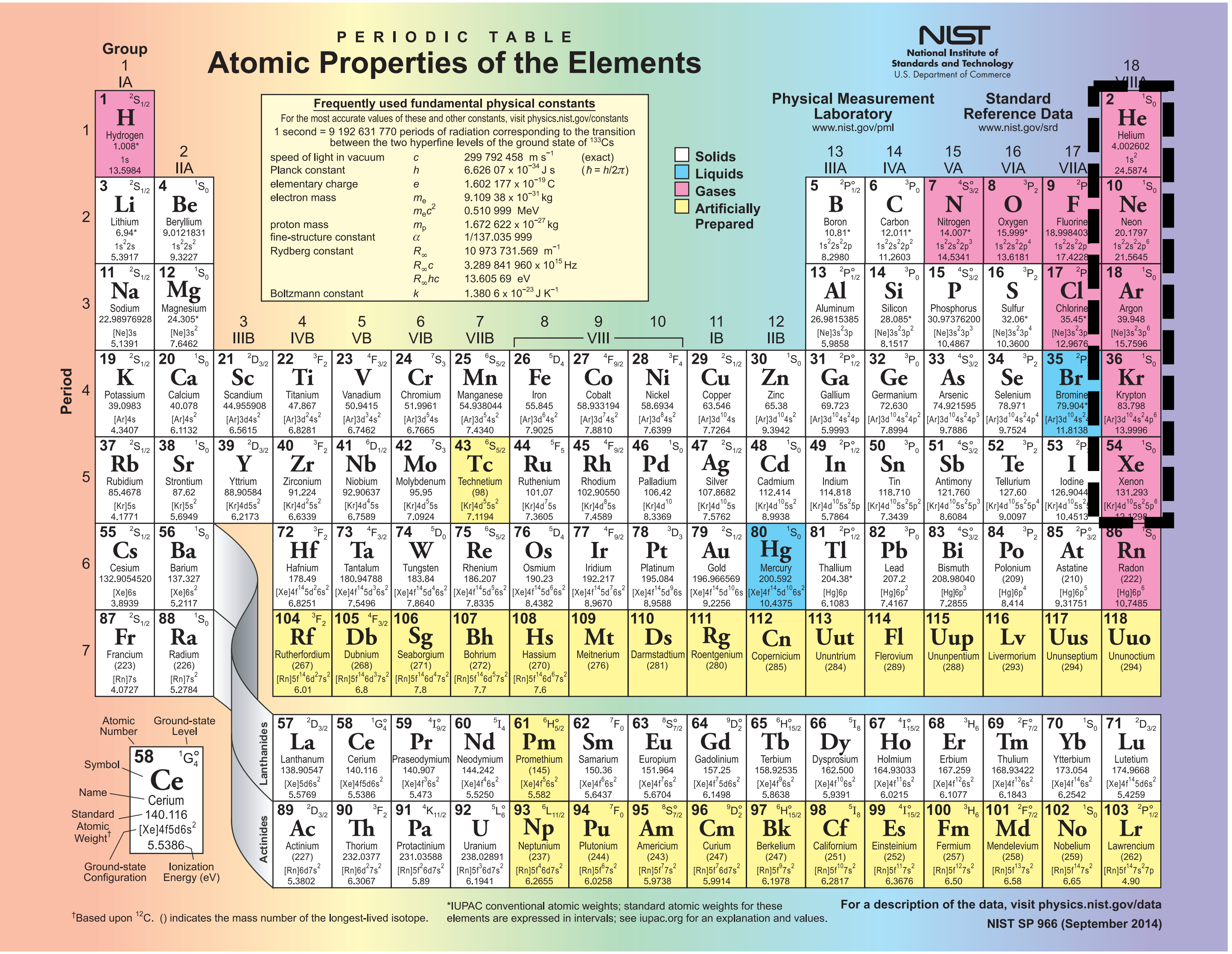
Noble Gases in Groundwater

EAR 419/619 Environmental Aqueous Geochemistry

What are noble gases?



Noble gases are INERT and STABLE

- Inert => they do not react with the reservoir rocks
- Stable => they do not undergo decay

- Noble gases are thus affected almost exclusively by physical processes, in particular, their transport in groundwater.

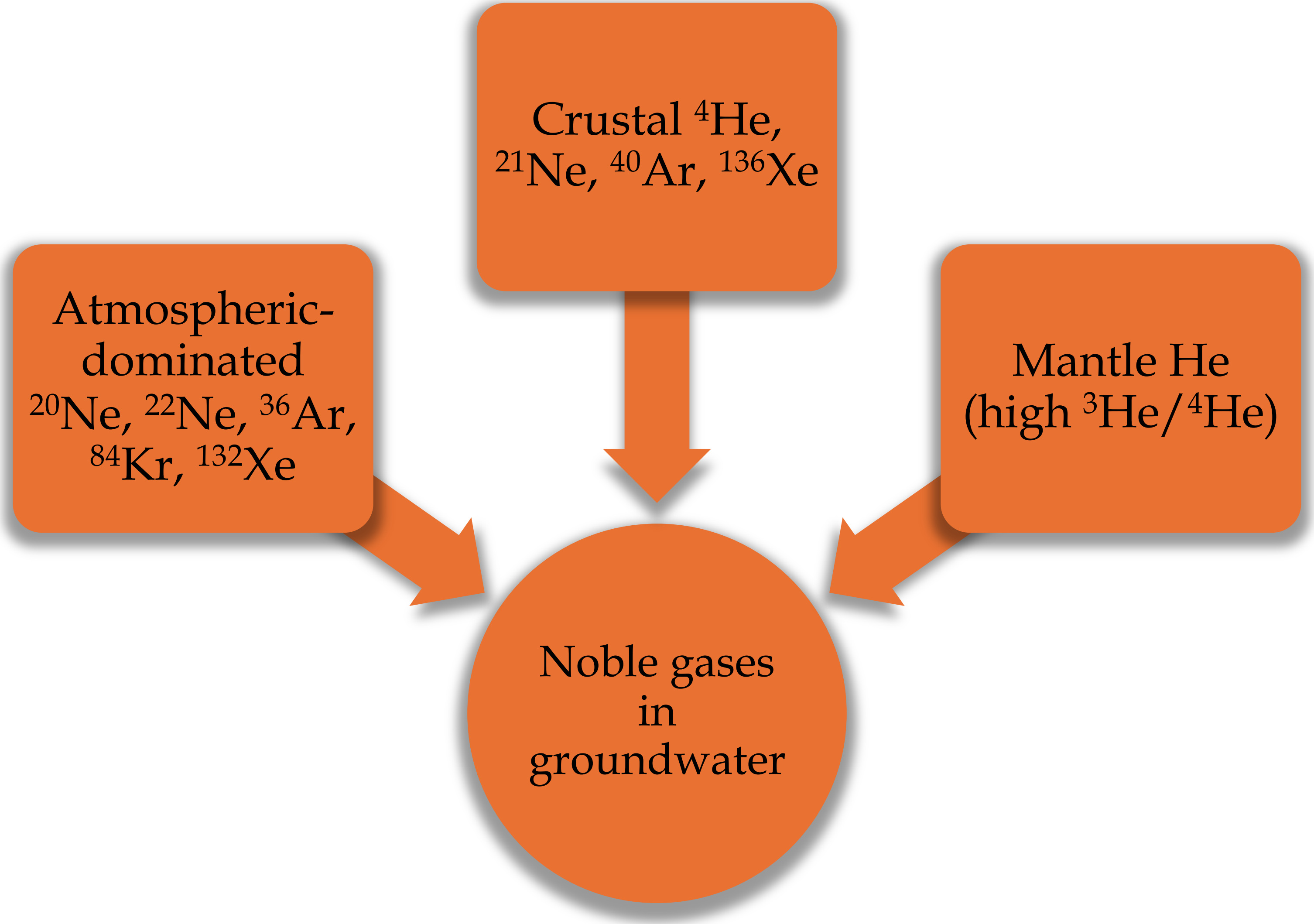
- This allows us to follow their path in groundwater for as long as they will remain in a particular groundwater flow system, even if they remain there for millions of years… these are two main characteristics of noble gases that make them excellent tracers.

In most of our groundwater studies we are mostly concerned with the following isotopes

- Helium (He): ^{3}He and ^{4}He
- Neon (Ne): ^{20}Ne, ^{21}Ne, ^{22}Ne
- Argon (Ar): ^{36}Ar, ^{38}Ar, ^{40}Ar

- Krypton (Kr) and Xenon (Xe) have also many isotopes but most of our studies look mainly at their absolute concentrations to help decipher the temperature of the ground at the moment recharge occurred (for paleoclimatic reconstructions). Maybe more on Kr and Xe isotopes some time later.

Noble gas systematics in groundwater



Noble gas systematics in groundwater

- Atmospheric
  - these correspond to the noble gases dissolved in the rainwater or as parts of air bubbles which infiltrates and is subsequently incorporated in aquifers)
- Crustal
  - in-situ production: noble gases that are produced in the rock reservoir of the aquifer itself, i.e., these noble gases are produced inside the aquifer itself)
  - external origin: noble gases that are produced at greater depths, either in deeper sedimentary layers or deeper in the crystalline crust and that are subsequently transported into the aquifer)
- Mantle
  - noble gases originate directly in the mantle and are subsequently transported into the aquifer)

Atmospheric noble gases

- ASW – stands for Air Saturated Water
  - It is water that is in equilibrium with air. So, we refer all the time to rainwater which recharges the aquifers as ASW because rainwater is in equilibrium with air.

- Excess air – EA
  - This refer to noble gases encompassed in air bubbles. Air bubble can be mixed into groundwater as the water table fluctuates.

Terrigenic noble gases

- Radiogenic noble gases:
  - Noble gases that are formed as a direct result of the natural, spontaneous decay of U, Th, and K and their daughter products (e.g., ^{4}He, ^{40}Ar).
  - ^{235}U, ^{238}U, ^{232}Th → ^{4}He
  - ^{40}K → ^{40}Ar

- Nucleogenic noble gases:
  - Noble gases that result from interactions between stable nuclei (e.g., Li, O, Mg) and decay related particles (e.g., alpha particles).
  - Examples of nucleogenic noble gases are ^{3}He and ^{21}Ne.
  - ^{3}He – it requires the presence of U and Th + Li (lithium)
  - ^{21}Ne - it requires the presence of U and Th + O and Mg

Terrigenic noble gases continued

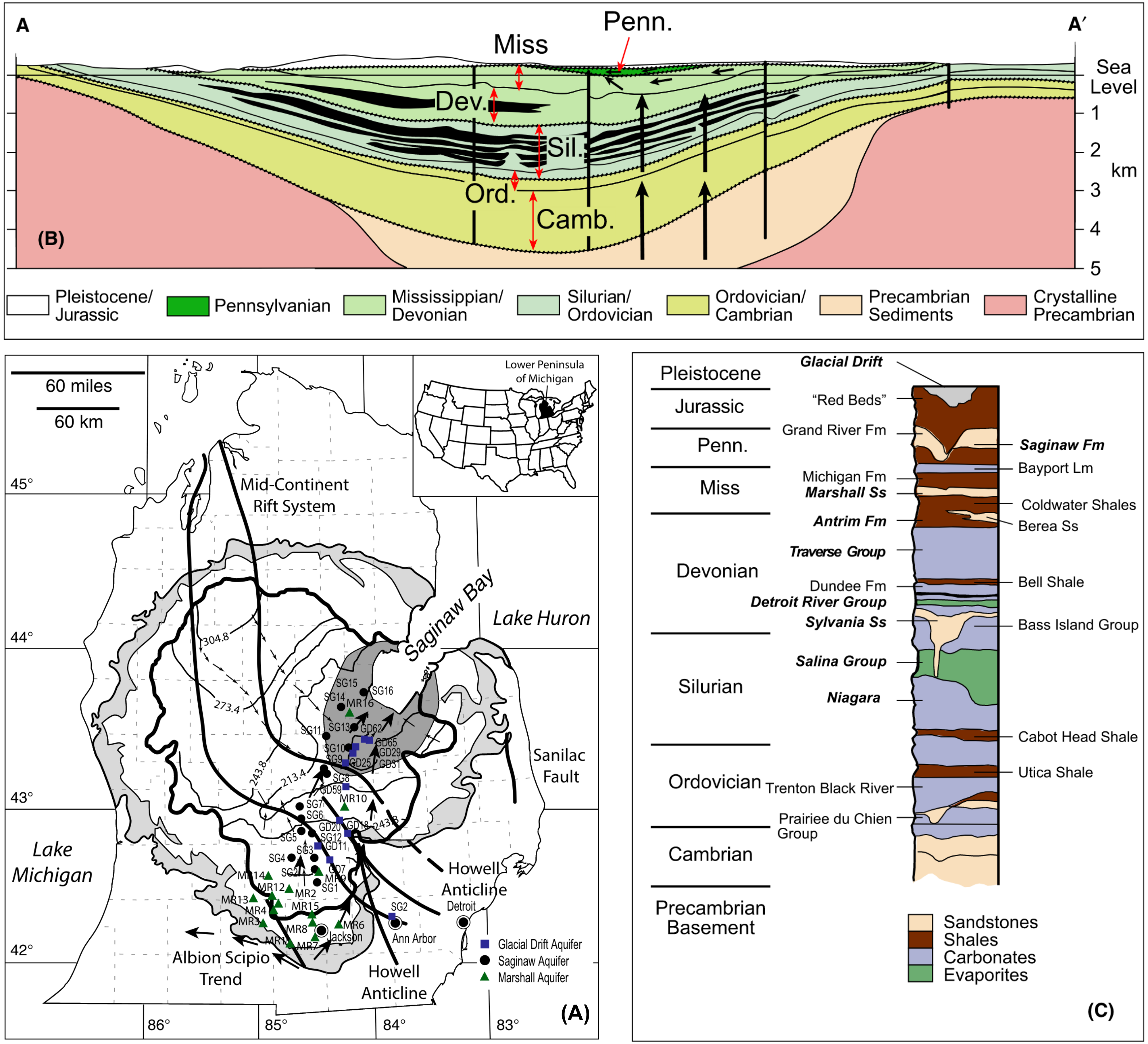
Production in the rocks of:

- ^{20}Ne
- ^{22}Ne
- ^{36}Ar
- ^{38}Ar

can be considered, to a first approximation,

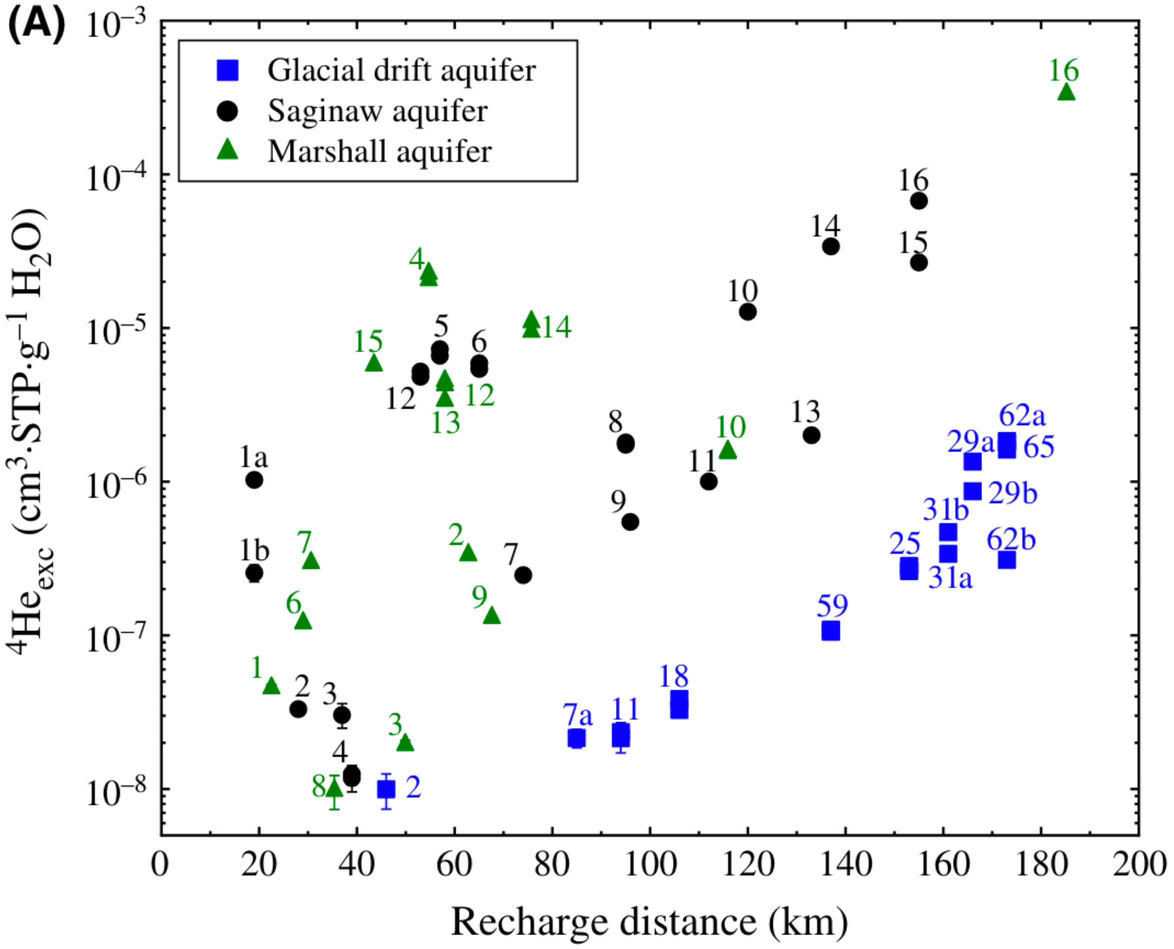
negligible

Case study 1: Michigan Basin



Wen et al. (2015)

Accumulation of terrigenic helium in MI groundwater

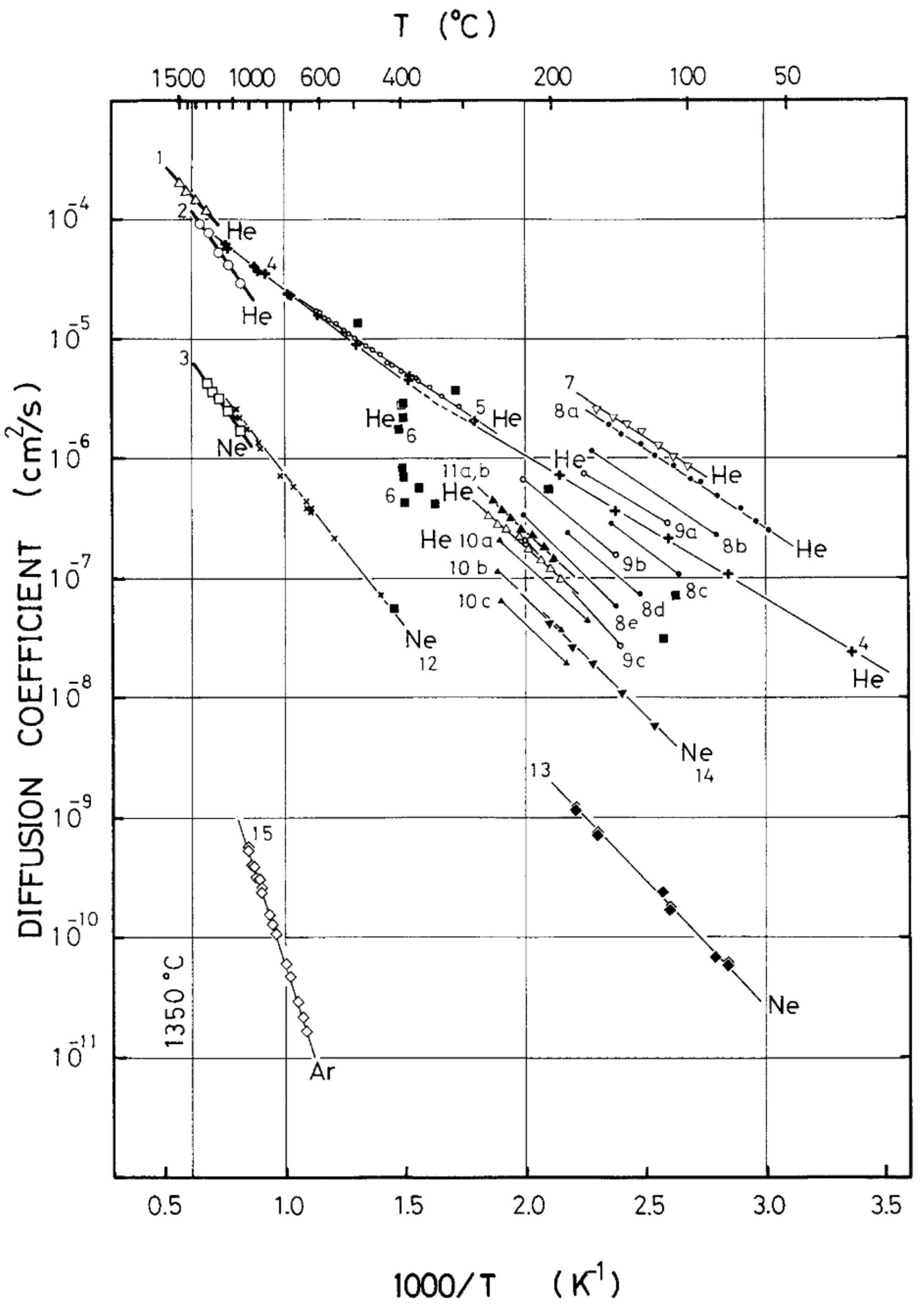


Wen et al. (2015)

Noble gas transport in groundwater

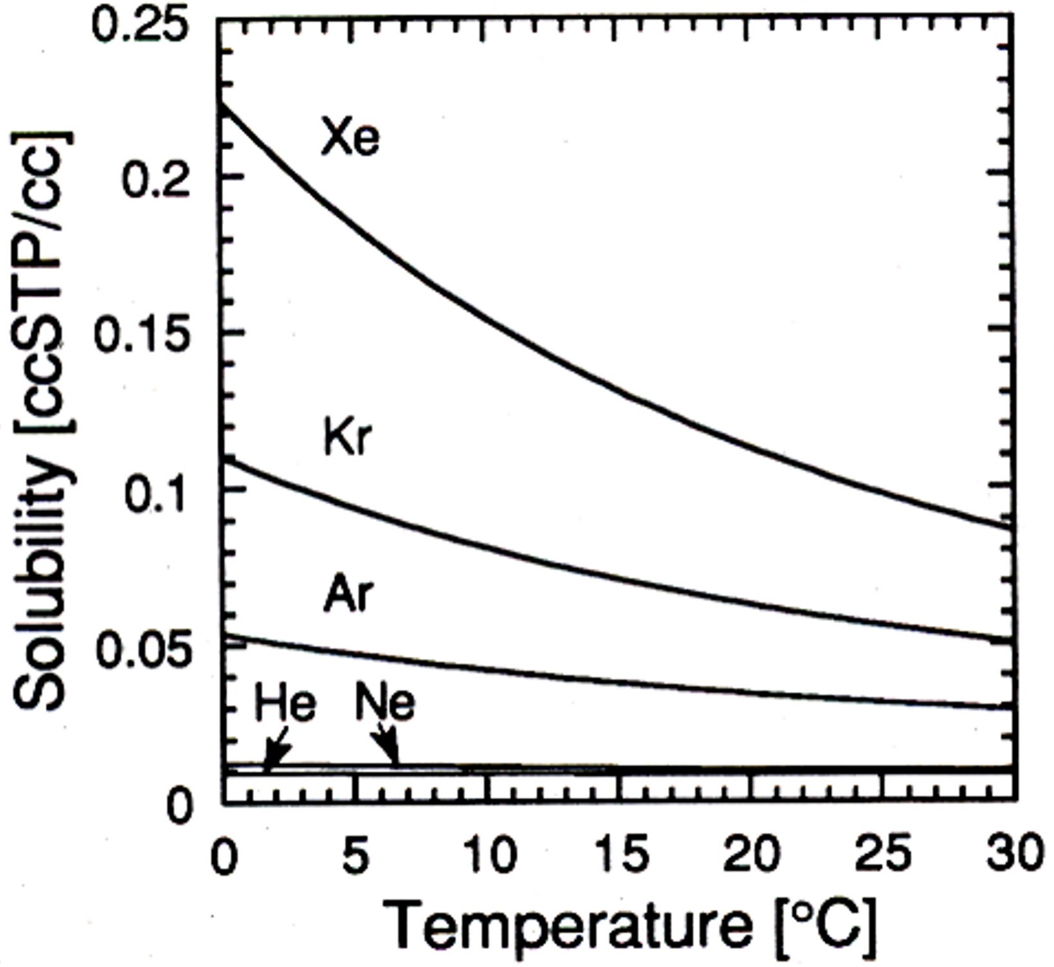
- Advection
  - In this case, water alone is responsible for their transport => they will move as fast or as slowly as groundwater; in this case, noble gases have a passive role
- Dispersion
  - Noble gases will move faster in certain directions due to a mixing phenomena that results from different microscopic velocities inside the pores - here too, water is the mechanism responsible for their movement
- Molecular diffusion
  - Water can be either at rest (immobile) or mobile
  - Noble gases move due to a concentration gradient, i.e., they will move from areas where the concentration is higher to areas where the concentration is lower – in this case, noble gases have the ability to move even if the water is immobile.

Noble gas diffusion coefficient is a function of temperature



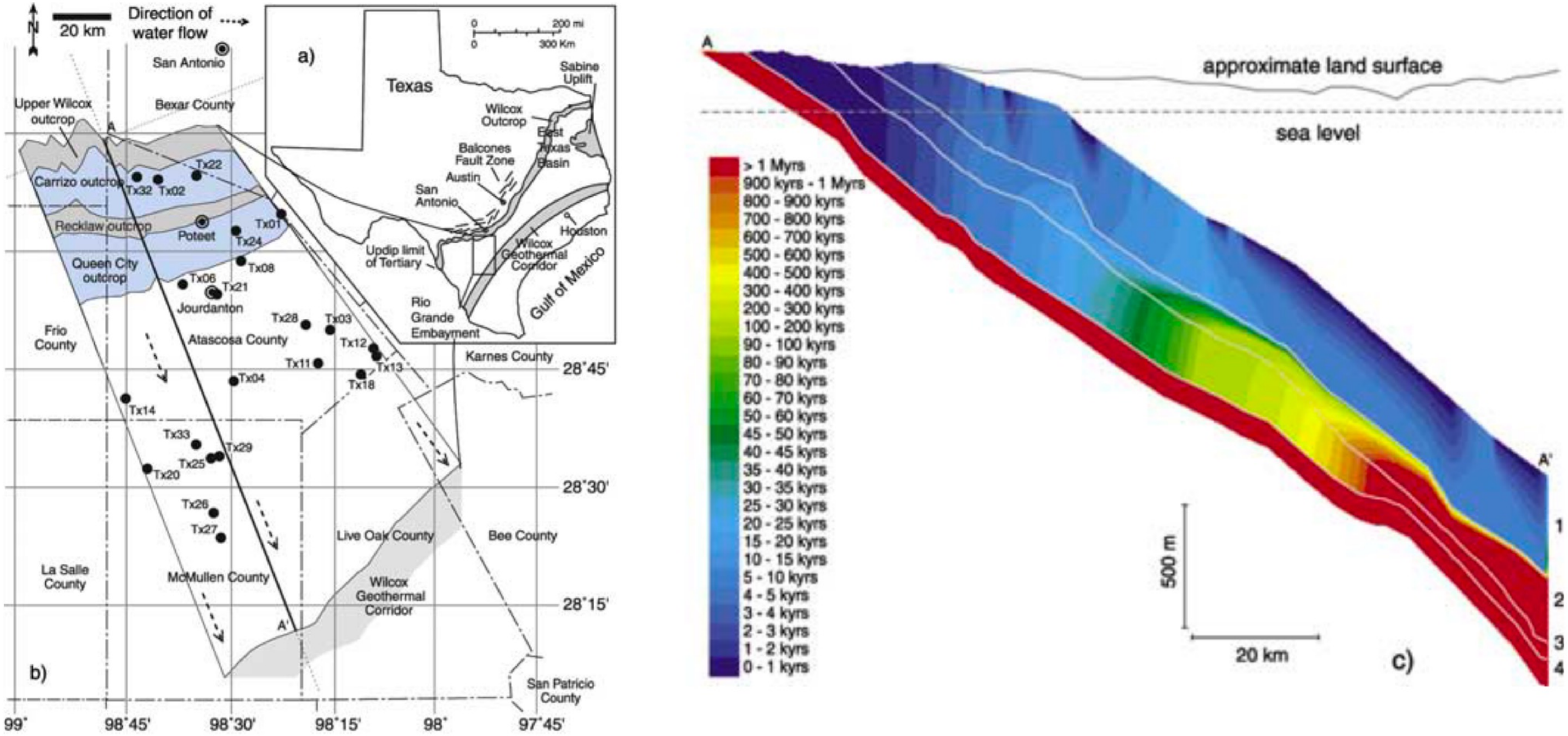
Ozima and Podosek (2002)

Noble gas solubility in water is a function of temperature



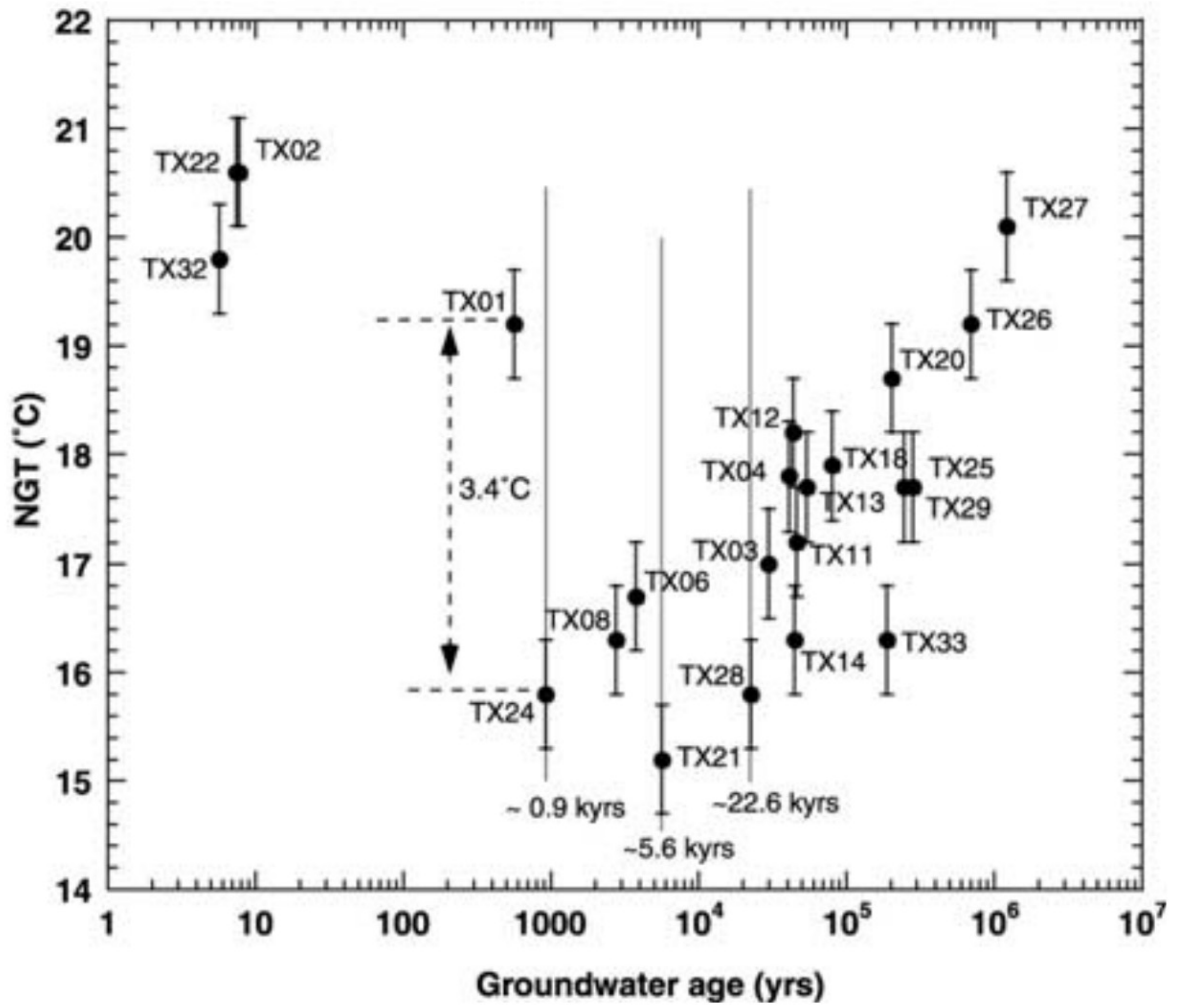
Noble gas concentration in water is a function of temperature, gas partial pressure in the gas phase, and salinity

Case study 2: Carrizo Aquifer in Texas



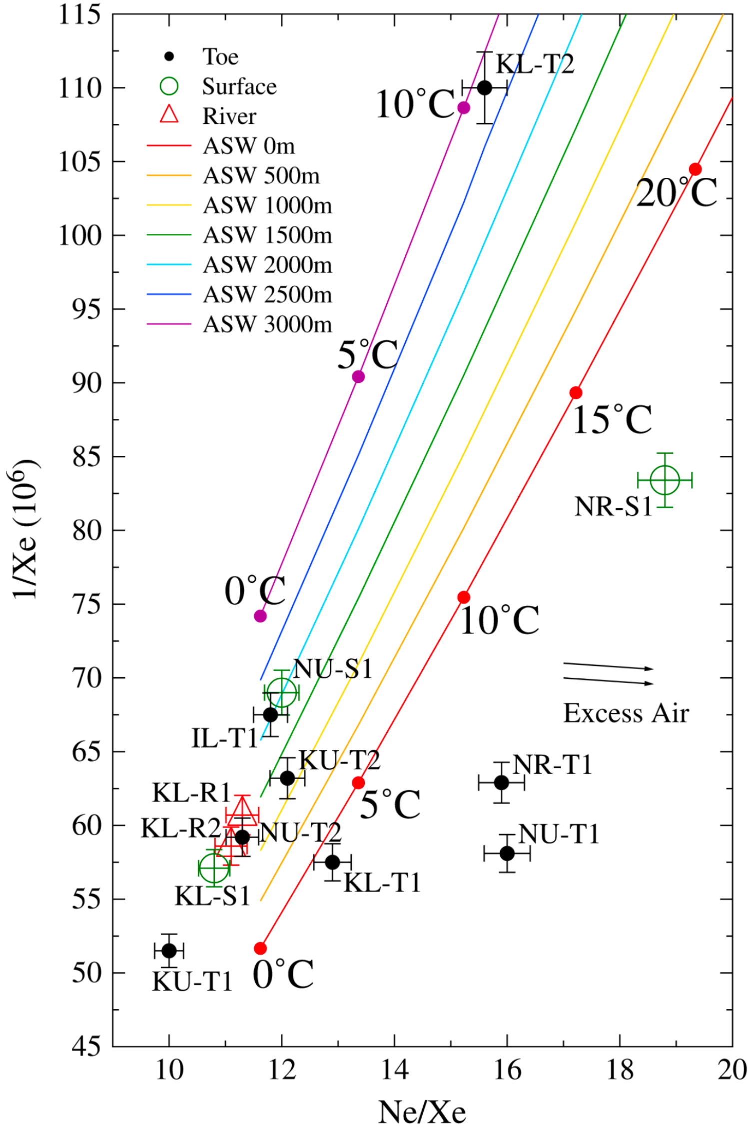
Castro and Goblet (2003)

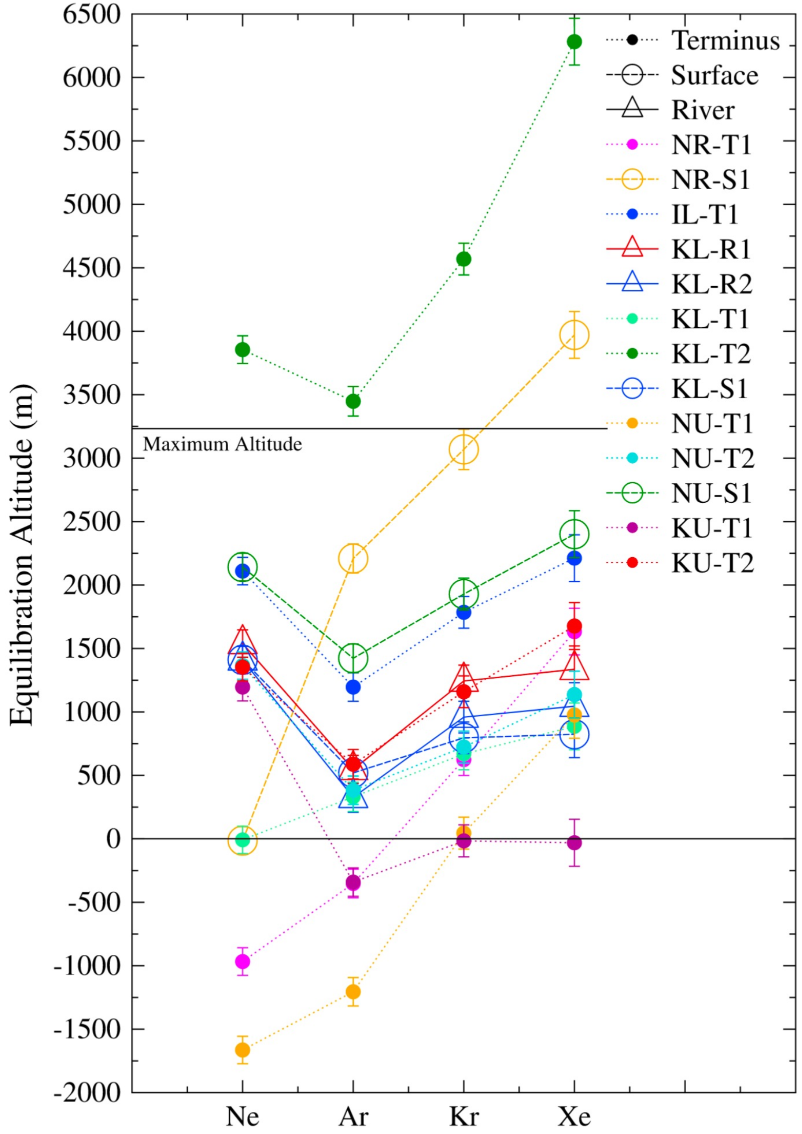
Case study 2: Carrizo Aquifer in Texas



Castro and Goblet (2003)

Case study 3: Greenland meltwater





Niu et al. (2015)

More noble gas systematics in groundwater

- Atmosphere (ASW)
  - The He isotopic ratio is generally presented as R/Ra, where R=$^{3}He/^{4}He$ and Ra is the atmospheric $^{3}He/^{4}He$ ratio (Ra = 1.384 * 10^{-6}).

R/Ra= 1 $^{21}Ne/^{22}Ne$= 0.029 $^{20}Ne/^{22}Ne$= 9.8

$^{38}Ar/^{36}Ar$=0.1869 $^{40}Ar/^{36}Ar$ = 295.5

- Crustal (radiogenic/nucleogenic component)

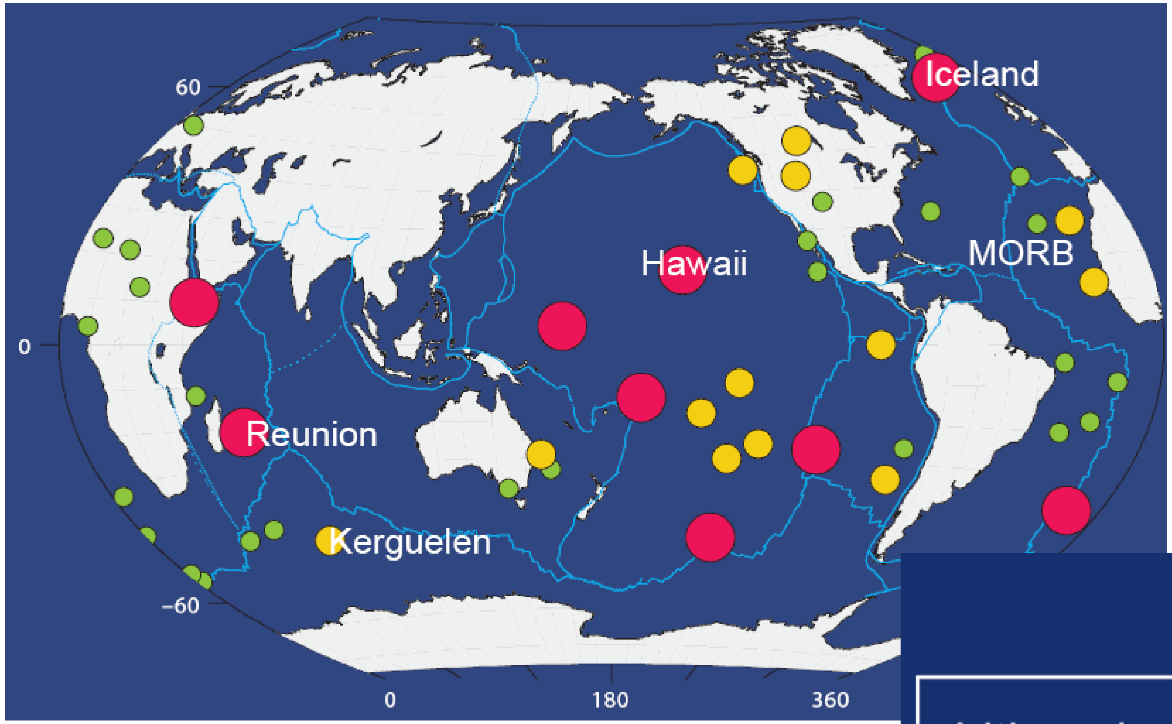
$0.02 \leq R/Ra \leq 0.05$ $^{21}Ne/^{22}Ne > 0.0290$ $^{40}Ar/^{36}Ar > 295.5$

- No values are given for crustal $^{20}Ne/^{22}Ne$ nor $^{38}Ar/^{36}Ar$. Why?

More noble gas systematics in groundwater

- Mantle
  - He: ~8≤R/Ra≤~35 ("pure" mantle component)
    - ~8 – "pure mantle" He component in Mid Ocean Ridge Basalts (MORBs)
    - ~35 - "pure mantle" He component in Ocean Island Basalts (OIBs) (e.g., Hawai)

Mantle structure and convection models

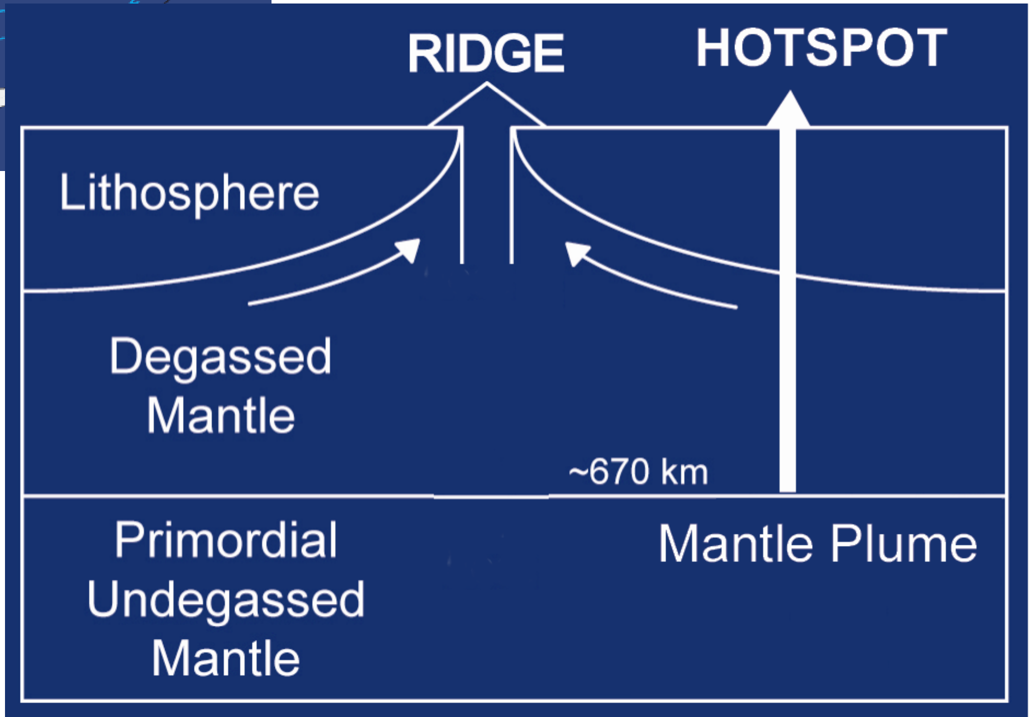


Hotspots (OIBs) around the world
(Courtillot et al., 2003)

R/Ra of MORBs (~8) versus
OIBs (~35)

Classic 2-layered mantle model

MORBs **OIBs**



More noble gas systematics in groundwater

- Mantle
  - Ne: $9.8 < {}^{20}Ne/{}^{22}Ne \leq 13.8$
    - ${}^{20}Ne/{}^{22}Ne = 13.8$ is the most “pure” Ne mantle component. It represents the most ancient Ne component in the Earth. We refer to it as being a “primordial or solar” component.

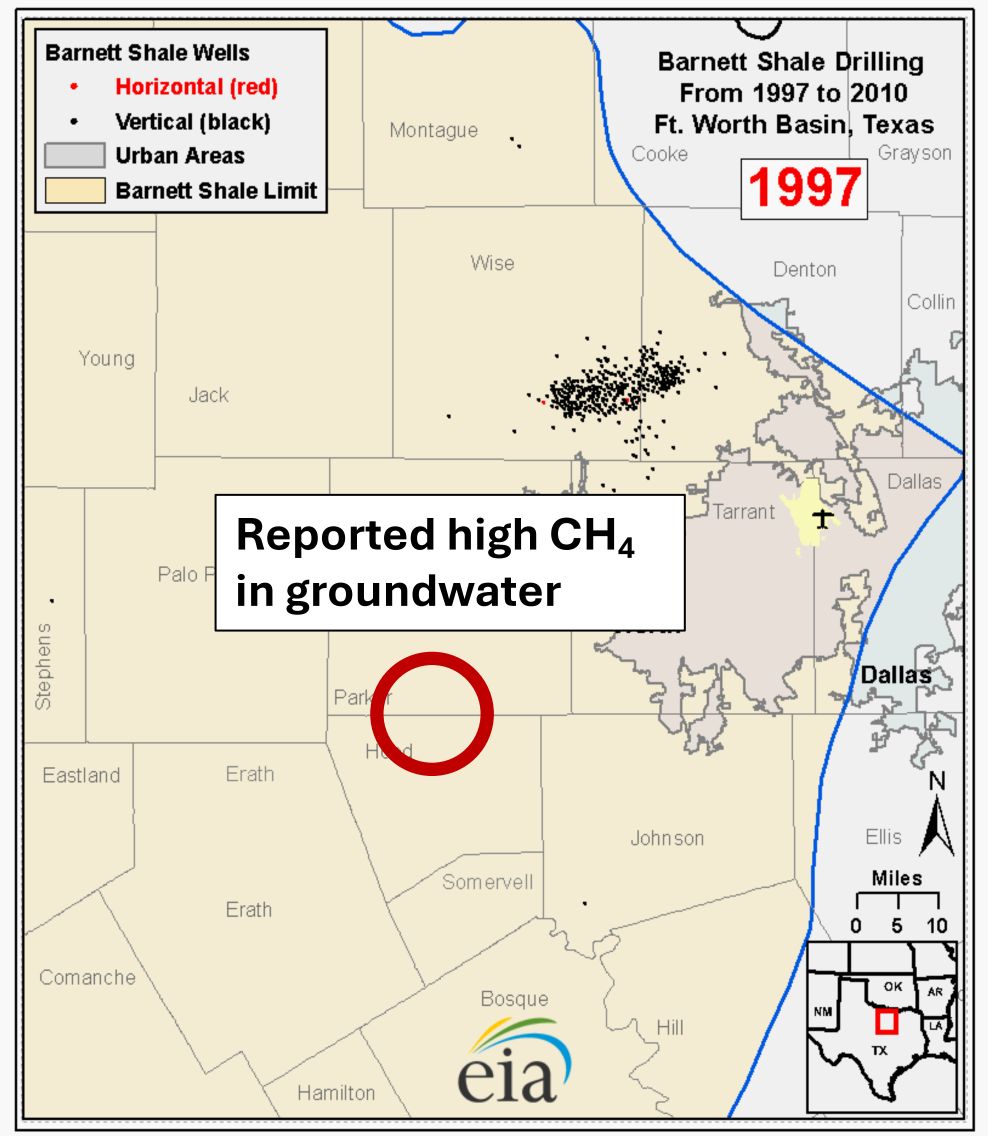
  - Ar: Not well known… we can simply say that

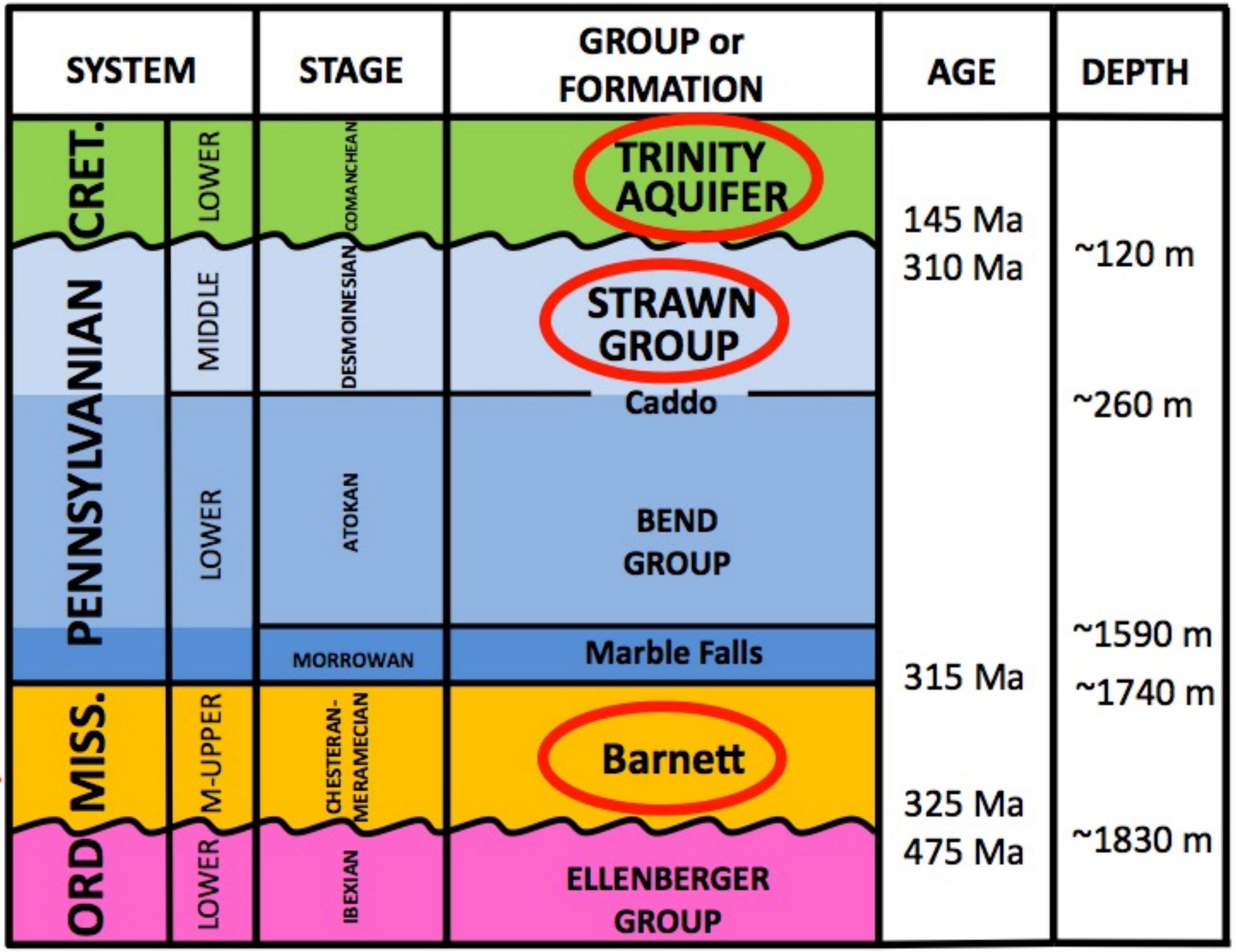
$${}^{40}Ar/{}^{36}Ar > 295.5$$

Take-away messages

- ^{36}Ar and ^{38}Ar are almost entirely atmospheric; thus, their concentrations in groundwater as well as $^{38}Ar/^{36}Ar$ isotopic ratios do not change over time
- In most groundwater systems, most of ^{20}Ne is of atmospheric origin; when this happens, ^{20}Ne concentration remains unchanged over time
- ^{20}Ne crustal production is negligible; thus, any addition of ^{20}Ne to the ASW value can only be of a mantle origin
- By contrast, any excess of ^{21}Ne with respect to the ASW has mostly a crustal origin
- ^{4}He is by far, the most massively produced isotope in the crust by contrast, production of ^{3}He in the crust is negligible with respect to that of ^{4}He
- Remember also that there is about 1 million times more ^{4}He than ^{3}He in the atmosphere (Ra = 1.384 * 10-6), while there is much more ^{3}He in the mantle than in the crust.

Case study 4: environmental impacts of shale gas drilling



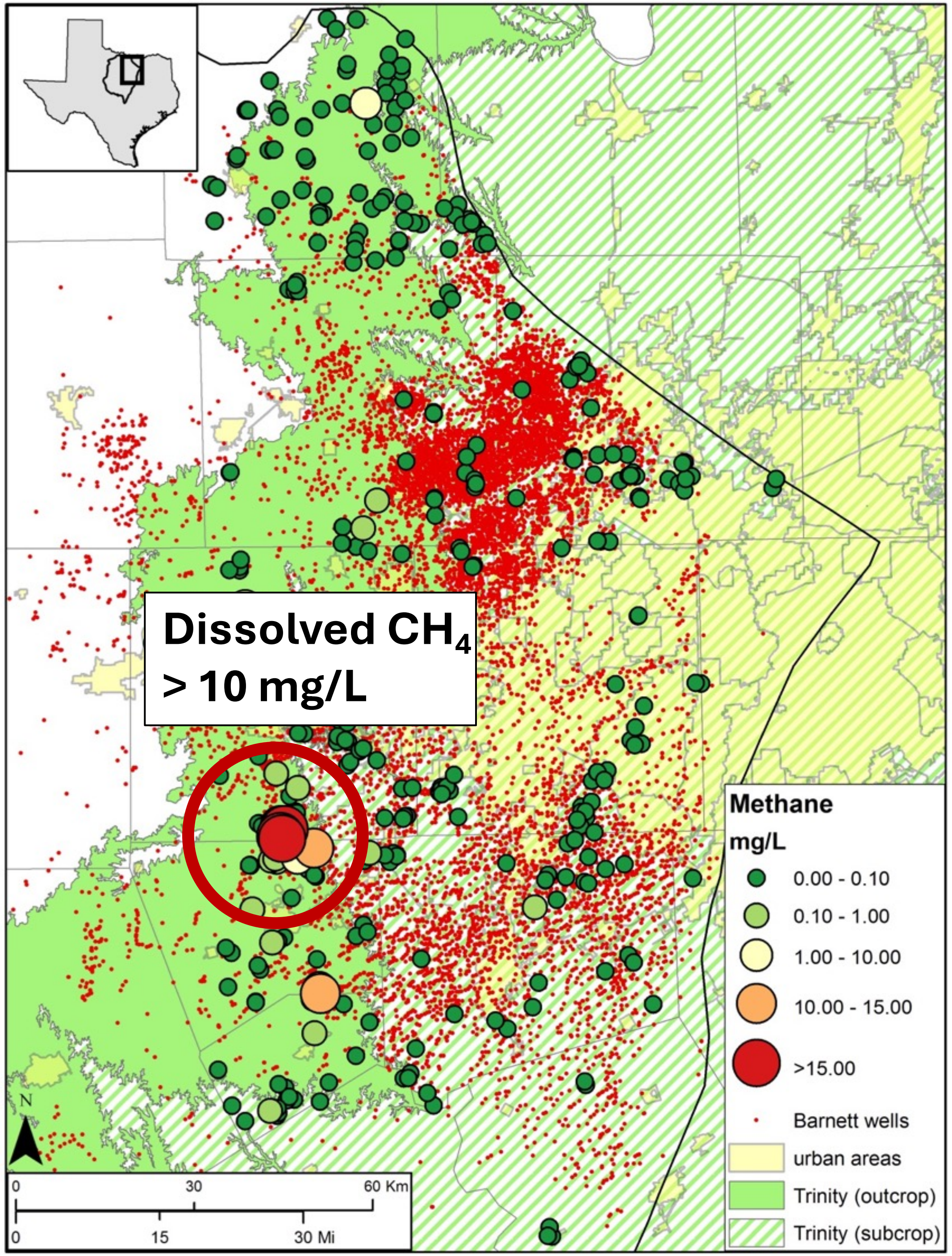


adapted from Kornacki *et al.*, (2014)

500+ groundwater samples collected and analyzed for dissolved stray gas (methane) in 2013 and 2014

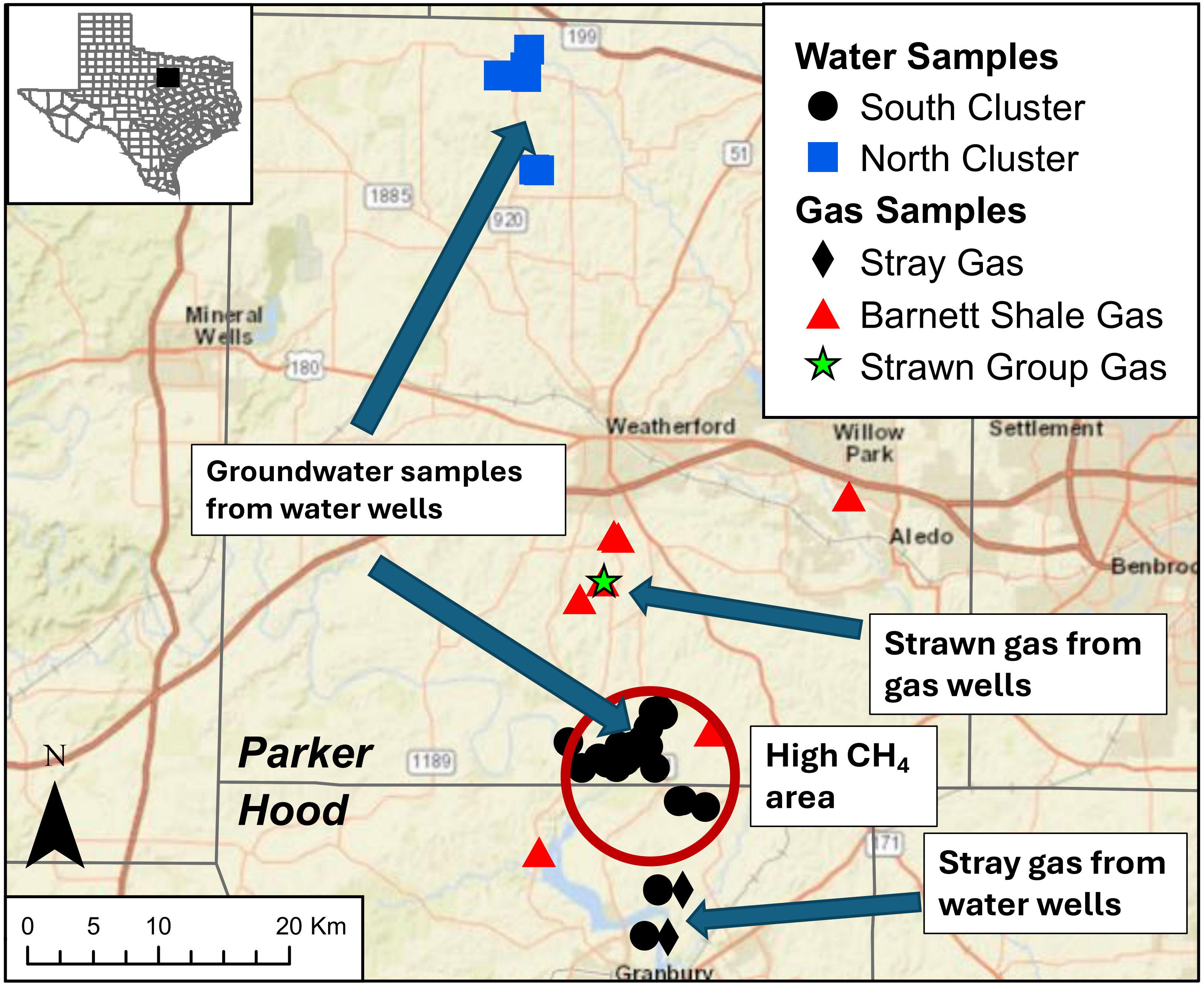
The source of stray gas?

- The deep Barnett Shale vs. the shallow Strawn Group?
- Naturally-occurring or migrating from nearby gas wells?



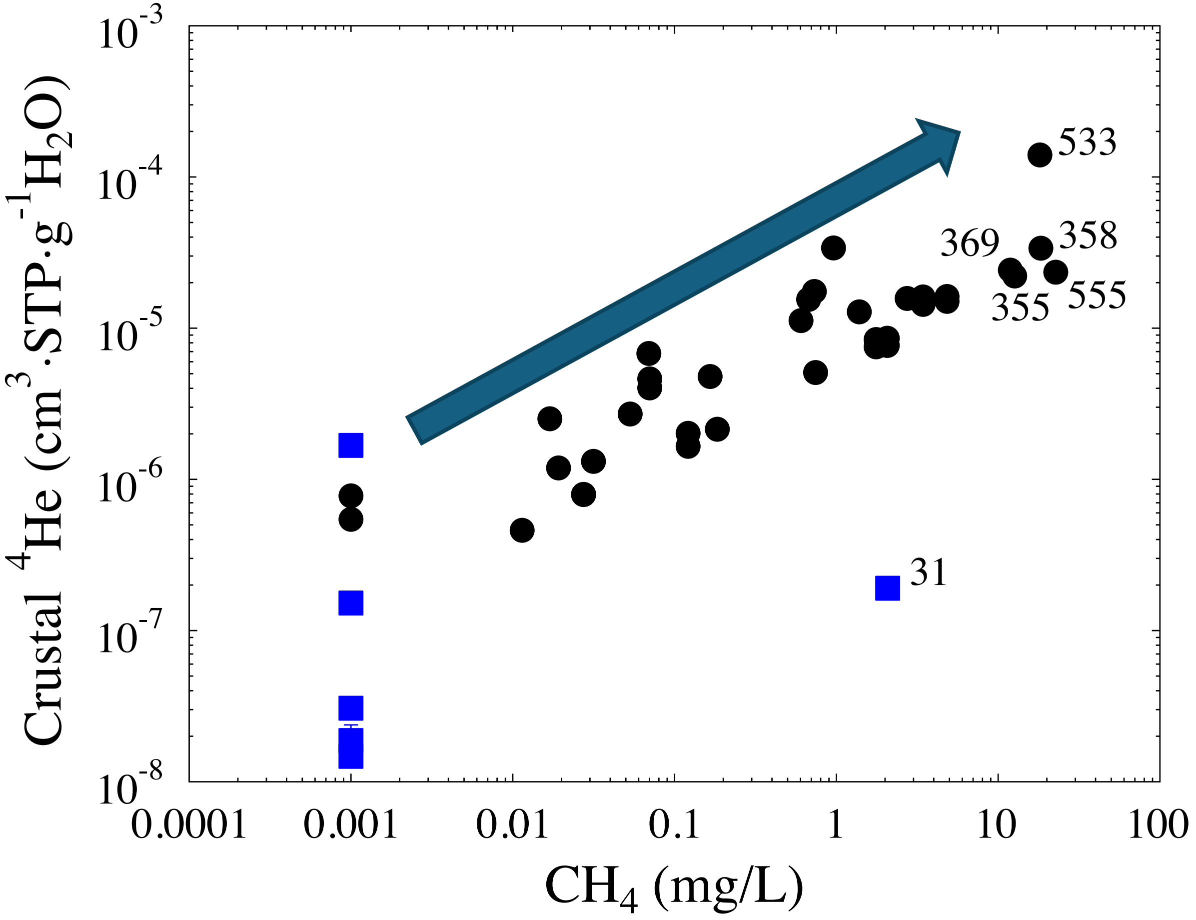
Nicot *et al.* (2017)

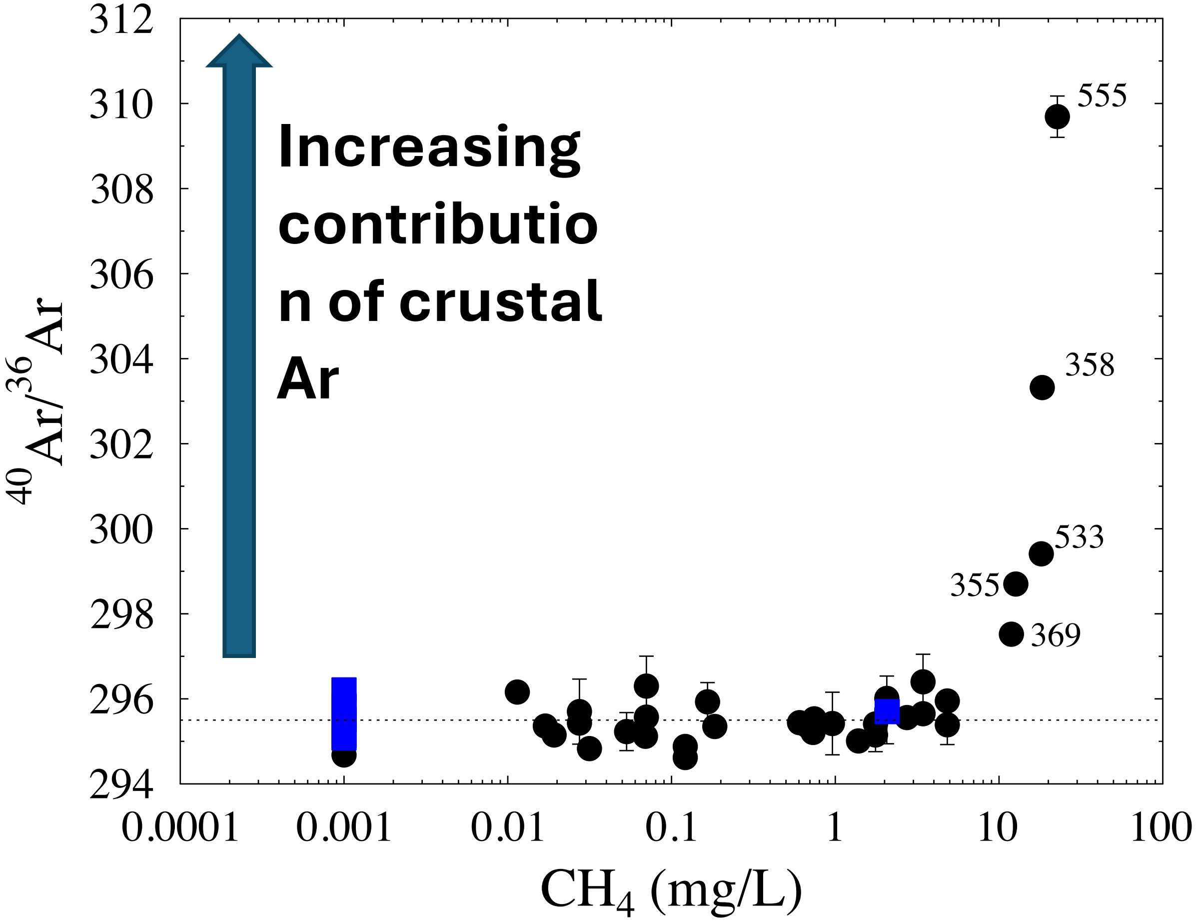
Collecting groundwater and gas samples for noble gas analyses



Wen *et al.* (2016; 2017)

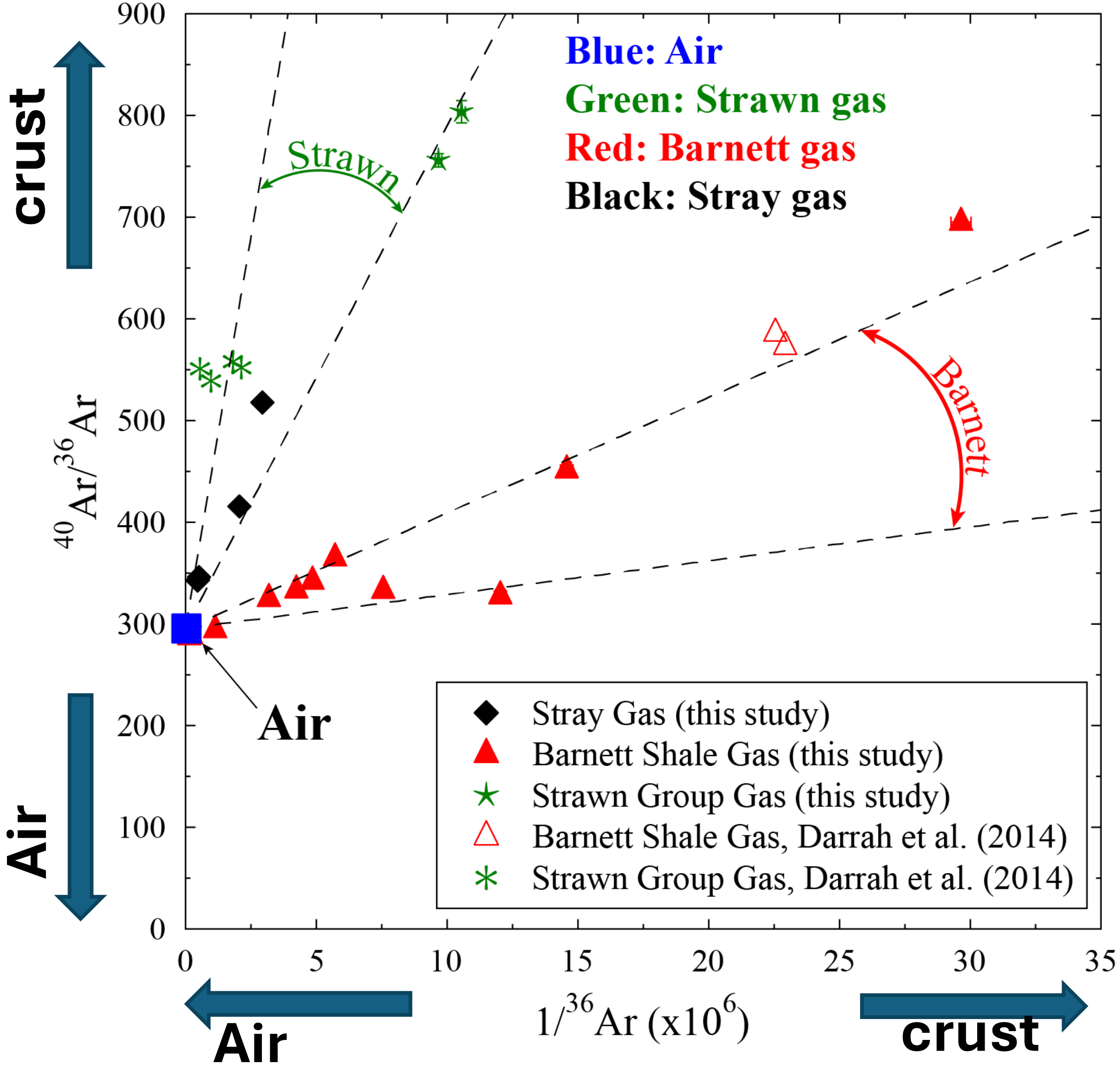
Correlated noble gases and CH_4 concentrations in water





Wen *et al.* (2016)

Strawn Group is likely the source of stray gas



Barnett and Strawn gas samples display very distinct noble gas signatures: Strawn gas older than Barnett gas?

The Strawn Group is likely the source of stray gas in the water wells

Well logs of four water wells with highest methane conc. (> 10 mg/L) show these wells all penetrate into the Strawn Group:

Local source other than migration from gas wells

Wen *et al.* (2017)

Water wells penetrating into the Strawn might reach small gas accumulation