

Applications of ^{81}Kr and ^{85}Kr in Groundwater Hydrology

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Wei Jiang⁶, Peter Mueller⁶, Zheng-Tian Lu^{6,7}

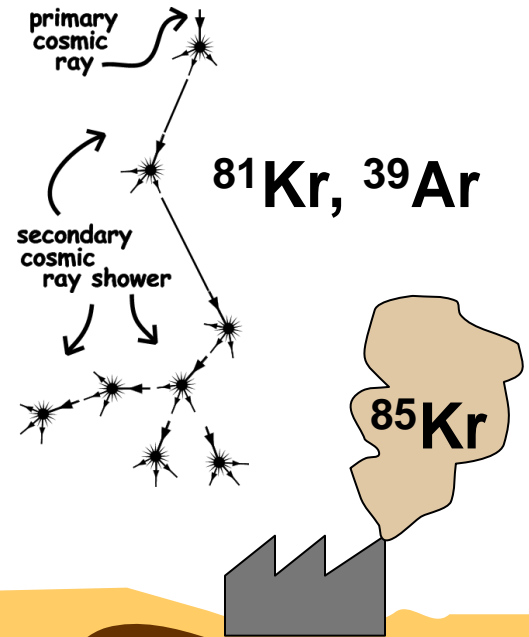
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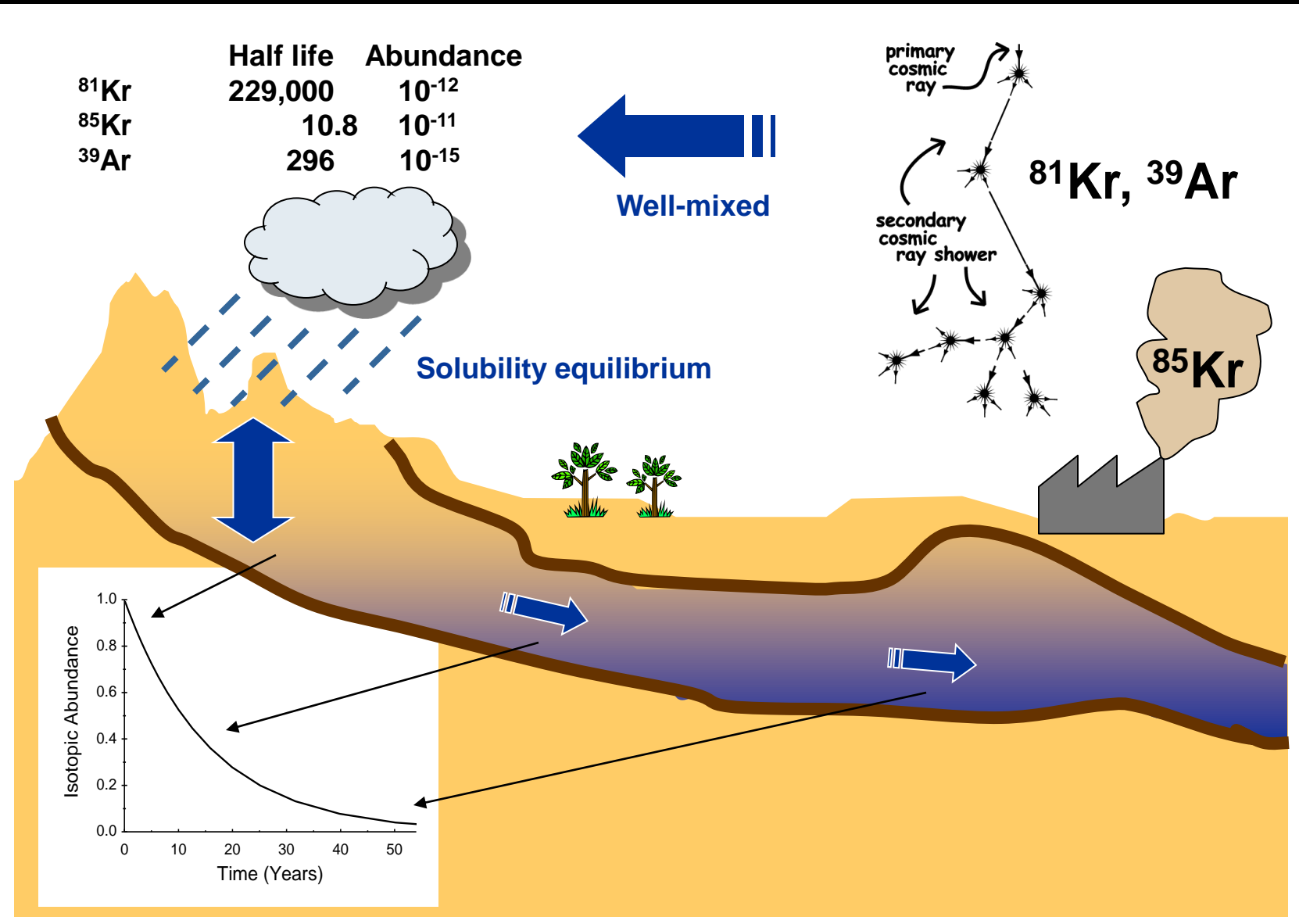
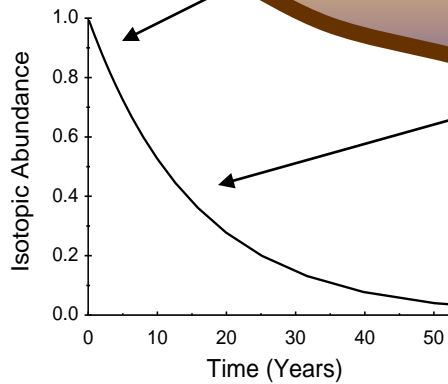
Noble gas radionuclides

	Half life	Abundance
^{81}Kr	229,000	10^{-12}
^{85}Kr	10.8	10^{-11}
^{39}Ar	296	10^{-15}

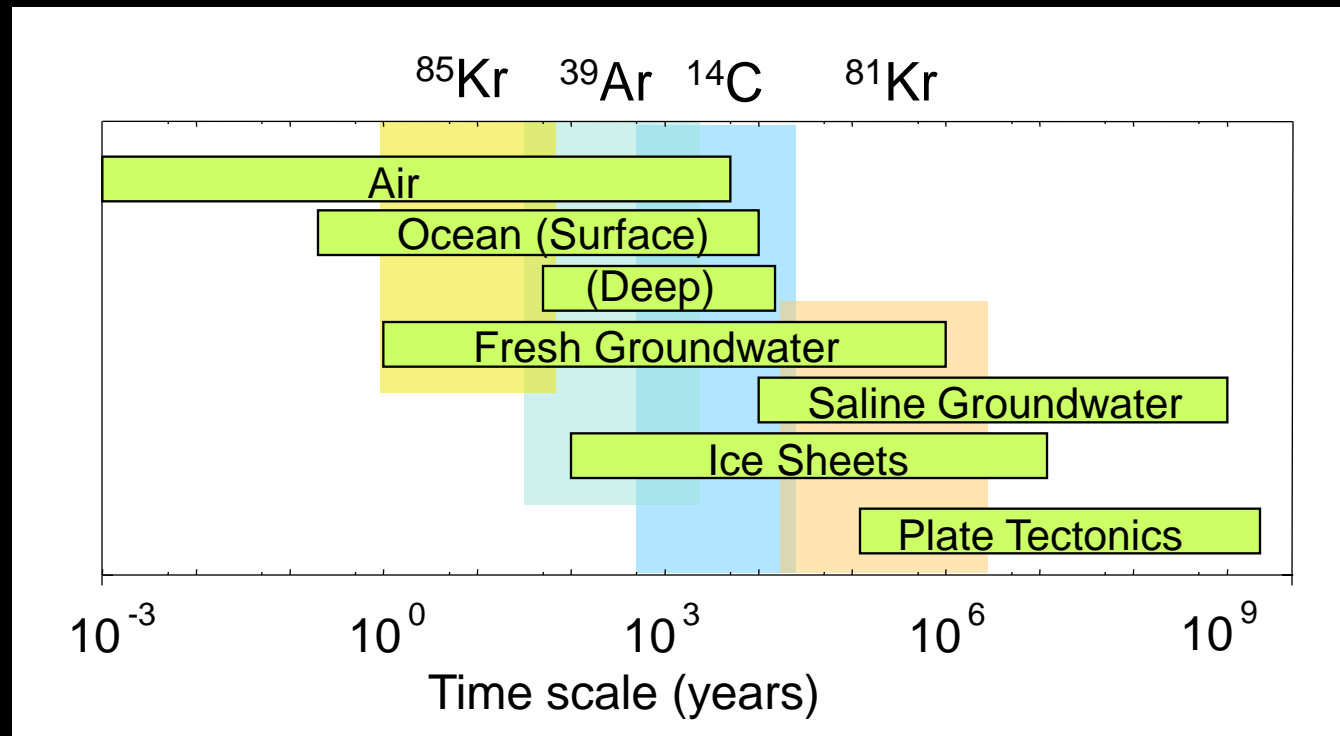
Well-mixed



Solubility equilibrium



Applicable Systems in Nature

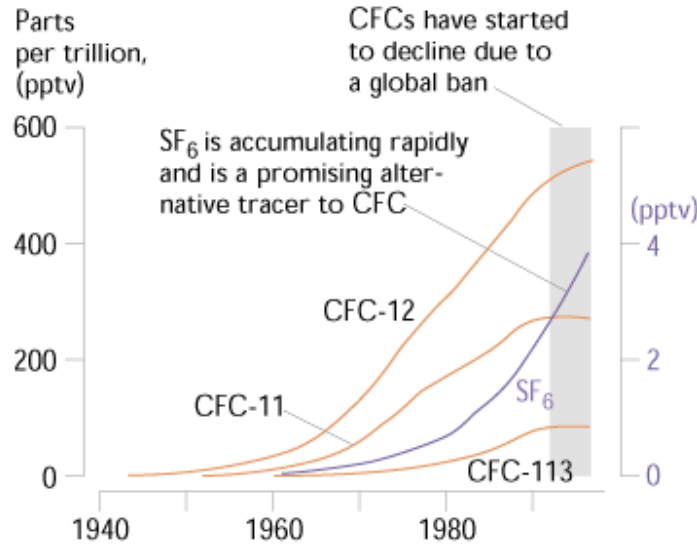


^{81}Kr : Old groundwater, glacial ice, brines

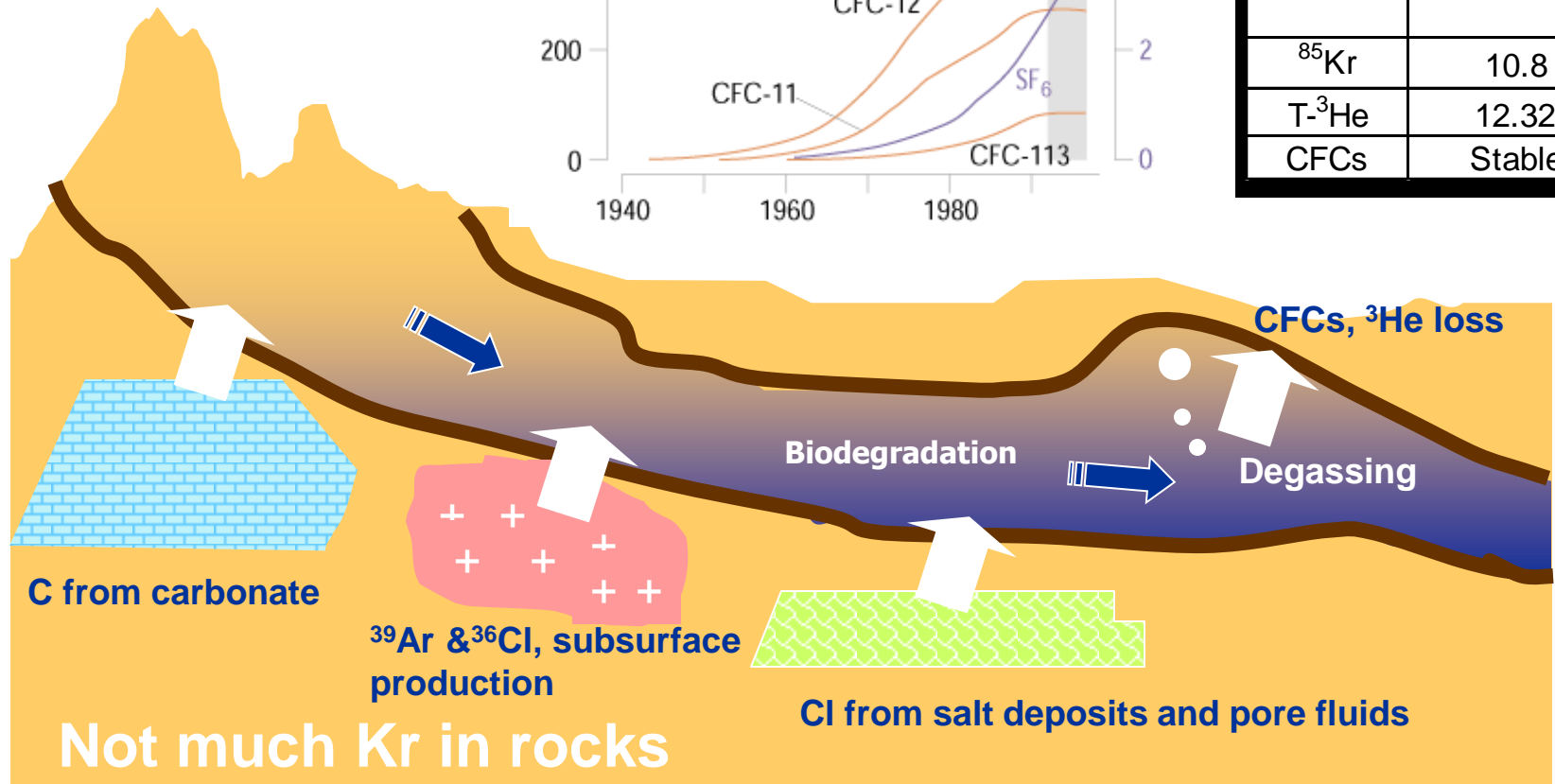
^{85}Kr : Young groundwater, atmosphere

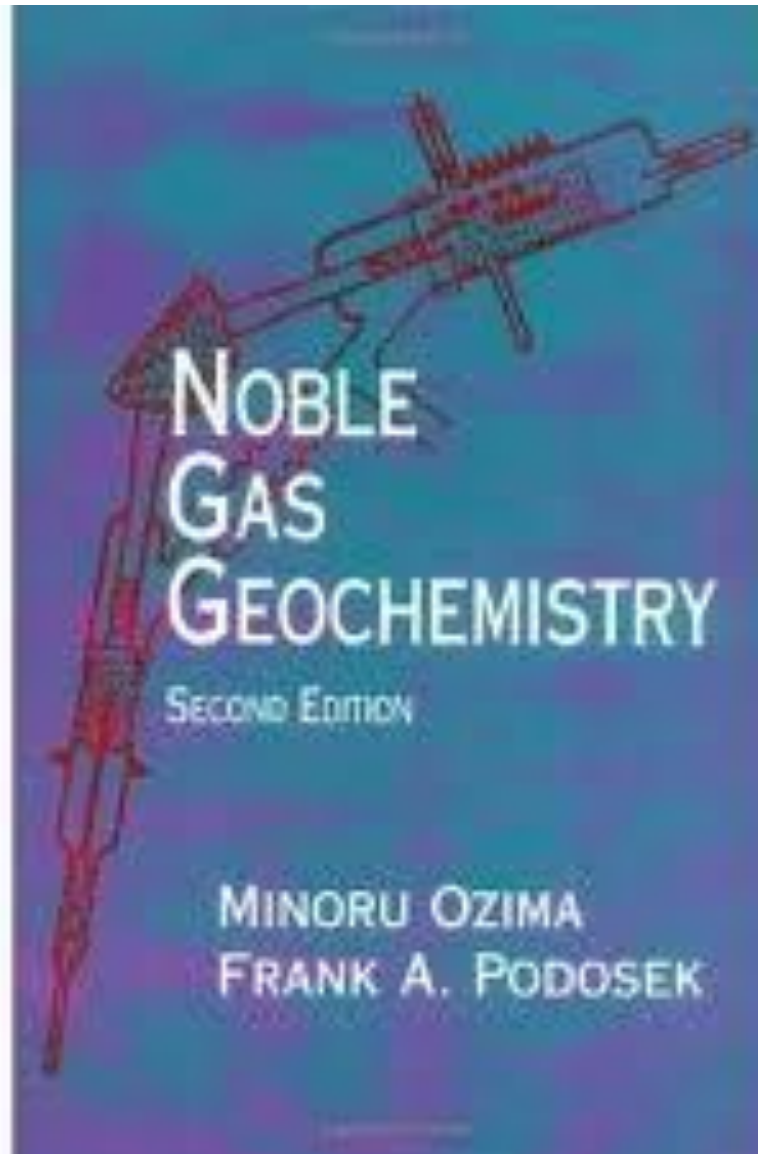
Competing Tracers and Advantages of Kr

	Half Life (yr)
^{81}Kr	229000
^{36}Cl	301000
^{14}C	5730
^{39}Ar	269
^{85}Kr	10.8
$\text{T-}^3\text{He}$	12.32
CFCs	Stable



Solubility equilibrium
 -> (P, T, S) required
Well-mixed?



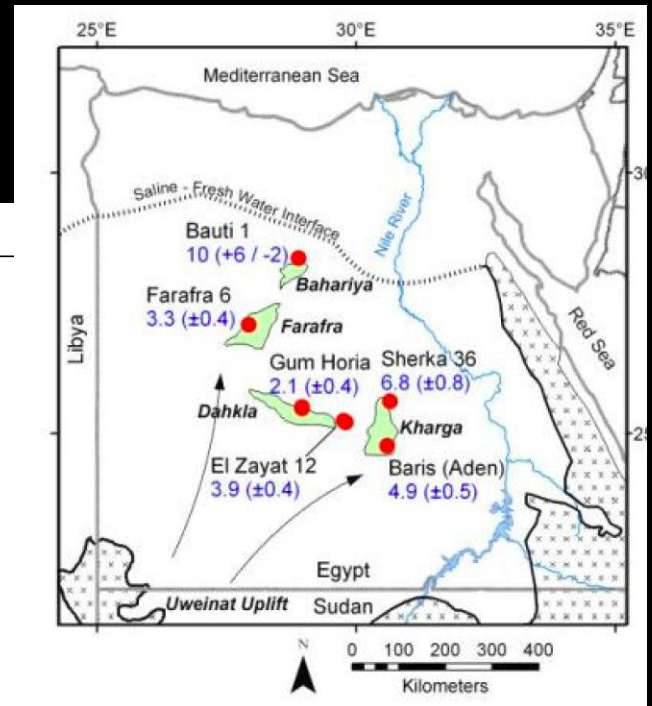
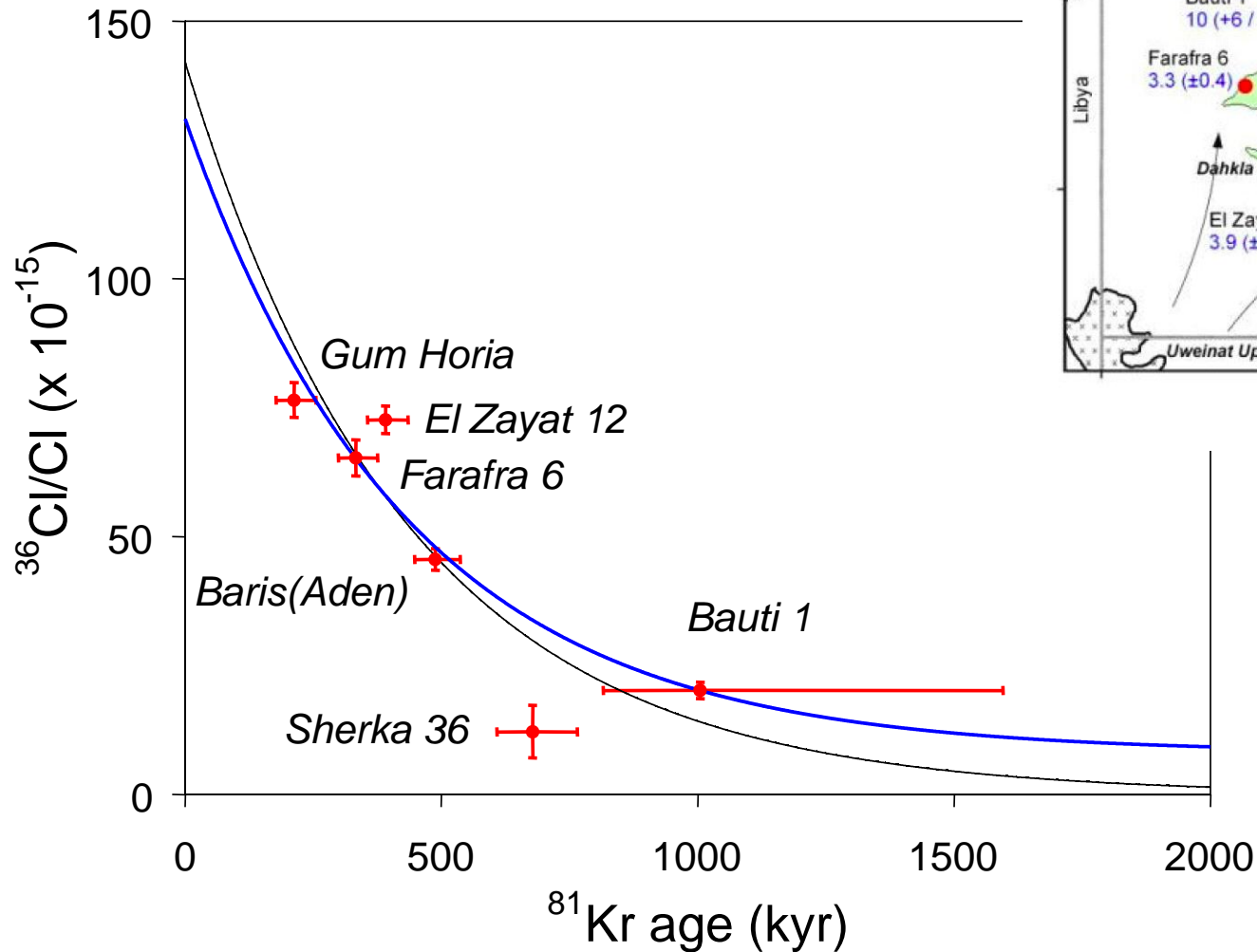


How I got started on the path of the holy grail in 1999.....

First application of ATTA in hydrology: Nubian Aquifer, Egypt

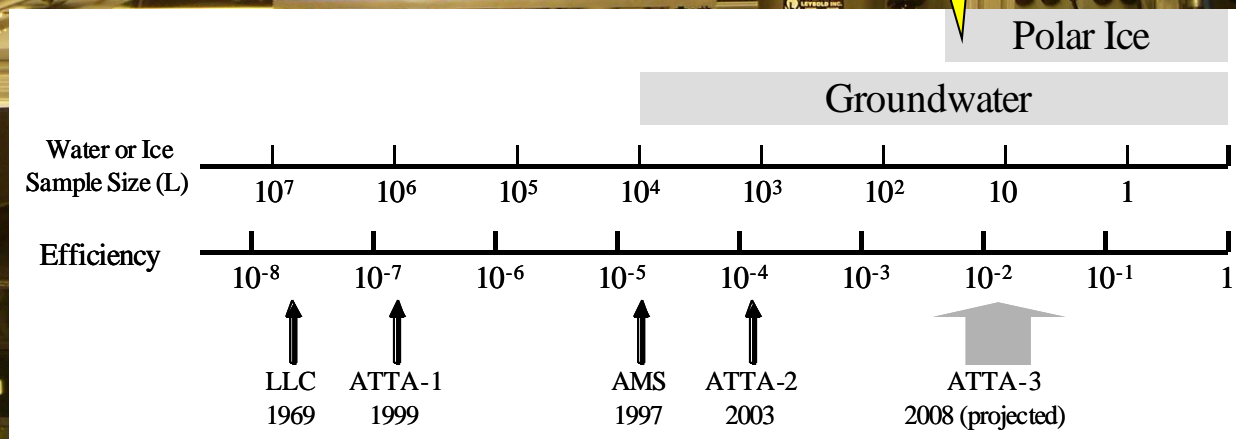


^{36}Cl - ^{81}Kr correlation



(Sturchio et al., GRL, 2004; Patterson et al., G³, 2005)

Getting ready for ATTA-3!



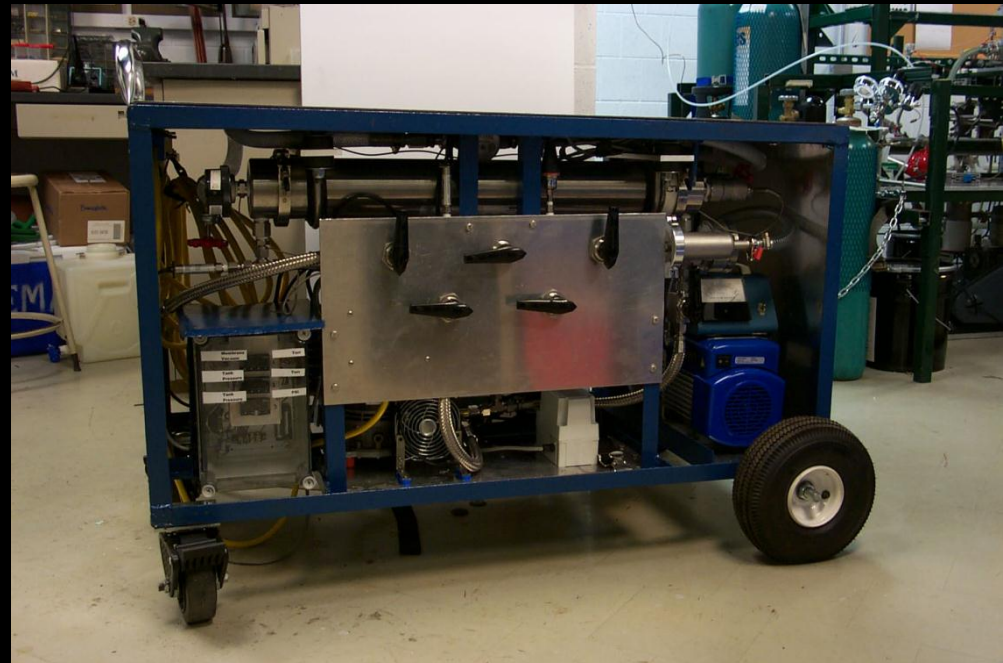
Improvements in on-site dissolved gas extraction

Extraction of Dissolved Gas for Analysis of Radiokrypton (EDGAR)

- Up to ~30 liter/min sampling rate
- Up to ~90% extraction of dissolved gases



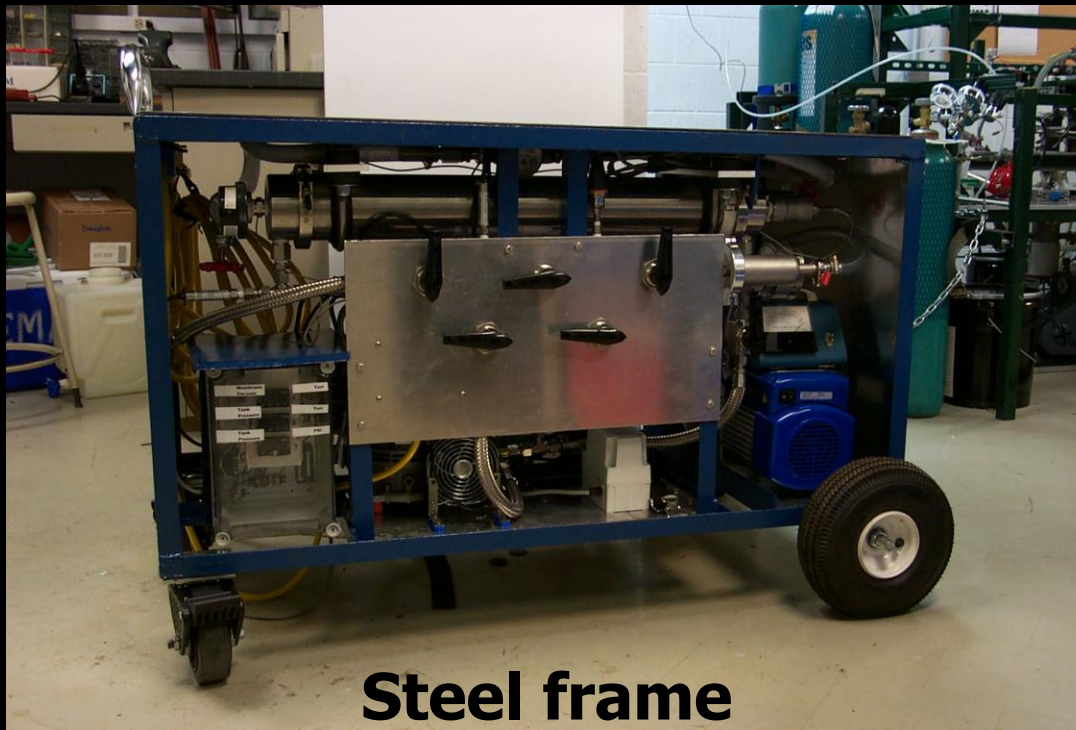
Bern apparatus



Pete Probst, MS thesis 2007, UIC

Portability: EDGAR II

Adjusted for checked luggage size in closed ATA-certified boxes, suitable for international travel

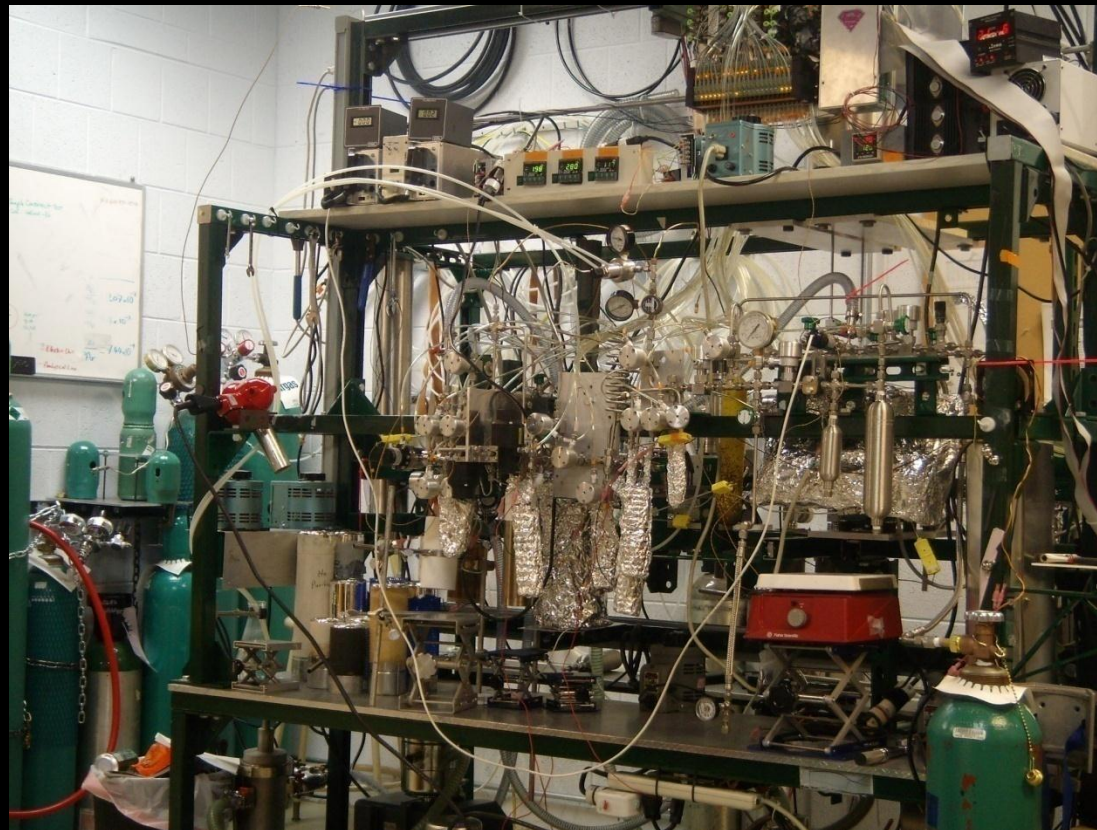


100 lbs. x2

400 lbs.

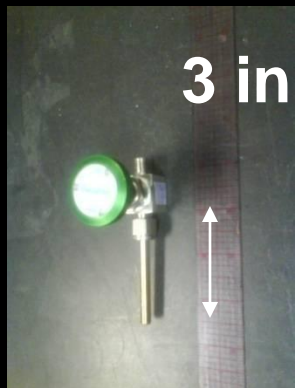
Improved Kr purification system (Yokochi et al., 2008)

- Kr extraction from 5-125 liter STP of bulk gas in 4-6 hours with > 90% Yield



5-125 LSTP
bulk gas

5-250 μ L STP
pure Kr

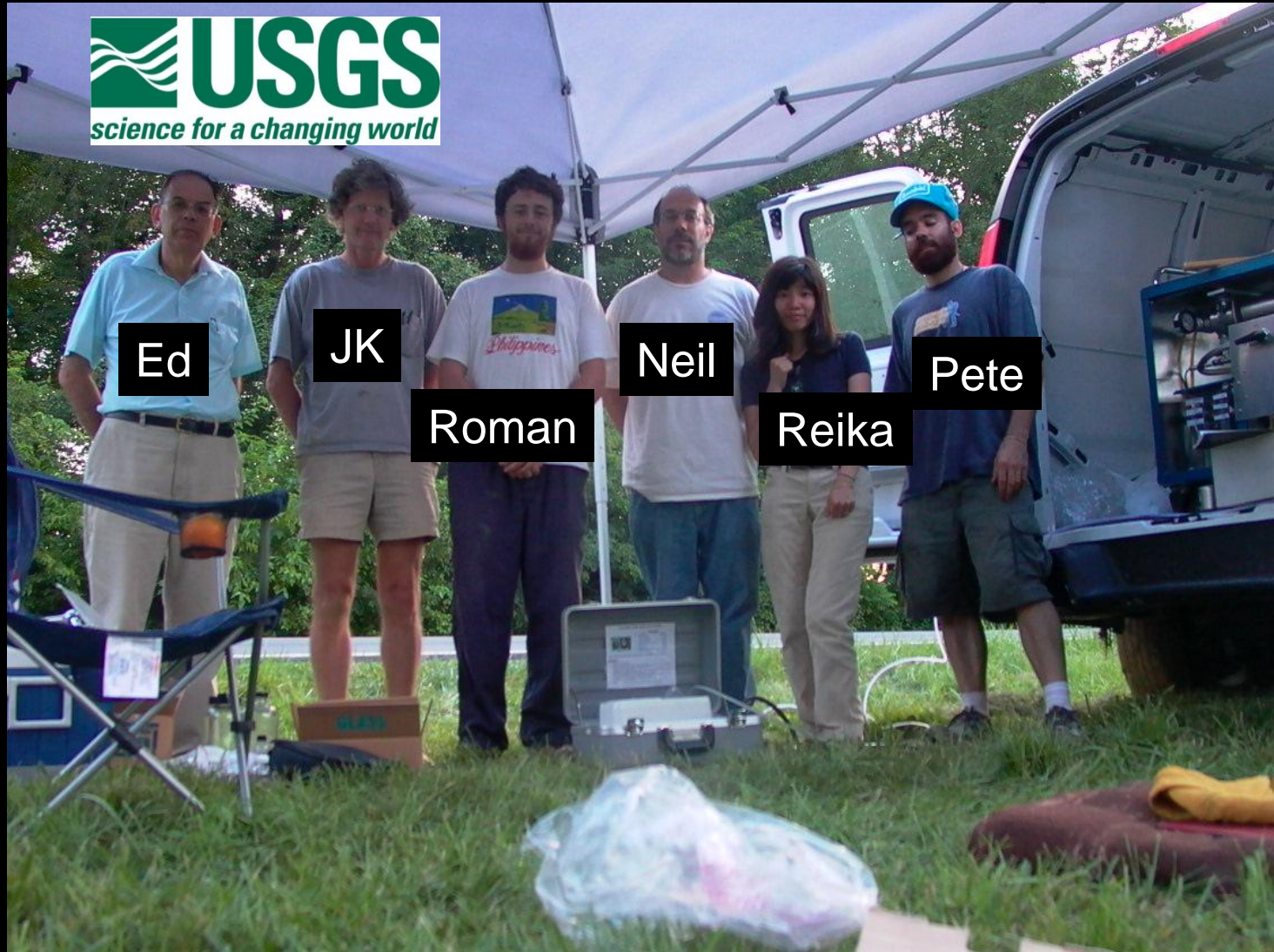


3 in

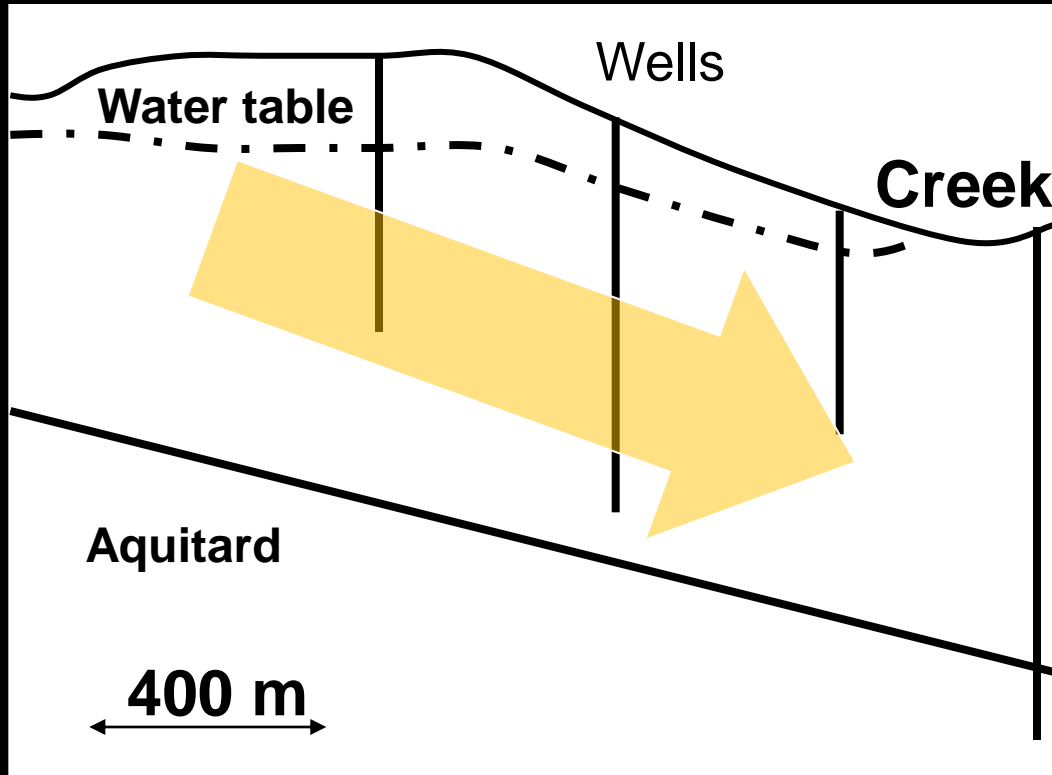


3 ft

EDGAR Field Test #1: Locust Grove, Maryland



Shallow unconfined aquifer



- Agricultural area
- Denitrification studied by Böhlke and Denver (1995)
- Comparative study of residence-time tracers $^3\text{H}/^3\text{He}$, CFCs, SF_6 , ^{85}Kr by Ekwurzel et al. (1994)

Dating of shallow groundwater: Comparison of the transient tracers $^3\text{H}/^3\text{He}$, chlorofluorocarbons, and ^{85}Kr

Brenda Ekwurzel,¹ Peter Schlosser,¹ and William M. Smethie Jr.

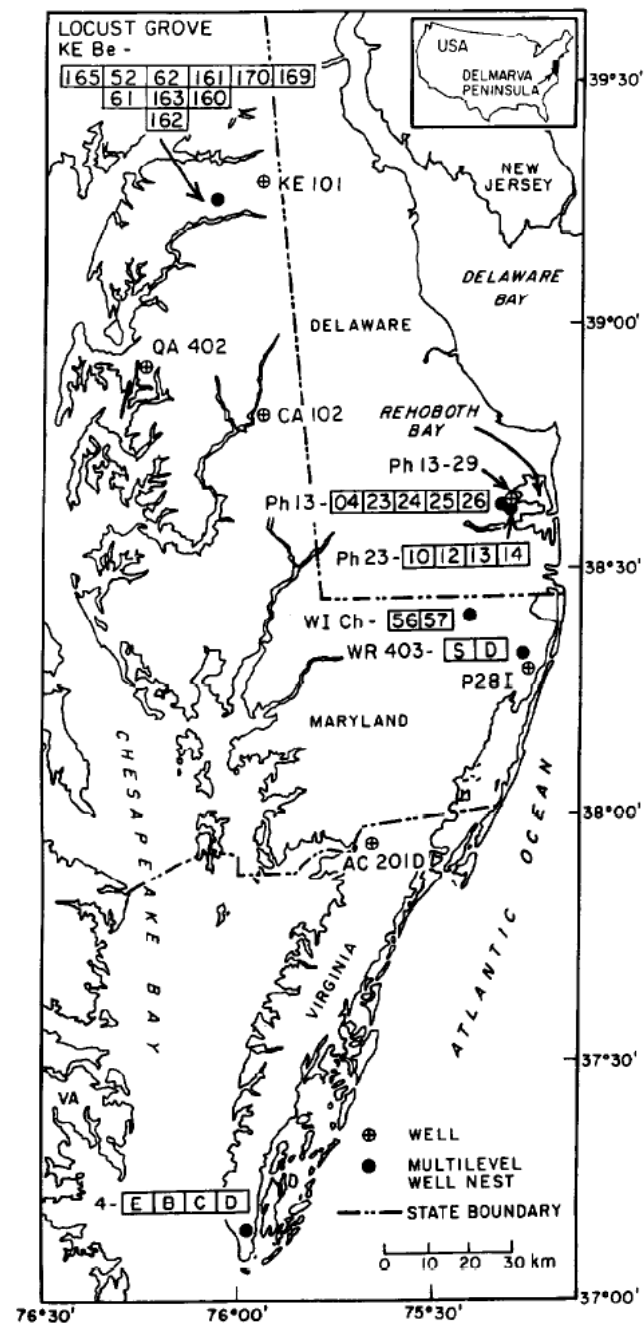
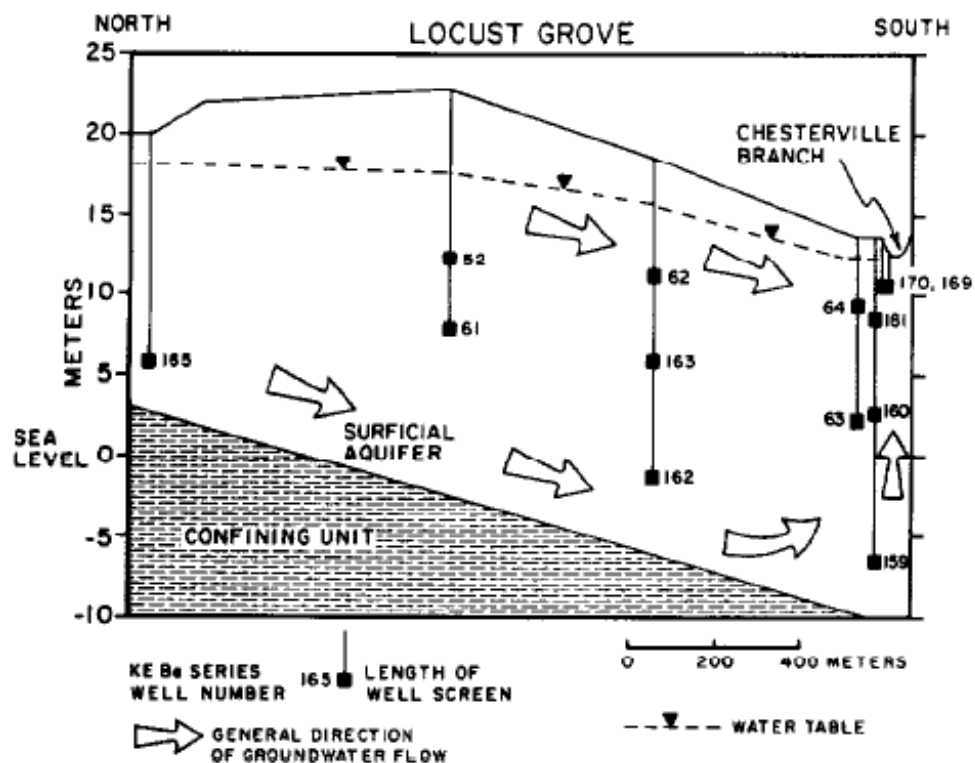
Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York

L. Niel Plummer, Eurybiades Busenberg, and Robert L. Michel

U.S. Geological Survey, Reston, Virginia

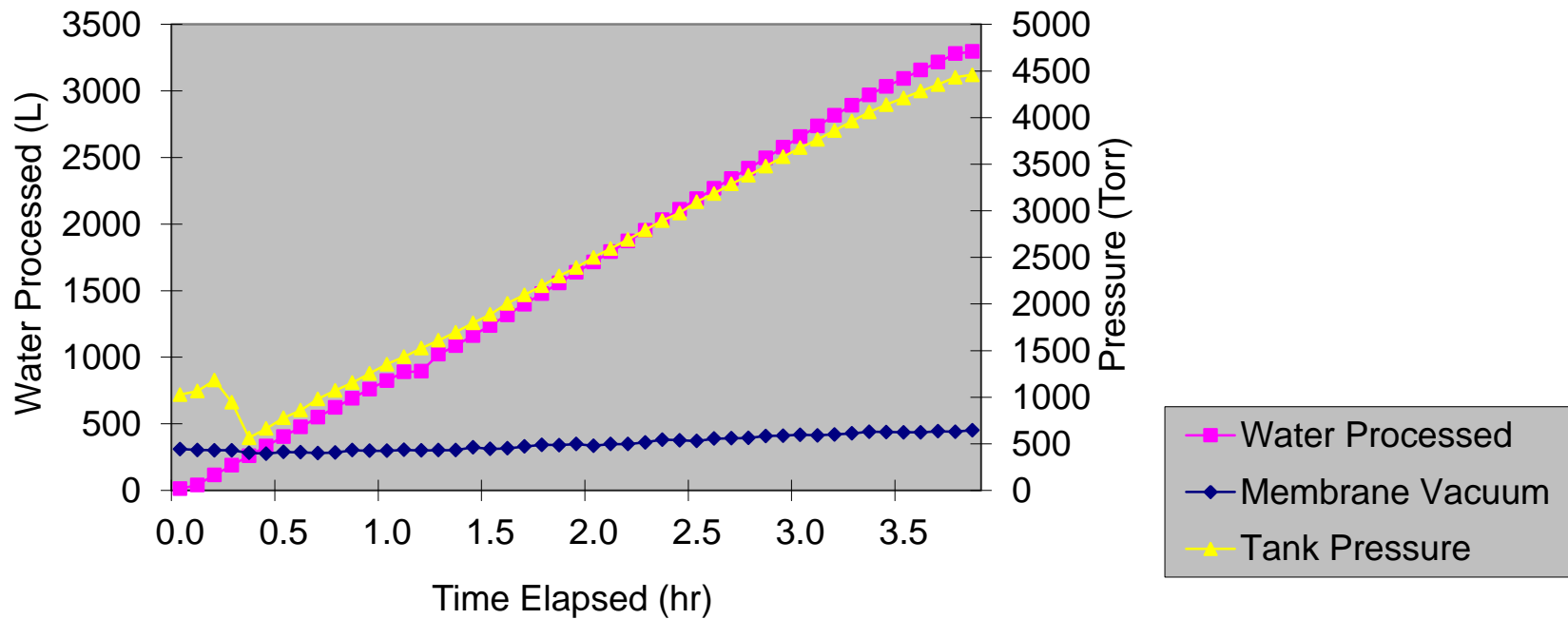
Ralf Weppernig and Martin Stute

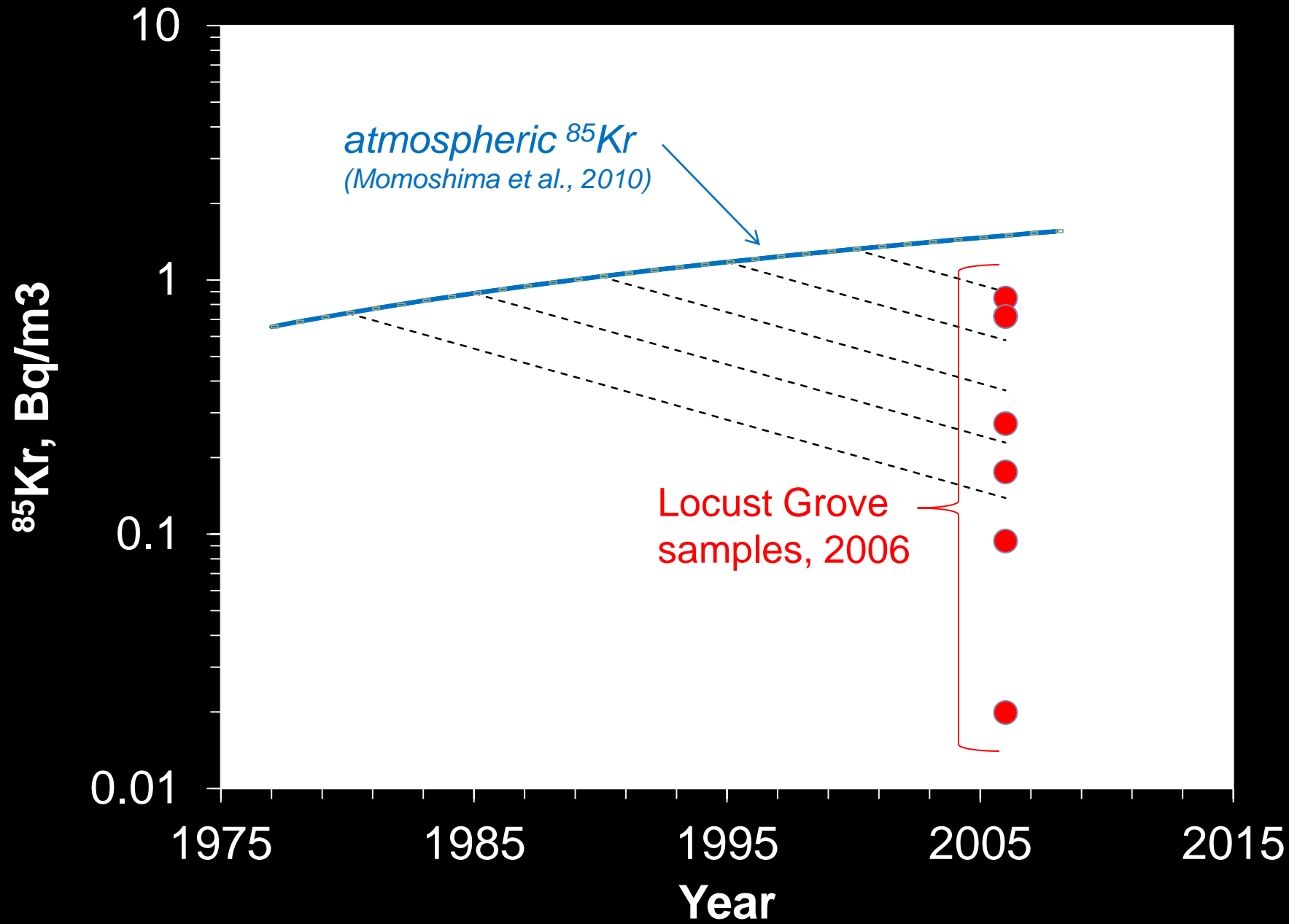
Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York



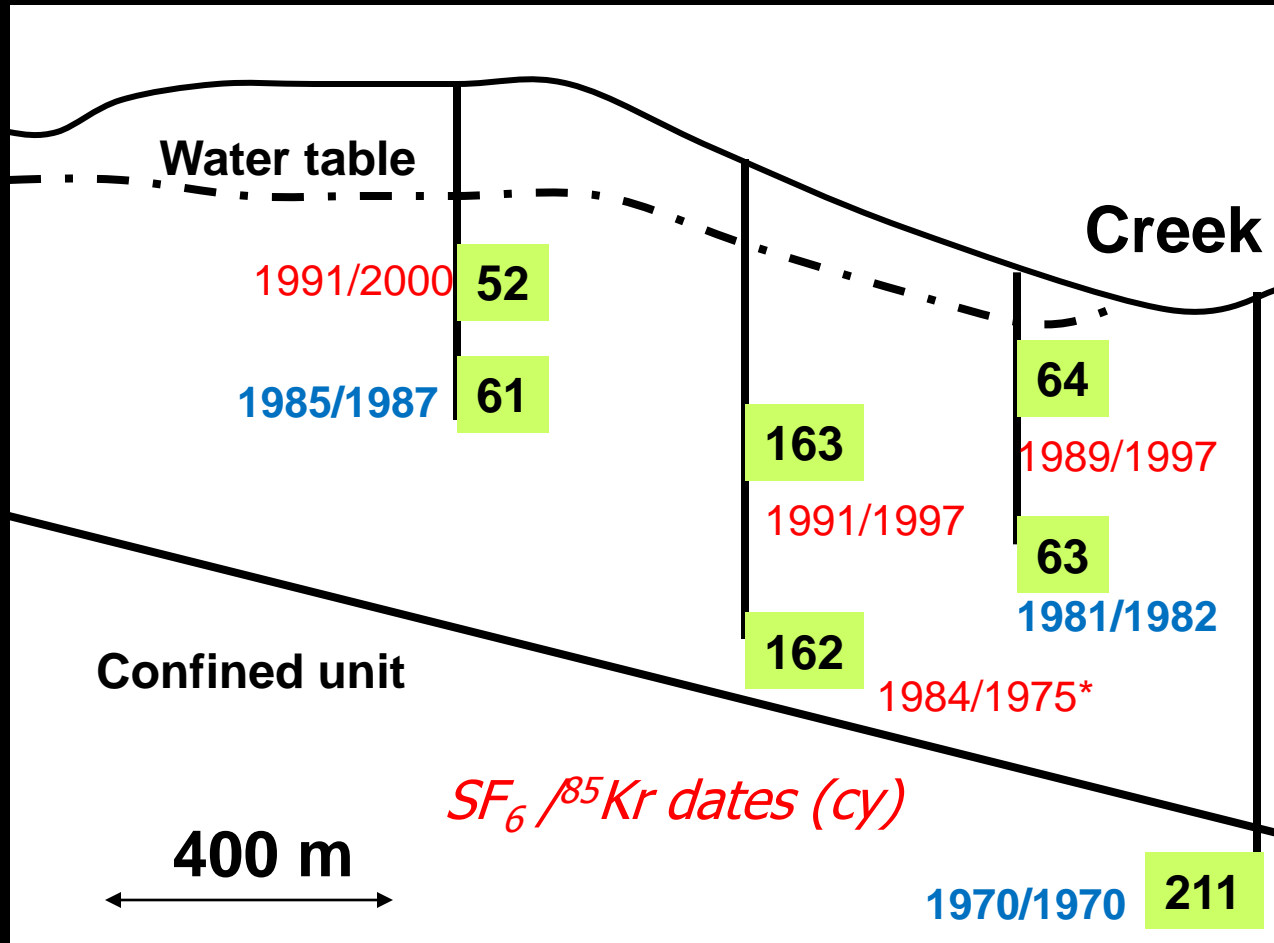
Example of typical sampling parameters using EDGAR-1

Well KeBe 61





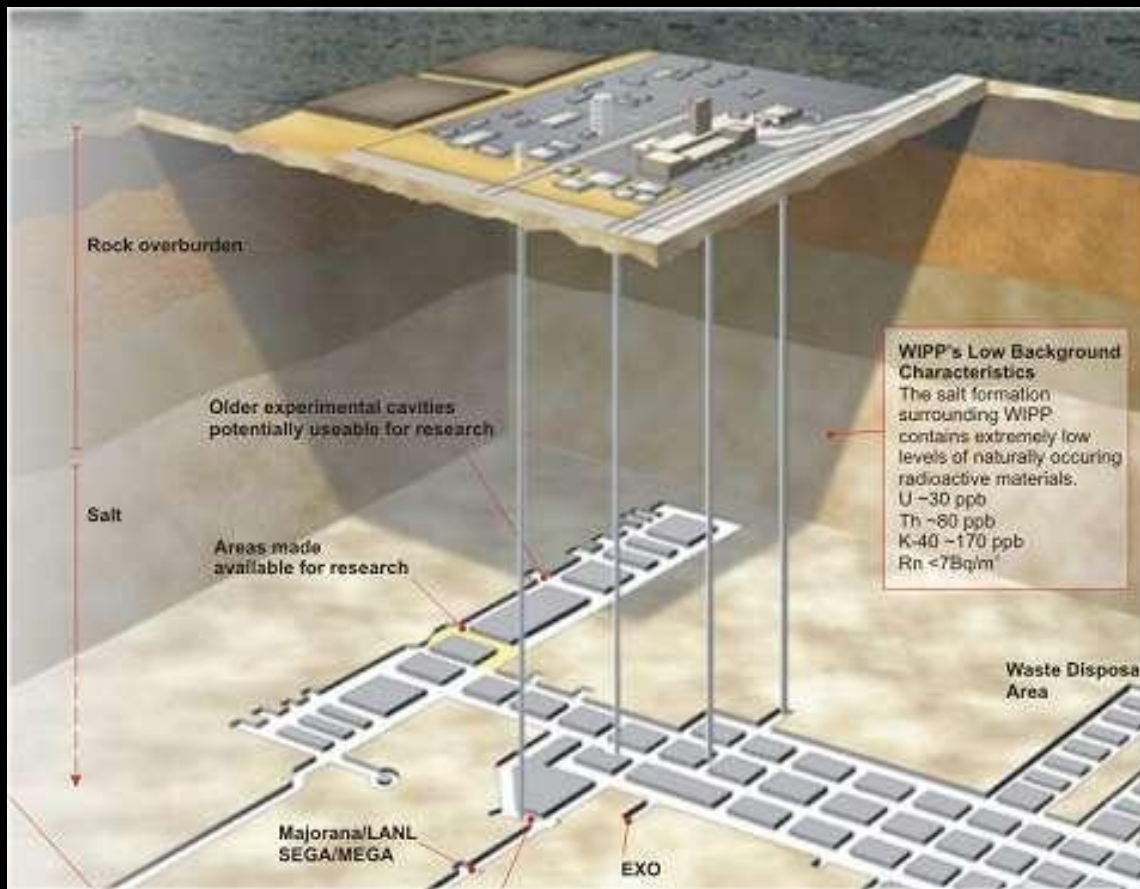
Comparison of SF₆ and ⁸⁵Kr in 2006



7 samples, >150 μl Kr separated

Field Test #3: WIPP (Waste Isolation Pilot Plant) storage site for TRU waste in a salt excavation near Carlsbad, NM

- What is the travel time of radionuclides from the repository to the accessible environment?



Location of WIPP site in southeastern New Mexico



Culebra Dolomite

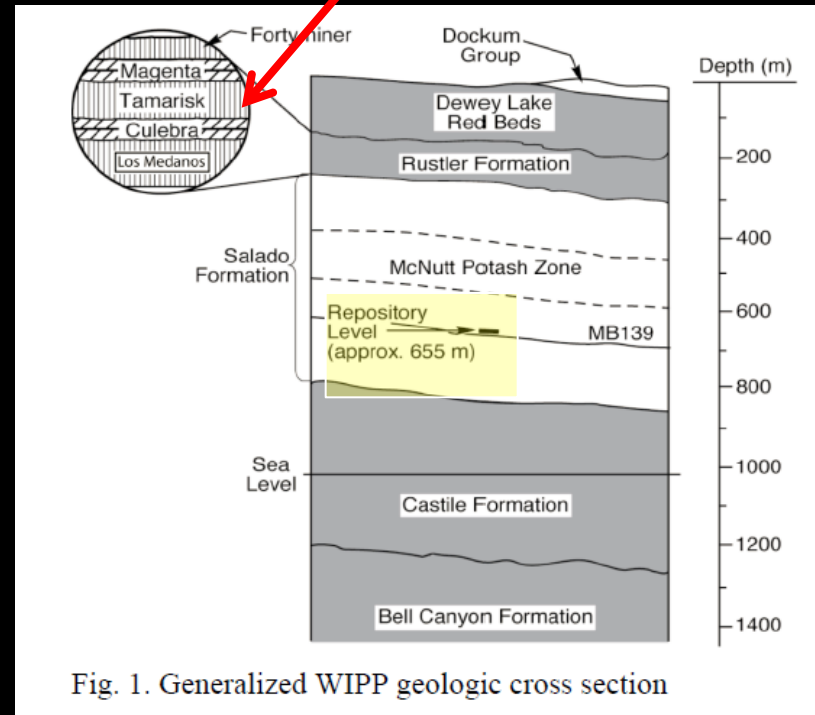
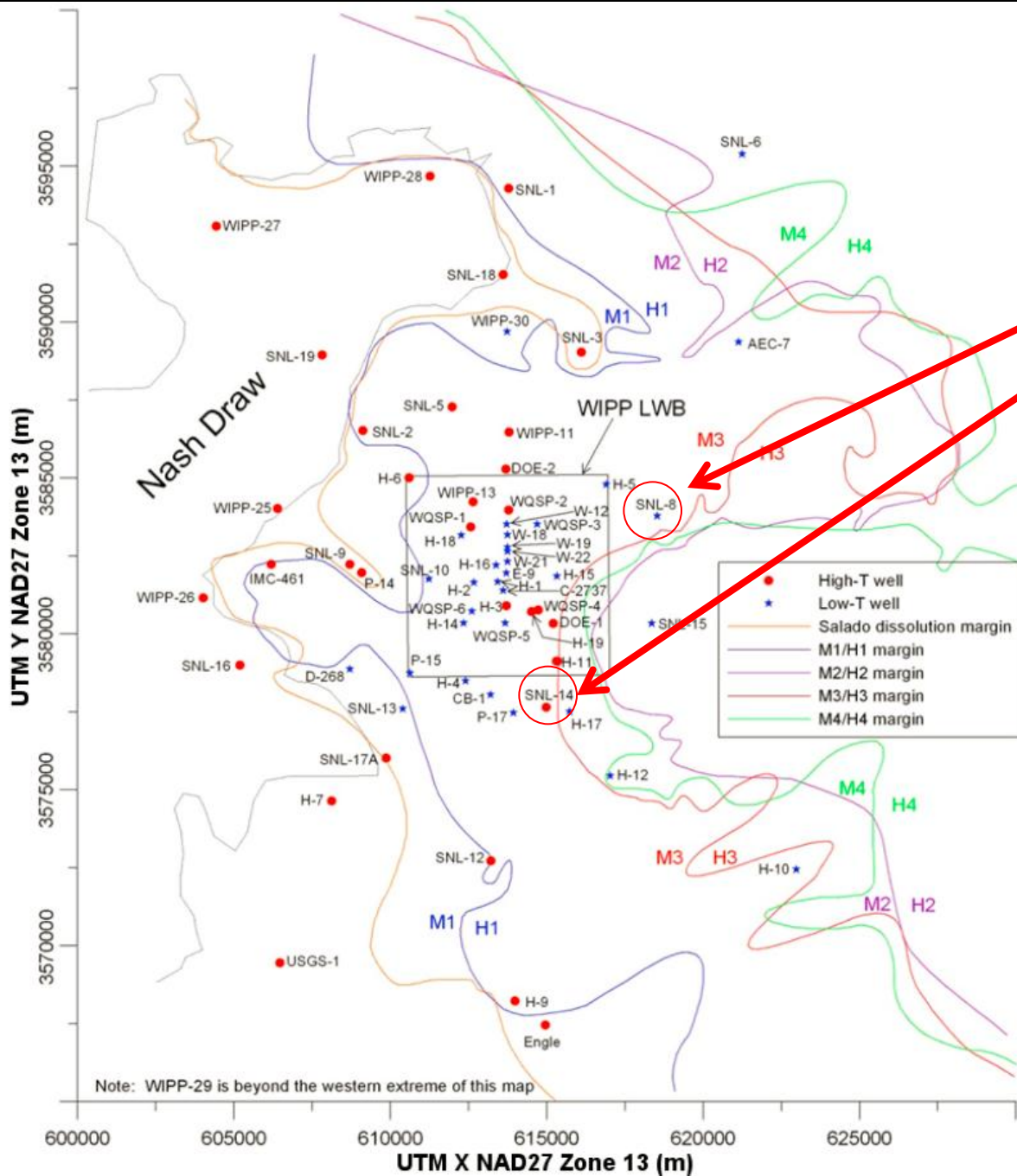


Fig. 1. Generalized WIPP geologic cross section



Sampled wells:
SNL-8 (low trans.) and
SNL-14 (high-trans.)

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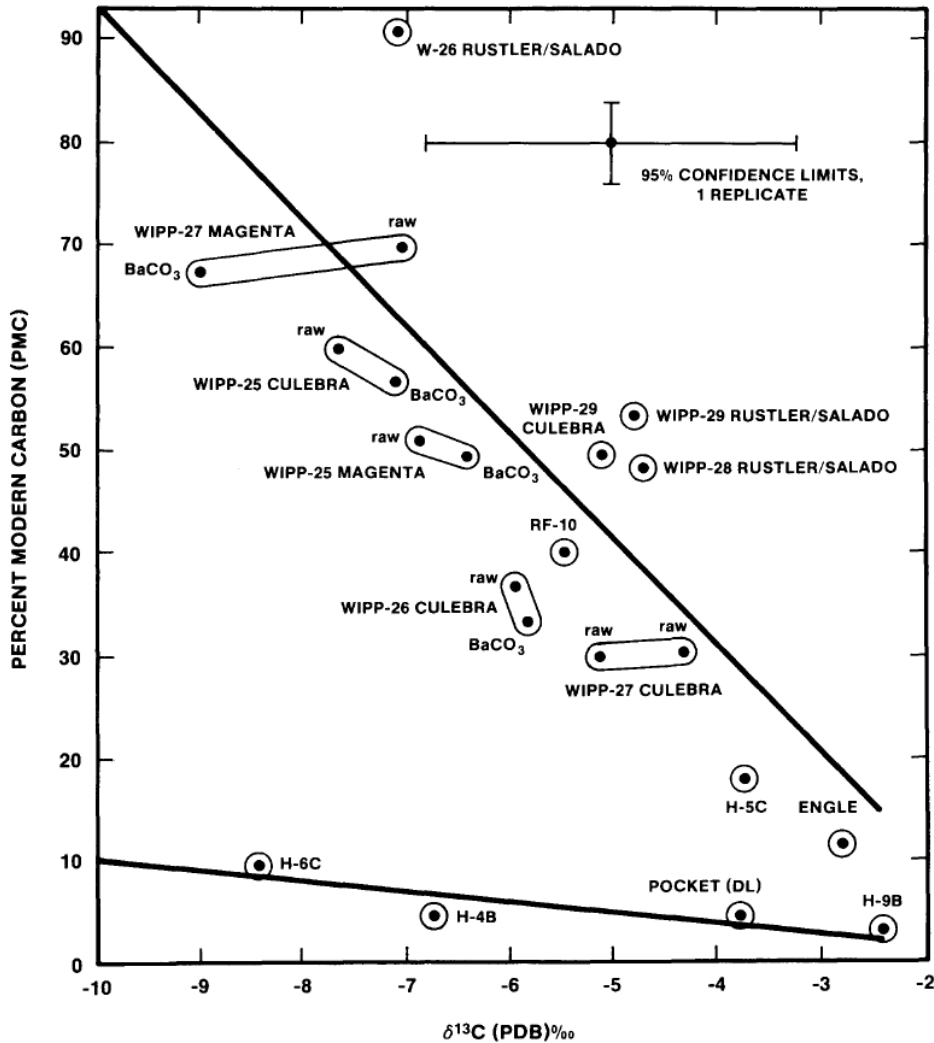


00000001 -

Feasibility Study: Applicability of Geochronologic Methods Involving Radiocarbon and Other Nuclides to the Groundwater Hydrology of the Rustler Formation, Southeastern New Mexico

Steven J. Lambert

Prepared by
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Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-76DP00789



TRI-6331-44-0

Figure 5. PMC values plotted versus $\delta^{13}\text{C}$. Two separate linear trends are indicated, one for samples with high-PMC values (greater than 10) and one for samples with low-PMC values (less than 10). The two trends appear to converge near PMC = 0 and $\delta^{13}\text{C}$ = 0.

← Relatively low ¹⁴C found in some brine samples from the Culebra dolomite aquifer

Conclusions from ^{14}C and ^{36}Cl measurements:

The minimum estimated age of surface-derived recharge for groundwaters in the Rustler and Dewey Lake aquifers near the WIPP site is 12 to 16 Ka, and this age range is supported by other paleoclimatic evidence (fossil packrat middens) in the region. The recharge may actually be part of an earlier Pleistocene event older than about 30 Ka, the age range of the radiocarbon method, given the possibility that even a small amount of contamination of these waters by modern carbon was introduced during well development. This contamination would make apparent radiocarbon ages spuriously young. These ages should not be used to calculate a travel time for Rustler groundwater across the WIPP site, because (a)

The ^{36}Cl values reported for Rustler groundwaters (H. Bentley, written communication) are all less than the limit of detectability for the measurement method (1 part ^{36}Cl in 10^{15} parts ^{35}Cl). This does not necessarily imply that the groundwaters have been out of contact with the atmosphere for a length of time greater than many half-lives of ^{36}Cl . Instead, it probably implies that the original level of cosmic-ray-generated ^{36}Cl has been diluted below the detection limit by dead ^{35}Cl and ^{37}Cl dissolved from the halite adjacent to the water-bearing intervals in the Rustler Formation.

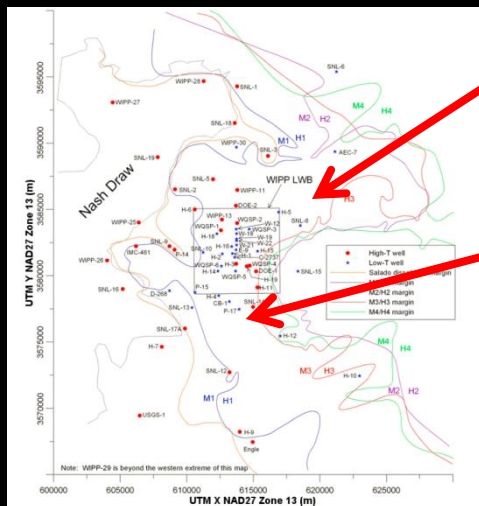
ATTA-3 results for WIPP brine samples:

	<u>Date of analysis</u>	<u>^{85}Kr (dpm/cc)</u>	<u>^{81}Kr (sample/air)</u>	<u>TDS,mg/L</u>
SNL-8	11/21/2011	10.3 ± 0.81	0.497 ± 0.038	140,000
SNL-14	11/23/2011	<1.62	0.668 ± 0.052	87,000

Problems found from CFCs, SF₆, ¹⁴C measurements:
air jetting and water injection during well completion

Apparent Mean Residence Times

(corrected assuming ⁸⁵Kr/Kr in air at time of well completion):



SNL-8

330 (+35/-33) × 10³ years

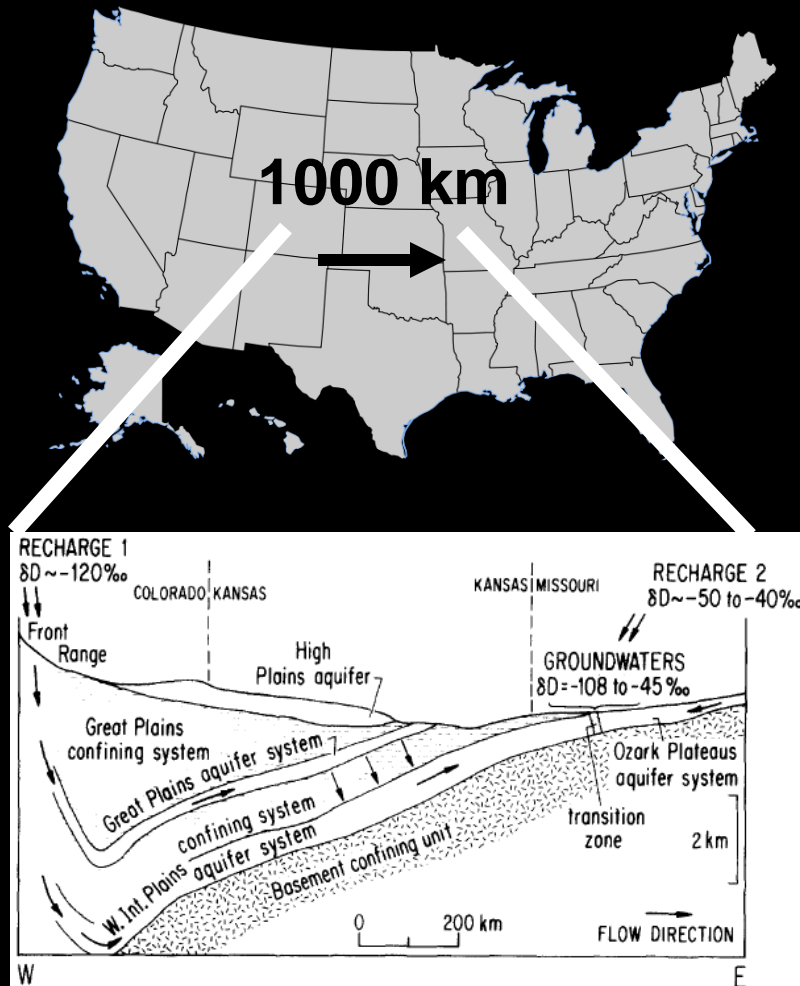
Low-Trans.

SNL-14

133 (+27/-24) × 10³ years

High-Trans.

Other Work in Progress: N.A. Midcontinent



Transcontinental travel time

- Great Plains and Interior Plains aquifers, USA
- Saline groundwaters, ~1000 km distance from Colorado Front Range recharge area to central Missouri discharge area
- Anticipated travel time
~ 10^6 yrs (1 m/yr)

(Musgrove & Banner, 1993)

Other Work in Progress : Atacama Desert, Chile

- Atacama Desert = Hyperarid region
 - Rainfall <10mm/yr
 - Water resource
 - = Vital for life and Cu industry



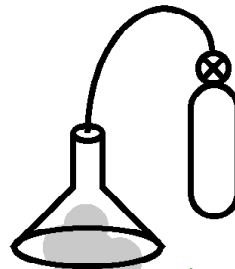
Beyond groundwater, oceans, and ice: Noble gas radionuclides in different reservoirs

Local
groundwater

$^{85}\text{Kr}/\text{Kr} \sim 0\%$
 $^{81}\text{Kr}/\text{Kr} \sim 100\%$
 $^{39}\text{Ar}/\text{Ar} < 100\%$

[ii] Gas stripping

Recycling



[i] Sampling

$^{85}\text{Kr}/\text{Kr} = 100\%$
 $^{81}\text{Kr}/\text{Kr} = 100\%$
 $^{39}\text{Ar}/\text{Ar} = 100\%$

Modern air

[iii] Assimilation

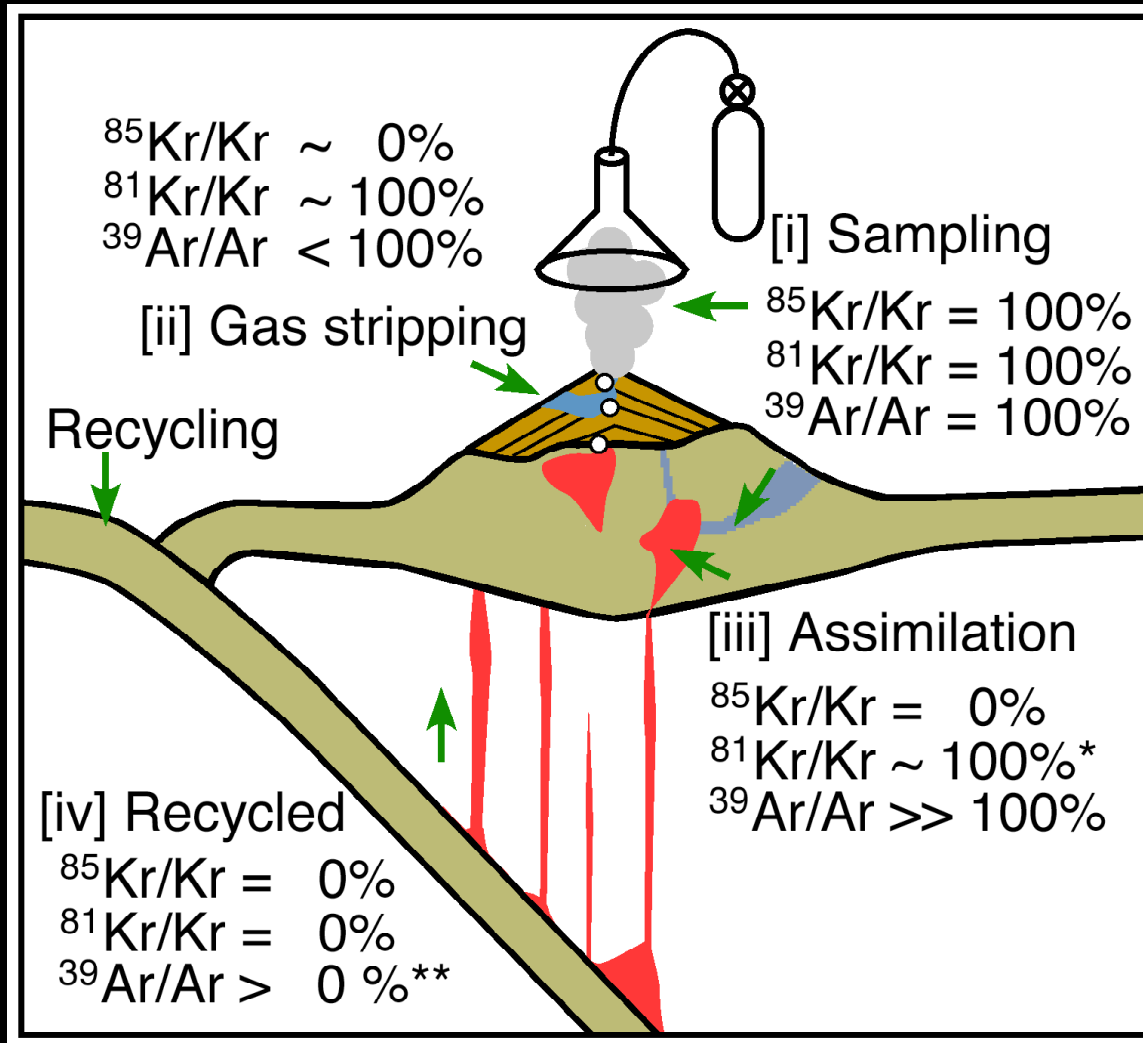
$^{85}\text{Kr}/\text{Kr} = 0\%$
 $^{81}\text{Kr}/\text{Kr} \sim 100\%^*$
 $^{39}\text{Ar}/\text{Ar} \gg 100\%$

Crust

[iv] Recycled

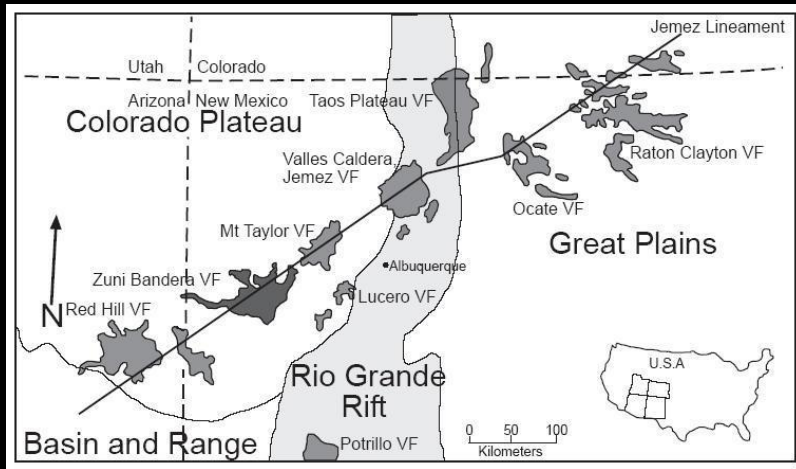
$^{85}\text{Kr}/\text{Kr} = 0\%$
 $^{81}\text{Kr}/\text{Kr} = 0\%$
 $^{39}\text{Ar}/\text{Ar} > 0\%^{**}$

> 2Myr



Planned sampling sites

Rio Grande Rift, New Mexico

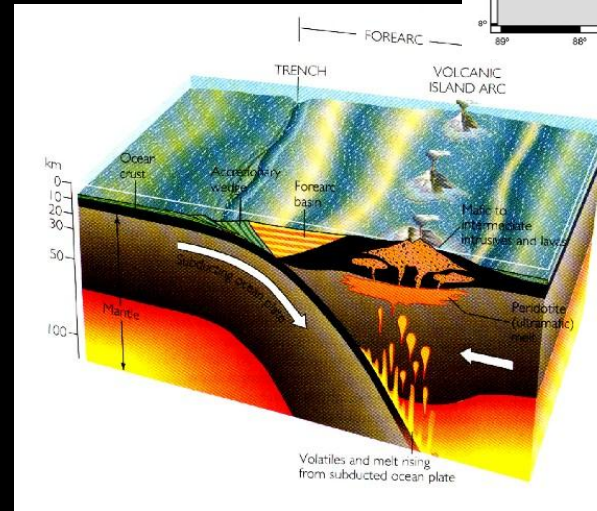


Volcan Poas, Costa Rica



Mantle gases?

+ Yellowstone
(Roland's talk)



Subduction

Applications in CO₂ sequestration studies?

