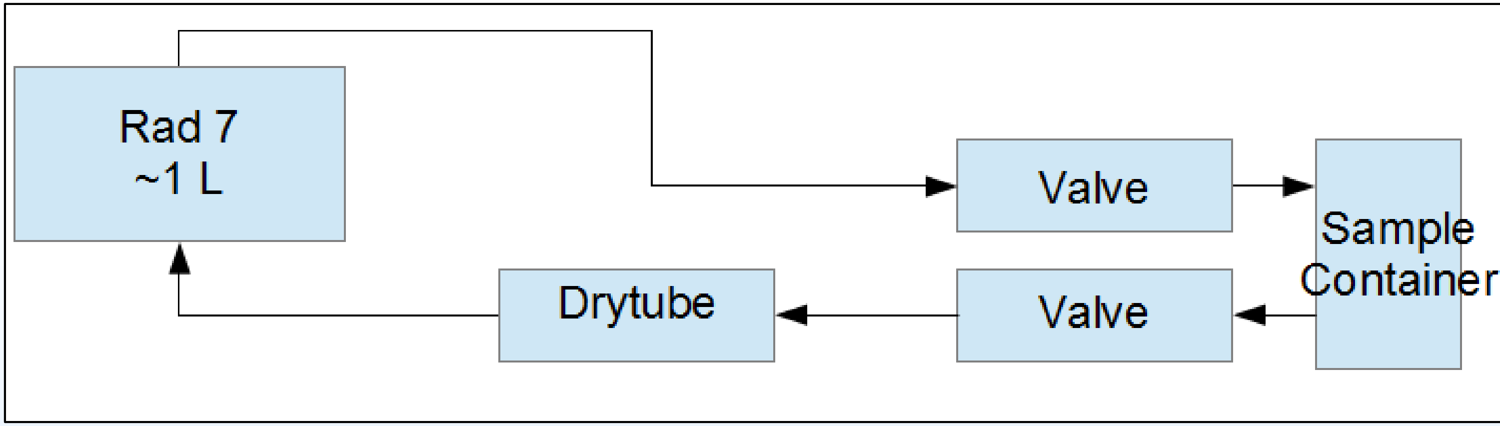
# Gantt Chart

| Subtask | Milestone | | | | | |
|---|---|---|---|---|---|---|
| 1 | HQ Milestone: Project Kick-off Meeting | | | | | |
| 1 | HQ Milestone: Educational Program Instituted | | | | | |
| 1 | HQ Milestone: Semi-Annual Progress Report | | | | | |
| 1 | HQ Milestone: Yearly Review Meeting | | | | | |
| 1 | HQ Milestone: Yearly Review Meeting | | | | | |
| | | | | | | |
| 1.1 | Update Project Management Plan | | | | | |
| 1.3 | Annual progress report submitted | | | | | |
| 1.3 | Annual progress report submitted | | | | | |
| | | | | | | |
| 2.1 & 2.2 | Obtain & calibrate radon and CO2 analyzers | | | | | |
| 2.3 | Begin 1st set of Field Measurements | | | | | |
| 2.4 | Complete 75% of Field Measurements | | | | | |
| | | | | | | |
| 3.1 | Begin 1st set of Laboratory Tests of Rn and Grain Size | | | | | |
| 3.2 | Submit report for Laboratory Tests of Rn and Grain Size | | | | | |
| 3.3 | Begin 1st set of Laboratory Tests of Effects of CO2-H2O-Rock Reaction | | | | | |
| 3.4 | Submit report for Laboratory Tests of Effects of CO2-H2O-Rock Reaction | | | | | |
| | | | | | | |
| 4.1 | Develop initial model | | | | | |
| 4.2 | Final report submitted | | | | | |
| | | 2010 | 2011 | 2012 | 2013 | 2014 |

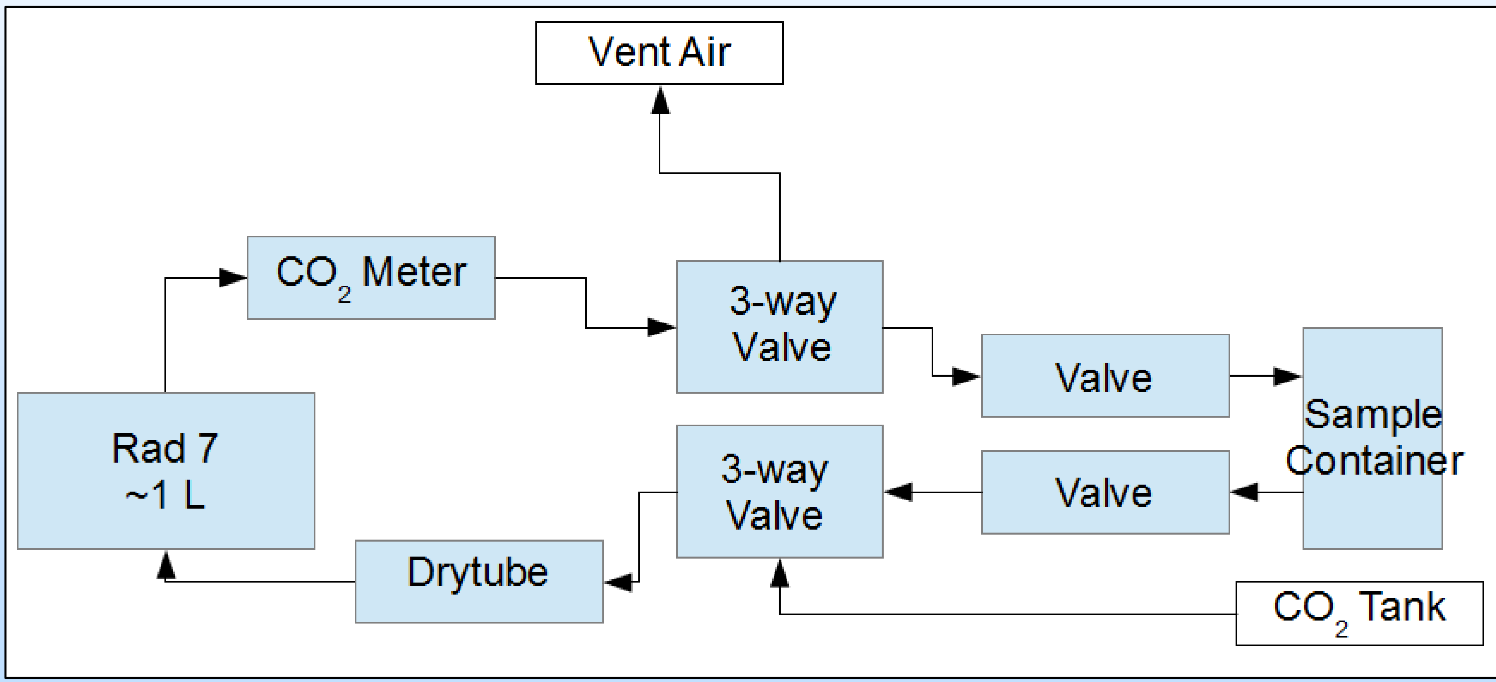
# Bibliography


- Lane-Smith, D., & Sims, K. W. W., 2013. The effect of $CO_2$ on the measurement of $^{220}Rn$ and $^{222}Rn$, with instruments utilizing electrostatic precipitation. *Acta Geophysica*. V. 61, p. 822-830, available at http://agp.igf.edu.pl/
- Giammanco, S., K. W. W. Sims, and M. Neri, 2007, Measurements of $^{220}Rn$ and $^{222}Rn$ and $CO_2$ emissions in soil and fumarole gases on Mt. Etna volcano (Italy): Implications for gas transport and shallow ground fracture,. Geochemistry, Geophysics, Geosystems, v. 8, Q10001, doi:10.1029/2007GC001644, available at: http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1525-2027
- Kaszuba, John P., Sims, Kenneth W. W., and Pluda, Allison, 2014, Aqueous geochemistry of the Thermopolis hydrothermal system, southern Bighorn Basin, Wyoming: Rocky Mountain Geology, v. 49, p. 1-16.

Ambient Air Schematic




$CO_2$ Schematic



# $CO_2$-$H_2O$-Rock Experiments

- Design
  - Single grain size (45-75 µm) and lithology (Cerros Del Rio Basalt)
  - Samples reacted with water for 20 days
  - 3 temperatures
    - 25 °C
    - 40 °C
    - 60 °C

# Notes

- 1 Becquerel = 1 decay/second = 27.027027 picocuries
- Otowi Member Guaje Member = 1.4 Ma (Guaje Pumice)
- Cerros Del Rio Basalt Fields = 1.96 to 4.62 Ma
- Banco Bonito = Still debated most likely <140 ka
- 1 mmol NaCl = 0.58 Salinity (g NaCl/kg $H_2O$)

# Notes cont.

- The DURRIDGE RAD7 uses a solid state alpha detector. A solid state detector is a semiconductor material (usually silicon) that converts alpha radiation directly to an electrical signal. One important advantage of solid state devices is ruggedness. Another advantage is the ability to electronically determine the energy of each alpha particle. This makes it possible to tell exactly which isotope (polonium-218, polonium-214, etc.) produced the radiation, so that you can immediately distinguish old radon from new radon, radon from thoron, and signal from noise. This technique, known as alpha spectrometry
- When the radon and thoron daughters, deposited on the surface of the detector, decay, they emit alpha particles of characteristic energy directly into the solid state detector. The detector produces an electrical signal. Electronic circuits amplify and condition the signal, then convert it to digital form. The RAD7 's microprocessor picks up the signal and stores it in a special place in its memory according to the energy of the particle. The accumulations of many signals results in a spectrum.