



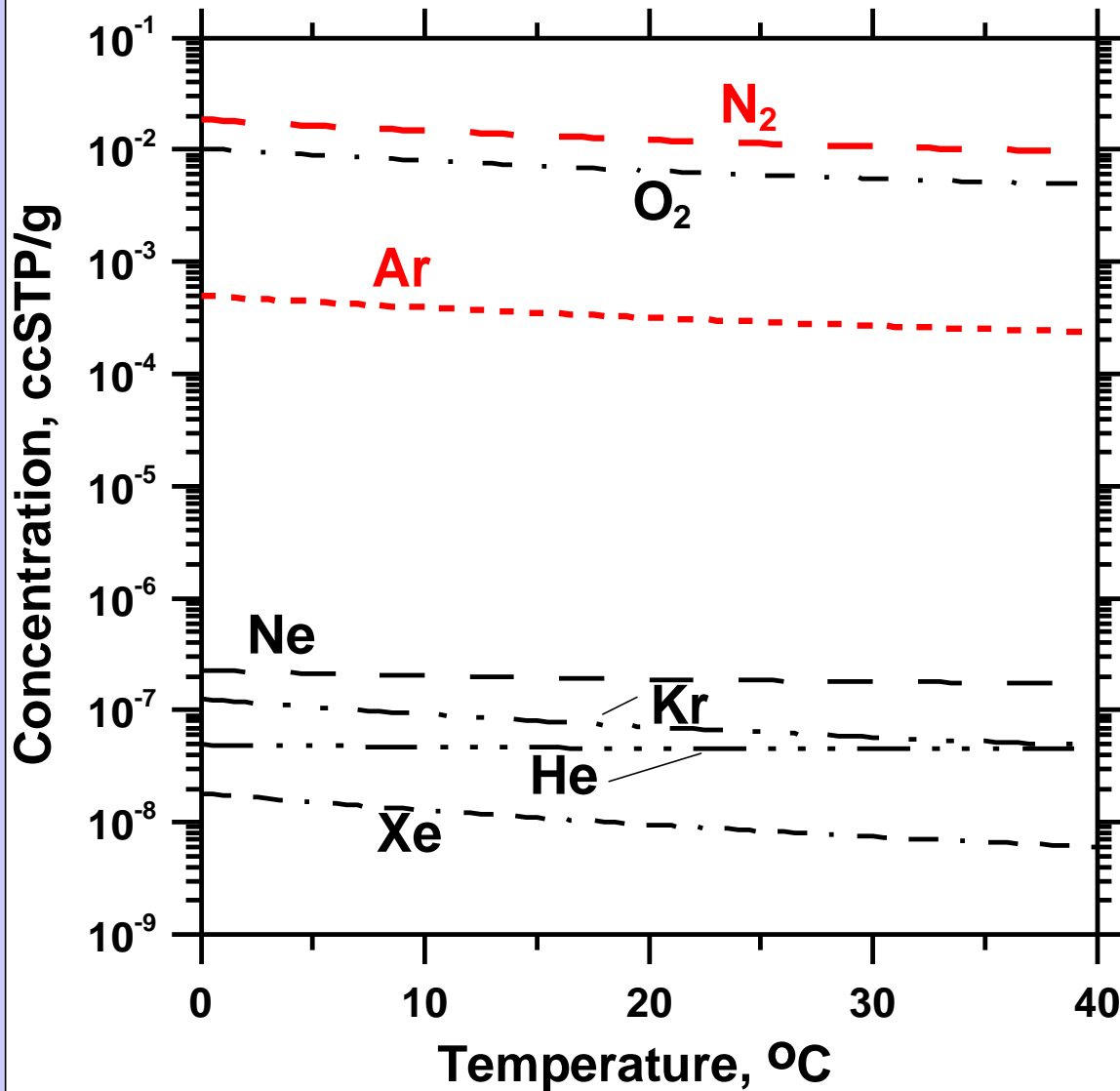
# **Applications of Dissolved N<sub>2</sub> and Ar in Groundwater**

**L. Niel Plummer, Eurybiades Busenberg,  
and Peggy K. Widman**

**U.S. Geological Survey  
Reston, VA**



## Air - Water Equilibrium



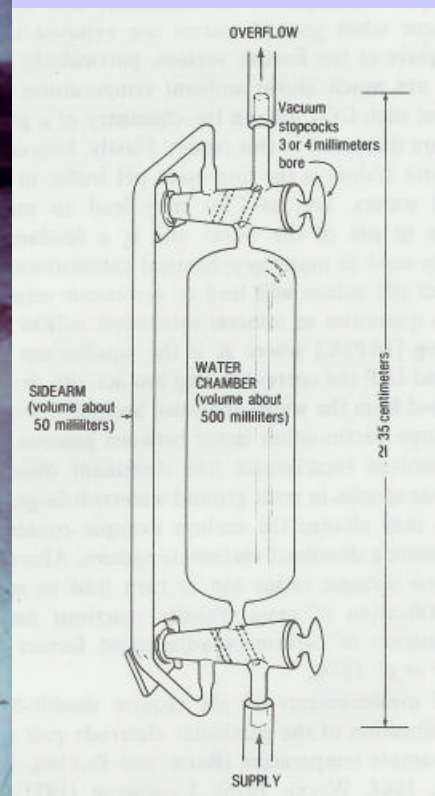
- $O_2$  unstable
- $N_2$  can be affected by  $NO_3$  reduction
- Terrigenous source of He
- Most reliable are Ar, Ne, Kr, Xe
- Ar and  $N_2$  solubilities from air are 3-5 orders of magnitude > than that of remaining noble gases. Can be measured by gas chromatography.

# Applications of N<sub>2</sub> – Ar Measurements in Groundwater

- Reconstruct recharge temperatures—
  - ✓ K<sub>H</sub> calculation in dating with atmospheric gases such as CFCs and SF<sub>6</sub>
  - ✓ Paleoclimatic reconstruction (check <sup>14</sup>C age)
- Reconstruct excess air—
  - ✓ Function of recharge rate and hydrogeology
  - ✓ Needed in dating with CFCs and esp. SF<sub>6</sub>.
- Trace water sources through aquifers
- Recharge mechanism— Focused/diffuse recharge; rapid recharge; (altitude of recharge)
- Reconstruct initial nitrate in agricultural studies

# BACKGROUND: N<sub>2</sub>-Ar

- **Heaton, Vogel, Talma (early 1980s)**  
Paleorecharge temperatures, excess air, denitrification.
- **Don Fisher, USGS (1970s)**  
Developed GC method, field sampling device.
- **Current state at USGS**  
Dual column GC method, new sample collection, QA/QC procedures, software.  
Extensive use in agricultural studies, dating with CFCs and SF<sub>6</sub>.

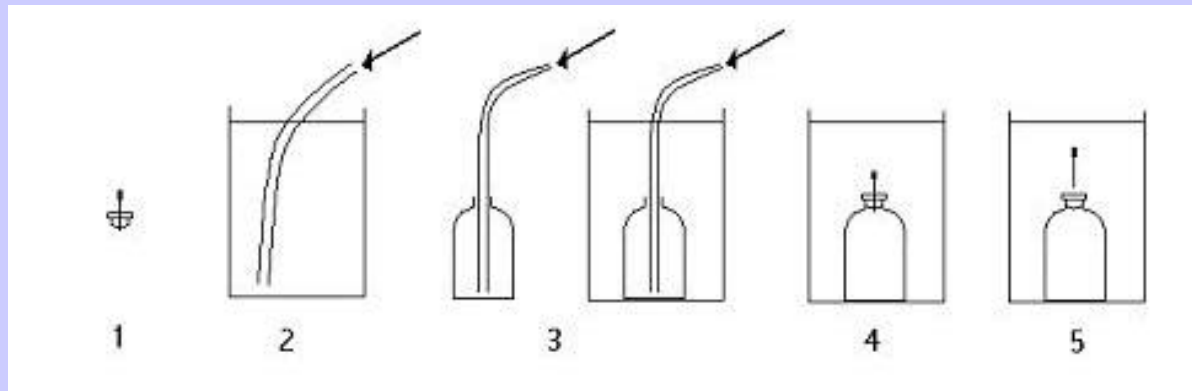


**Fisher dissolved gas sample container**

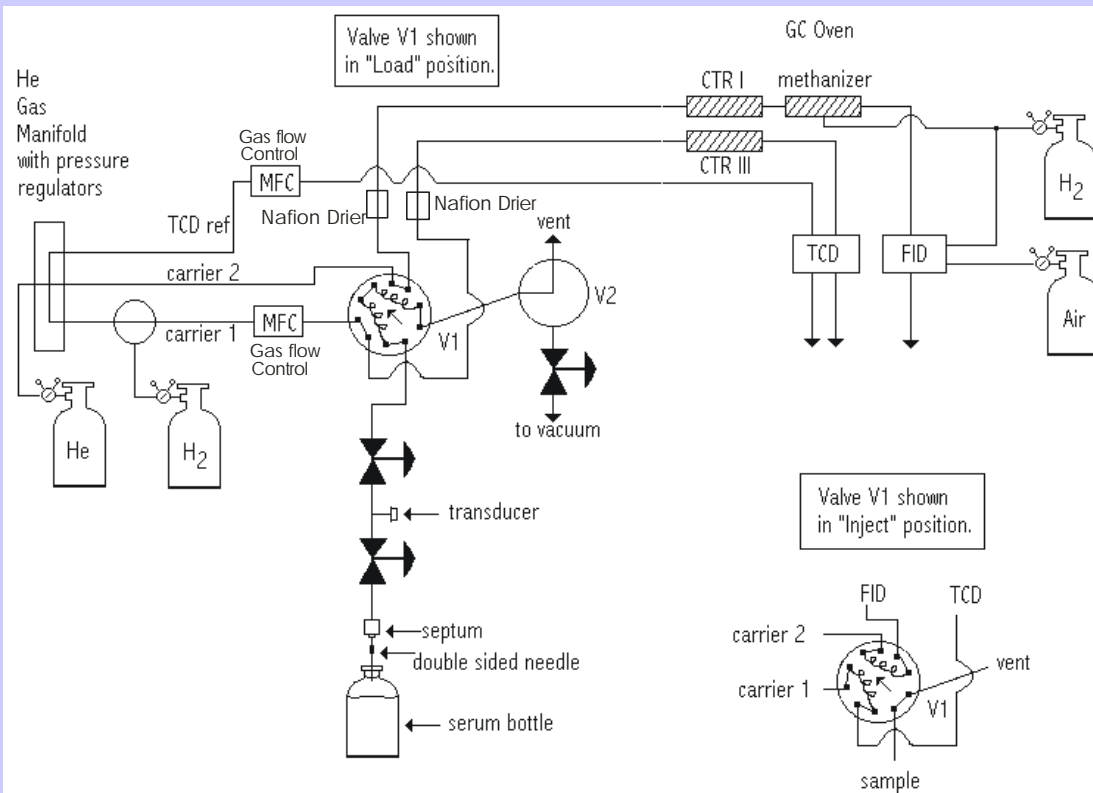


**Bruce B. Hanshaw (the late), at Philip flowing well, Philip, South Dakota, 68°C, Madison aquifer, circa 1979; Bruce had a good sense of humor.**

# Sample Collection



- 160 cc glass bottle with septum stopper
- Filled without headspace under water
- Needle used to release fluid as stopper inserted
- Needle removed.
- Bottle weight measured empty and full.

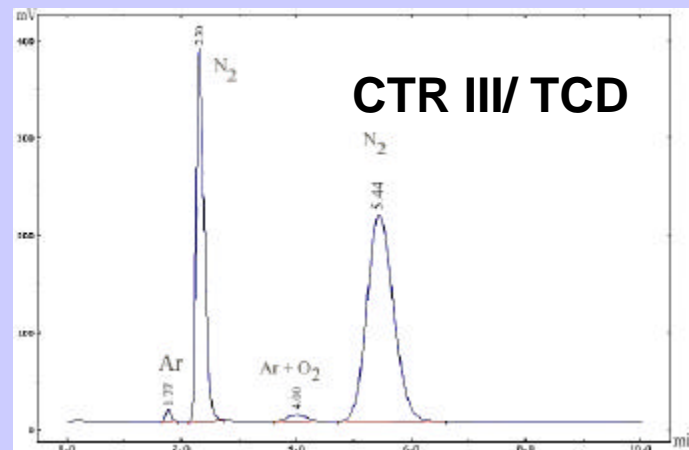


## Schematic of analytical system

- Headspace equilibrated >24 hrs
- Water temp. measured in bottle immediately after injection
- All measurements made on same initial vol. of gas
- Two columns (each a double column); two detectors.
- Calibrated with known gas standards.
- QA/QC daily with water samples equilibrated in water baths at 9, 16, and 24 °C in same sample container.

## CTR III / TCD

- Measures Ar, N<sub>2</sub>, and O<sub>2</sub>+Ar; O<sub>2</sub> determined by difference
- Thermal Conductivity Detector

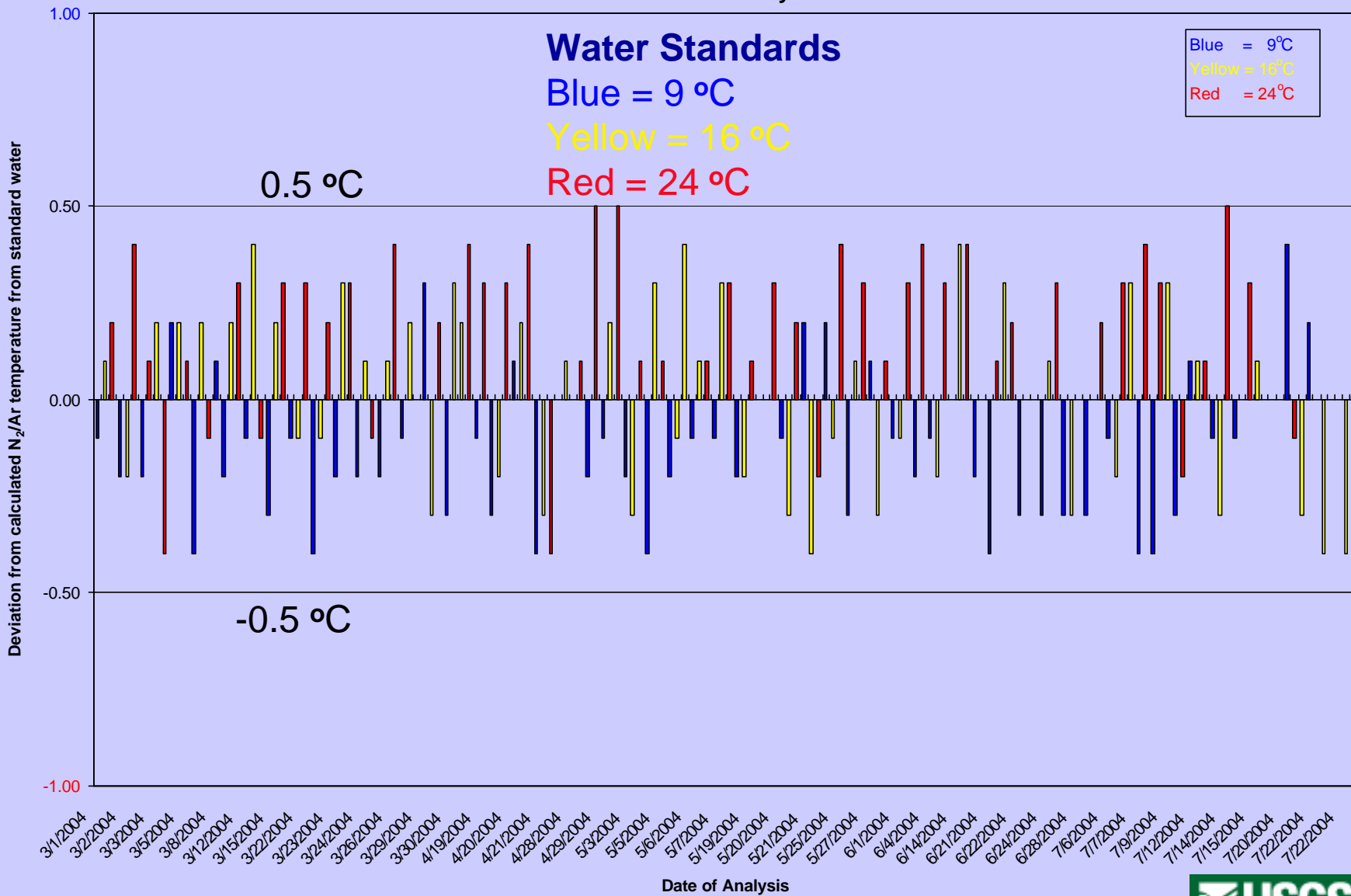


## CTR I / FID

- Separates all the gases
- Used only for CH<sub>4</sub> and CO<sub>2</sub>
- CO<sub>2</sub> converted to CH<sub>4</sub> for measurement with FID

# Temperature of Standard Water - N<sub>2</sub>/Ar Calculated Temperature

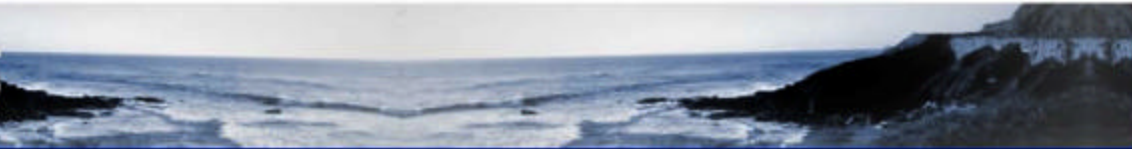
March 2004-July 2004





<http://water.usgs.gov/lab/cfc>

USGS d--USERINHOUSE-->(Internal Access)d--USERINHOUSE--> - CFC Lab | Reston, VA



## The Reston Chlorofluorocarbon Laboratory (Internal Access)

Site Map

Home

CFC

FAQ

Background

Lab

Research

Staff

Contact

Prices

Dissolved Gas

FAQ

Lab

Research

Staff

Sampling

Contact

Prices

SF<sub>6</sub>

FAQ

Background

Lab

Research



United States Geological Survey  
CFC Laboratory



**Dating of  
young  
groundwater  
with  
CFCs, SF<sub>6</sub>, <sup>3</sup>H,  
& <sup>3</sup>H/<sup>3</sup>He**  
PDF (3.07 MB)  
(June 2004)

**Dating of  
Young  
Groundwater**  
PDF (5.29 MB)  
(November  
2003)

Welcome

See extensive bibliography



# Why Measure N<sub>2</sub> – Ar, when suites of noble gases can be measured?

- Relatively high concentrations; Waters can be analyzed by relatively simple GC methods.
- In some cases, most of the information obtained from noble gases can also be obtained from N<sub>2</sub>-Ar
- Reconstruct amounts of denitrification. Initial NO<sub>3</sub>; Agricultural studies; fertilizers fate.
- Cost effective. Large numbers of samples can be collected and analyzed; potential for mapping flow in aquifers.

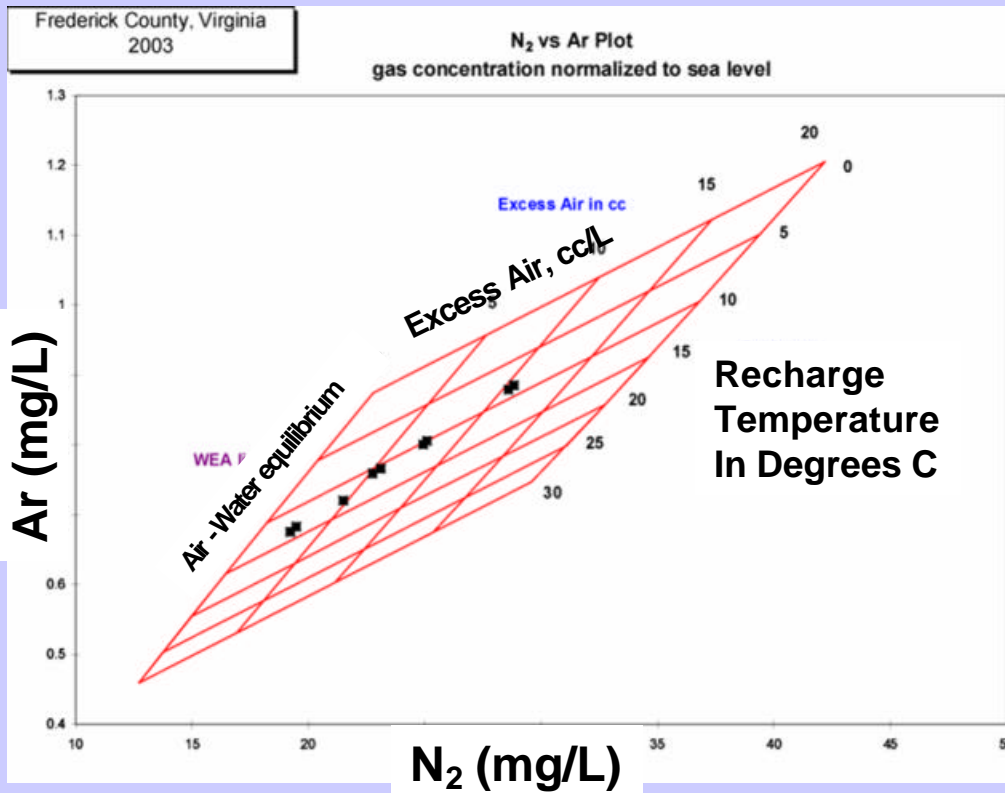
# Limitations of N<sub>2</sub> – Ar data

- Only 2 independent measurements, but as many as 4 unknowns (Recharge temperature; Excess air; Altitude of recharge; Excess N<sub>2</sub>).
- Gas fractionation? Need additional gases to even detect. Most applications of N<sub>2</sub> – Ar assume complete dissolution of excess air. This is an approximation, but considering the relatively high concentrations of N<sub>2</sub> and Ar in groundwater, appears to be a reasonable assumption.

# Recharge Temperature - Excess Air

$$N_2(\text{meas}) = N_2(\text{equil}) + N_2(\text{Ex air}) + N_2(\text{denit})$$

$$Ar(\text{meas}) = Ar(\text{equil}) + Ar(\text{Ex air})$$

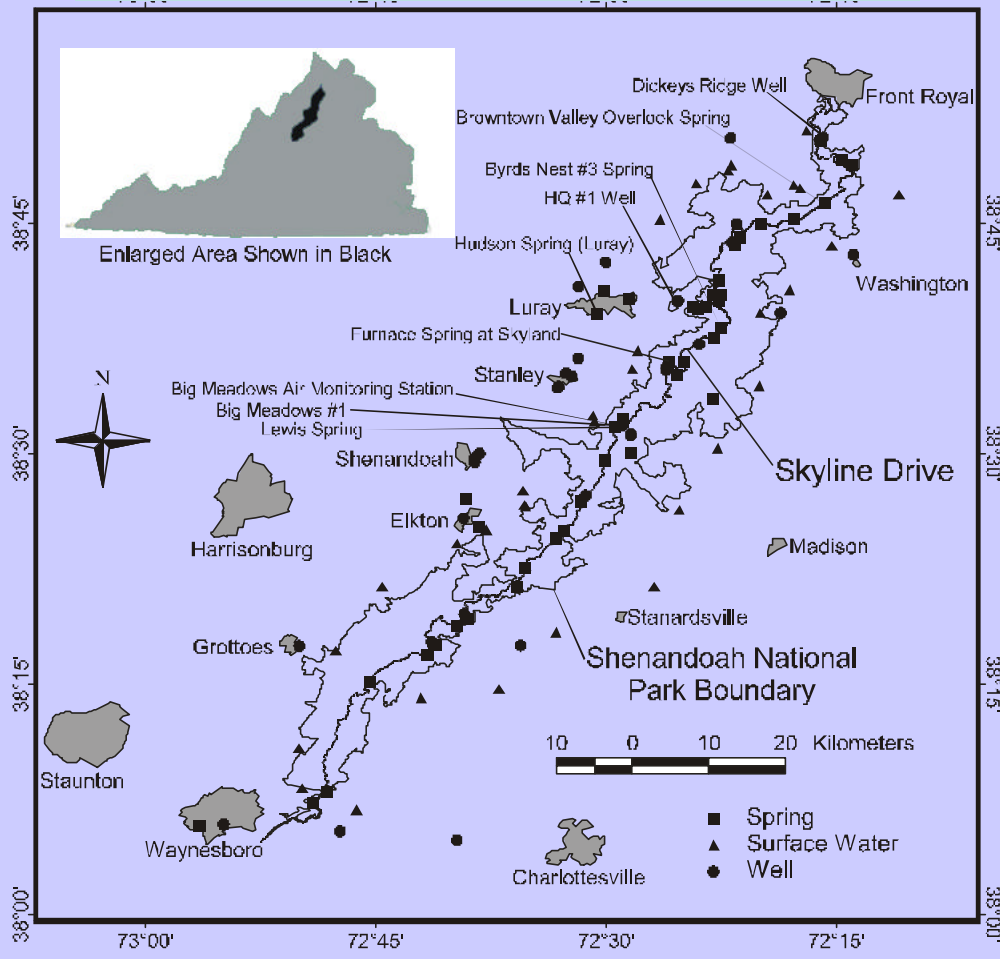


**Aerobic waters**  
**N<sub>2</sub>(denit) = 0**

**Altitude of recharge assumed**

**Samples from wells in fractured rock in Virginia**  
**RT 9 – 14 °C**  
**3-10 cc/L excess air**

# Springs and wells from Blue Ridge Mountains of Virginia; Shenandoah National Park

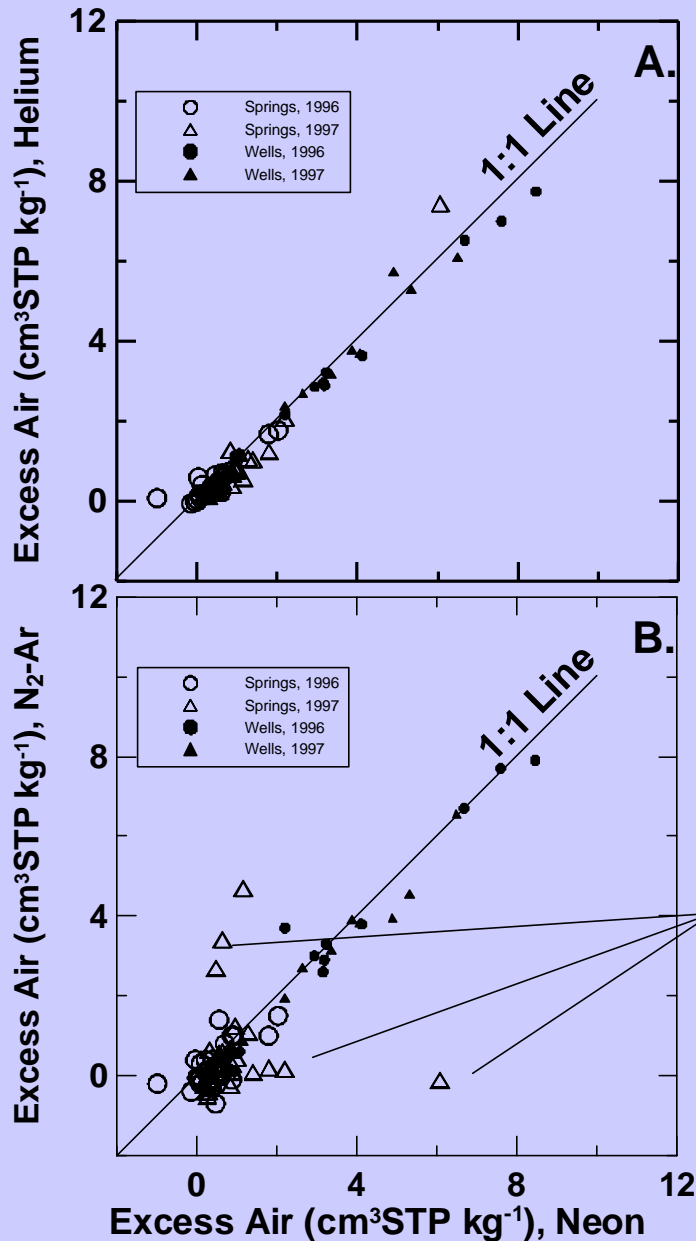


Lewis Mountain Spring



Sampling from a Typical Spring Box and Weir

## Springs and wells, Blue Ridge, VA

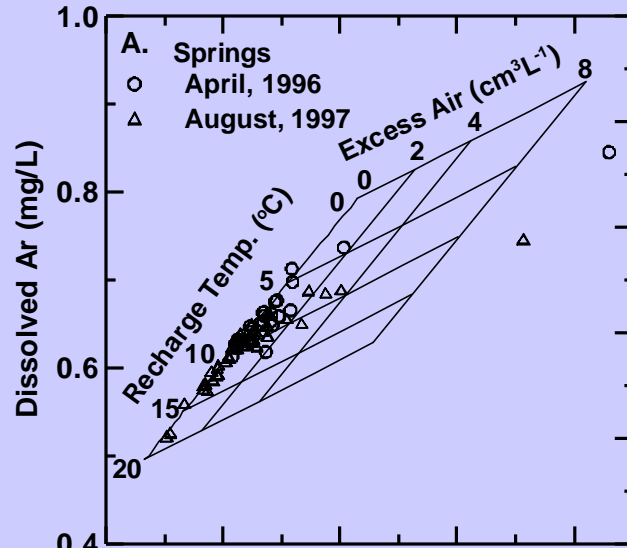


Comparison of excess air calculated from mass spectrometric He and Ne with excess air from GC N<sub>2</sub>-Ar

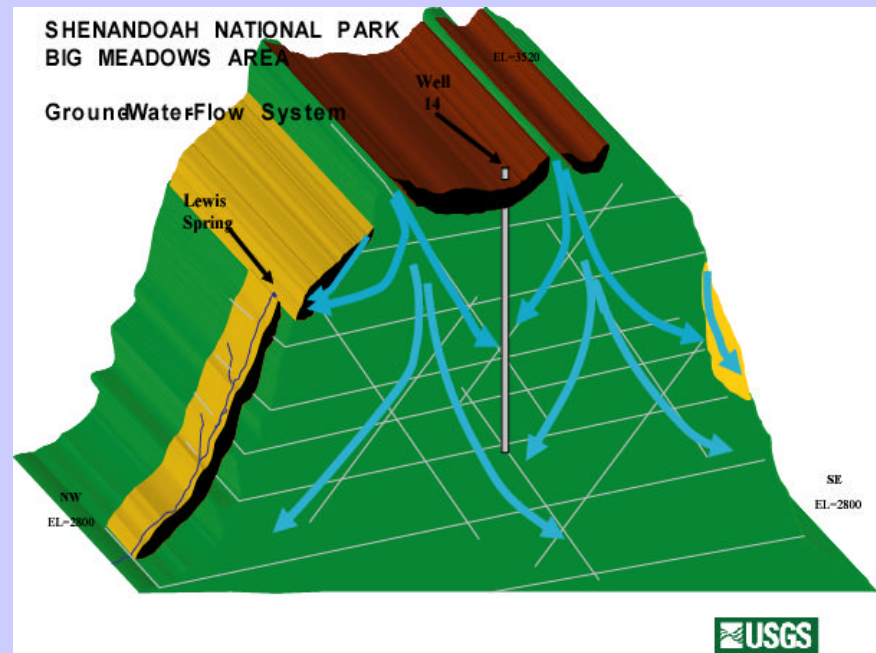
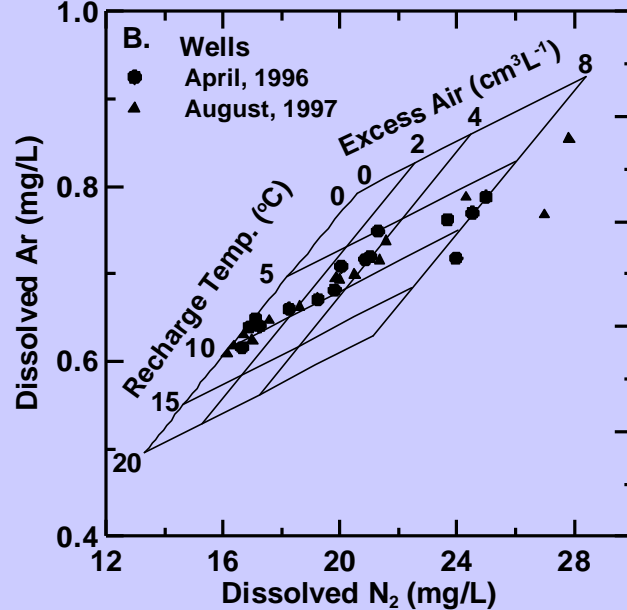
No evidence of gas fractionation

Largest deviations probably gas leaks in sample container.

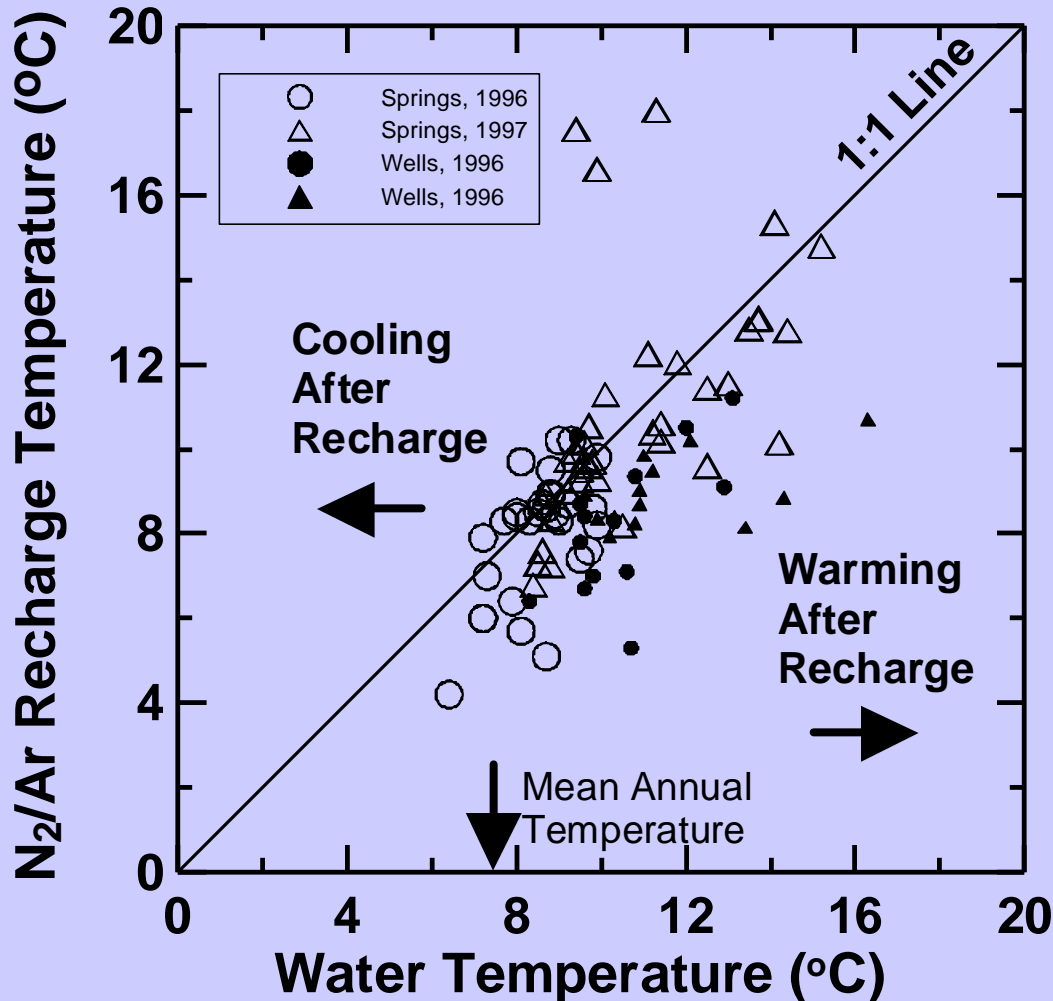
## Springs and Wells— Blue Ridge Mts., VA



- Springs—residuum and colluvium; 0-2 cc/L excess air [sand aquifers]
- Wells-- fractured rock; 0-8 cc/L excess air [river floods; arroyos; fractured rock]
- Wide range of RT for springs;
- Narrow range of RT for wells
- Mean annual Temp about 7.8 °C



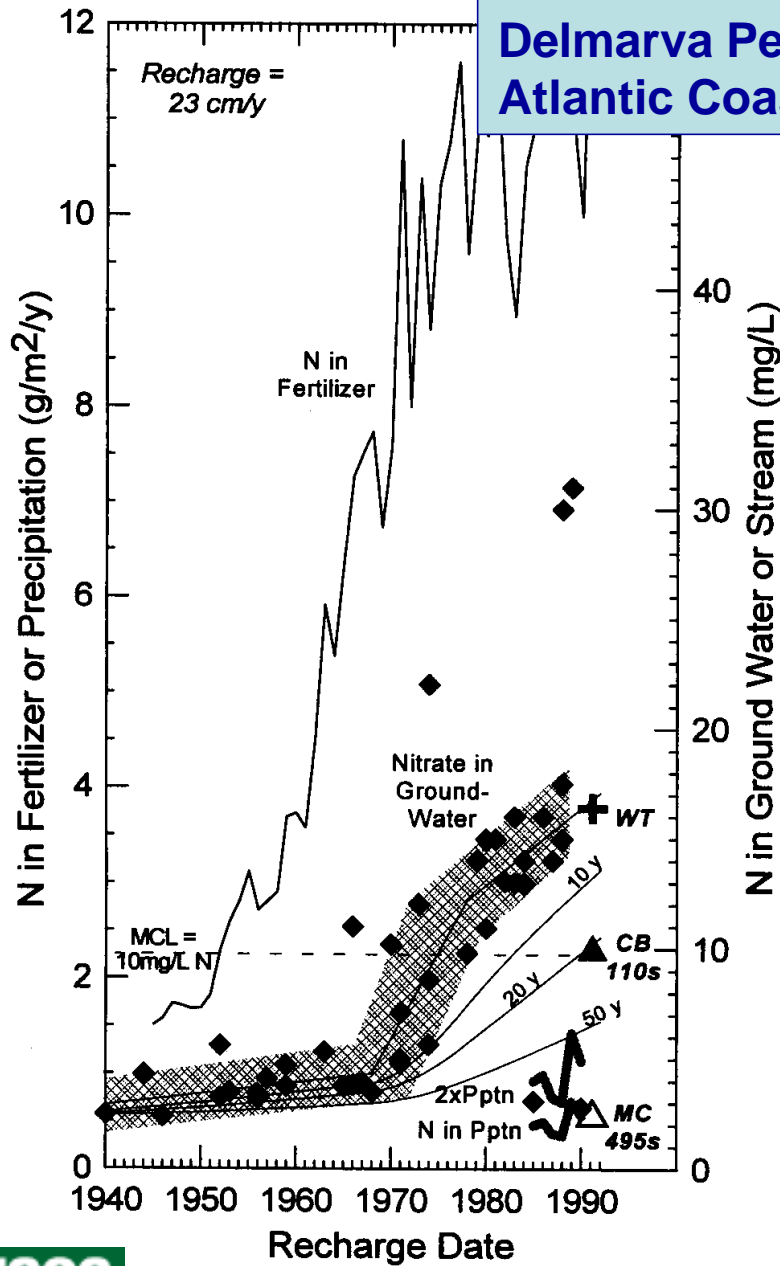
# Springs and wells Blue Ridge, VA



- Most springs have recharge temperatures near the water temperature (shallow)
- Seasonal dependence of RT (shallow recharge)
- A few springs warmed in circulation (deeper)
- Discharge from most wells warmed in ground (deeper)
- 3 samples cooled following a summer thunderstorm



## Delmarva Peninsula Atlantic Coastal Plain



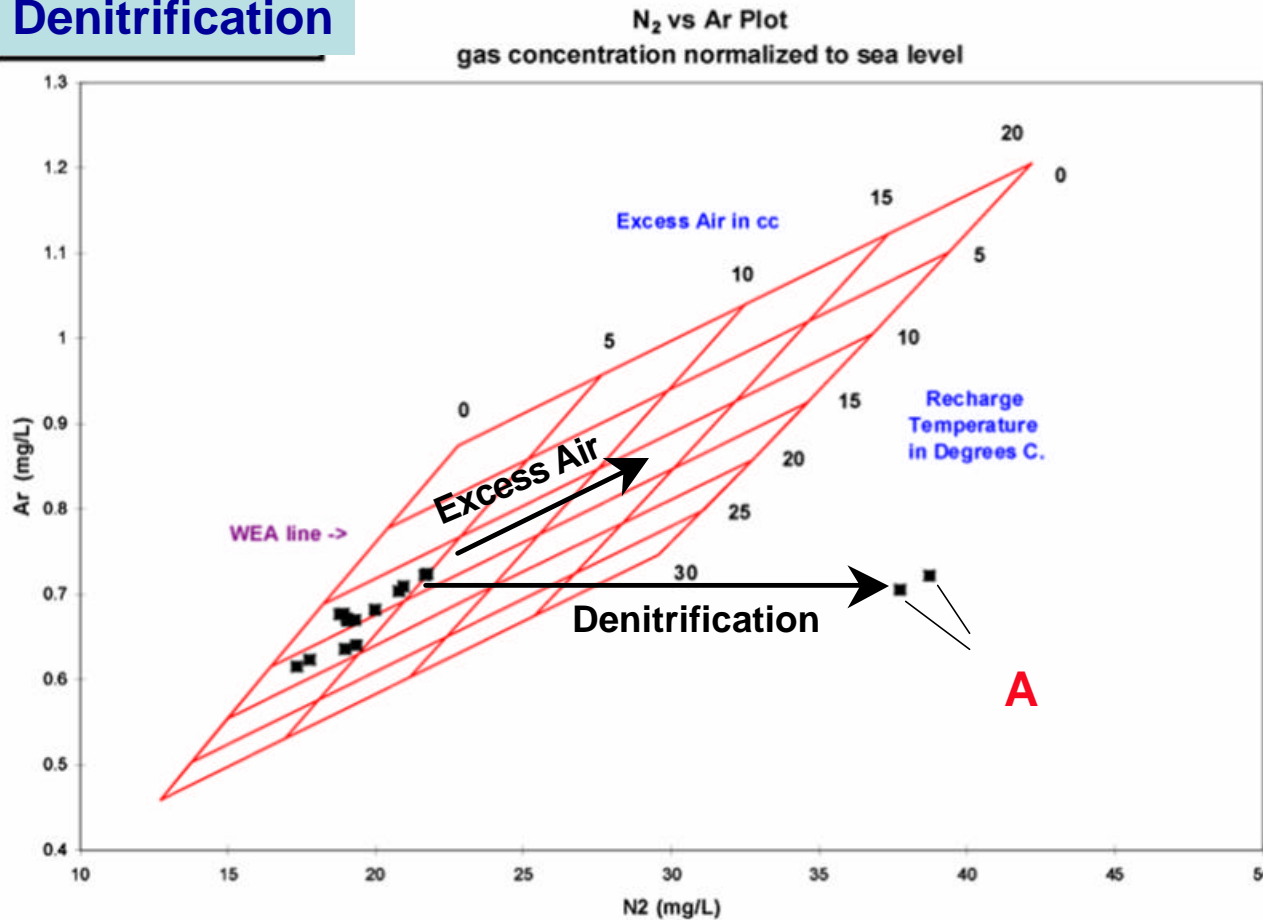
- CFC ages and  $\text{NO}_3$ : 40-yr record of  $\text{NO}_3$  recharge rate.
- Records increase in fertilizer application from the 1970's.
- 20-35 % of applied fertilizer reached the aquifer.
- Mean residence time of 20 yrs for gw discharge to local streams.

Böhlke and Denver (1995)

# What to do about denitrification?

- **Aerobic samples; No denitrification**
  - ✓ Assume altitude of recharge and solve  $N_2$  and Ar for T and Excess air
- **Anaerobic samples**
  - ✓ If Ne data available, solve  $N_2$ , Ar, Ne for T, Excess air and Excess  $N_2$  (at assumed recharge altitude)
  - ✓ If no Ne data, determine an average T or excess air from other aerobic samples in the data set.
- **Can Probably ignore denitrification in most paleowaters**

# Denitrification



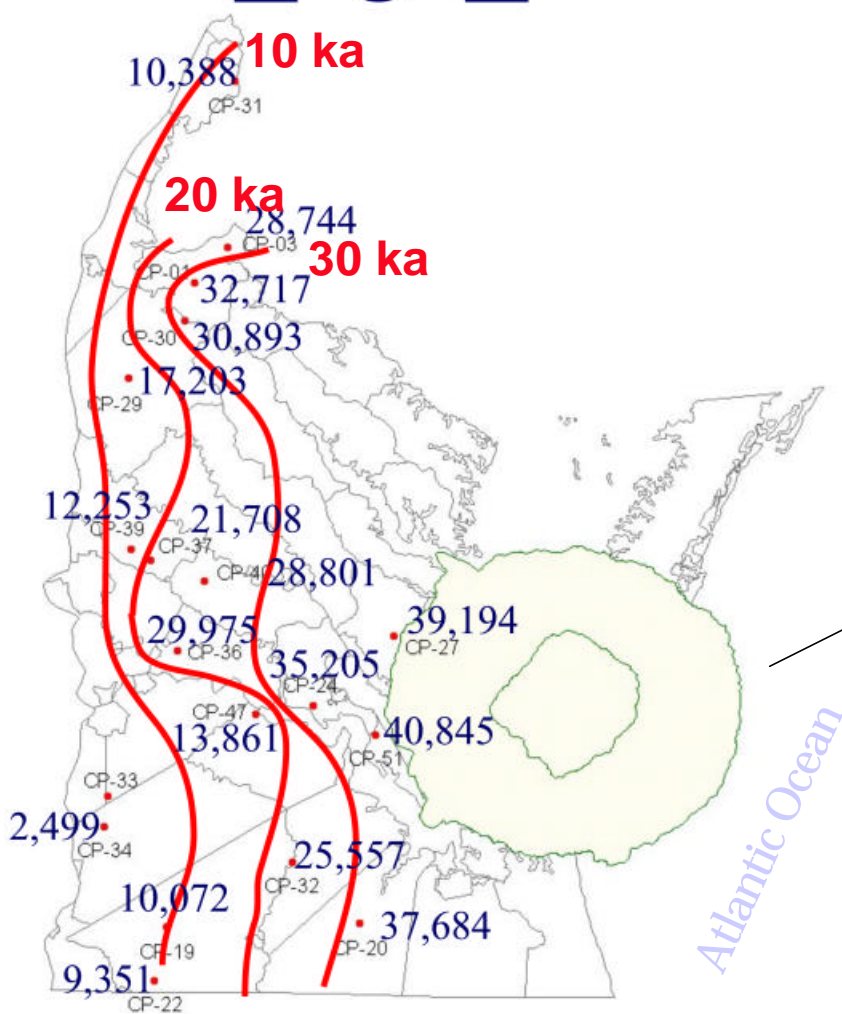
All samples aerobic  
(3-8 mg/L O<sub>2</sub>)  
except Sample A  
(in duplicate)

Average Recharge  
Temperature 14.3 ± 2.0

Average Excess Air  
3.0 ± 1.1 cc STP/L

**Sample A:**  
16 mg/L of N<sub>2</sub> from  
denitrification  
brings recharge  
temperature to  
13.2 °C and excess  
air to 4.3 ccSTP/L

# FG\_age\_final



Paleoclimatic Reconstruction

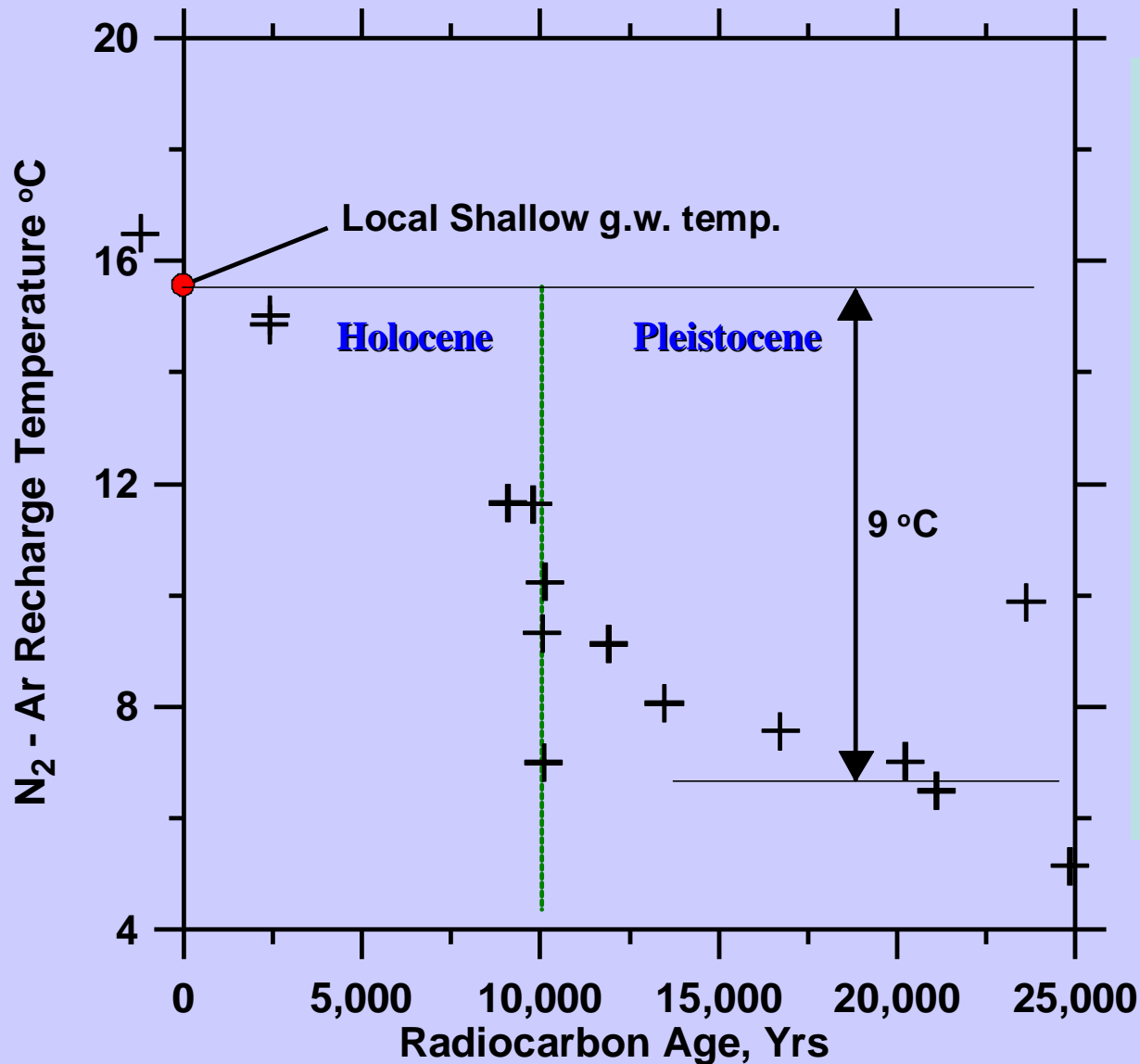
Fontes-Garnier Model <sup>14</sup>C Ages

Middle Potomac Aquifer

Chesapeake Bay Impact Crater (Eocene, some 40 million yrs ago)



# Nitrogen-Argon Recharge Temperatures (Coastal Plain)

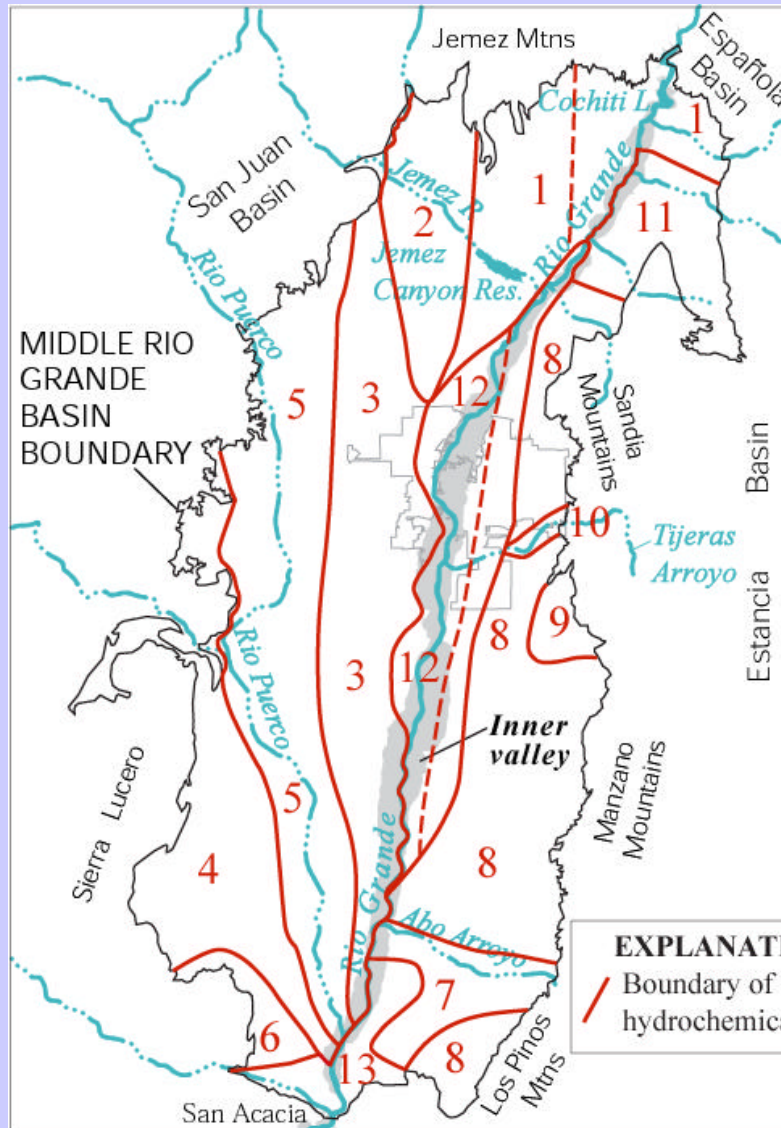


- Anaerobic, but initial NO<sub>3</sub> low in paleowaters
- Aeschbach-Hertig et al found 9 °C cooling in NGTs in Aquia aquifer just north of here in the Maryland Coastal Plain

# Altitude of recharge dependence

- Assume altitude of recharge—
  - ✓  $\pm 500$  m  $\rightarrow \pm 2.3$  °C;  $\pm 100$  m  $\rightarrow$  analytical uncertainty ( $\pm 0.5$  °C)
  - ✓ Estimate from hydrologic conceptualization
- Reconstruct using local lapse rate and (for deep UZ) temp-depth profile—
  - ✓ Calc. RT as function of altitude finding intersection with atmospheric lapse (Zuber et al.)
  - ✓ Calc. depth below land surface and RT using local thermal profiles.

# Tracing Sources of Recharge to Ground-water Systems



## HYDROCHEMICAL ZONES

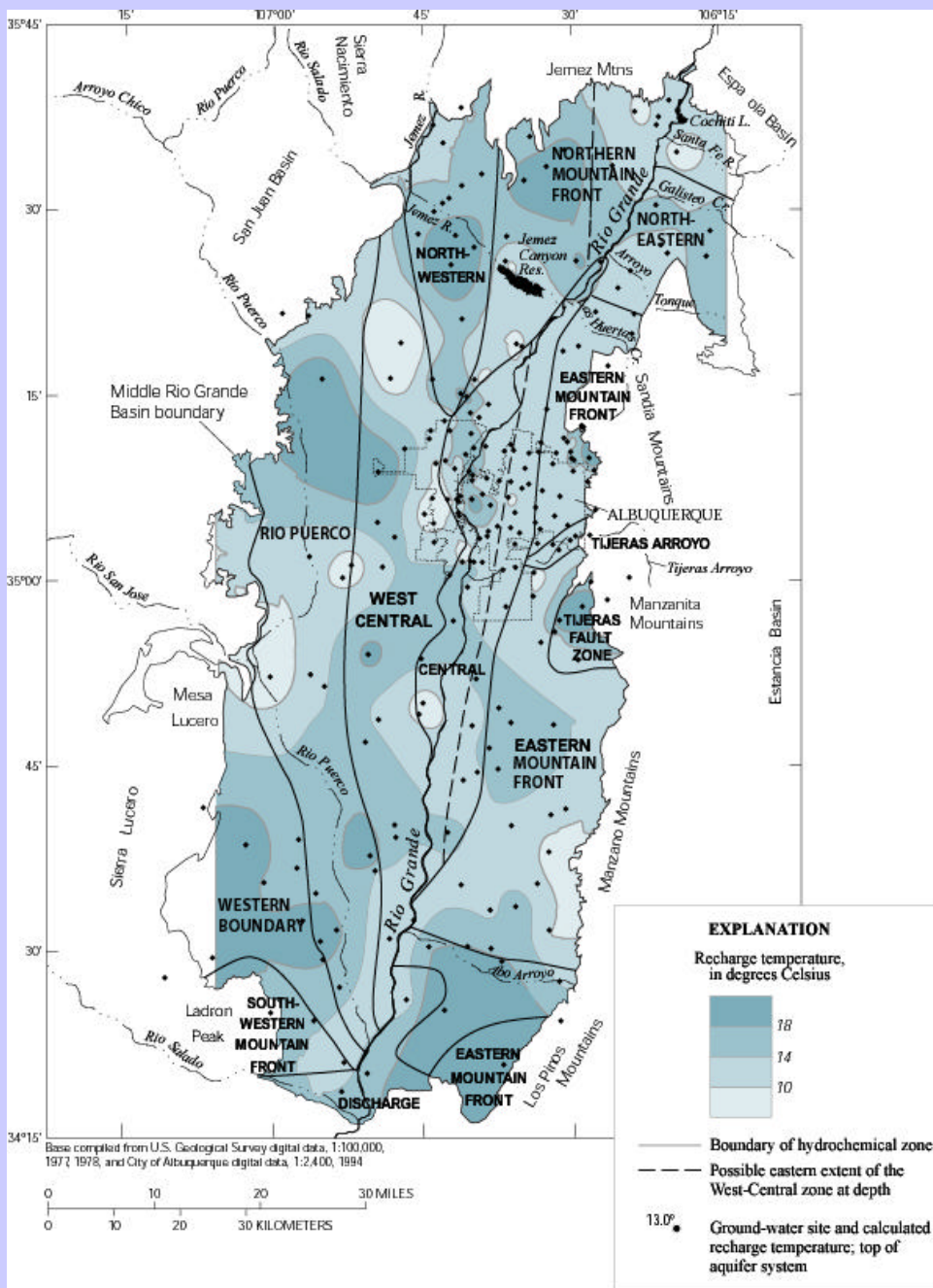
- 1 = Northern Mountain Front
- 2 = Northwestern
- 3 = West Central (extends eastward to dashed line at depth)
- 4 = Western Boundary
- 5 = Rio Puerco
- 6 = SW Mountain Front
- 7 = Abo Arroyo
- 8 = Eastern Mountain Front
- 9 = Tijeras Fault Zone
- 10 = Tijeras Arroyo
- 11 = Northeastern
- 12 = Central
- 13 = Discharge

**EXPLANATION**  
 / Boundary of hydrochemical zone



- Stable isotopes
- Water comp.
- <sup>14</sup>C data
- Dissolved gases
- RT, Ex Air
- Alt/depth of RC
- Focused/diffuse recharge





## Recharge Temperatures across top of aquifer

**Altitude of recharge assumed:**  
**5000 feet** (SW sources, NW, Abo Arroyo, NE zones)  
**6500 feet** (NMF, EMF, Tijeras)  
**8000 feet** (West Central zone)

• Mean Annual temp at Alb.  
 13.6 °C

• Large areas of the basin have recharge temperatures well above this.

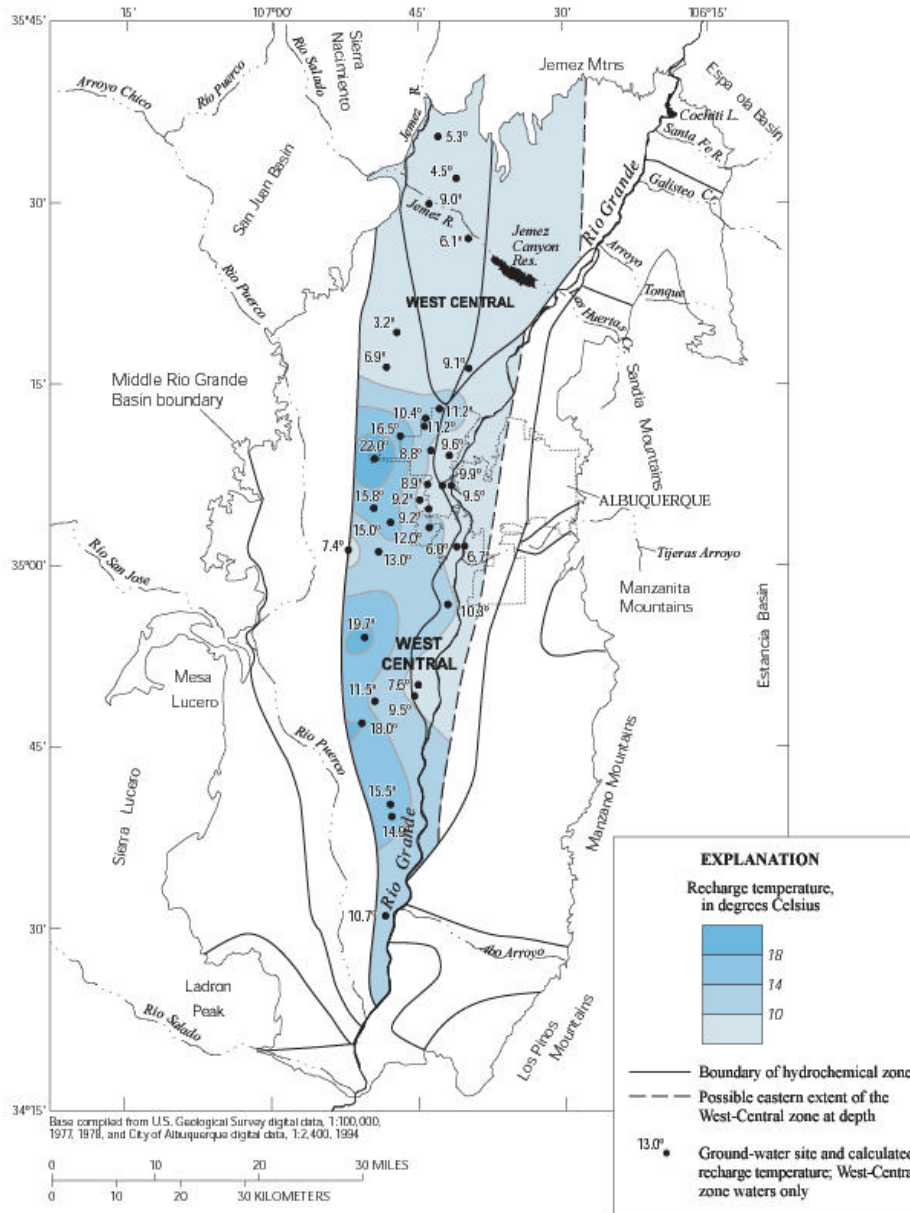
• Warm recharge in NMF and NW zones found above cold RC of West Central zone



# West Central Zone Waters

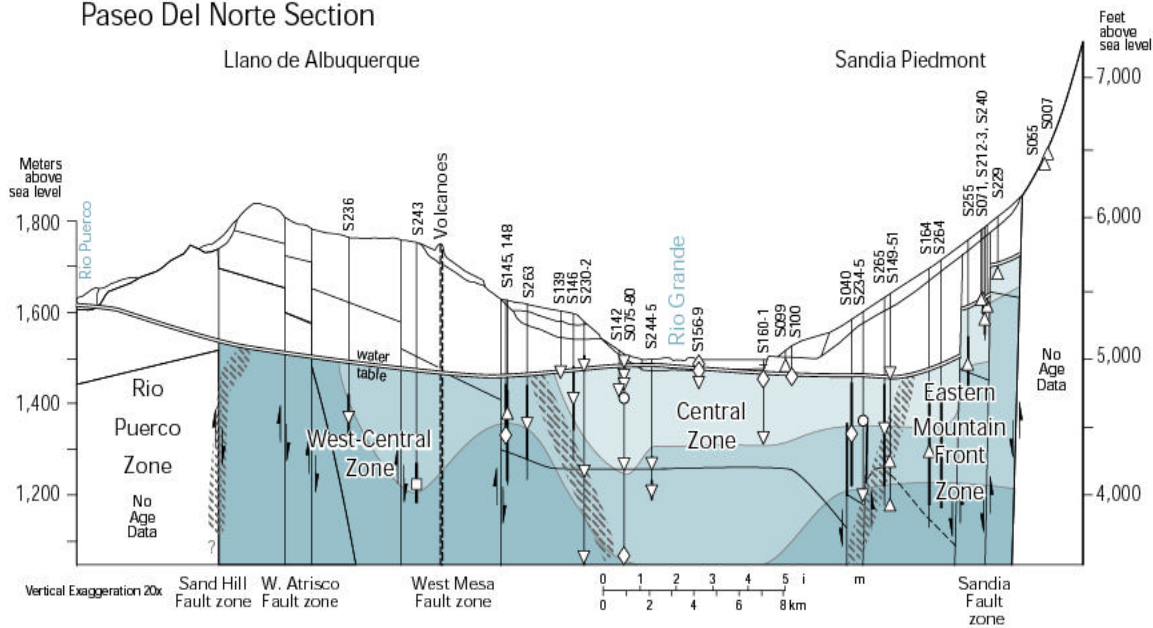
- Paleowaters
- 15 to >30ka <sup>14</sup>C yrs
- Depleted stable isotopes
- Recharge altitude assumed: 8,000 feet
- Both cold and warm recharge occurred. Cold=focused recharge or high alt. recharge. Warm=diffuse recharge through deep UZ

± 1500 feet alt. = ± 2.3 °C

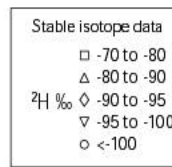
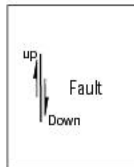
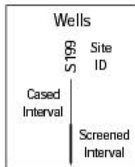
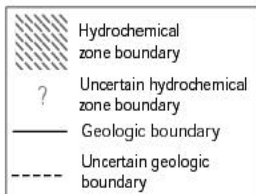
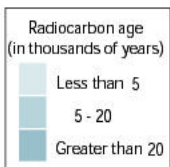


# Paseo Del Norte Section

Llano de Albuquerque

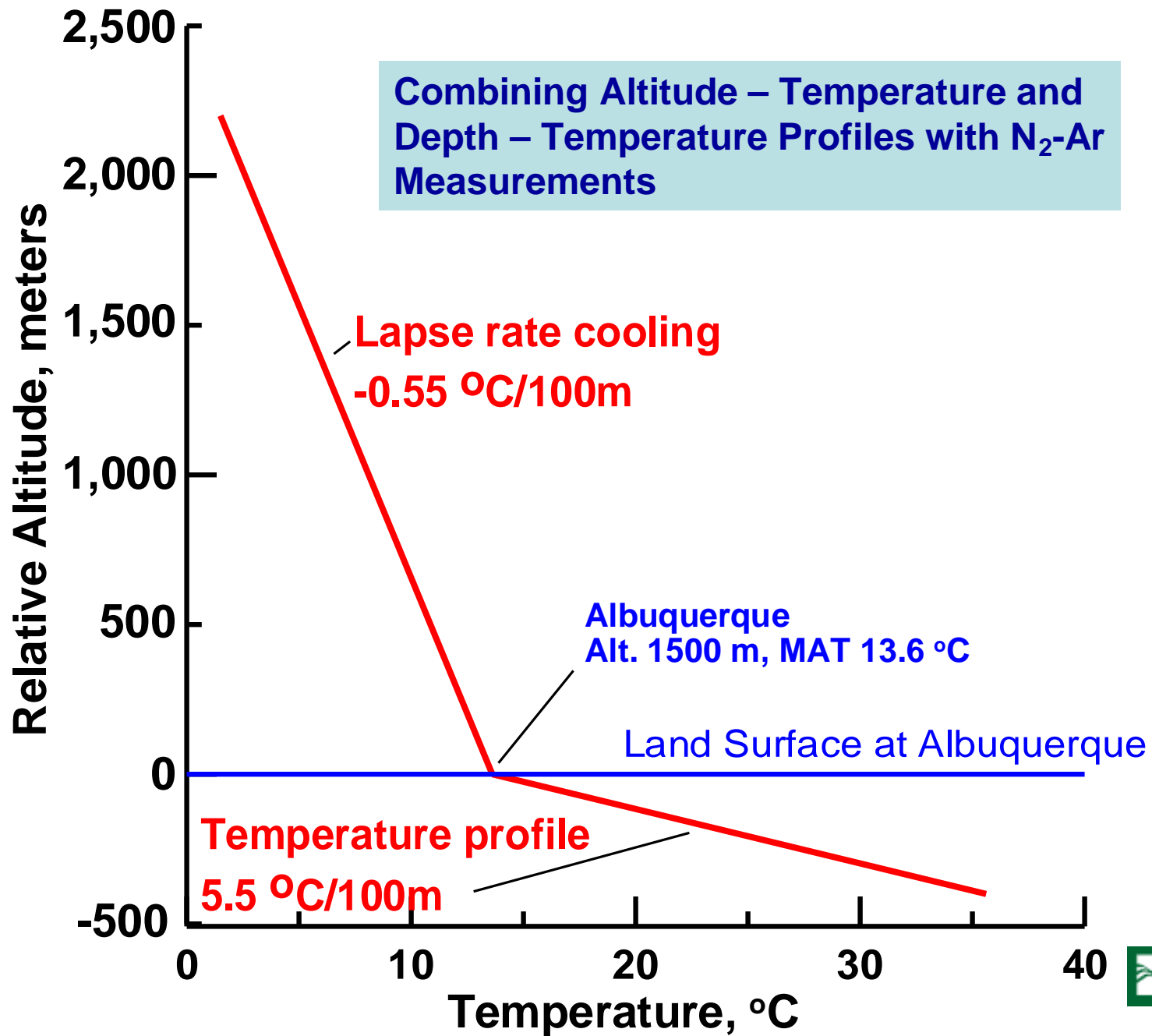


## EXPLANATION

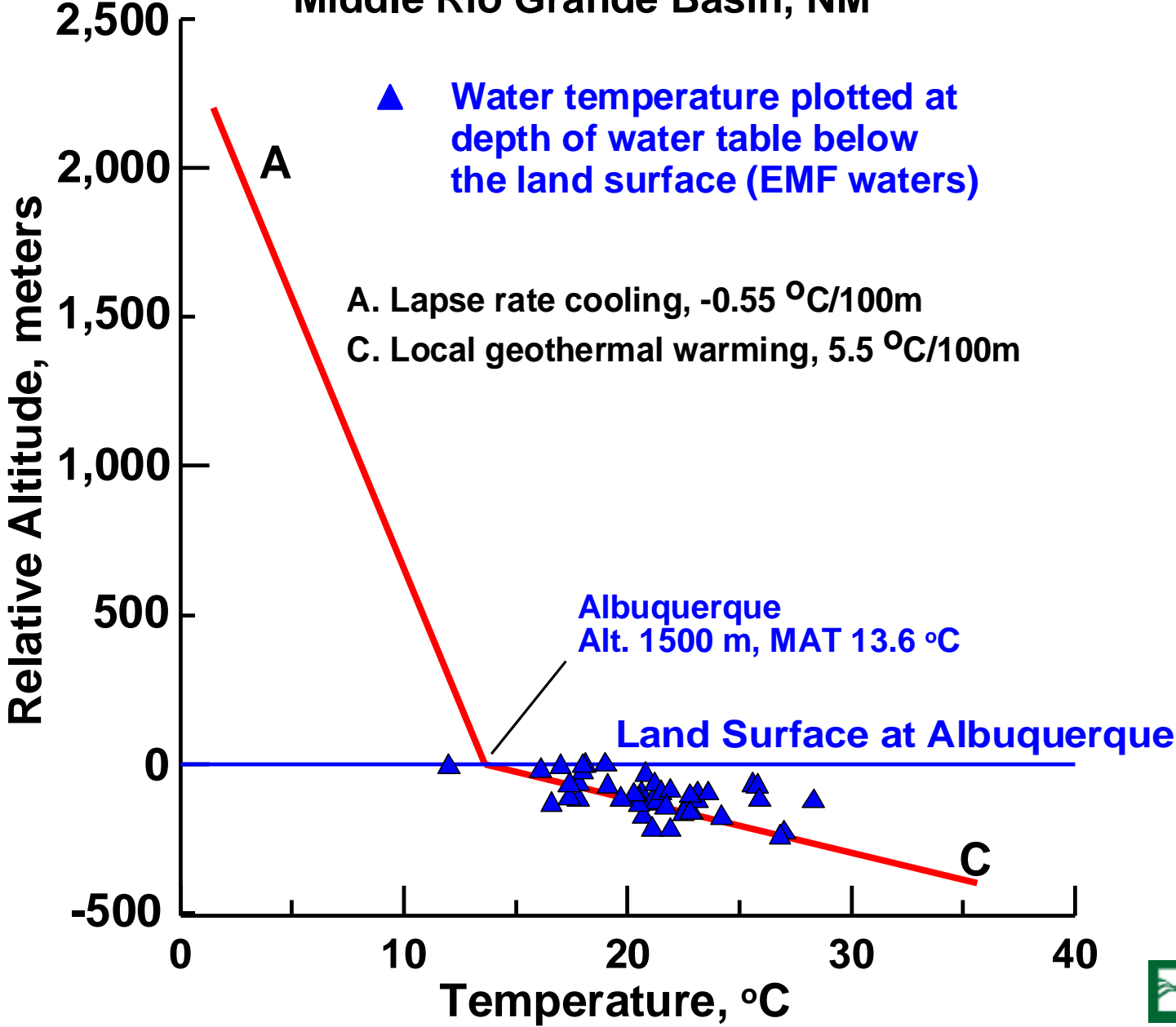


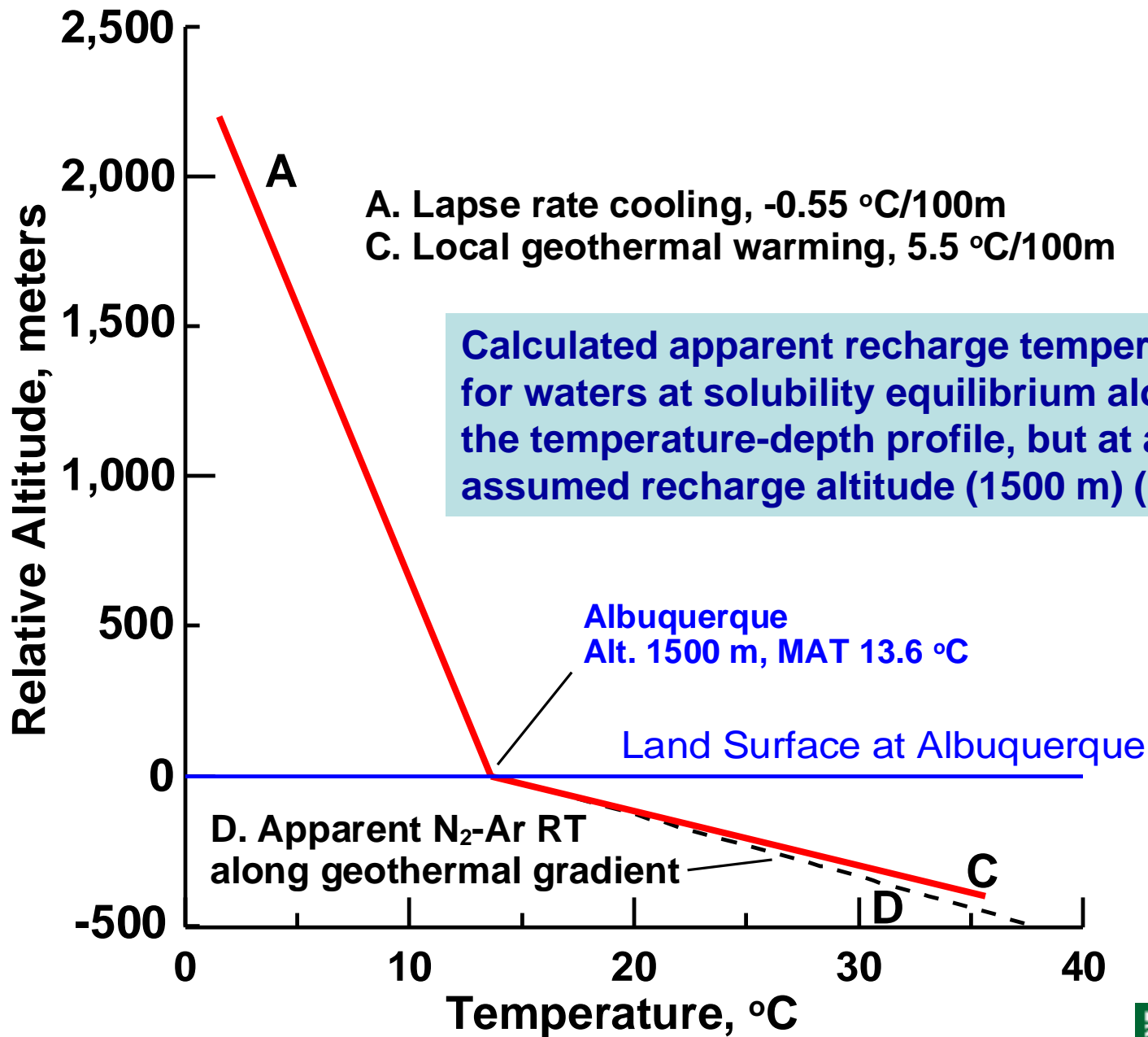
**Deep UZ  
To about 900 feet**

**Direct infiltration  
From rivers,  
arroyos**

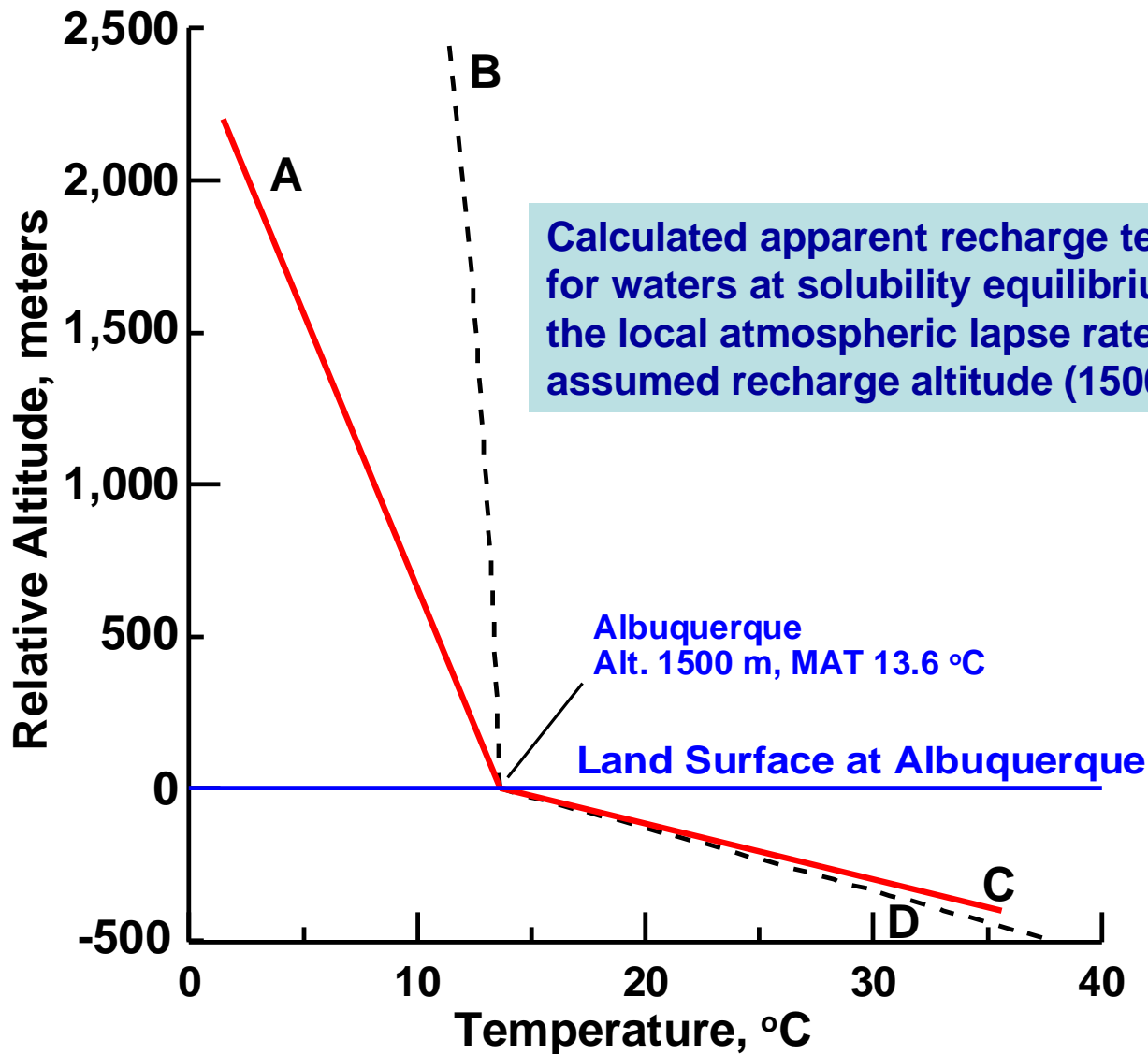


# Eastern Mountain Front Zone Middle Rio Grande Basin, NM

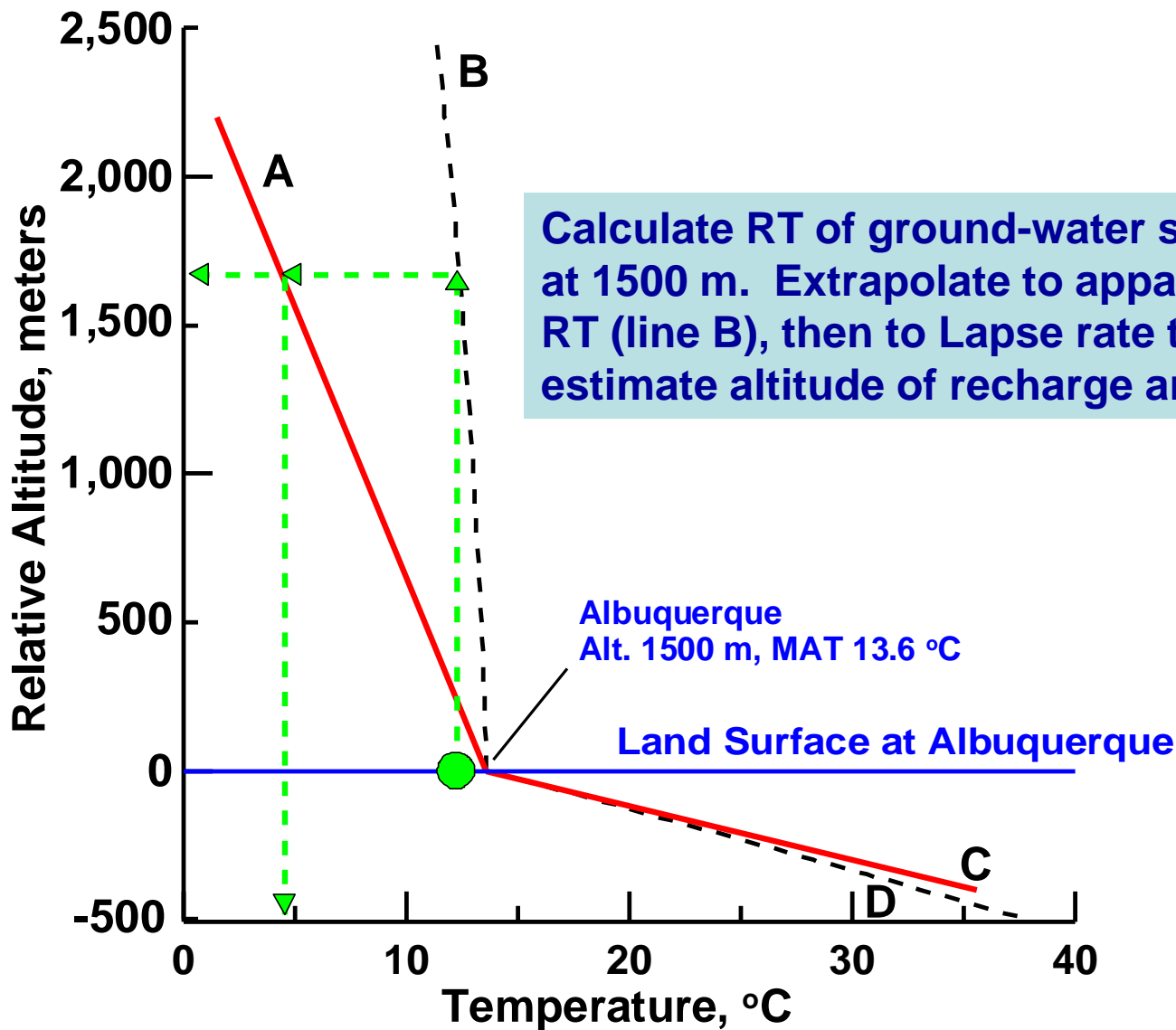




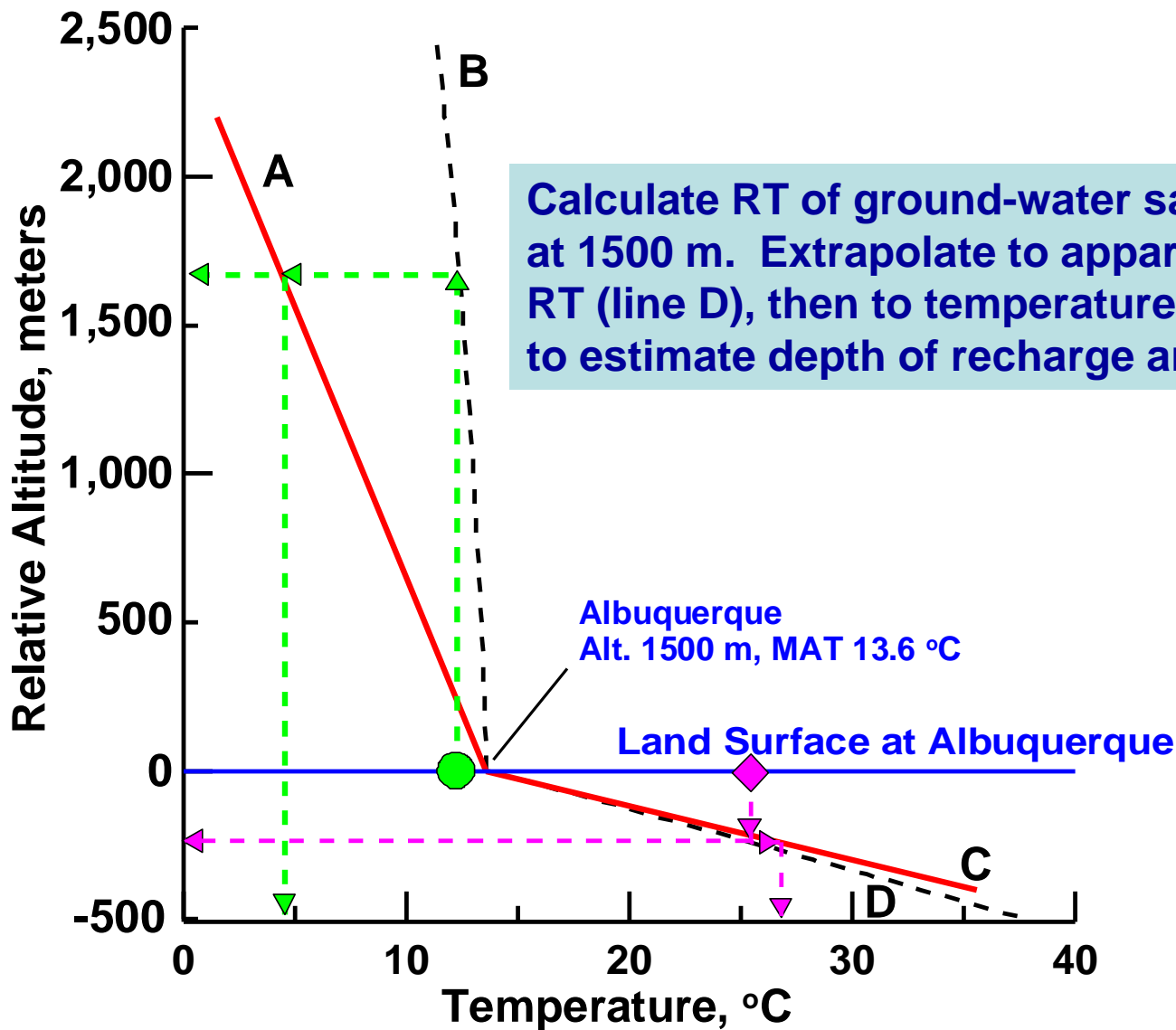
- A. Lapse rate cooling,  $-0.55\text{ }^{\circ}\text{C}/100\text{m}$
- B. Apparent  $\text{N}_2\text{-Ar}$  RT along lapse rate
- C. Local geothermal warming,  $5.5\text{ }^{\circ}\text{C}/100\text{m}$
- D. Apparent  $\text{N}_2\text{-Ar}$  RT along geothermal gradient



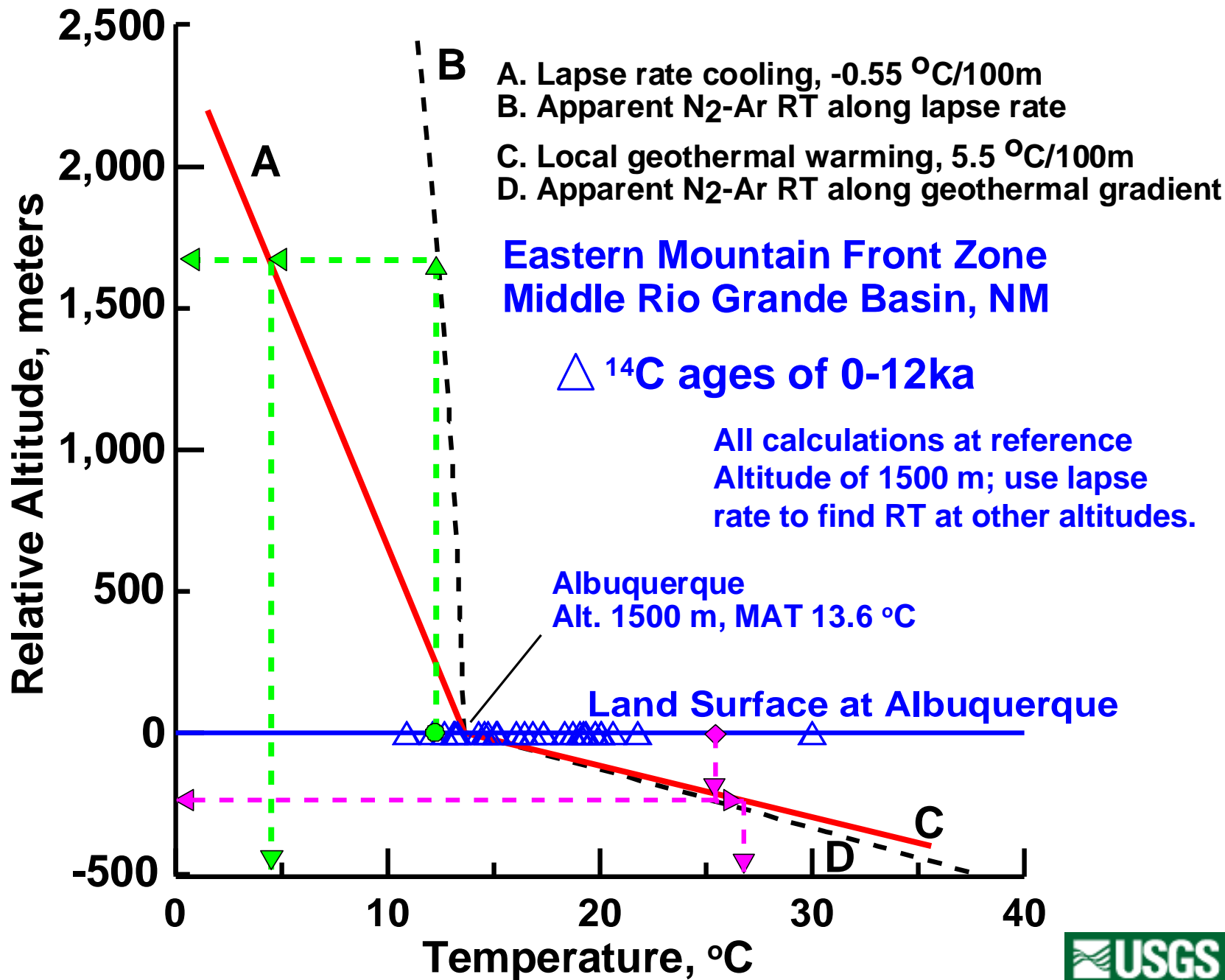
- A. Lapse rate cooling,  $-0.55\text{ }^{\circ}\text{C}/100\text{m}$
- B. Apparent  $\text{N}_2\text{-Ar}$  RT along lapse rate
- C. Local geothermal warming,  $5.5\text{ }^{\circ}\text{C}/100\text{m}$
- D. Apparent  $\text{N}_2\text{-Ar}$  RT along geothermal gradient

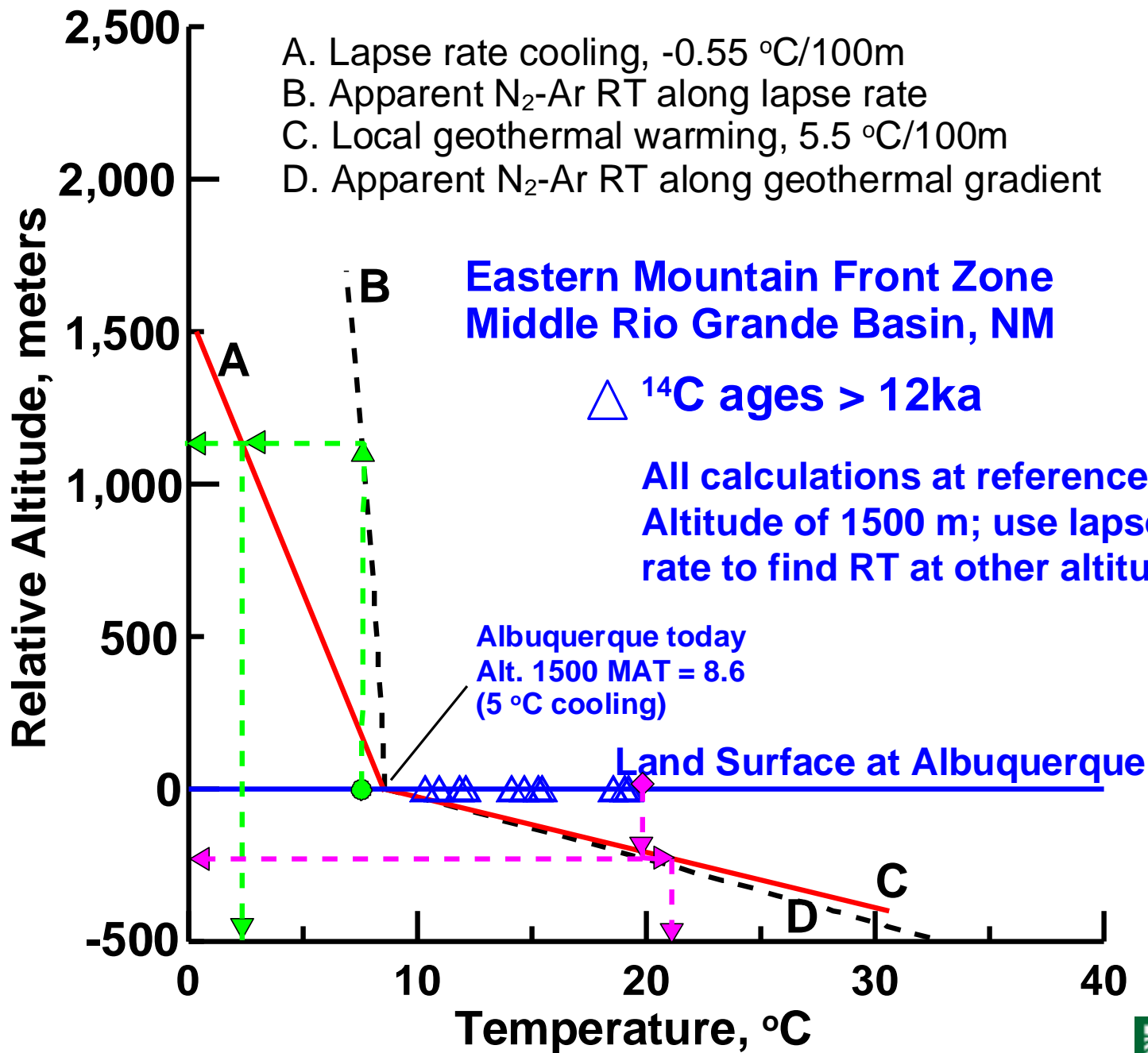


- A. Lapse rate cooling,  $-0.55\text{ }^{\circ}\text{C}/100\text{m}$
- B. Apparent  $\text{N}_2\text{-Ar}$  RT along lapse rate
- C. Local geothermal warming,  $5.5\text{ }^{\circ}\text{C}/100\text{m}$
- D. Apparent  $\text{N}_2\text{-Ar}$  RT along geothermal gradient









# CONCLUSIONS

- RT determined by GC from N<sub>2</sub>-Ar measurements in ground water typically  $\pm 0.5$  °C on laboratory standards; best suited for aerobic or low nitrate waters where altitude of recharge is known.
- Large uncertainties in RT and Ex air can result if denitrification is significant.
- Possible to combine a local depth-temperature profile with N<sub>2</sub>-Ar data to estimate depth of recharge below deep unsaturated zones in arid regions, but estimation of altitude of recharge from the local atmospheric lapse rate is poorly constrained.
- Most waters recharged along the Eastern Mountain Front of the MRGB, NM were recharge at depths of up to 150 meters below the land surface.
- Thousands of measurements of N<sub>2</sub>-Ar in US groundwater have been made at the USGS over the past decade to estimate 1) recharge temperature for CFC/SF<sub>6</sub> dating studies, 2) agricultural denitrification studies, 3) paleo-temperature reconstruction, 4) tracing sources of water in aquifers, and 5) interpreting recharge mechanism.

## CONCLUDING REMARKS

➤ Increasingly, geochemists and hydrologists are including measurements of concentrations of dissolved gases in hydrologic investigations. These include suites of noble gases (Ar, Ne, Kr, Xe, He) to study recharge conditions and deep groundwater circulation, gases that are indicators of microbial processes ( $O_2$ ,  $CH_4$ ,  $CO_2$ ,  $H_2S$ ,  $N_2O$ ,  $N_2$ , etc.), and gases that can be used to interpret groundwater age (CFCs,  $SF_6$ ,  $^4He$ ,  $^{85}Kr$ ,  $^{39}Ar$ ,  $^{81}Kr$ , etc.).

➤ Thousands of measurements of  $N_2$  and Ar in groundwater have been made at the USGS over the past decade to estimate 1) recharge temperature and excess air for CFC/ $SF_6$  dating studies, 2) estimate quantities of denitrification in agricultural studies, 3) reconstruct paleo-environmental conditions, 4) identify and trace sources of water in aquifers, 5) interpret recharge mechanisms, and 6) estimate altitude or depth of recharge.