Natural radionuclides in North Carolina private wells: Influence of geology and water chemistry on radium mobilization in a granitic area

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Introduction

- Interdisciplinary research in North Carolina:
  - Occurrence of natural contaminants in private wells
  - Geochemical controls
  - Social/economic aspects for private well users
  - Treatment options for individuals and communities
- Uranium (U), radium (Ra),and radon (Rn) in drinking water results in elevated cancer risk
- Private well usage is widespread in rural areas of North Carolina

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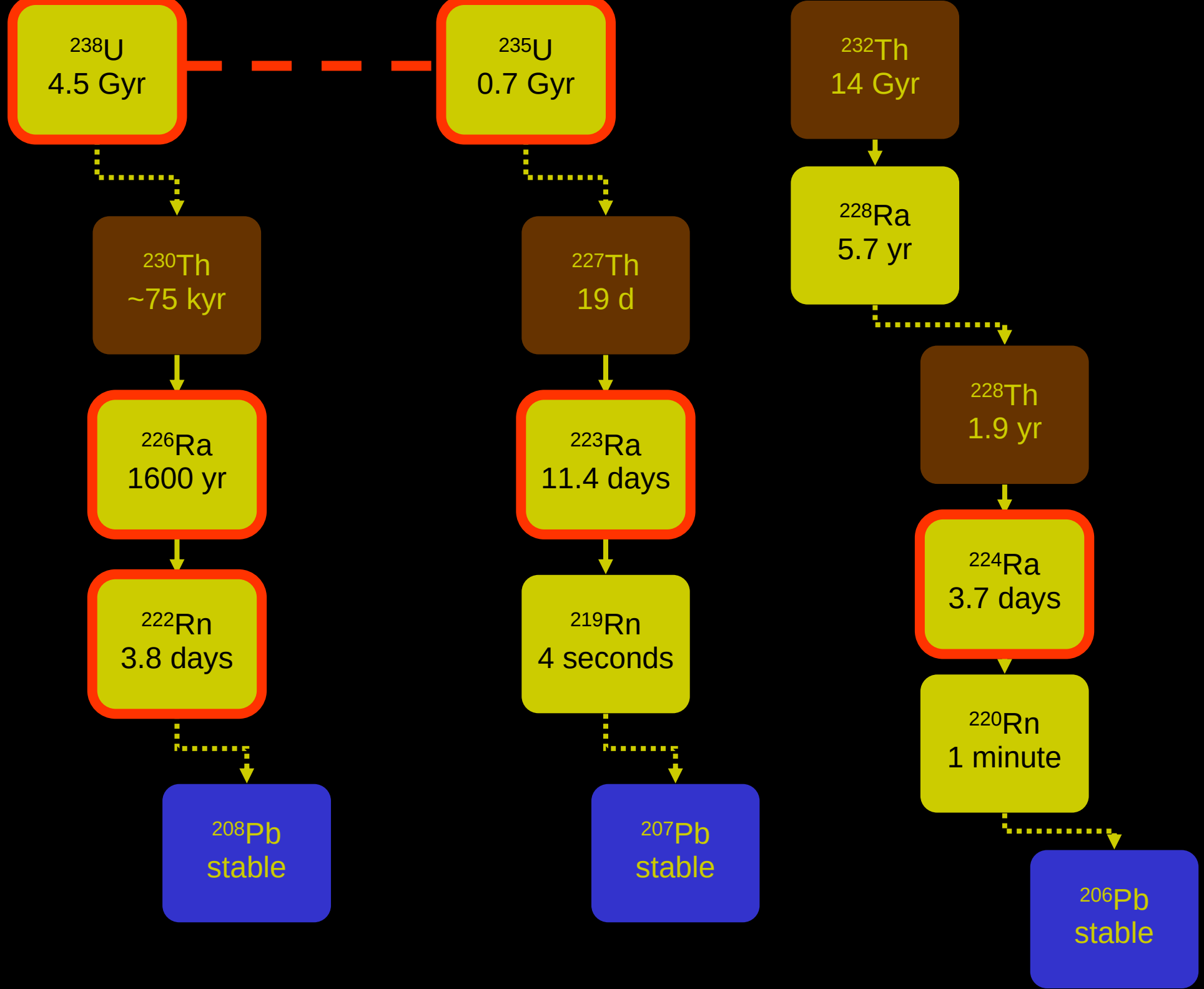
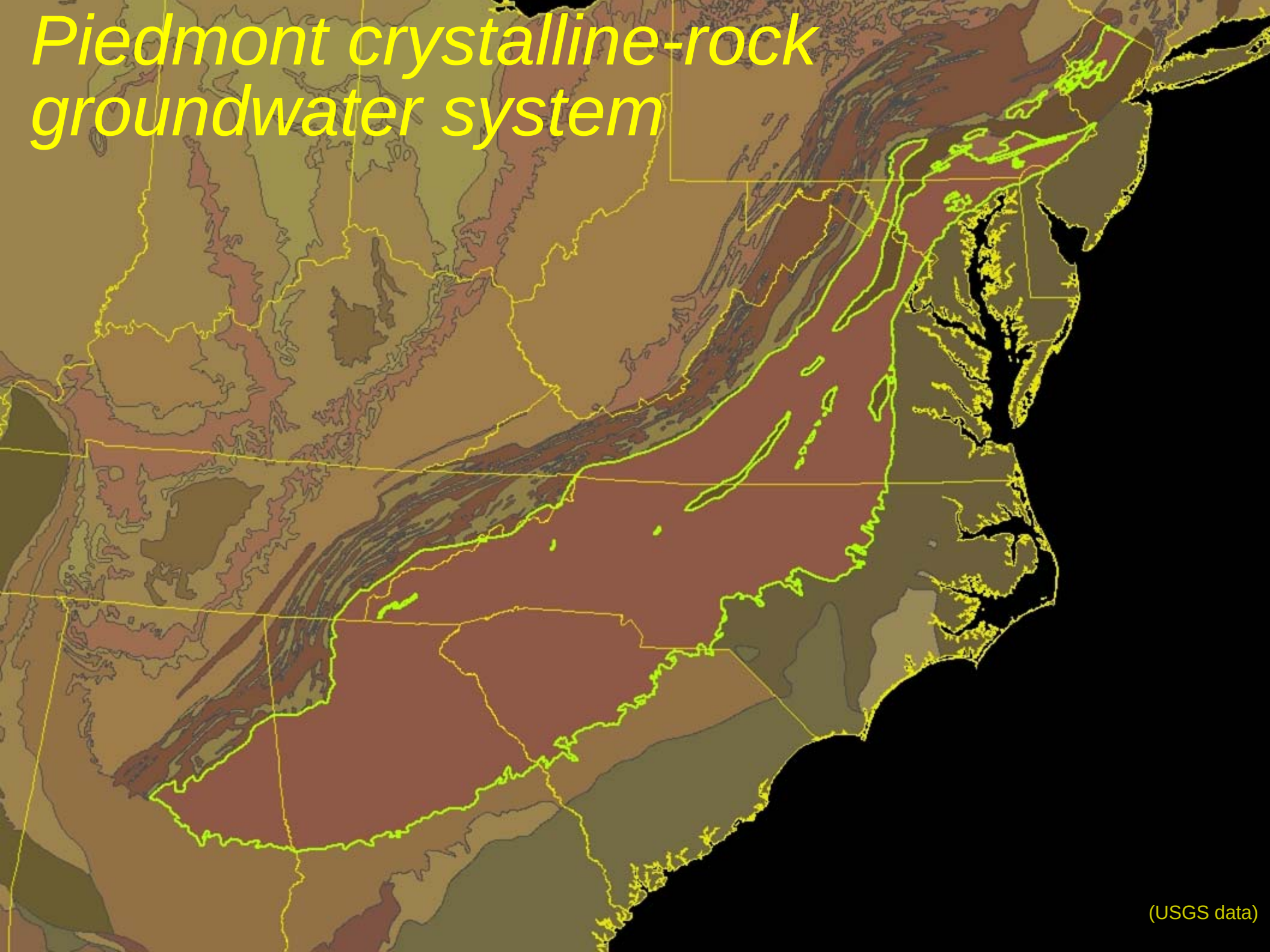
Questions...

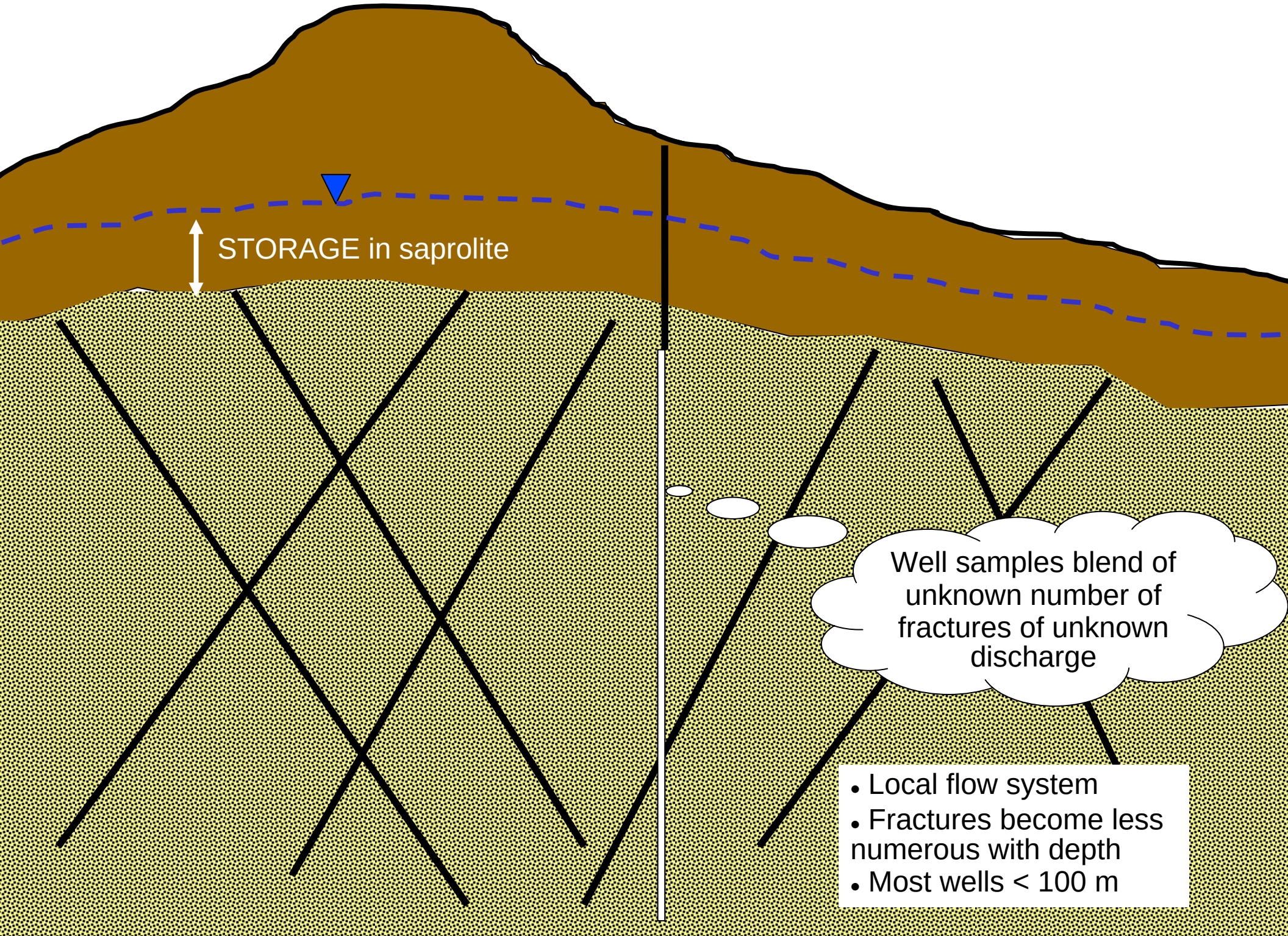
- Previous studies indicate that U, Ra, and Rn may exceed drinking water standards in the Raleigh, NC area, especially in the Rolesville Granite
- Will comprehensive geochemical study of well water reveal additional, unrecognized controls on radionuclide occurrence?
- Can radionuclide levels change with time?
- Can radionuclide levels be predicted?

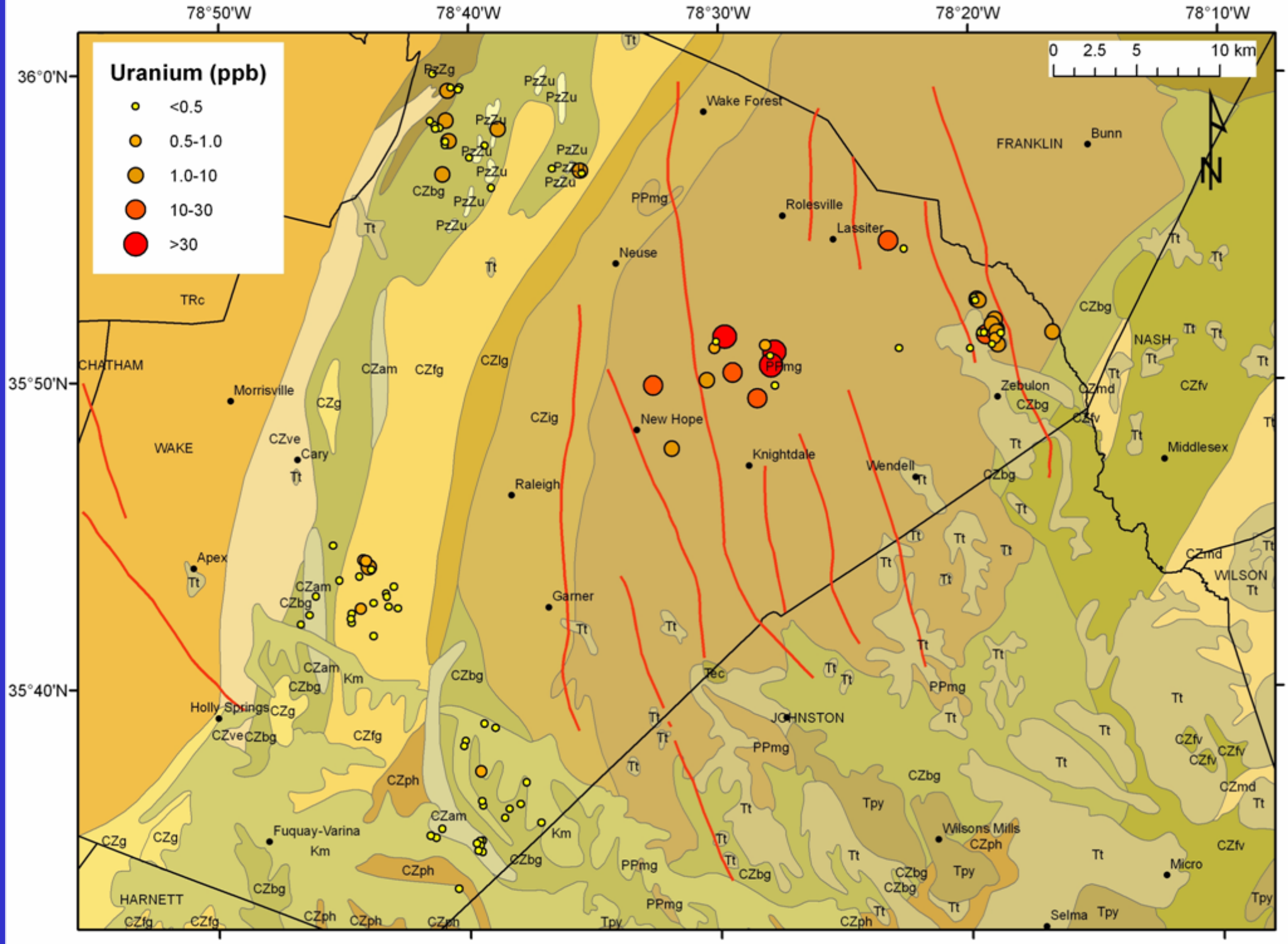

238U
4.5 Gyr
235U
0.7 Gyr
232Th
14 Gyr
230Th
~75 kyr
227Th
19 d
228Ra
5.7 yr
226Ra
1600 yr
223Ra
11.4 days
228Th
1.9 yr
222Rn
3.8 days
219Rn
4 seconds
224Ra
3.7 days
220Rn
1 minute
208Pb
stable
207Pb
stable
206Pb
stable

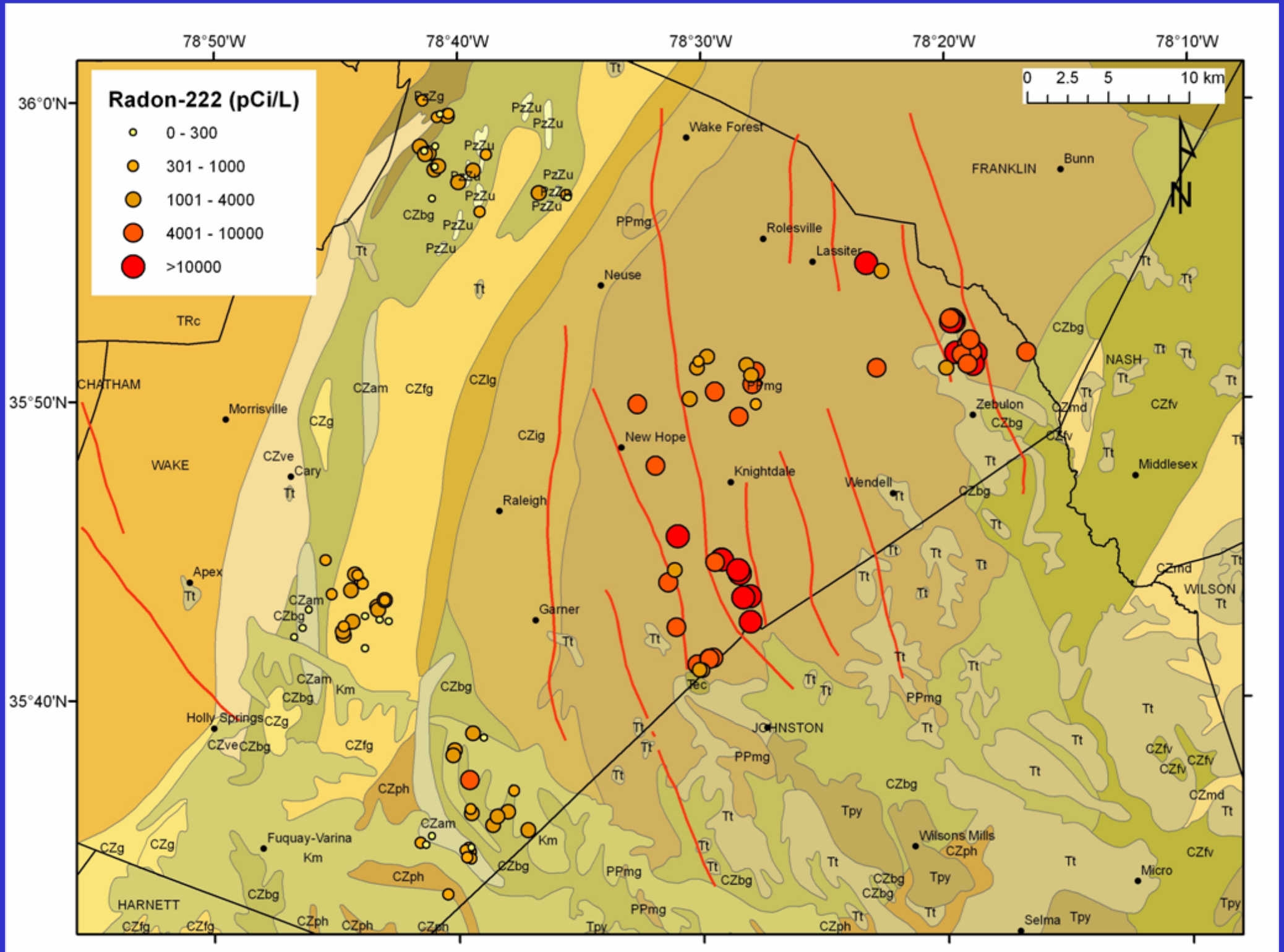
Piedmont crystalline-rock groundwater system



(USGS data)


STORAGE in saprolite
Well samples blend of unknown number of fractures of unknown discharge
• Local flow system
• Fractures become less numerous with depth
• Most wells < 100 m


Uranium (ppb)
<0.5
0.5-1.0
1.0-10
10-30
>30
78°50'W
78°40'W
78°30'W
78°20'W
78°10'W
36°0'N
35°50'N
35°40'N
0 2.5 5 10 km
N
Wake Forest
Bunn
FRANKLIN
Rolesville
Lassiter
Neuse
TRc
CHATHAM
Morrisville
WAKE
Cary
Raleigh
New Hope
Knightdale
Wendell
Zebulon
NASH
Middlesex
WILSON
Apex
Garner
Holly Springs
JOHNSTON
Fuquay-Varina
Wilsons Mills
Micro
Selma
HARNETT
PzZg
PzZu
CZbg
CZam
CZfg
CZlg
CZig
CZg
CZve
CZph
CZfv
CZmd
Km
PPmg
Tt
Tec
Tpy


Radon-222 (pCi/L)
0 - 300
301 - 1000
1001 - 4000
4001 - 10000
>10000
78°50'W
78°40'W
78°30'W
78°20'W
78°10'W
36°0'N
35°50'N
35°40'N
0 2.5 5 10 km
N
Wake Forest
Bunn
FRANKLIN
Rolesville
Lassiter
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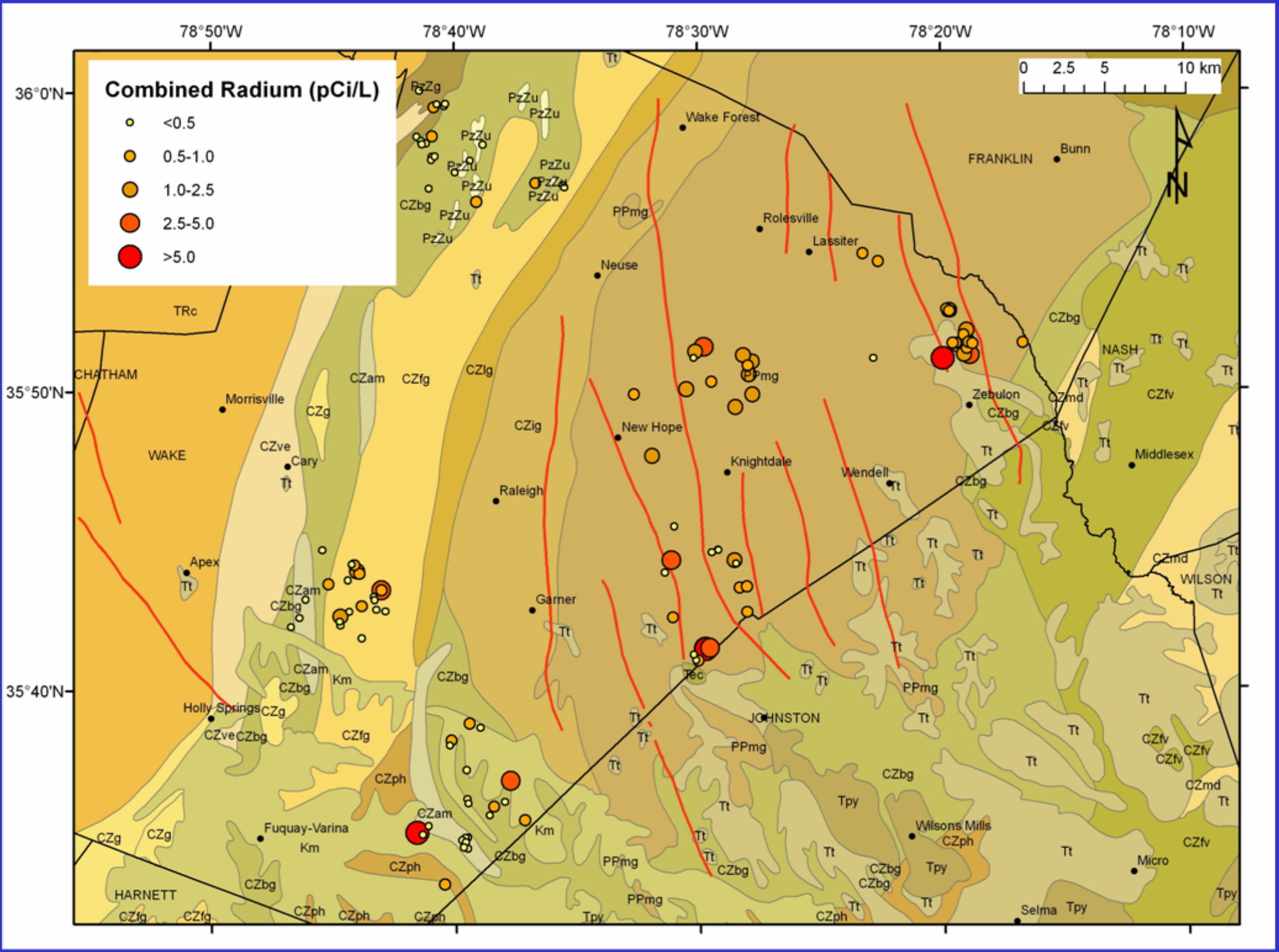
Tpy
Tec


Combined Radium (pCi/L)
<0.5
0.5-1.0
1.0-2.5
2.5-5.0
>5.0
78°50'W
78°40'W
78°30'W
78°20'W
78°10'W
36°0'N
35°50'N
35°40'N
0 2.5 5 10 km
N
Wake Forest
Bunn
FRANKLIN
Rolesville
Lassiter
Neuse
TRc
CHATHAM
Morrisville
WAKE
Cary
Raleigh
New Hope
Knightdale
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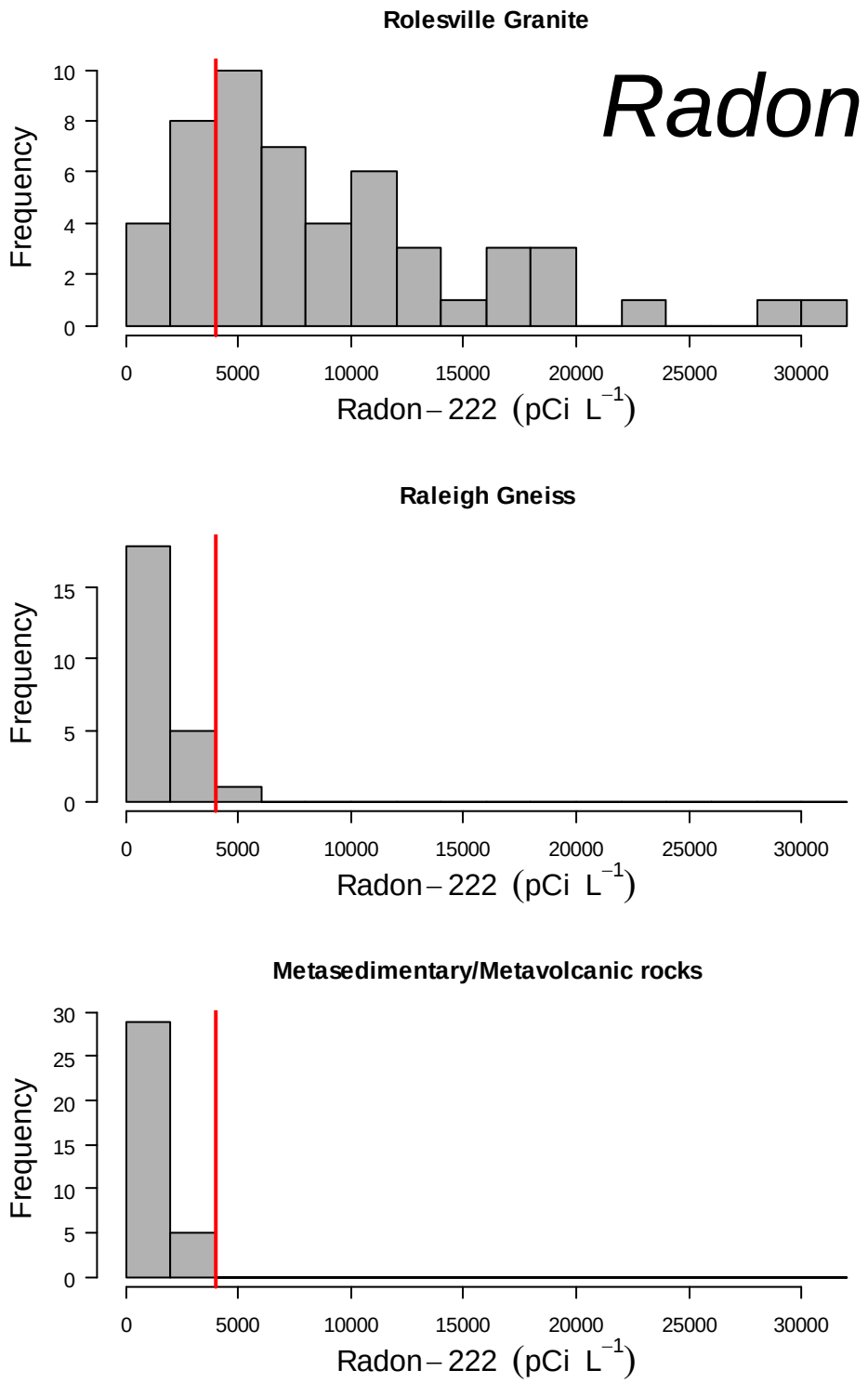
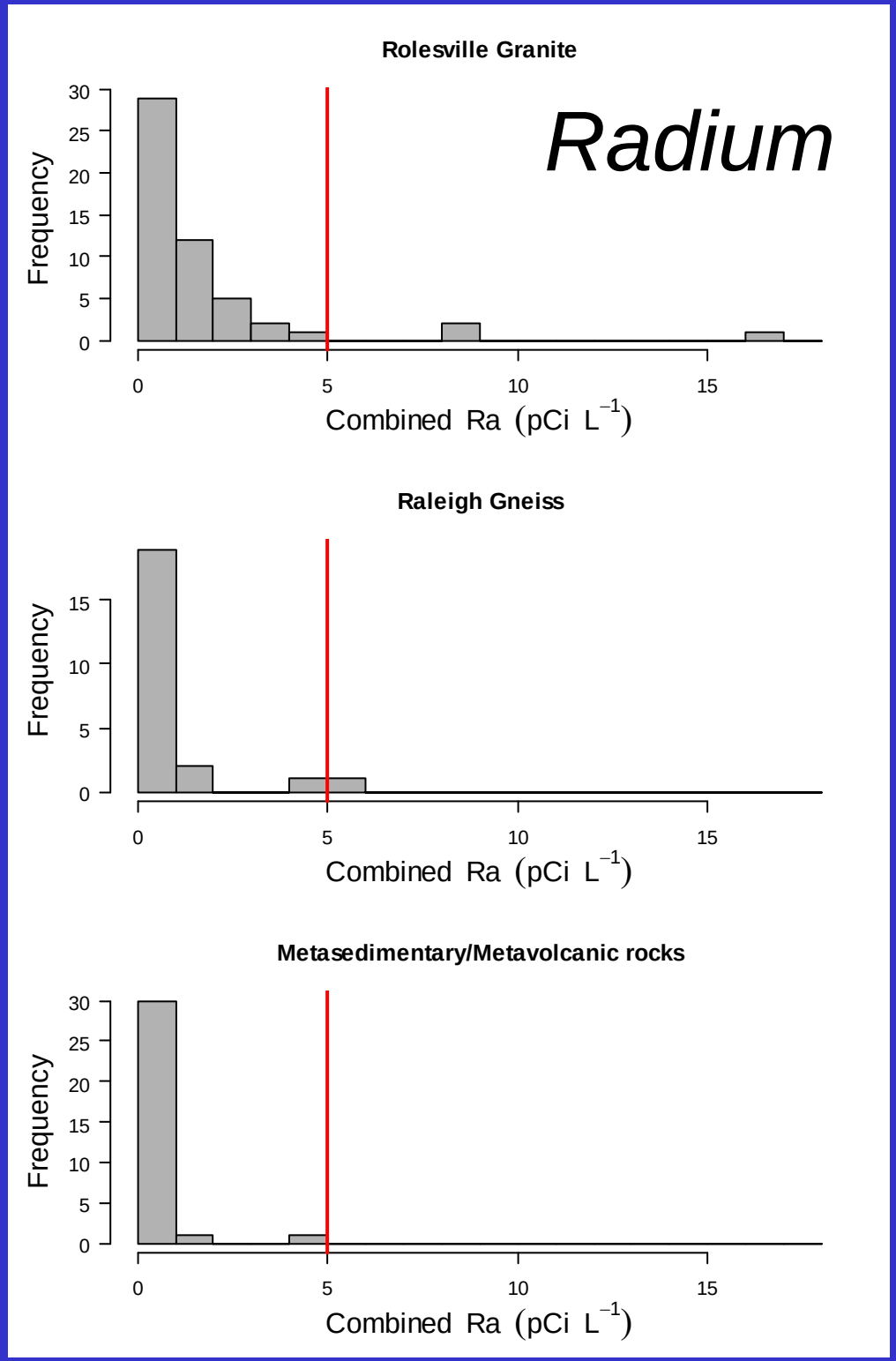
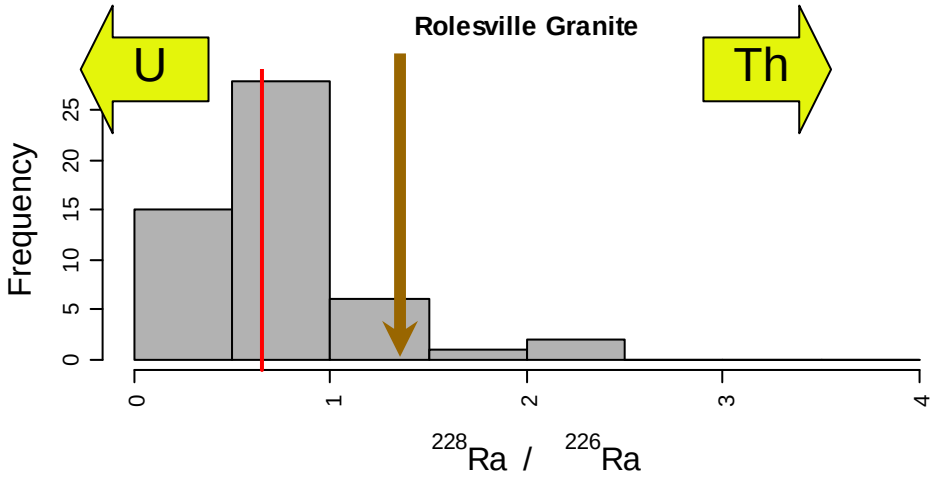
Fuquay-Varina
Wilsons Mills
Micro
Selma
HARNETT
PzZg
PzZu
CZbg
CZam
CZfg
CZlg
CZg
CZve
CZig
CZph
CZfv
CZmd
Km
Tt
PPmg
Tpy
Tec

Radon


Rolesville Granite
Frequency
0
2
4
6
8
10
0
5000
10000
15000
20000
25000
30000
Radon – 222 (pCi L^{-1})
Raleigh Gneiss
Frequency
0
5
10
15
0
5000
10000
15000
20000
25000
30000
Radon – 222 (pCi L^{-1})
Metasedimentary/Metavolcanic rocks
Frequency
0
5
10
15
20
25
30
0
5000
10000
15000
20000
25000
30000
Radon – 222 (pCi L^{-1})


Rolesville Granite
Radium
Frequency
30
25
20
15
10
5
0
0
5
10
15
Combined Ra (pCi L^{-1})
Raleigh Gneiss
Frequency
15
10
5
0
0
5
10
15
Combined Ra (pCi L^{-1})
Metasedimentary/Metavolcanic rocks
Frequency
30
25
20
15
10
5
0
0
5
10
15
Combined Ra (pCi L^{-1})

Radium isotope ratio
^{228}Ra / ^{226}Ra



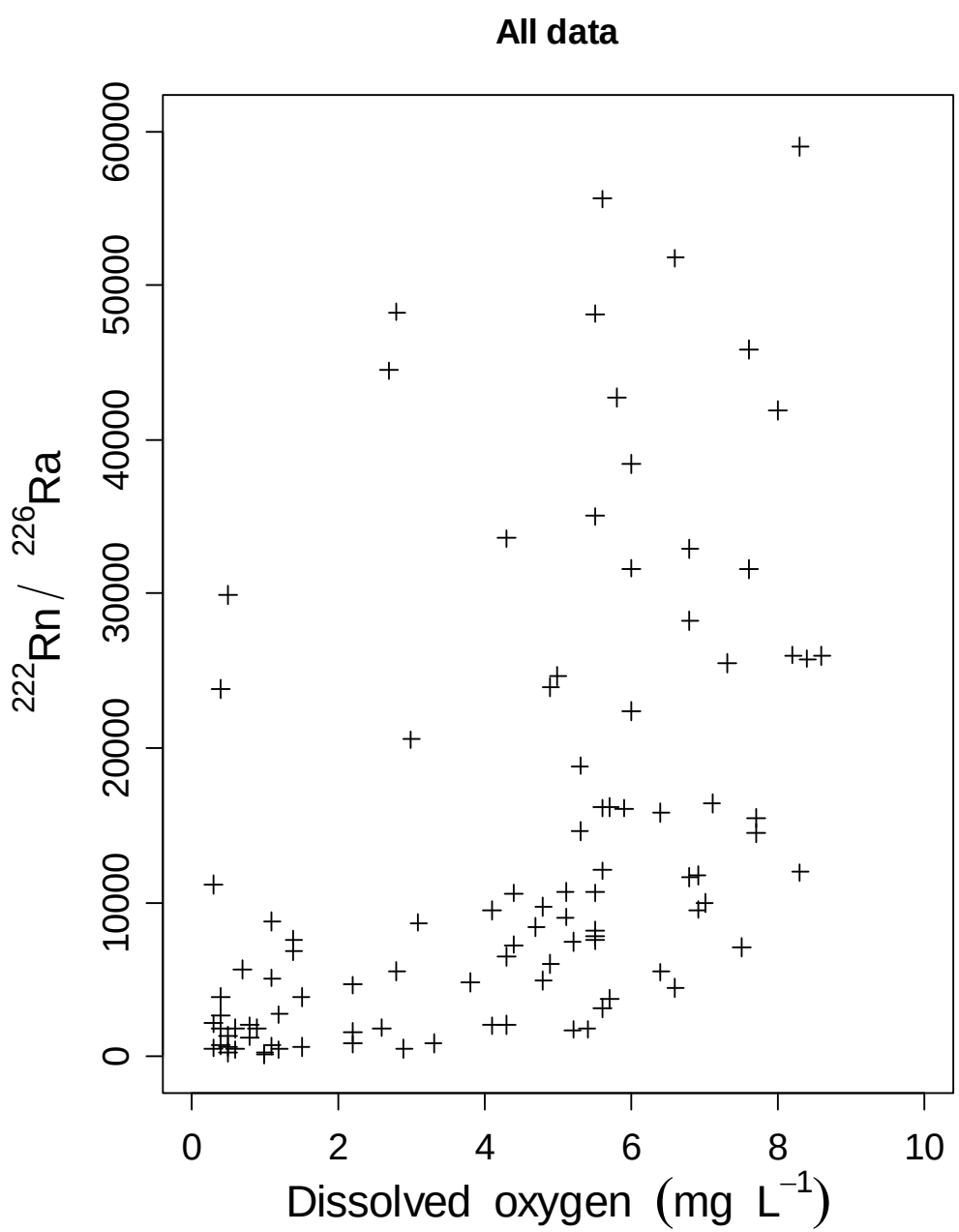
Median $^{228}Ra/^{226}Ra$ activity ratio:

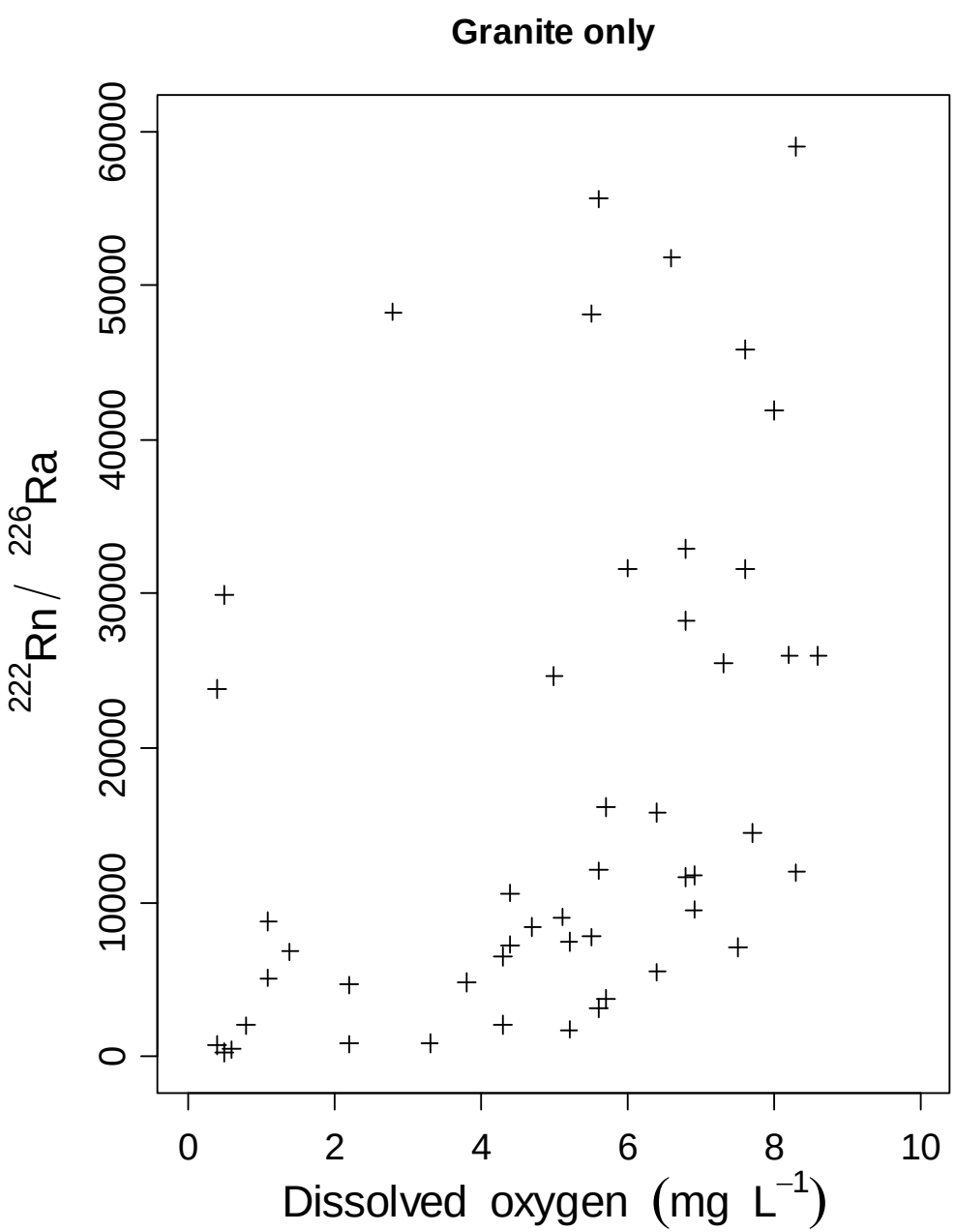
0.7 for waters

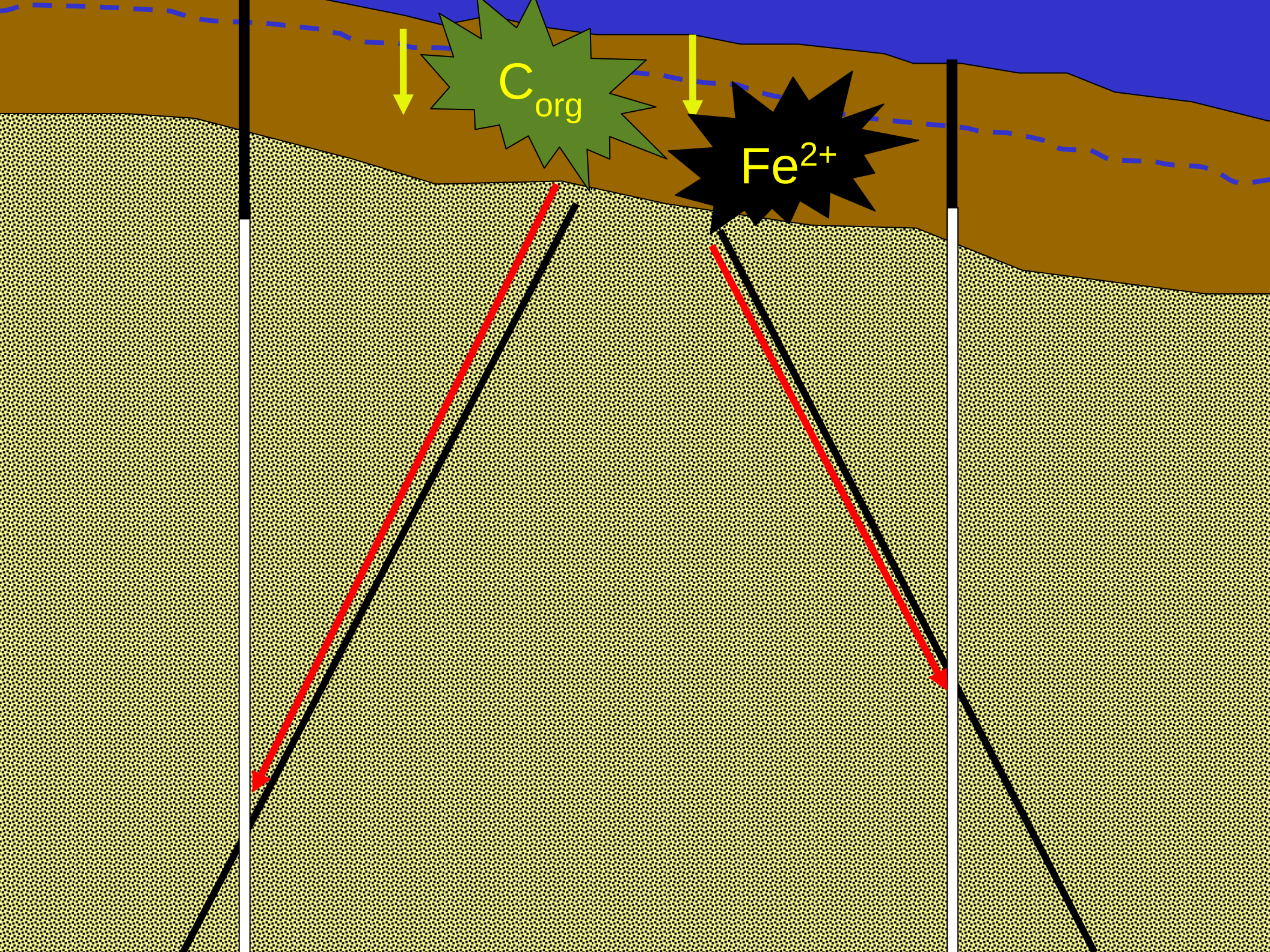
1.4 for cores

- Ra from the U series is more susceptible to entering water than Ra from the Th series
- However, all isotopes of Ra “behave” the same chemically
- Thus, Ra from the U series must be better sited due to processes that move U to fracture surfaces more effectively than Th

Redox effects on $^{222}Rn/^{226}Ra$ ratio






C_{org}
Fe^{2+}

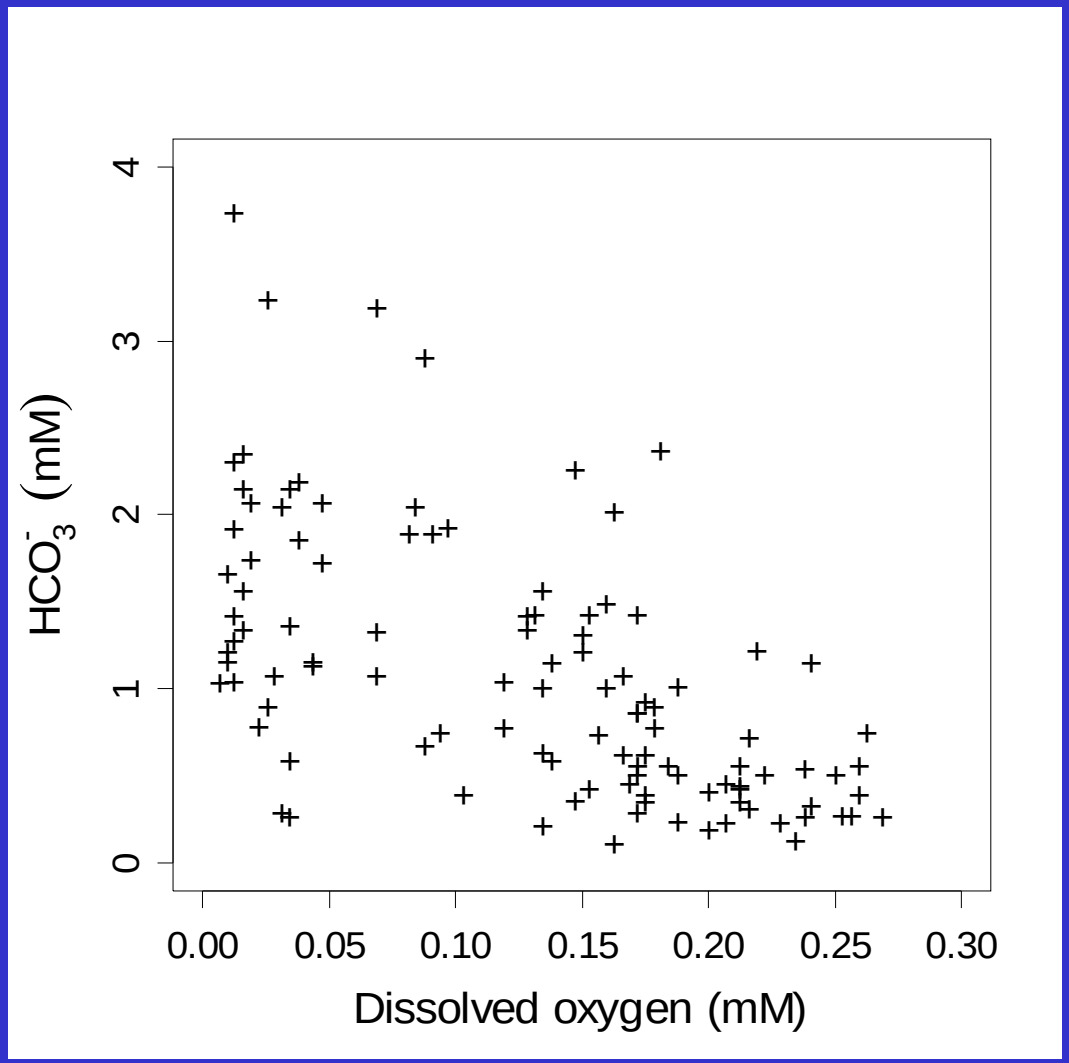
Mechanisms of oxygen reduction

Biotic:

$CH_2O + O_2 = CO_2 + H_2O$

- O_2 and HCO_3^- are negatively correlated

Inorganic carbon



Mechanisms of oxygen reduction

Biotic:

$CH_2O + O_2 = CO_2 + H_2O$

- O_2 and HCO_3^- are negatively correlated

Abiotic:

$4Fe^{2+} + 3O_2 + 6H_2O = 4Fe(OH)_3$

- Well-documented weathering reaction
- Observed in microfractures of similar granites
- Resulting Fe oxide *adsorbs* U and Ra

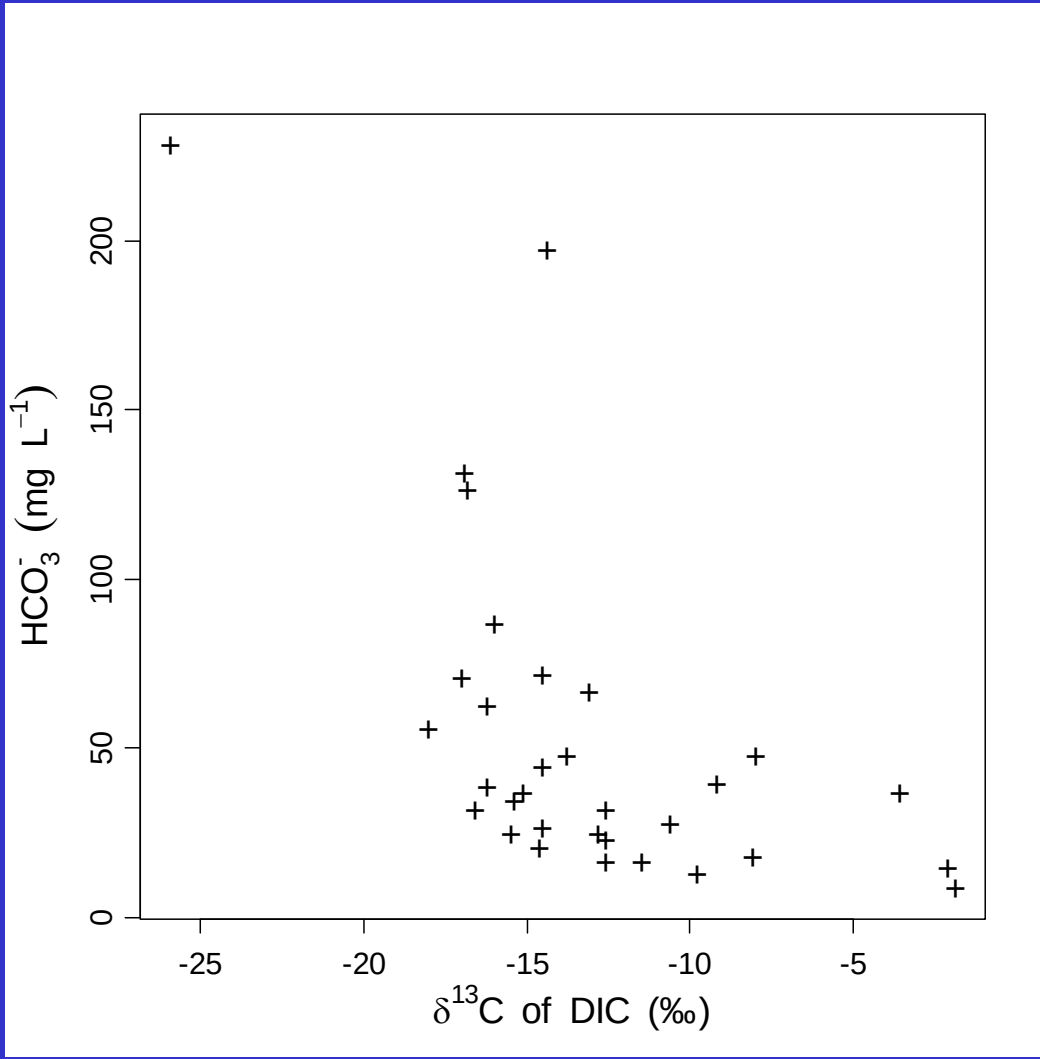
Stable isotopes of carbon in dissolved bicarbonate

Calcite dissolution $\delta^{13}C \approx 0$ ‰

$\delta^{13}C$ of bicarbonate

Soil CO_2, microbial respiration $\delta^{13}C \approx -25$ ‰

Inorganic carbon



Some inorganic carbon (bicarbonate) is from microbial respiration, probably during recharge through the soil & saprolite

Conclusions (1)

- Rn and U in water strongly linked to rock type
- Ra also higher overall in granite, but capable of exceeding drinking water standards in other rocks (depending on water chemistry)
- Radon much more likely to exceed (proposed) drinking water standards
- Low $^{228}Ra/^{226}Ra$ implies that U-series radionuclides have been relocated beyond their original locations in unweathered bedrock

Conclusions (2)

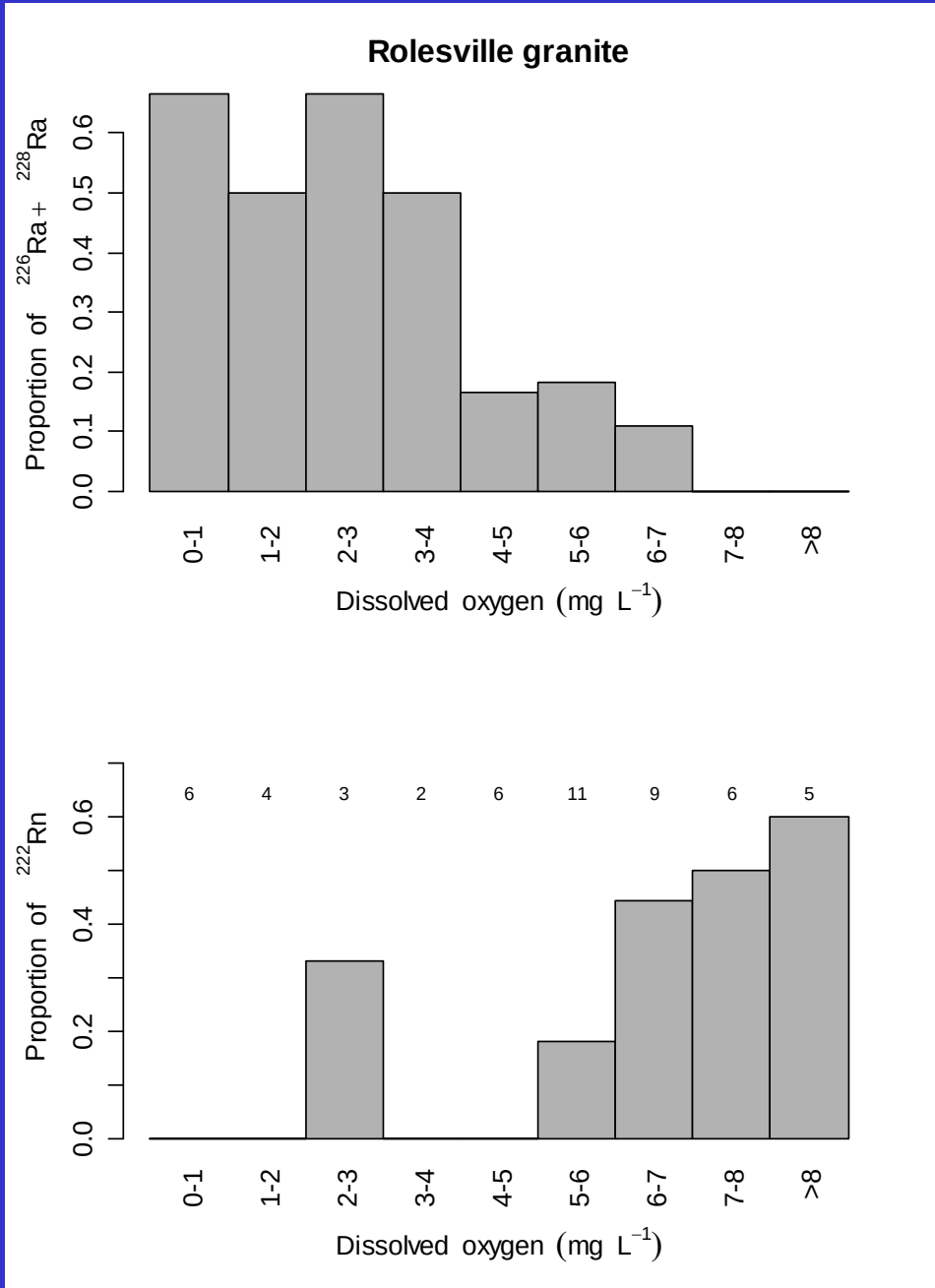
- Unambiguous documentation of redox effect across a large range of Ra and Rn activities
  - Large sample size
  - Low detection limits
- Ra mobility relative to Rn varies by 2 orders of magnitude
- 2 possible mechanisms:
  - Oxidation of organic carbon during recharge through soil and saprolite (FAST)
  - Oxidation of Fe^{2+} by dissolved oxygen during biotite weathering (SLOW)

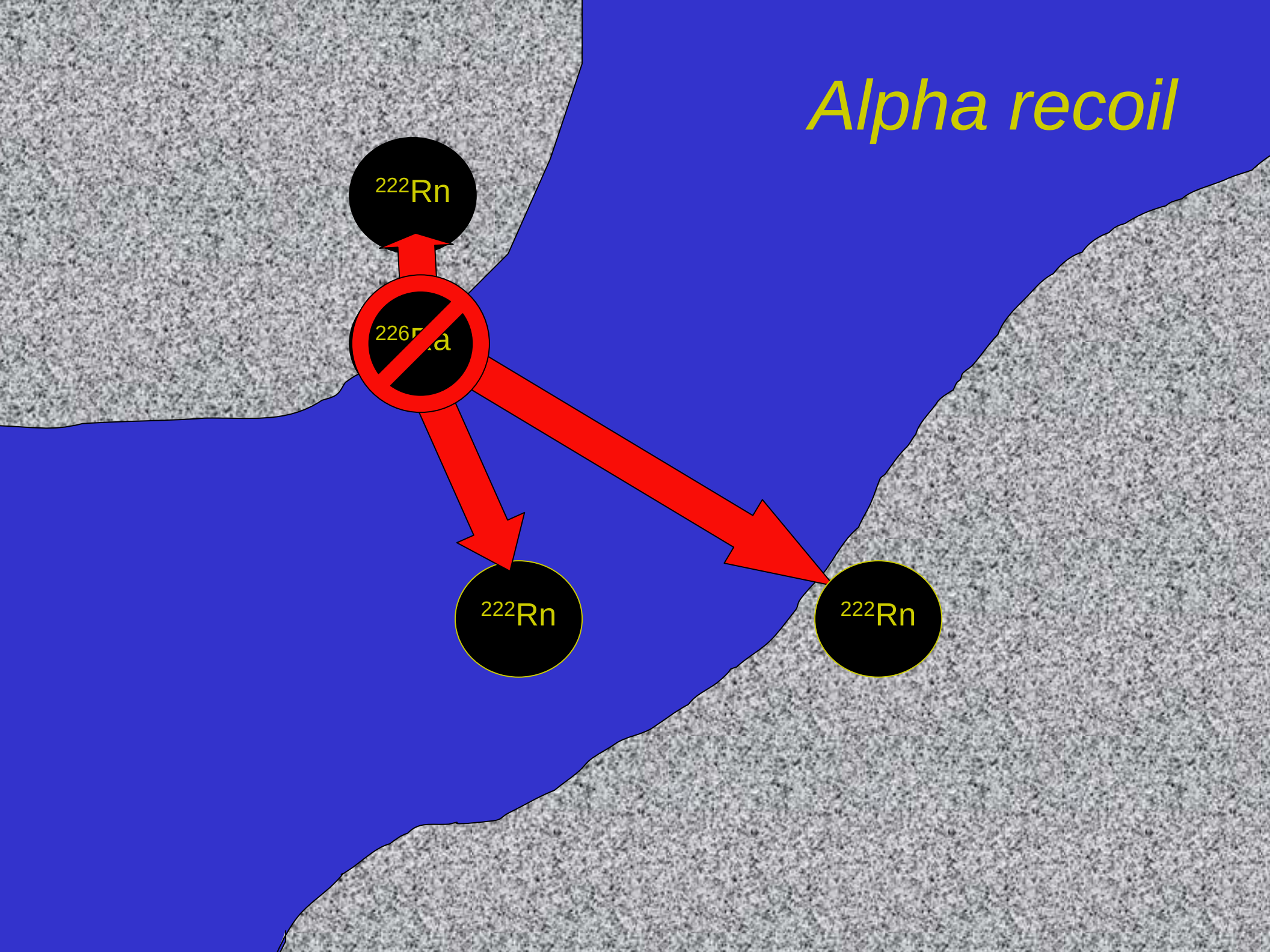
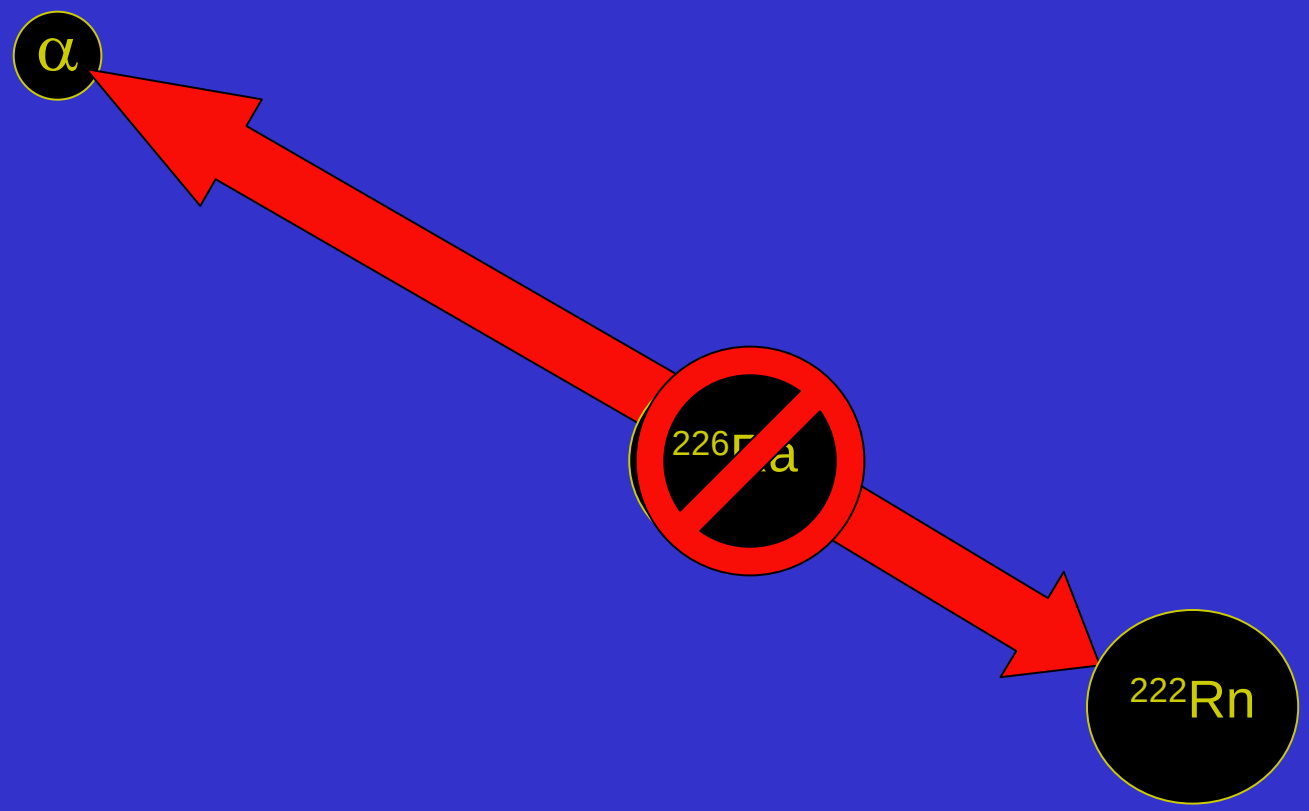
Conclusions (3)

- Both mechanisms suggest that groundwater acquires redox chemistry during recharge through soil and saprolite
- However, radionuclides are acquired in the bedrock fracture network (indicated by half-lives as short as 3 days), with Ra adsorption influenced by redox condition
- Changing redox conditions in fractures may influence observed Ra levels in wells, but time scale is not constrained

Recommendations

- Dissolved oxygen measurements are a useful screen in radionuclide occurrence studies
- Elevated Ra coincides with low DO
- High Rn coincides with high DO




Alpha recoil
222Rn
226Ra
222Rn
222Rn

Alpha recoil