



Solute Chemistry and Isotope Tracers of Groundwater Systems in the Middle San Pedro Basin, Arizona



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Acknowledgements



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- Thank you to the citizens of the San Pedro Basin and to my colleagues at the U of A for field help and lab help
- Jennifer McIntosh, Chris Eastoe, Tom Meixner, and Jesse Dickinson are thanked for their support and advice

PLAN

- 1. Introduction to isotopes**
- 2. Candice's research approach**
- 3. Water quality issues**
- 4. Questions addressed by isotope data**



Introduction to isotopes

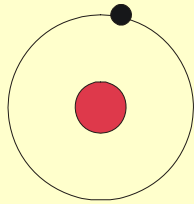
O and H isotopes

Tritium

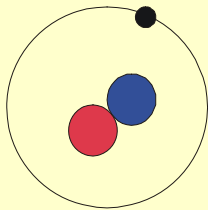
Carbon-14

Sulfur – not discussed here.

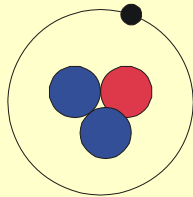
Isotopes of Hydrogen



Hydrogen-1 (protium)



Hydrogen-2 (deuterium)



Hydrogen-3 (tritium)

Radioactive > helium + electron

Half-life about 12.5 years



Isotopes of Oxygen

Oxygen-16 8 protons, 8 neutrons

Oxygen-17 8 protons, 9 neutrons

Oxygen-18 8 protons, 10 neutrons

All stable



Isotopes of Carbon

stable

Carbon-12 6 protons, 6 neutrons

Carbon -13 6 protons, 7 neutrons

radioactive

Carbon -14 6 protons, 8 neutrons

Half-life about 5730 years

Where do tritium and carbon-14 come from?



Cosmic rays strike upper atmosphere



Atmospheric testing of nuclear weapons, 1950s-1970s



Use of tritium

Groundwater once fell as rain containing measurable tritium.

Tritium decays – half life 12.4 years

Tritium below detection indicates pre-1955 rainwater.

Detectable tritium indicates presence of post-1955 rainwater



Use of carbon-14

Groundwater once fell as rain that soaked into soil and dissolved soil gas containing C-14.

C-14 decays – half life 5730 years

High C-14 indicates younger water; low C-14 indicates older water (exact ages difficult to calculate).

Age range 0 to about 20,000 years

δ -values

$$\delta^{18}\text{O} = \left\{ \left(R_{\text{sample}}/R_{\text{standard}} \right) - 1 \right\} \times 1000 \text{ ‰}$$

$$R = {}^{18}\text{O}/{}^{16}\text{O}$$

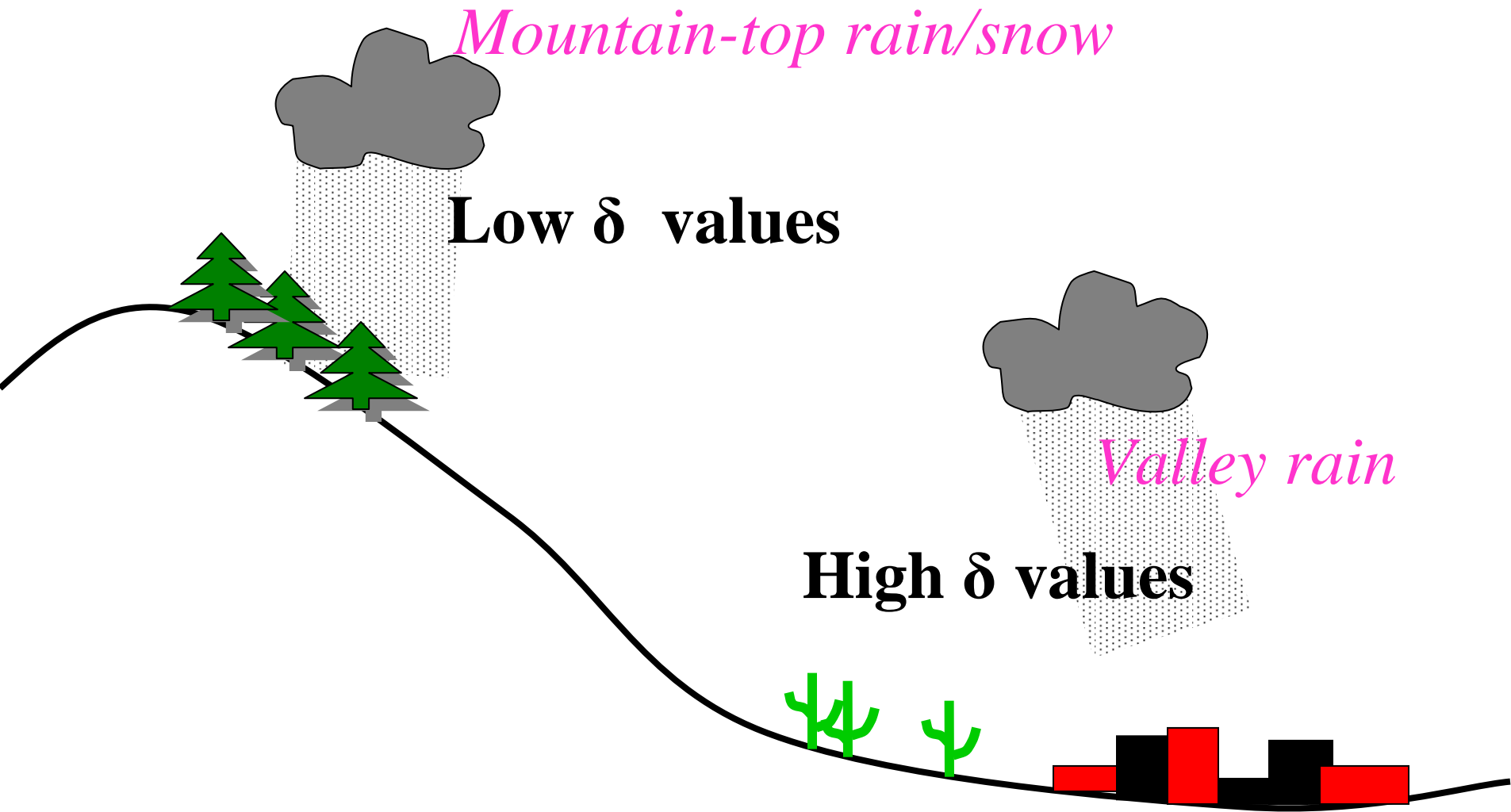
Similarly, δD with $R = \text{D}/\text{H}$

Higher δ - value implies more of the heavy isotope

$\delta^{18}\text{O}$	=	-40	-12 to -6	0
Antarctic ice			NM rain	ocean



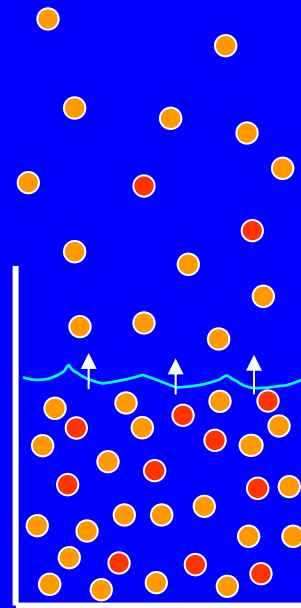
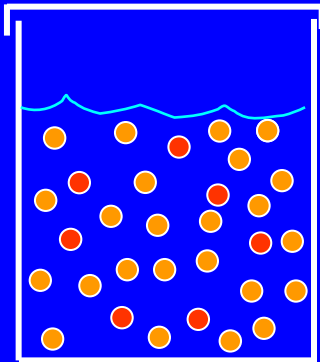
Why isotope ratios in water vary: Condensation



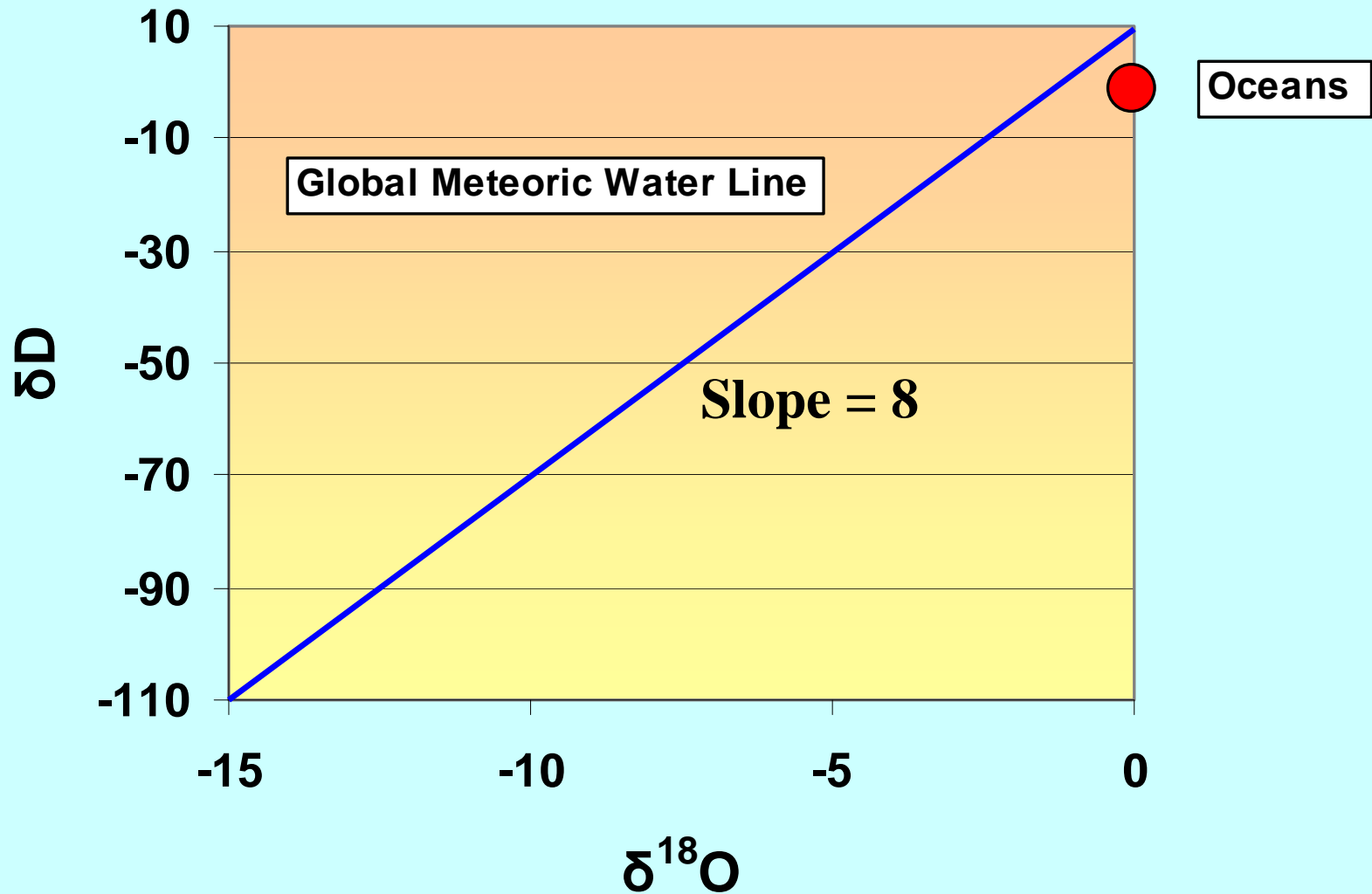


Why isotope ratios in water vary: Evaporation

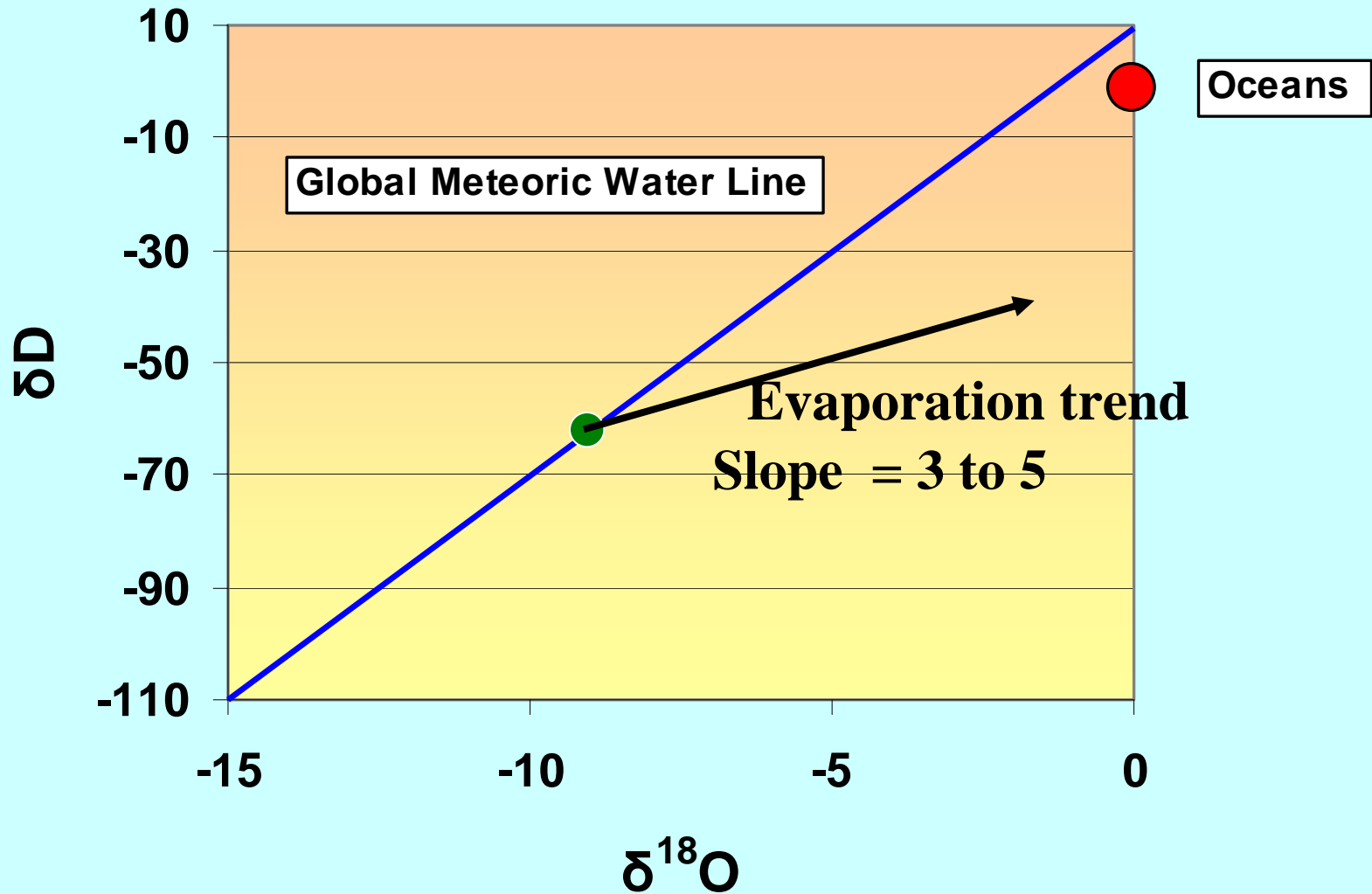
- **Lighter molecule (^1H , ^{16}O)**
- **Heavier molecule (^2H , ^{18}O)**



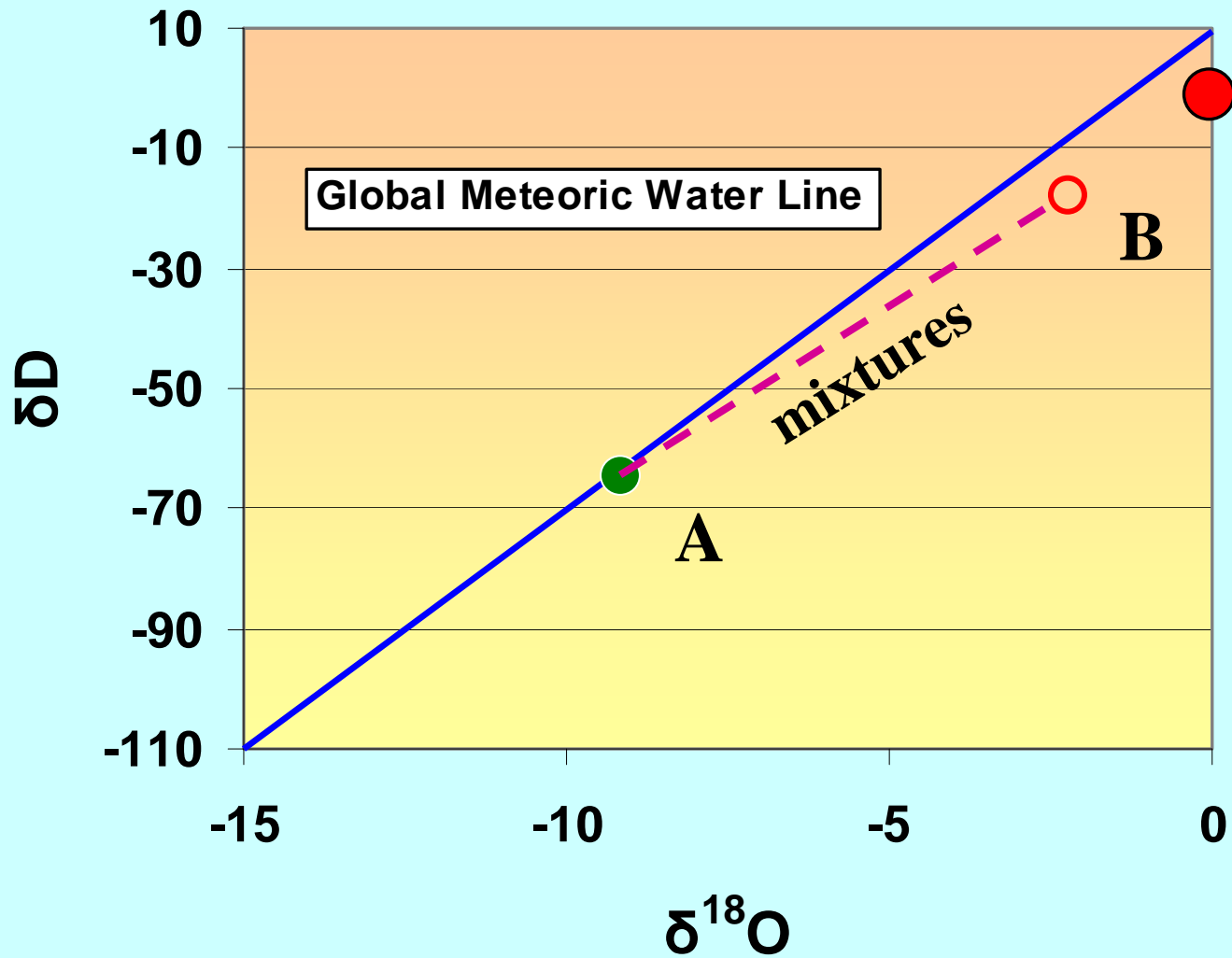
The basic diagram



Evaporation



Mixing



How Candice approached the research problem:

- 1. Detailed sampling in all four aquifers, and of river water**
- 2. Analyses of major ions: sodium, potassium, calcium, magnesium, strontium, bicarbonate, chloride, sulfate, nitrate, bromide, fluoride**
- 3. Analyses of isotopes: stable isotopes of hydrogen, oxygen, carbon and sulfur; radioactive isotopes carbon-14 and tritium**
- 4. NETPATH modeling to correct carbon-14 data.**

Water Quality Issues

Potential problems: fluoride (F) and nitrate (NO3)

No data for arsenic

EPA Maximum contaminant levels (MCLs):

F 4 mg/L

NO3 44 mg/L

	Fracture Sys.	Unconfined	Confined	Flood plain
No. samples	25	7	35	11
F > 4 mg/L	1	0	5	2
NO3 > 44 mg/L	0	0	0	0
NO3 > 10 mg/L	4	1	2	3

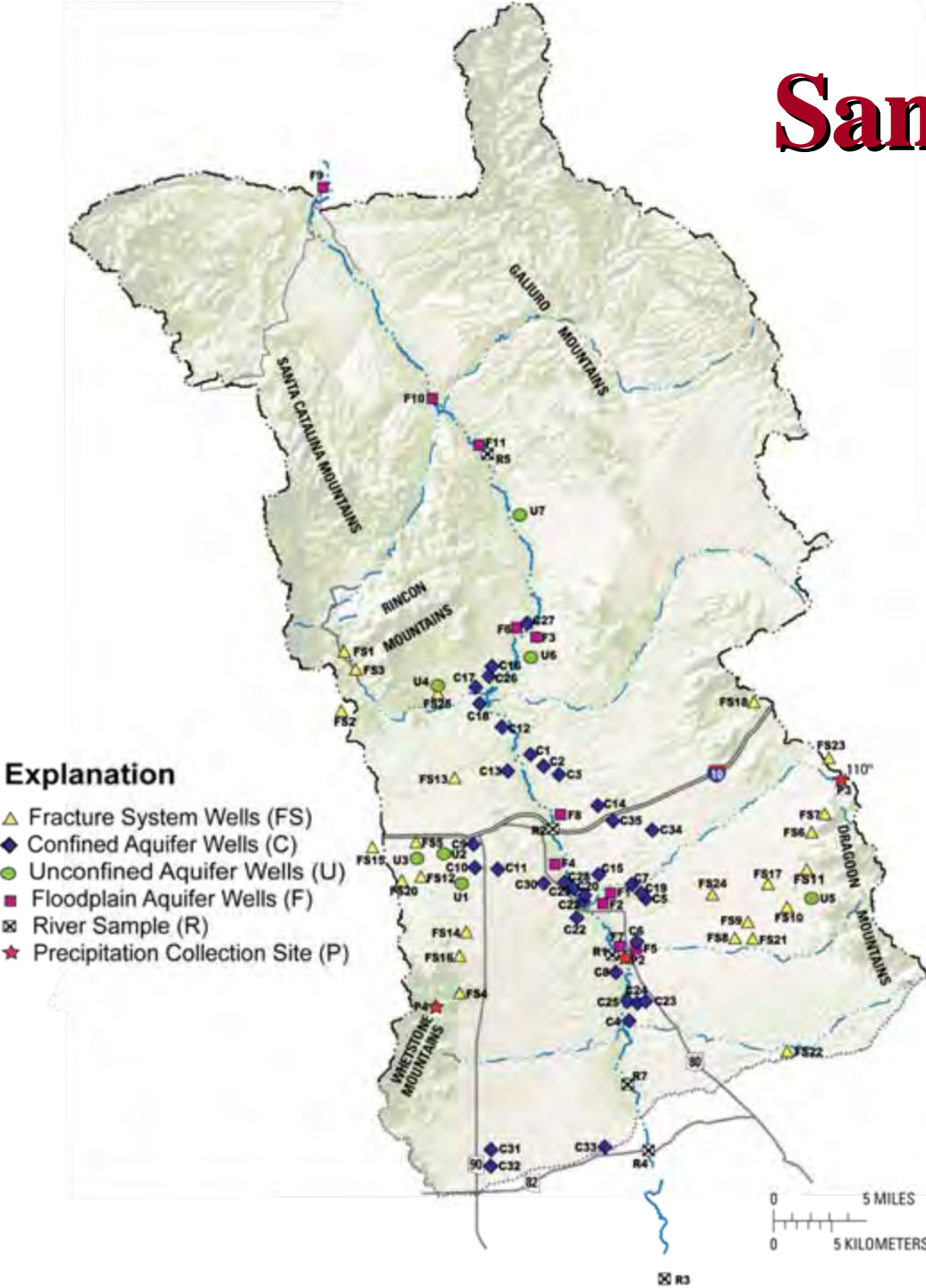
The news is generally good!

Isotopes help us to answer the following questions about groundwater in the Middle San Pedro basin:

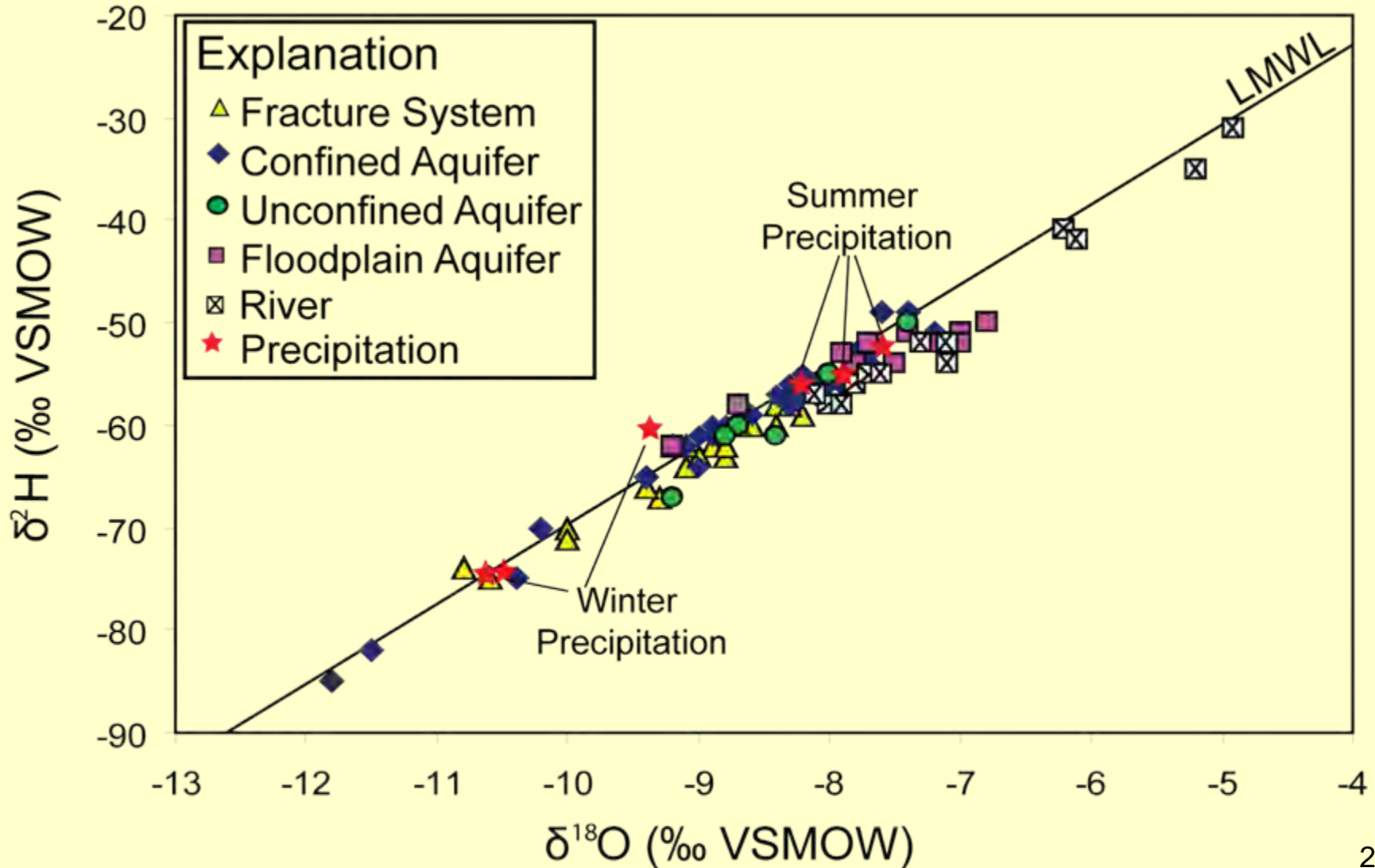
- 1. Where does recharge occur?**
- 2. Is recharge limited to summer or winter?**
- 3. Is the confined aquifer connected hydrologically to the flood plain aquifer?**
- 4. How long does water take to flow from the basin margins to the confined aquifer beneath the river?**

Sampling Strategy

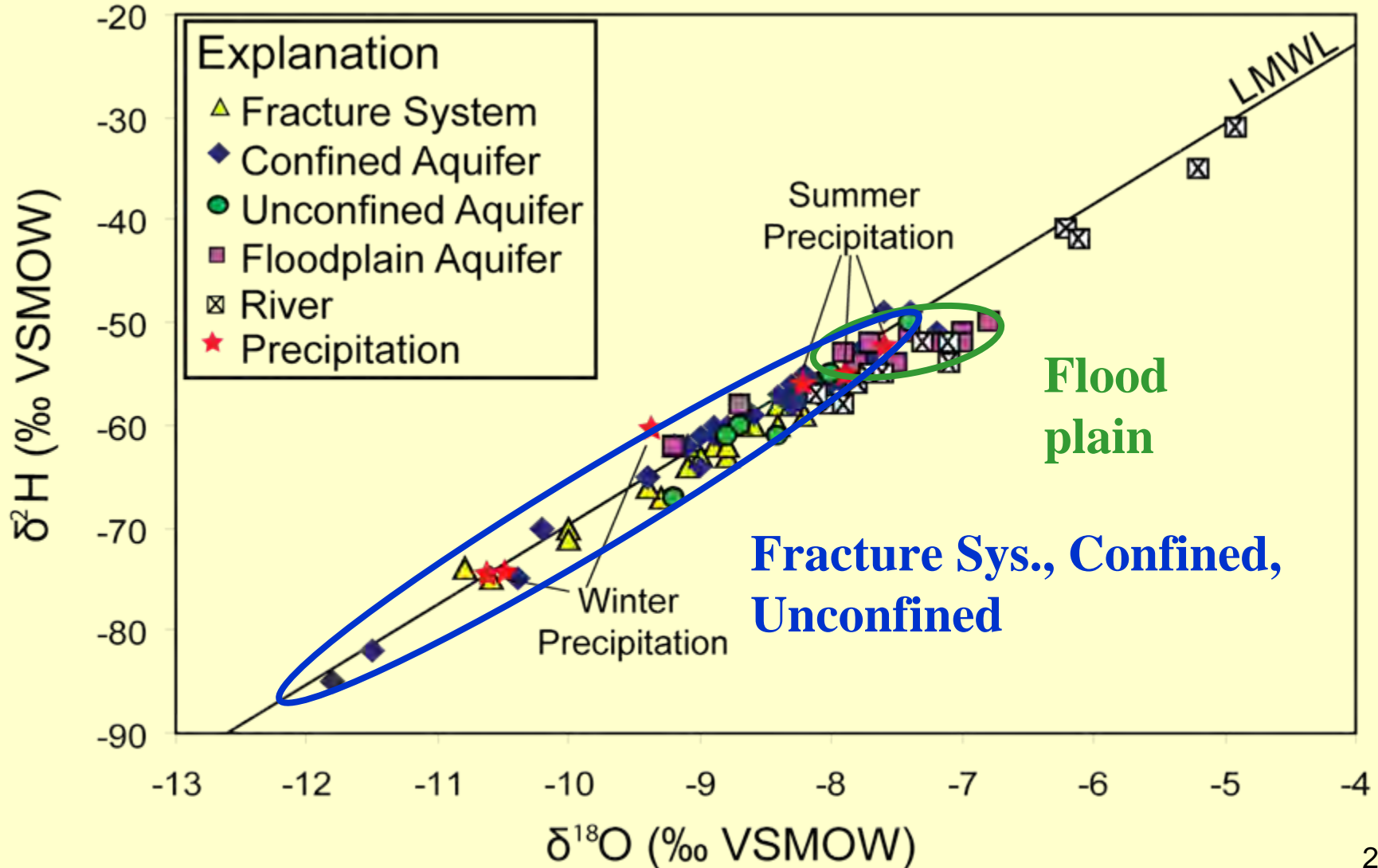
- Sampled groundwater from various points in basin, targeting transects, washes, and wells along the river
- Collected base flow of the river throughout the year
- Determined isotopic composition of precipitation from various elevations and different seasons
- Sampled wells of varying depths to target relationship between deep confined and shallow alluvial aquifer



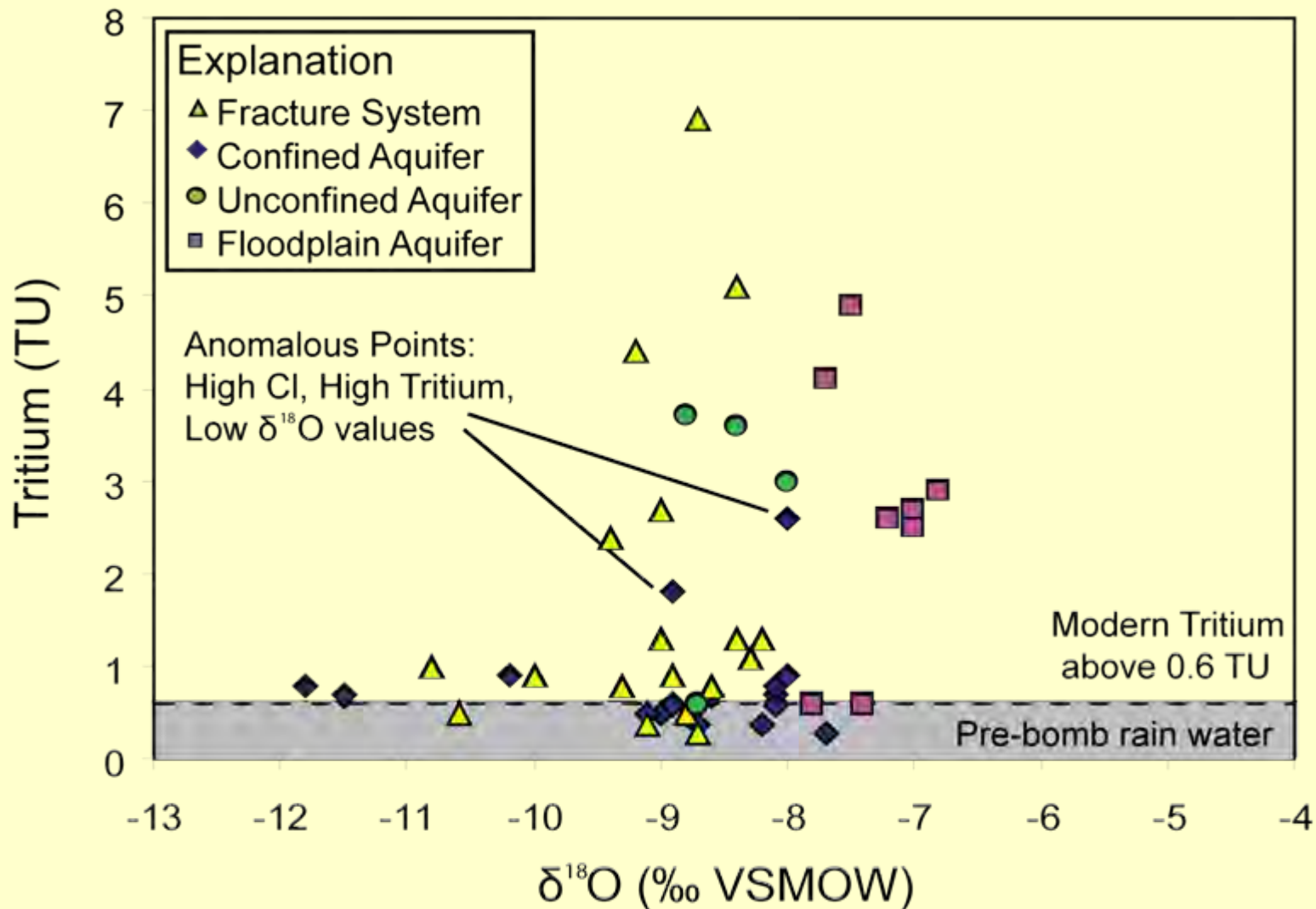
Stable Isotopes to Determine Areas of Recharge



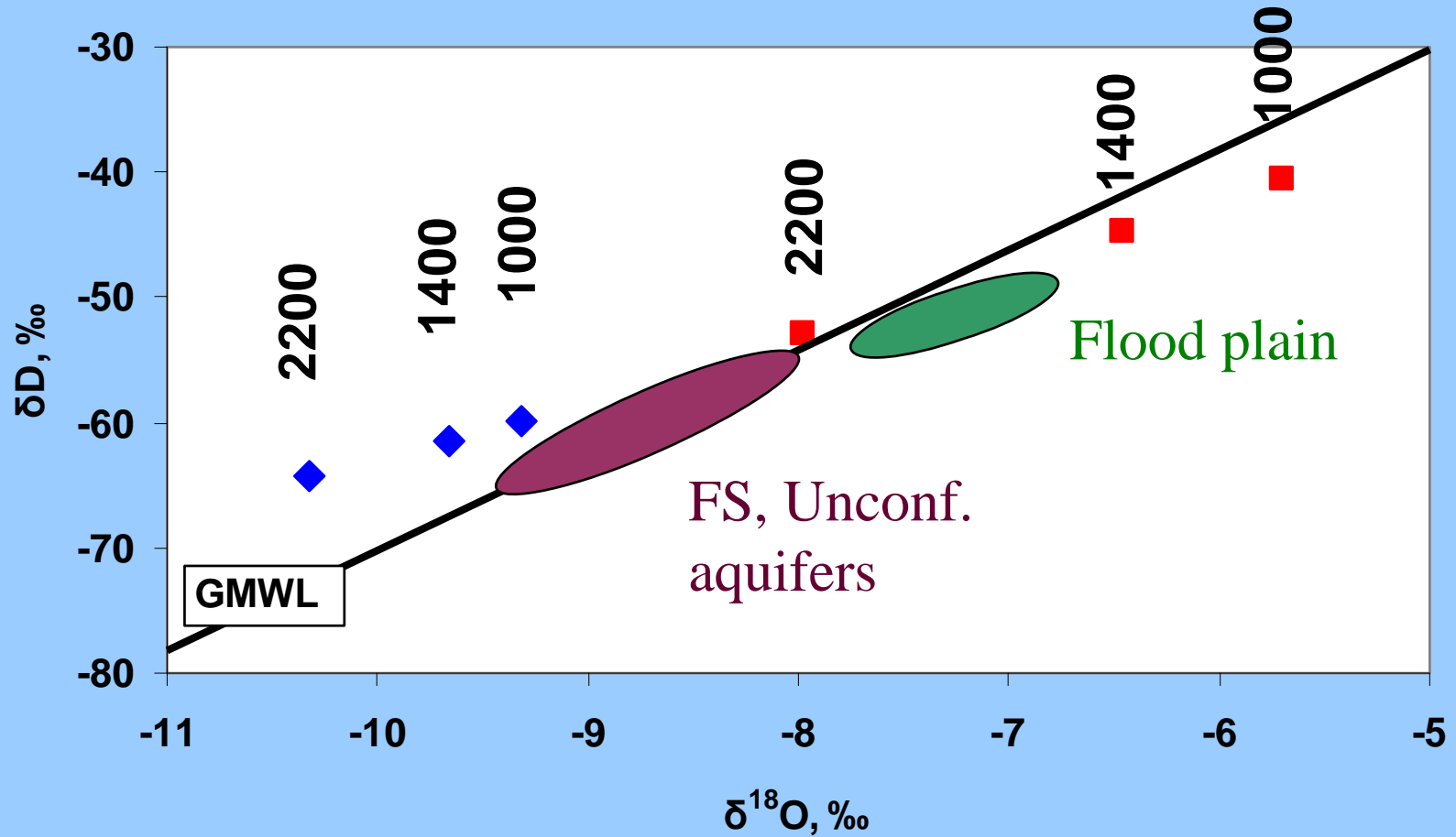
Stable Isotopes to Determine Areas of Recharge



Tritium and Oxygen Isotopes as Residence Time Tracers

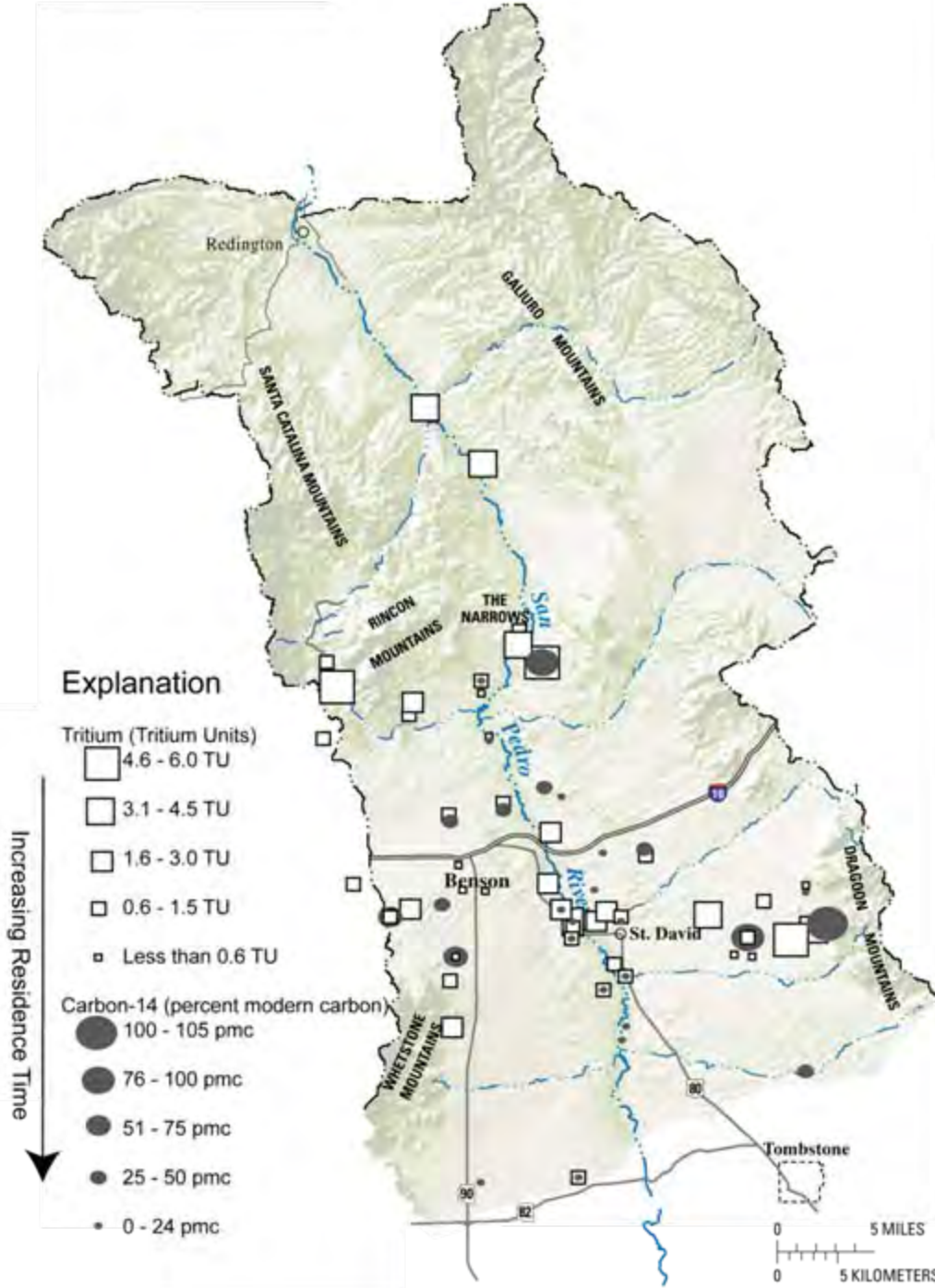


Seasonality of recharge



◆ Winter ■ Summer

Age Tracer Results

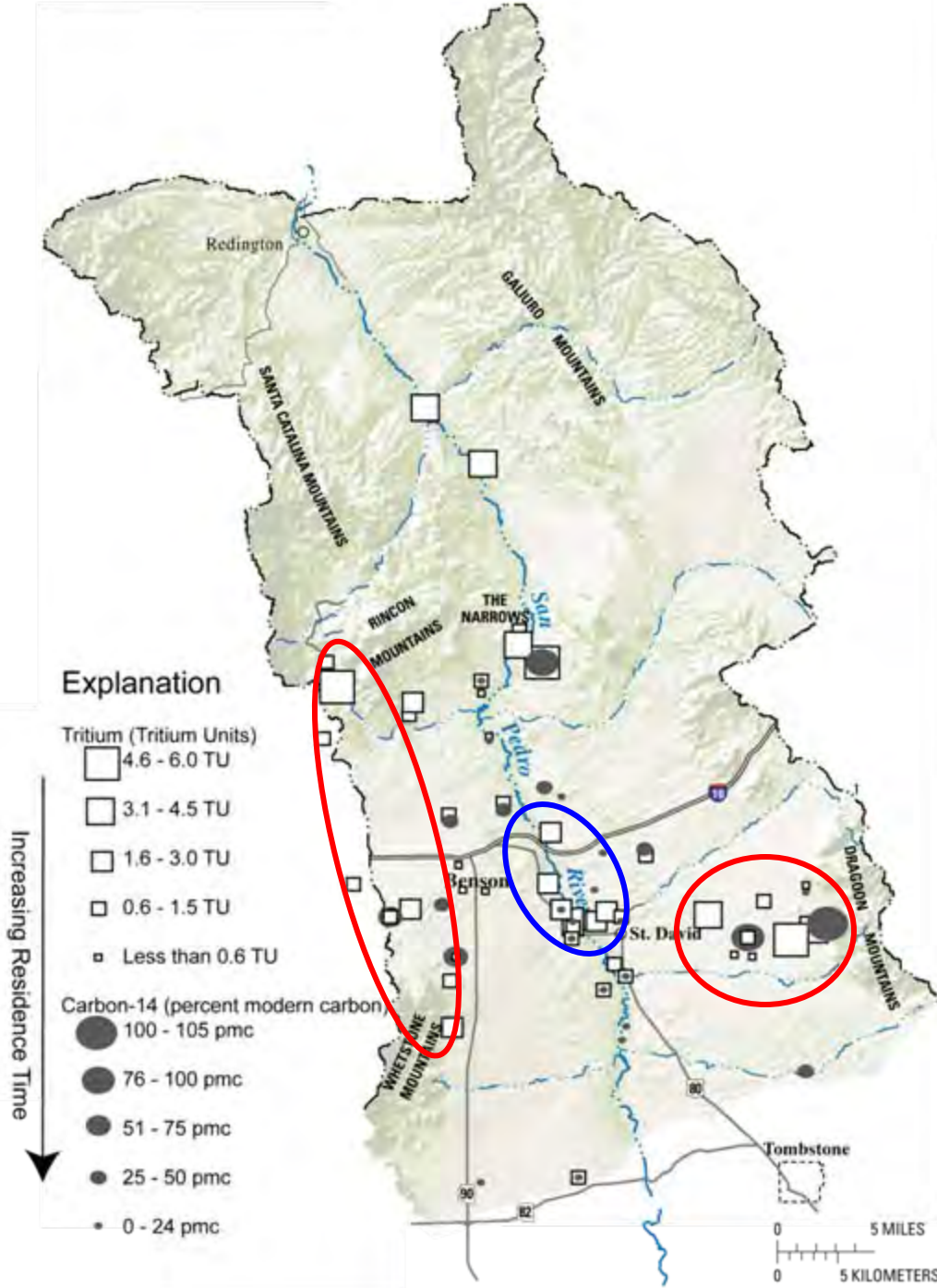


- Detectable tritium values found in shallow wells near river and in mountain system wells

- C-14 values high in mountain systems and decrease toward basin center

- Deep wells exhibit low C-14 values while shallow wells exhibit high C-14 values

Age Tracer Results

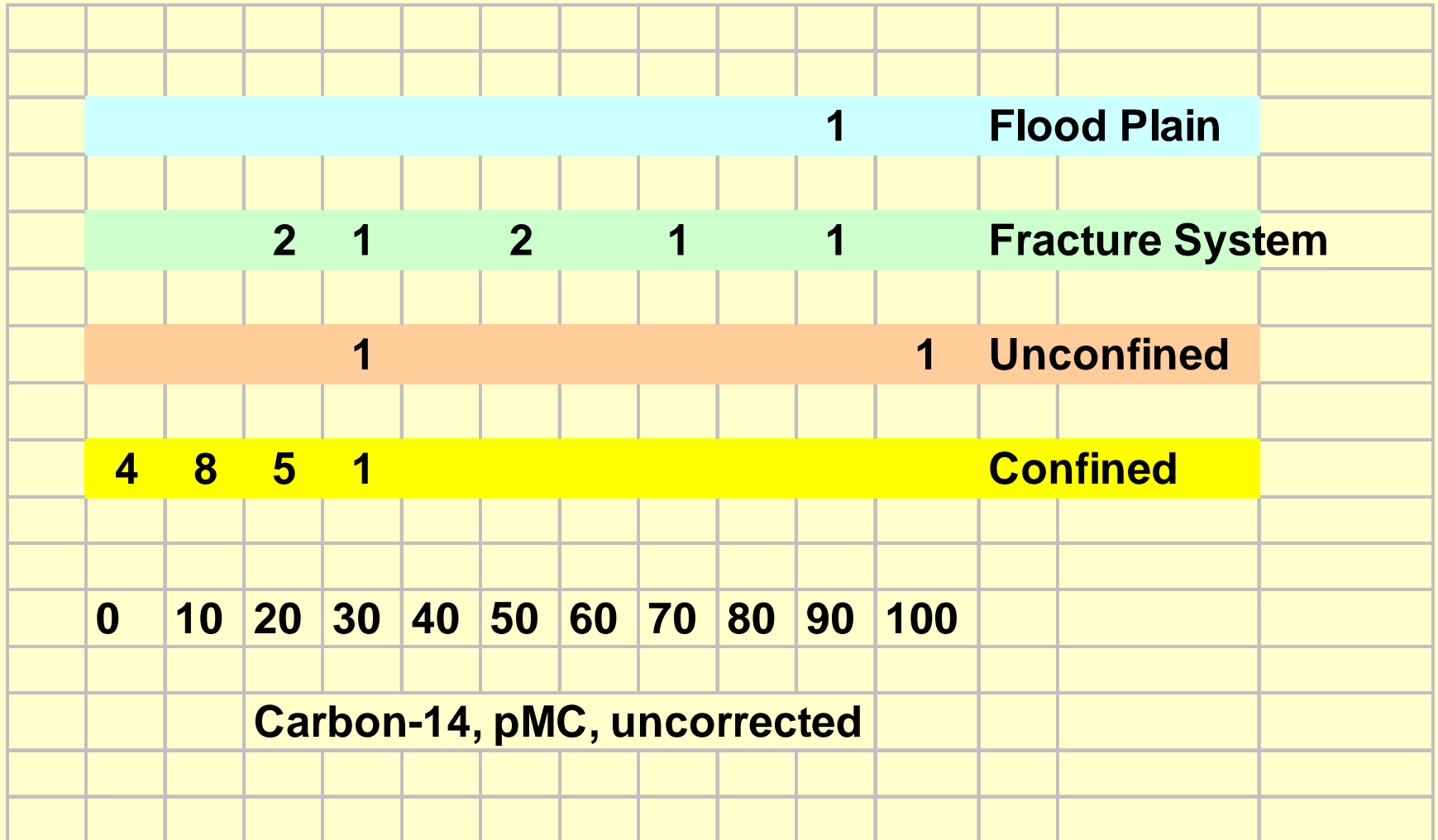


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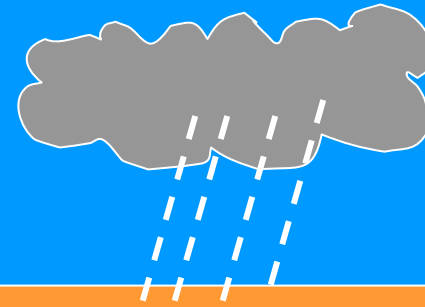
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Carbon-14 distribution



Atmosphere CO₂



Soil CO₂
High C-14

**Dissolves soil
gas**

SOIL

**Rock calcite
(CaCO₃)
no C-14**

**Dissolves
calcite**

Aquifer

**BASIN
SEDIMENT**

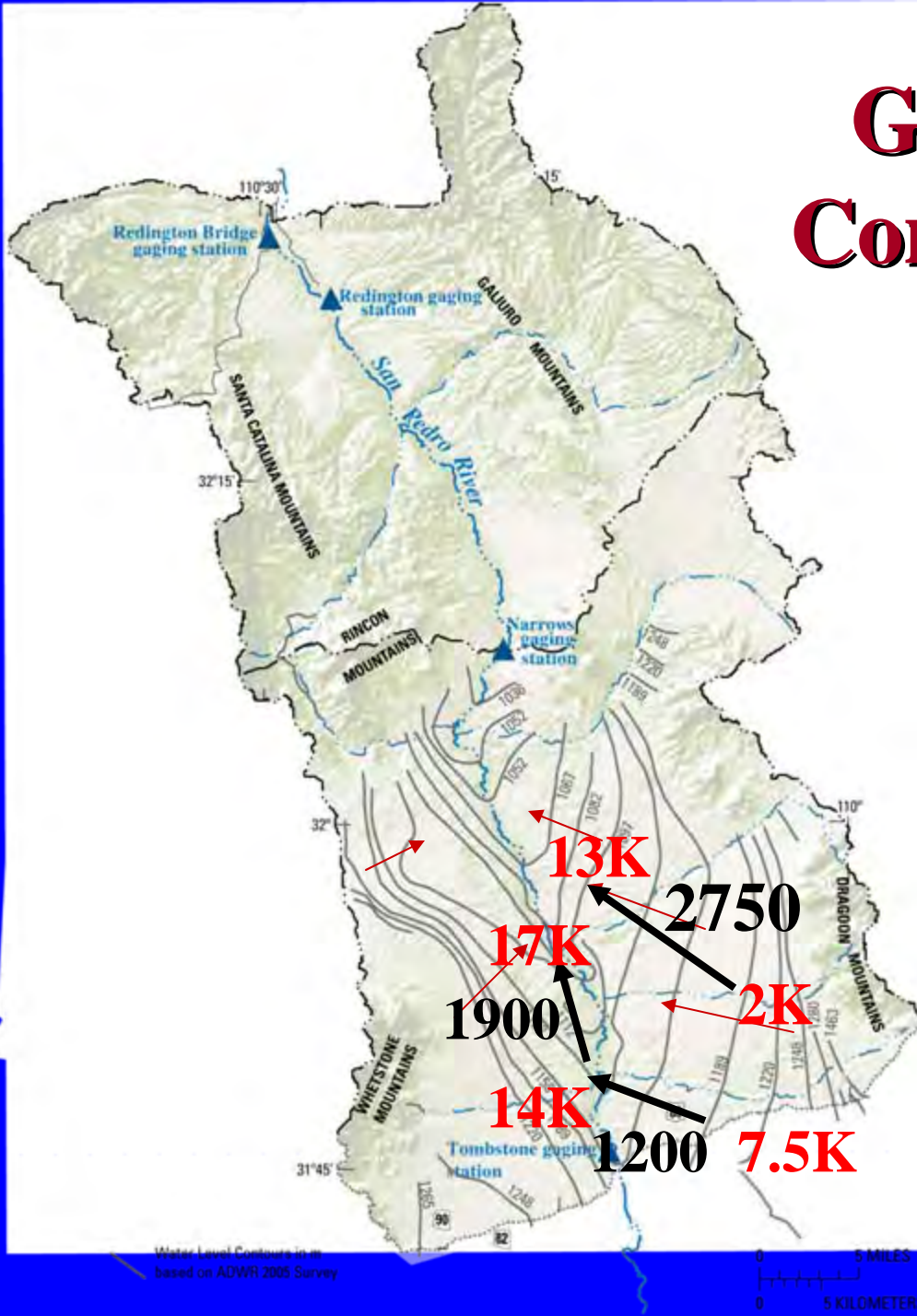


Groundwater Level Contours and Inferred Flow Directions

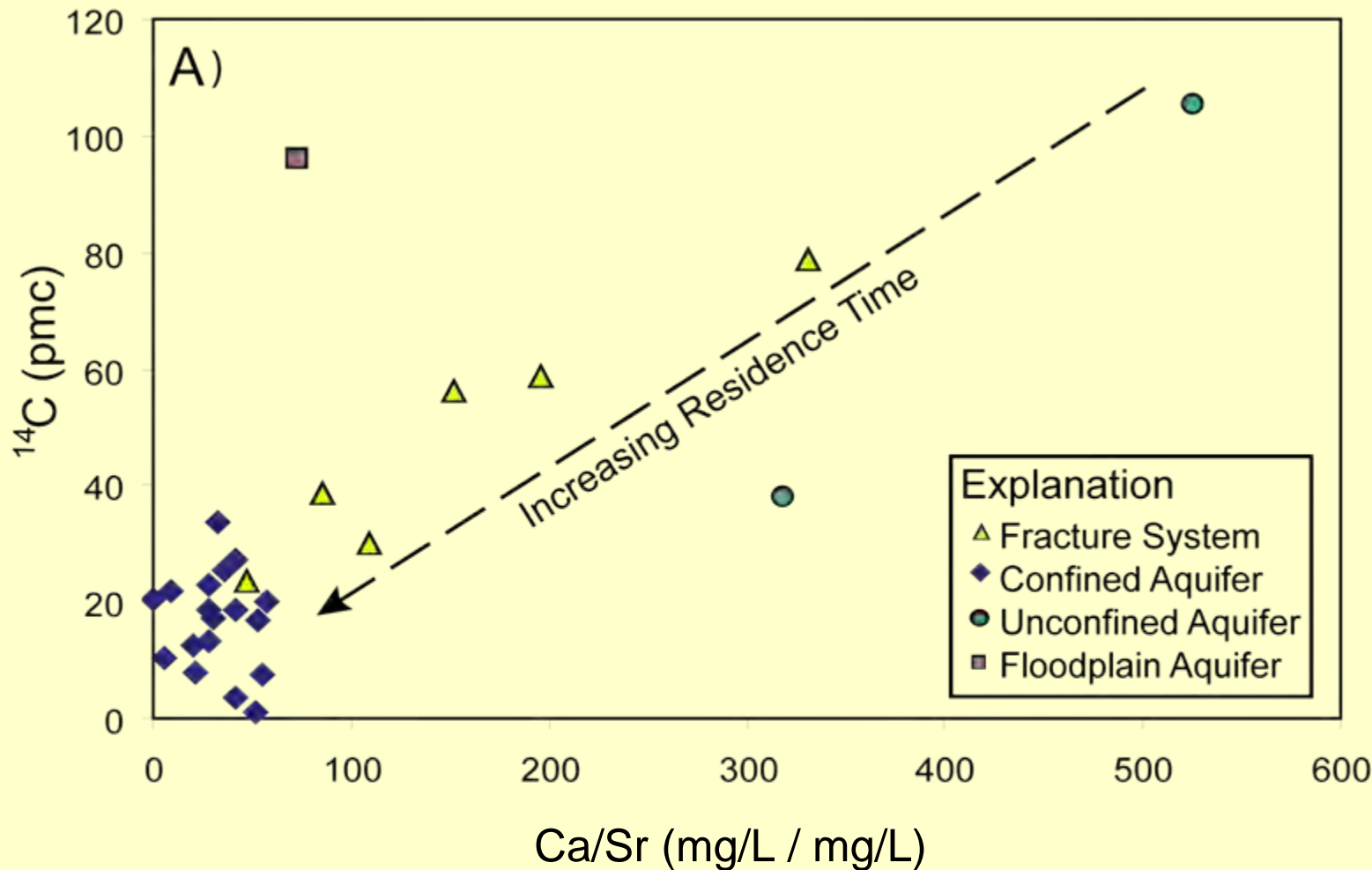
NETPATH – USGS
MODELING
PROGRAM

Uncorrected ages

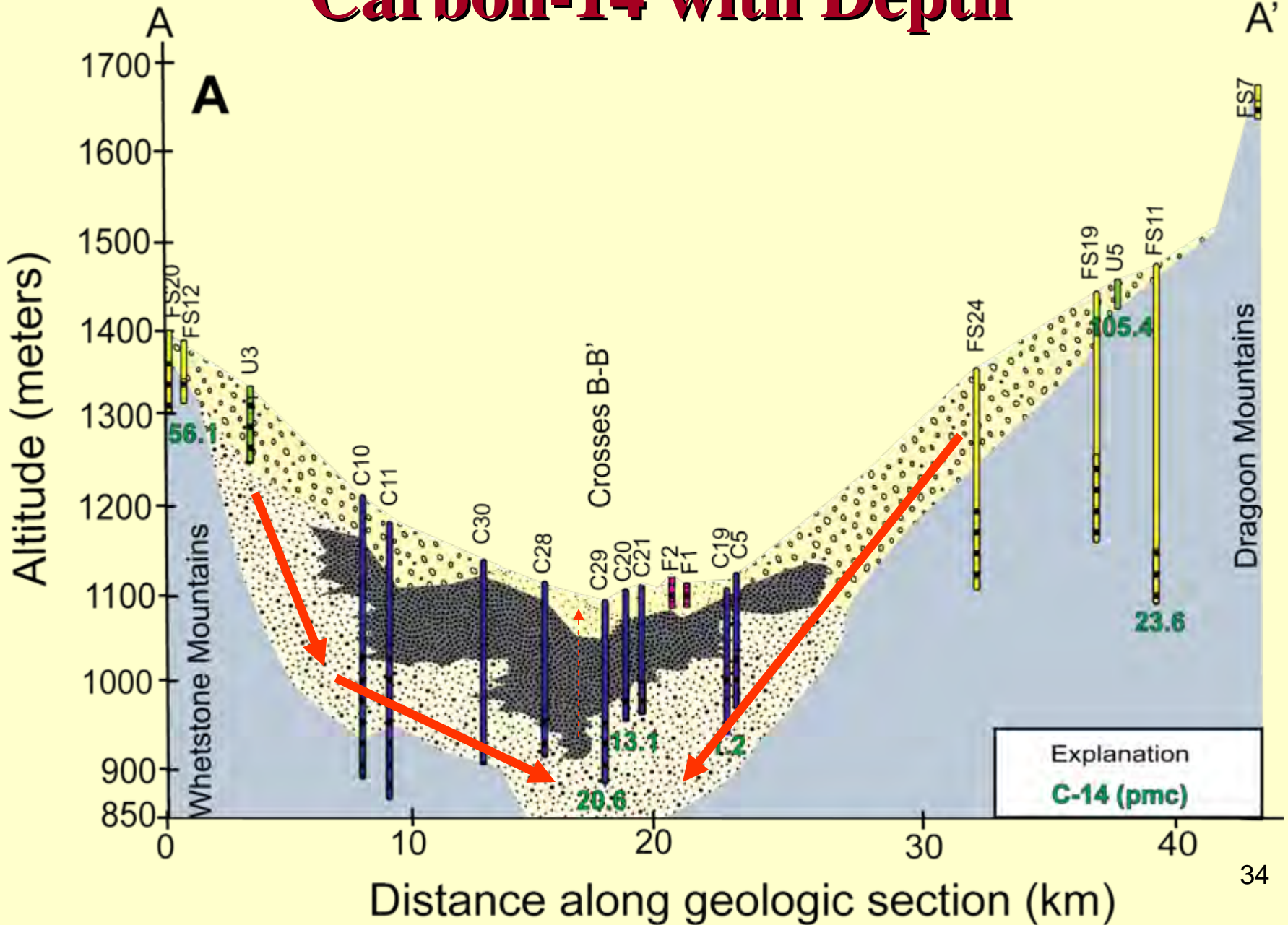
Modeled
(corrected) ages



Ca/Sr Ratios Compared with Traditional Age Tracers



Carbon-14 with Depth



Conclusions

1. Recharge to flood-plain aquifer from river, summer recharge dominant.
2. Recharge to fracture-system aquifer (and thence to confined aquifer) from basin margins, with winter recharge dominant.
3. Confined aquifer has little connection with flood-plain aquifer – expressed in O,H isotopes and tritium.
4. Water in the confined aquifer has been resident for thousands of years . In FS aquifer – some water resident only a few decades.