

Noble Gases in Groundwater

EAR 419/619 Environmental Aqueous Geochemistry

What are noble gases?

PERIODIC TABLE
Atomic Properties of the Elements

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

Frequently used fundamental physical constants

For the most accurate values of these and other constants, visit physics.nist.gov/constants

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ¹³³Cs

speed of light in vacuum c 299 792 458 m s⁻¹ (exact)

Planck constant h 6.626 07 × 10⁻³⁴ J s ($h = h/2\pi$)

elementary charge e 1.602 177 × 10⁻¹⁹ C

electron mass m_e 9.109 38 × 10⁻³¹ kg

$m_e c^2$ 0.510 999 MeV

proton mass m_p 1.672 622 × 10⁻²⁷ kg

fine-structure constant α 1/137.035 999

Rydberg constant R_∞ 10 973 731.569 m⁻¹

$R_\infty c$ 3.289 841 960 × 10¹⁵ Hz

$R_\infty h c$ 13.605 69 eV

Boltzmann constant k 1.380 6 × 10⁻²³ J K⁻¹

Physical Measurement Laboratory
www.nist.gov/pml

Standard Reference Data
www.nist.gov/srd

Legend:

- Solids
- Liquids
- Gases
- Artificially Prepared

Period	Group 1 IA		Groups 2-10										Groups 11-18					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H Hydrogen 1.008 ¹ s																	He Helium 4.002602 1s
2	Li Lithium 6.94 1s ² 2s	Be Beryllium 9.0121831 1s ² 2s ²											B Boron 10.81 1s ² 2s ² 2p	C Carbon 12.011 1s ² 2s ² 2p	N Nitrogen 14.007 1s ² 2s ² 2p ³	O Oxygen 15.999 1s ² 2s ² 2p ⁴	F Fluorine 18.998403 1s ² 2s ² 2p ⁵	Ne Neon 20.1797 1s ² 2s ² 2p ⁶
3	Na Sodium 22.98976928 [Ne]3s	Mg Magnesium 24.305 [Ne]3s ²										Al Aluminum 26.9815385 [Ne]3s ² 3p	Si Silicon 28.085 [Ne]3s ² 3p ²	P Phosphorus 30.97376200 [Ne]3s ² 3p ³	S Sulfur 32.06 [Ne]3s ² 3p ⁴	Cl Chlorine 35.45 [Ne]3s ² 3p ⁵	Ar Argon 39.948 [Ne]3s ² 3p ⁶	
4	K Potassium 39.0983 [Ar]4s	Ca Calcium 40.078 [Ar]4s	Sc Scandium 44.955908 [Ar]3d ¹ 4s	Ti Titanium 47.867 [Ar]3d ² 4s	V Vanadium 50.9415 [Ar]3d ³ 4s	Cr Chromium 51.9961 [Ar]3d ⁵ 4s	Mn Manganese 54.938044 [Ar]3d ⁵ 4s	Fe Iron 55.845 [Ar]3d ⁶ 4s	Co Cobalt 58.933194 [Ar]3d ⁷ 4s	Ni Nickel 58.6934 [Ar]3d ⁸ 4s	Cu Copper 63.546 [Ar]3d ¹⁰ 4s	Zn Zinc 65.38 [Ar]3d ¹⁰ 4s	Ga Gallium 69.723 [Ar]3d ¹⁰ 4s ² 4p	Ge Germanium 72.630 [Ar]3d ¹⁰ 4s ² 4p ²	As Arsenic 74.921595 [Ar]3d ¹⁰ 4s ² 4p ³	Se Selenium 78.971 [Ar]3d ¹⁰ 4s ² 4p ⁴	Br Bromine 79.904 [Ar]3d ¹⁰ 4s ² 4p ⁵	Kr Krypton 83.798 [Ar]3d ¹⁰ 4s ² 4p ⁶
5	Rb Rubidium 85.4678 [Kr]5s	Sr Strontium 87.62 [Kr]5s	Y Yttrium 88.90584 [Kr]4d ¹ 5s	Zr Zirconium 91.224 [Kr]4d ² 5s	Nb Niobium 92.90637 [Kr]4d ⁴ 5s	Mo Molybdenum 95.95 [Kr]4d ⁵ 5s	Tc Technetium (98) [Kr]4d ⁵ 5s	Ru Ruthenium 101.07 [Kr]4d ⁷ 5s	Rh Rhodium 102.90550 [Kr]4d ⁸ 5s	Pd Palladium 106.42 [Kr]4d ¹⁰	Ag Silver 107.8682 [Kr]4d ¹⁰ 5s	Cd Cadmium 112.414 [Kr]4d ¹⁰ 5s ²	In Indium 114.818 [Kr]4d ¹⁰ 5s ² 5p	Sn Tin 118.710 [Kr]4d ¹⁰ 5s ² 5p ²	Sb Antimony 121.760 [Kr]4d ¹⁰ 5s ² 5p ³	Te Tellurium 127.60 [Kr]4d ¹⁰ 5s ² 5p ⁴	I Iodine 126.9044 [Kr]4d ¹⁰ 5s ² 5p ⁵	Xe Xenon 131.293 [Kr]4d ¹⁰ 5s ² 5p ⁶
6	Cs Cesium 132.9054520 [Xe]6s	Ba Barium 137.327 [Xe]6s		Hf Hafnium 178.49 [Xe]4f ¹⁴ 5d ² 6s	Ta Tantalum 180.94788 [Xe]4f ¹⁴ 5d ³ 6s	W Tungsten 183.84 [Xe]4f ¹⁴ 5d ⁴ 6s	Re Rhenium 186.207 [Xe]4f ¹⁴ 5d ⁵ 6s	Os Osmium 190.23 [Xe]4f ¹⁴ 5d ⁶ 6s	Ir Iridium 192.227 [Xe]4f ¹⁴ 5d ⁷ 6s	Pt Platinum 195.084 [Xe]4f ¹⁴ 5d ⁹ 6s	Au Gold 196.966569 [Xe]4f ¹⁴ 5d ¹⁰ 6s	Hg Mercury 200.592 [Xe]4f ¹⁴ 5d ¹⁰ 6s	Tl Thallium 204.38 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p	Pb Lead 207.2 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	Bi Bismuth 208.98040 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	Po Polonium (209) [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	At Astatine (210) [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	Rn Radon (222) [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
7	Fr Francium (223) [Rn]7s	Ra Radium (226) [Rn]7s		Rf Rutherfordium (261) [Rn]5f ¹⁴ 6d ² 7s	Db Dubnium (262) [Rn]5f ¹⁴ 6d ³ 7s	Sg Seaborgium (263) [Rn]5f ¹⁴ 6d ⁴ 7s	Bh Bohrium (264) [Rn]5f ¹⁴ 6d ⁵ 7s	Hs Hassium (270) [Rn]5f ¹⁴ 6d ⁶ 7s	Mt Meitnerium (268) [Rn]5f ¹⁴ 6d ⁷ 7s	Ds Darmstadtium (281) [Rn]5f ¹⁴ 6d ⁸ 7s	Rg Roentgenium (280) [Rn]5f ¹⁴ 6d ⁹ 7s	Cn Copernicium (285) [Rn]5f ¹⁴ 6d ¹⁰ 7s	Uut Ununtrium (284) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p	Fl Flerovium (289) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	Uup Ununpentium (288) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ³	Lv Livermorium (293) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	Uus Ununseptium (294) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵	Uuo Ununoctium (294) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶
			58 Ce Cerium 140.116 [Xe]4f ¹ 5d ¹ 6s ²	57 La Lanthanum 138.90547 [Xe]5d ¹ 6s ²	59 Pr Praseodymium 140.907 [Xe]4f ³ 6s ²	60 Nd Neodymium 144.242 [Xe]4f ⁴ 6s ²	61 Pm Promethium (145) [Xe]4f ⁵ 6s ²	62 Sm Samarium 150.36 [Xe]4f ⁶ 6s ²	63 Eu Europium 151.964 [Xe]4f ⁷ 6s ²	64 Gd Gadolinium 157.25 [Xe]4f ⁷ 5d ¹ 6s ²	65 Tb Terbium 158.92535 [Xe]4f ⁹ 6s ²	66 Dy Dysprosium 162.500 [Xe]4f ¹⁰ 6s ²	67 Ho Holmium 164.93033 [Xe]4f ¹¹ 6s ²	68 Er Erbium 167.259 [Xe]4f ¹² 6s ²	69 Tm Thulium 168.93422 [Xe]4f ¹³ 6s ²	70 Yb Ytterbium 173.054 [Xe]4f ¹⁴ 6s ²	71 Lu Lutetium 174.9668 [Xe]4f ¹⁴ 5d ¹ 6s ²	
			89 Ac Actinium (227) [Rn]6d ¹ 7s ²	90 Th Thorium 232.0377 [Rn]6d ² 7s ²	91 Pa Protactinium 231.03688 [Rn]5f ² 6d ¹ 7s ²	92 U Uranium 238.02891 [Rn]5f ³ 6d ¹ 7s ²	93 Np Neptunium (237) [Rn]5f ⁴ 6d ¹ 7s ²	94 Pu Plutonium (244) [Rn]5f ⁶ 7s ²	95 Am Americium (243) [Rn]5f ⁷ 7s ²	96 Cm Curium (247) [Rn]5f ⁸ 7s ²	97 Bk Berkelium (247) [Rn]5f ⁹ 7s ²	98 Cf Californium (251) [Rn]5f ¹⁰ 7s ²	99 Es Einsteinium (252) [Rn]5f ¹¹ 7s ²	100 Fm Fermium (257) [Rn]5f ¹² 7s ²	101 Md Mendelevium (258) [Rn]5f ¹³ 7s ²	102 No Nobelium (259) [Rn]5f ¹⁴ 7s ²	103 Lr Lawrencium (262) [Rn]5f ¹⁴ 7s ² 7p	

Atomic Number **Ground-state Level**

Symbol **Name** **Standard Atomic Weight** **Ground-state Configuration** **Ionization Energy (eV)**

58 Ce Cerium 140.116 [Xe]4f¹5d¹6s² 5.5386

*IUPAC conventional atomic weights; standard atomic weights for these elements are expressed in intervals; see iupac.org for an explanation and values.
 For a description of the data, visit physics.nist.gov/data
 NIST SP 966 (September 2014)

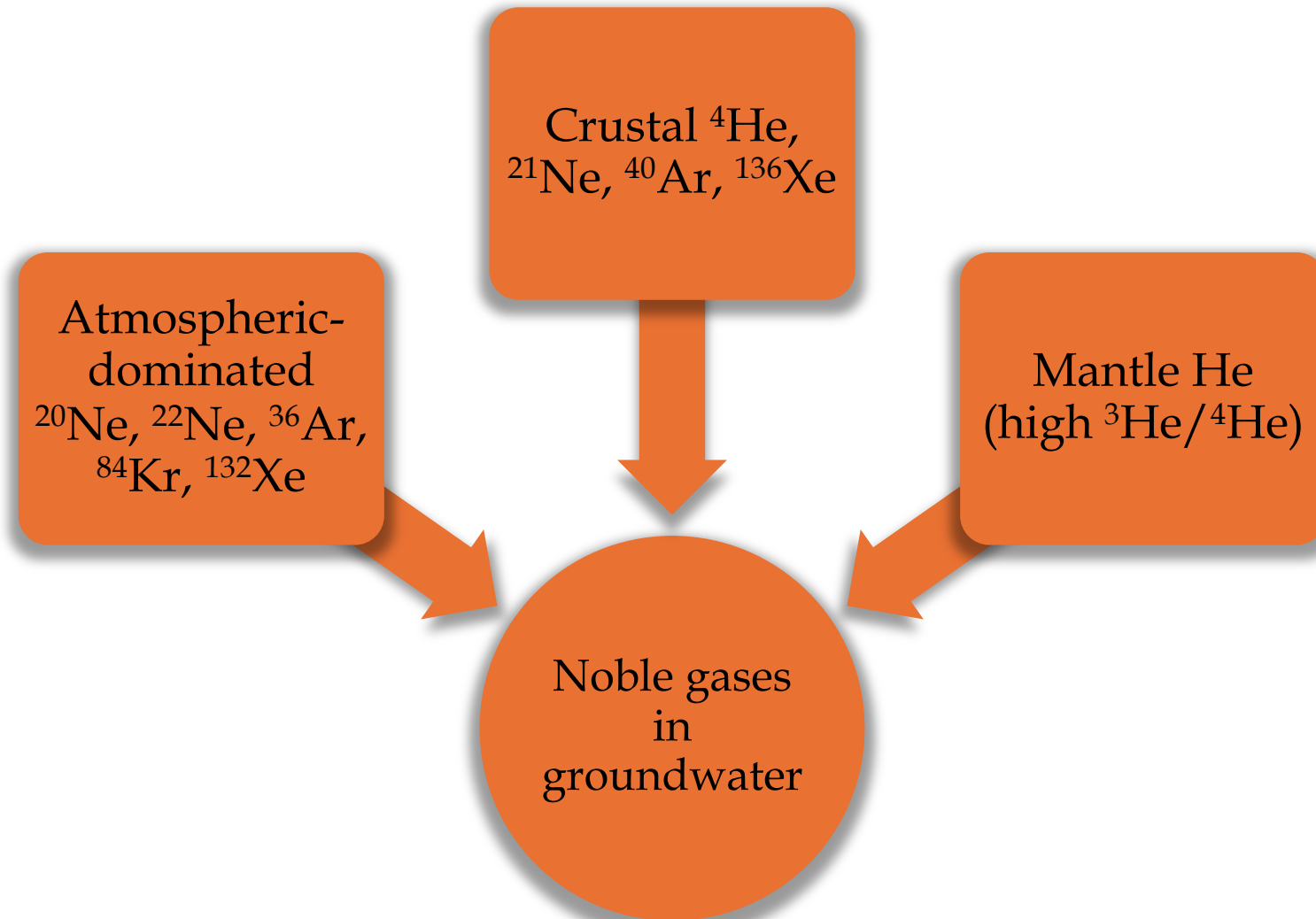
Noble gases are INERT and STABLE

- 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): ^3He and ^4He
- 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., ^4He , ^{40}Ar).
 - ^{235}U , ^{238}U , $^{232}\text{Th} \rightarrow ^4\text{He}$
 - $^{40}\text{K} \rightarrow ^{40}\text{Ar}$
- 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 ^3He and ^{21}Ne .
 - ^3He – it requires the presence of U and Th + Li (lithium)
 - ^{21}Ne - it requires the presence of U and Th + O and Mg

Terrigenous noble gases continued

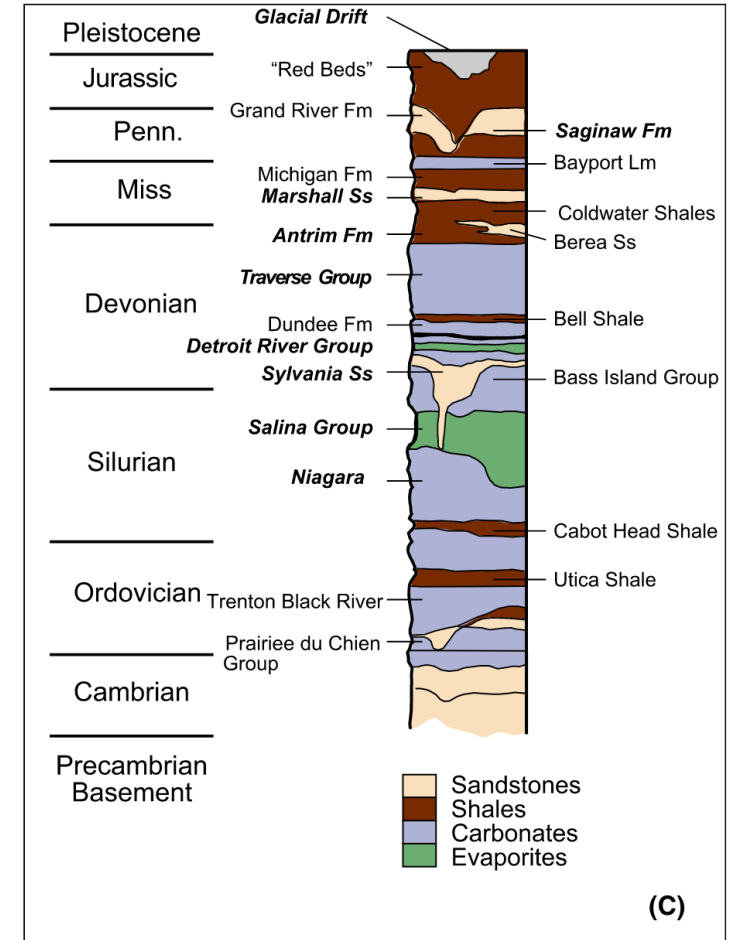
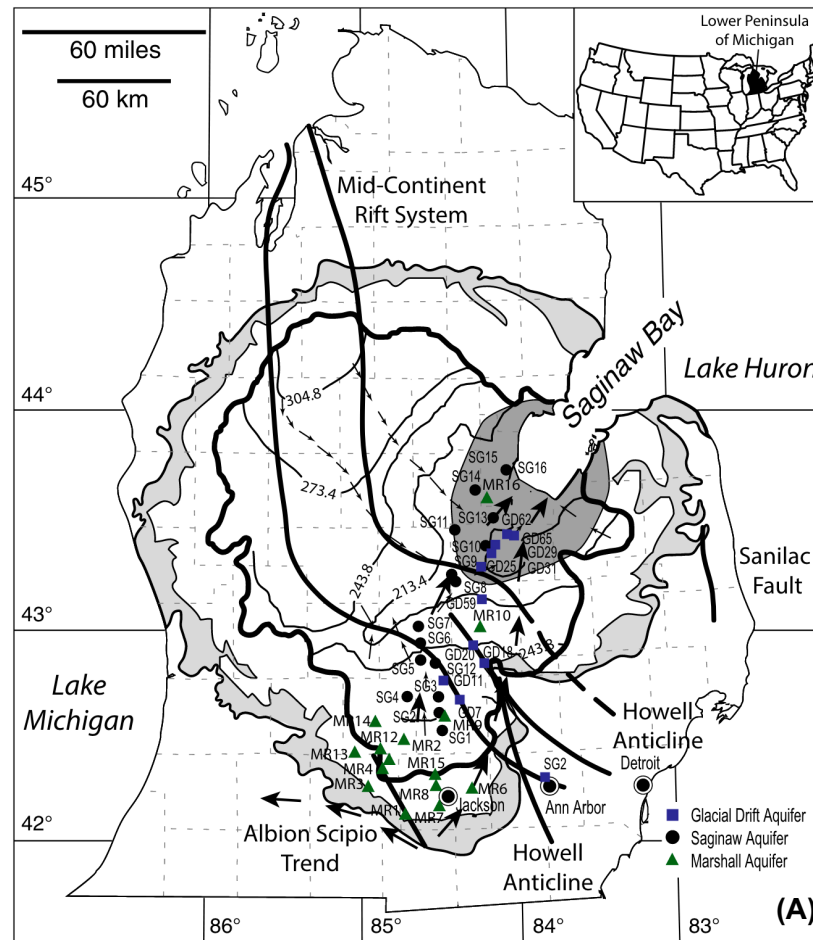
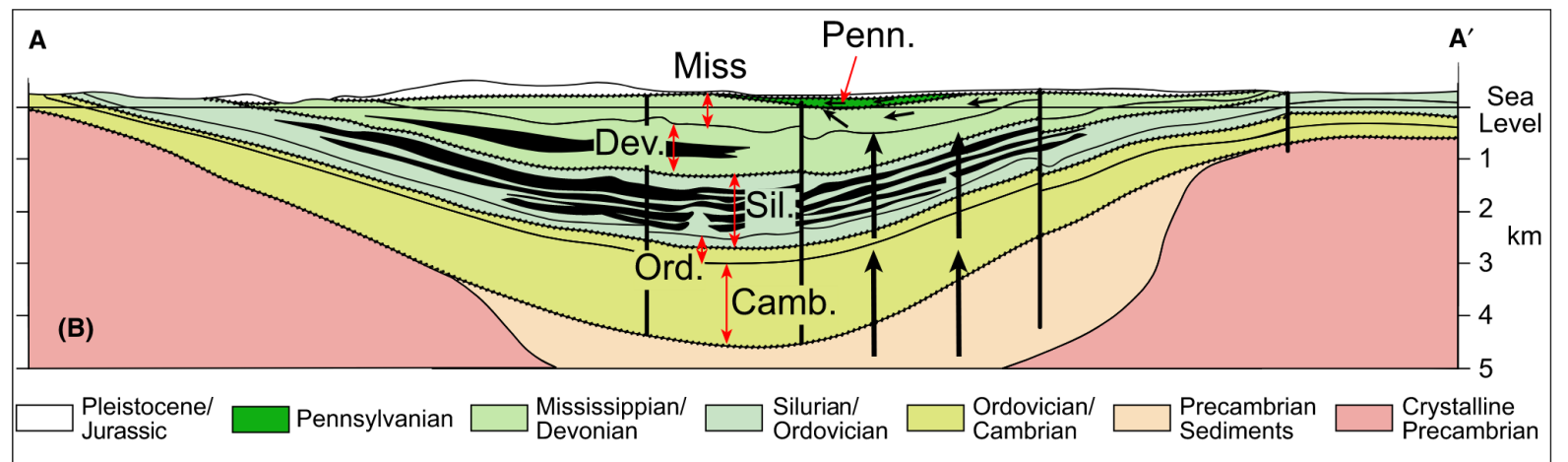
Production in the rocks of:

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

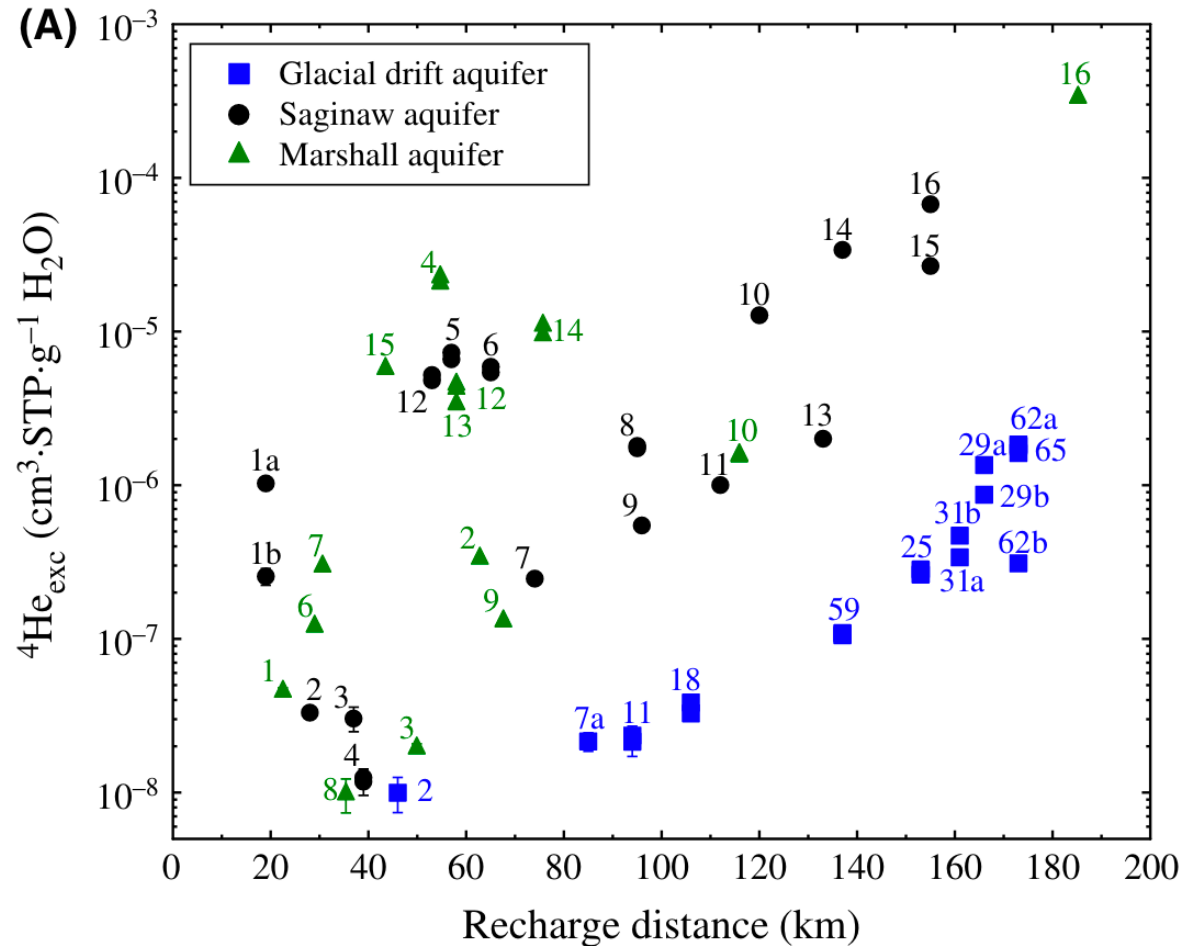
can be considered, to a first approximation,

negligible

Case study 1: Michigan Basin



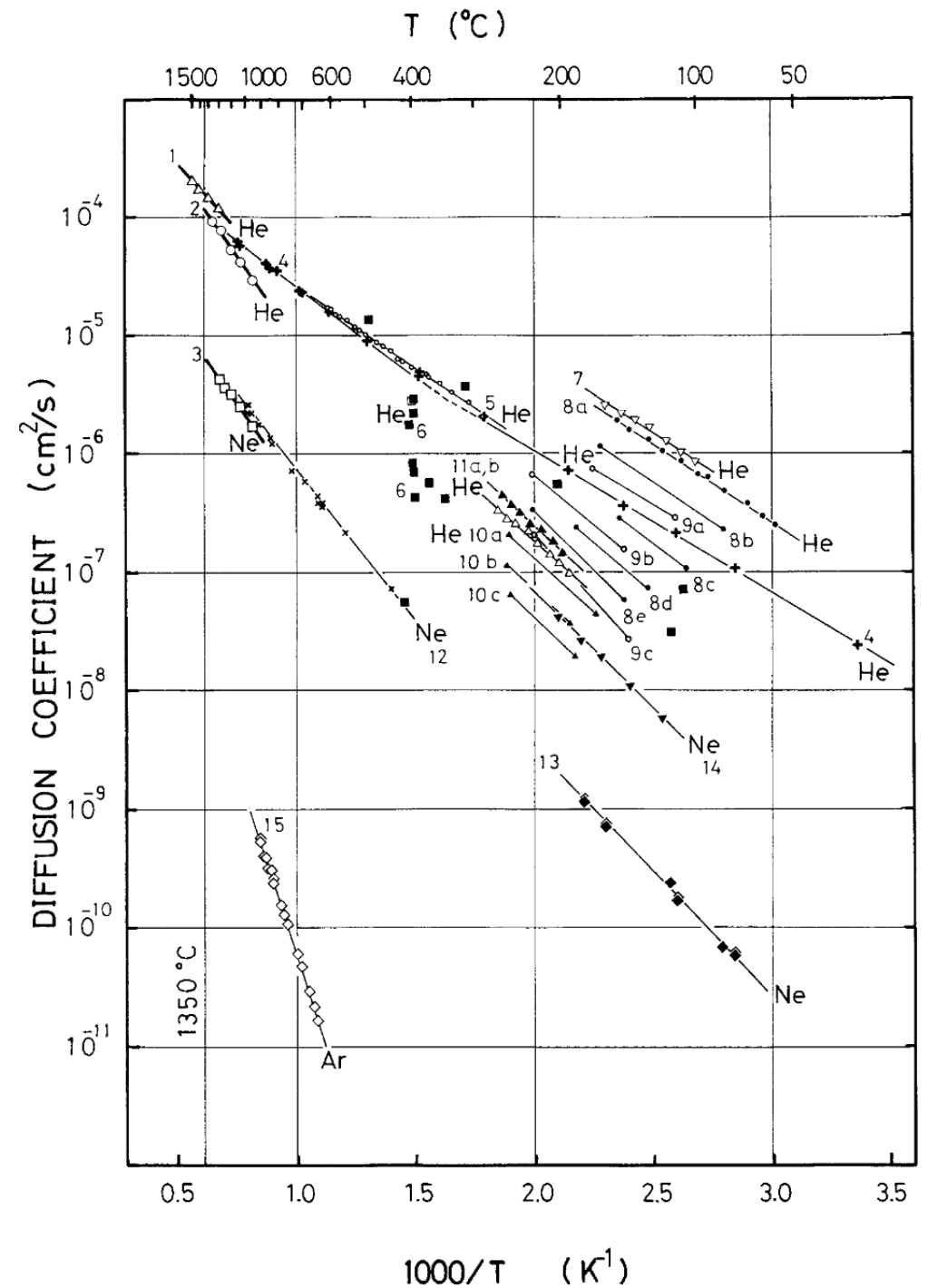
Accumulation of terrigenous helium in MI groundwater



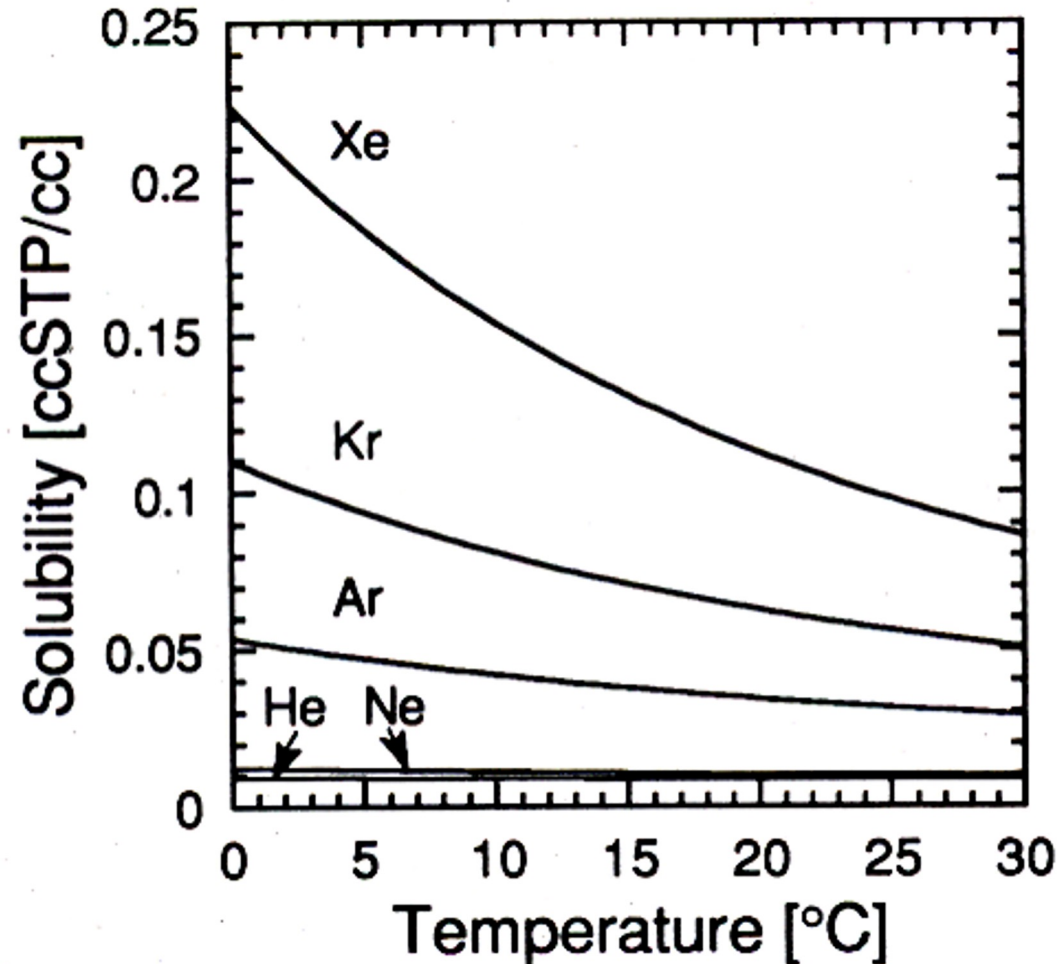
Noble gas transport in groundwater

- 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

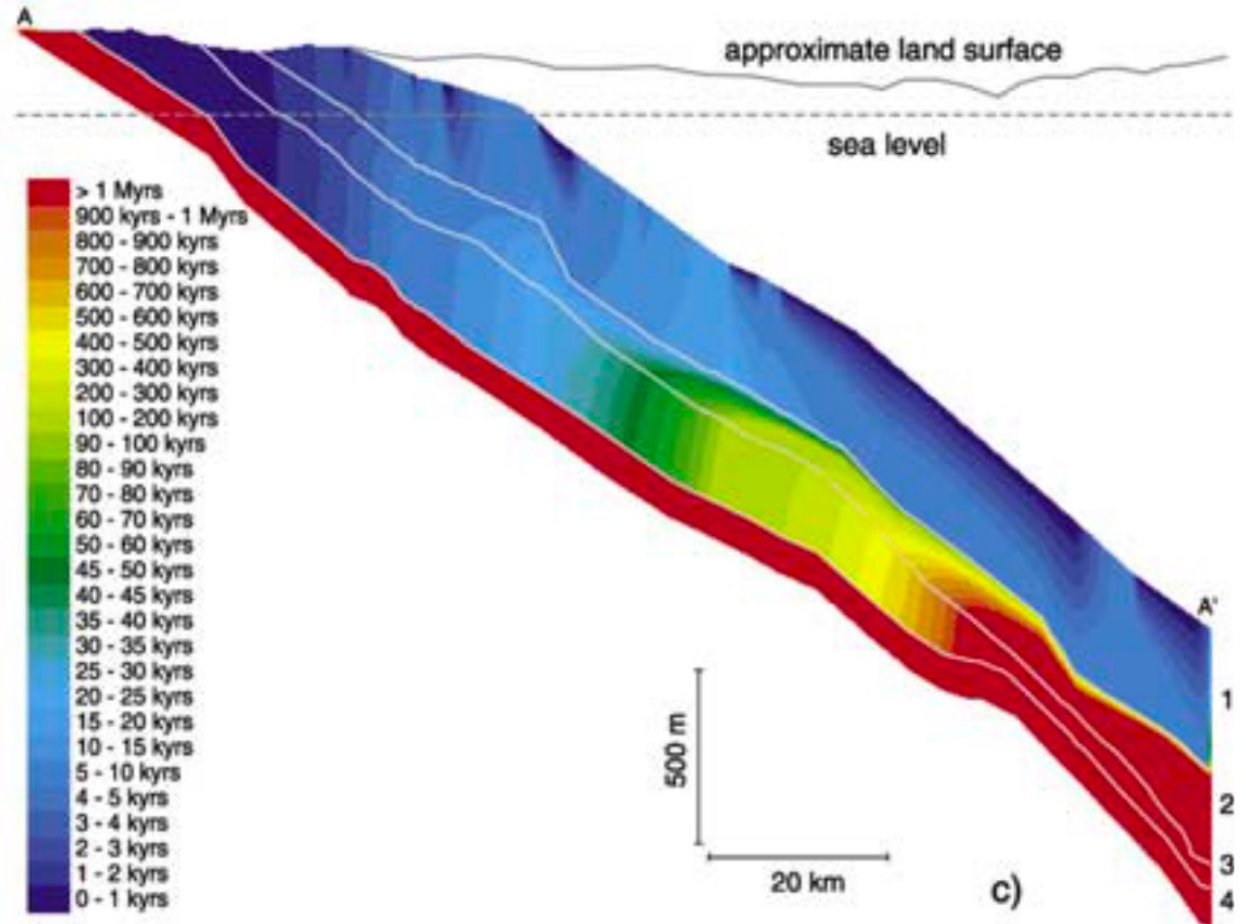
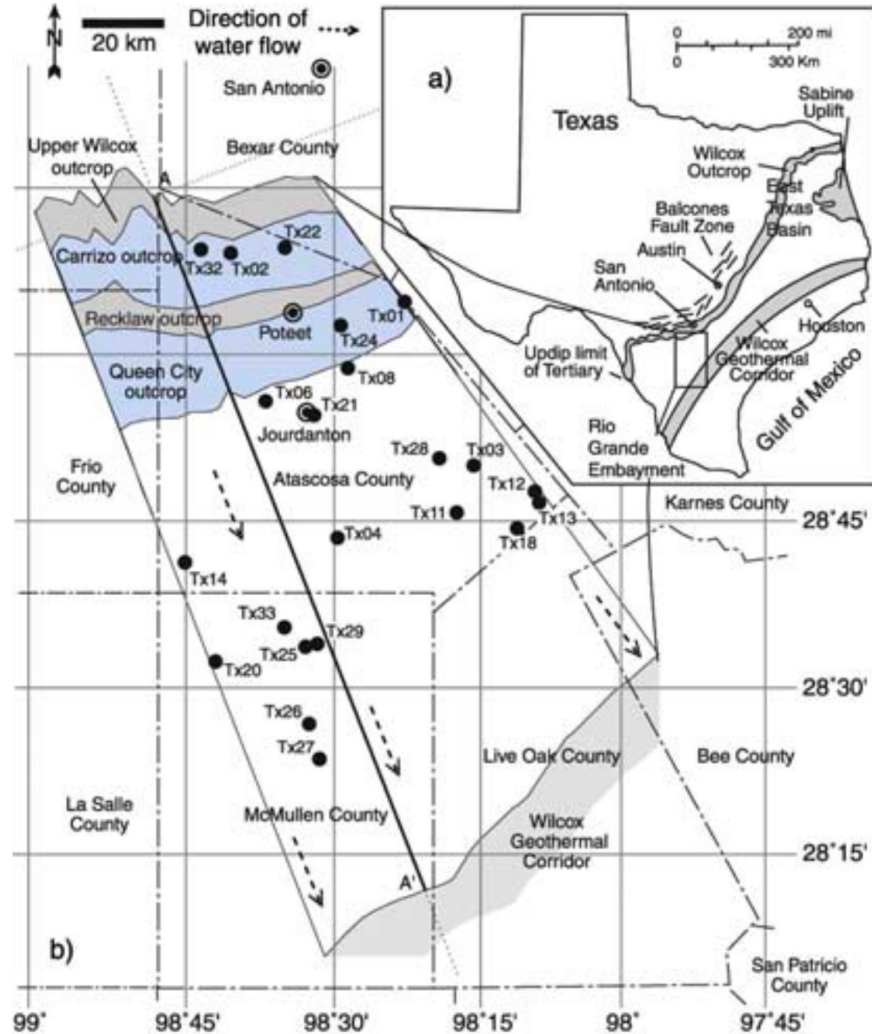


Noble gas solubility in water is a function of temperature

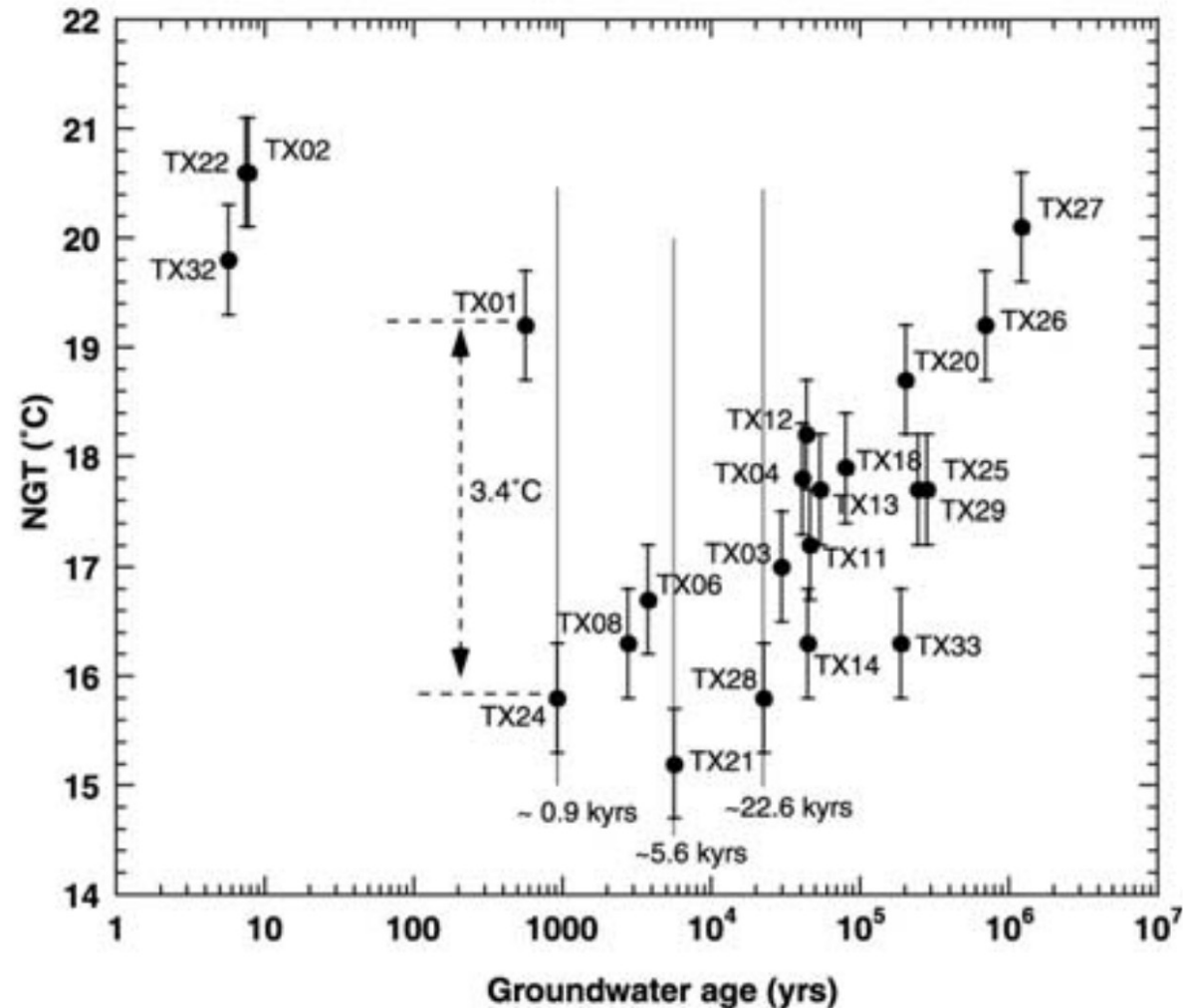


Noble gas concentration in water is a function of temperature, gas partial pressure in the gas phase, and salinity

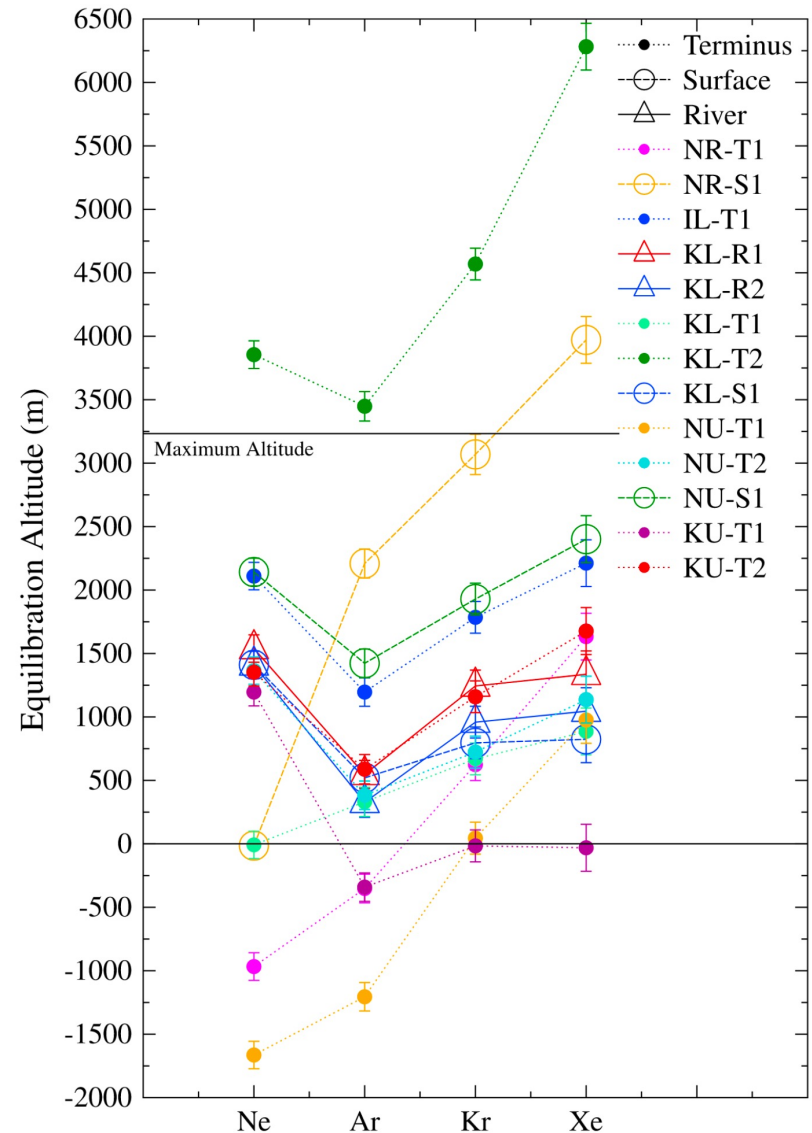
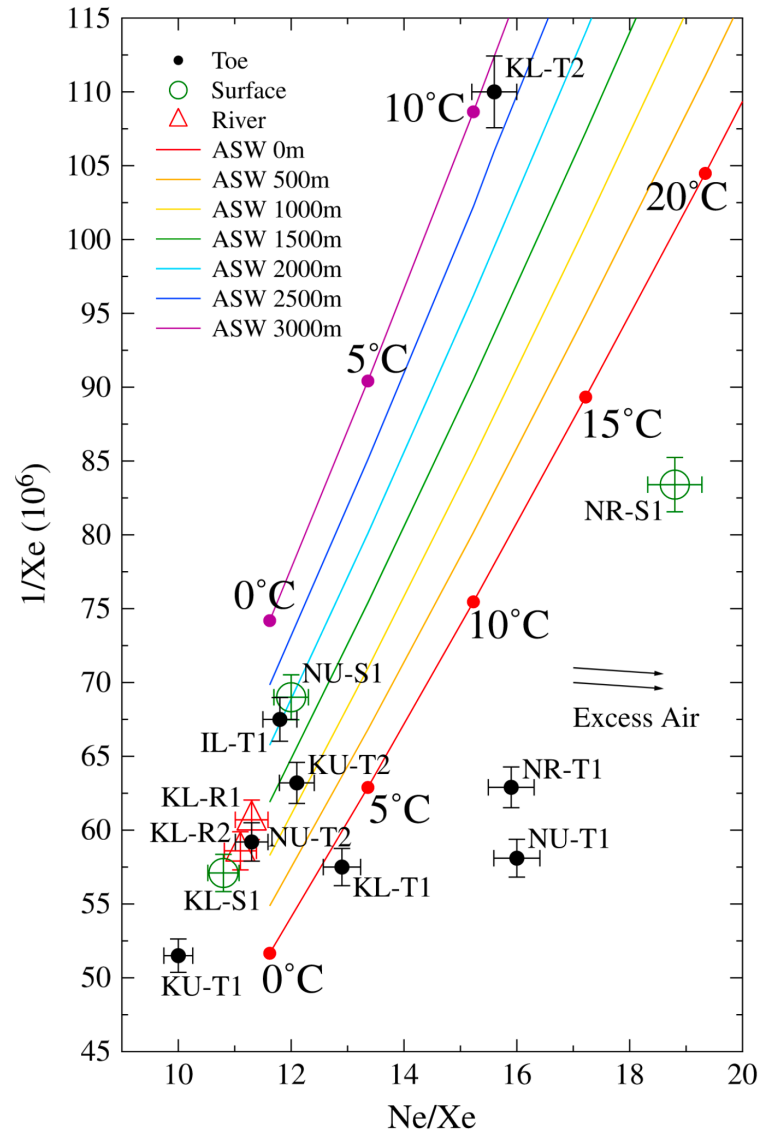
Case study 2: Carrizo Aquifer in Texas



Case study 2: Carrizo Aquifer in Texas



Case study 3: Greenland meltwater



More noble gas systematics in groundwater

- Atmosphere (ASW)

- The He isotopic ratio is generally presented as R/R_a , where $R = {}^3\text{He}/{}^4\text{He}$ and R_a is the atmospheric ${}^3\text{He}/{}^4\text{He}$ ratio ($R_a = 1.384 \times 10^{-6}$).

$$R/R_a = 1 \quad {}^{21}\text{Ne}/{}^{22}\text{Ne} = 0.029 \quad {}^{20}\text{Ne}/{}^{22}\text{Ne} = 9.8$$

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

- Crustal (radiogenic/nucleogenic component)

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

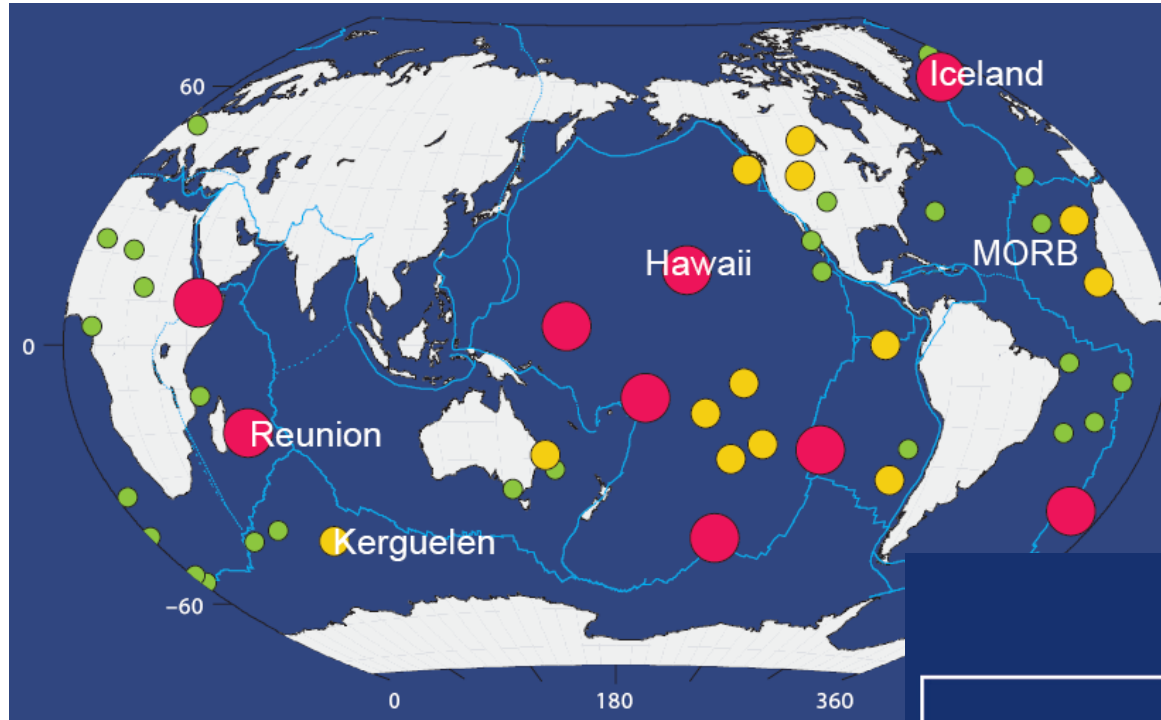
- No values are given for crustal ${}^{20}\text{Ne}/{}^{22}\text{Ne}$ nor ${}^{38}\text{Ar}/{}^{36}\text{Ar}$. Why?

More noble gas systematics in groundwater

- Mantle

- He: $\sim 8 \leq R/R_a \leq \sim 35$ (“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., Hawaii)

Mantle structure and convection models



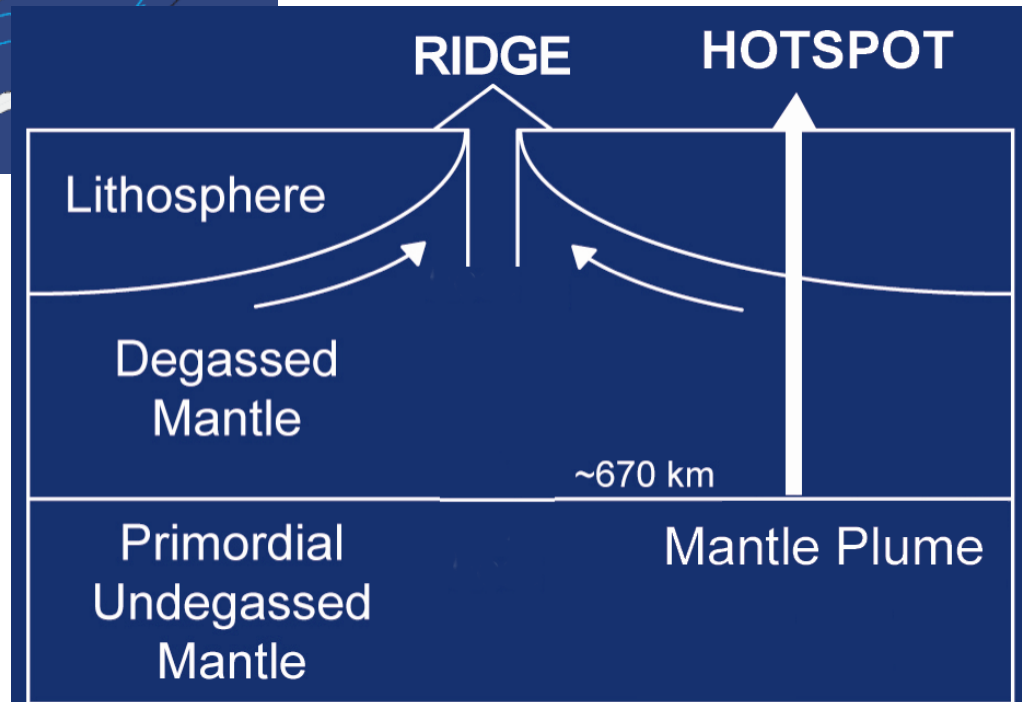
R/Ra of MORBs (~8) versus
OIBs (~35)

Classic 2-layered mantle model

MORBs

OIBs

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



More noble gas systematics in groundwater

- Mantle

- Ne: $9.8 < {}^{20}\text{Ne}/{}^{22}\text{Ne} \leq 13.8$

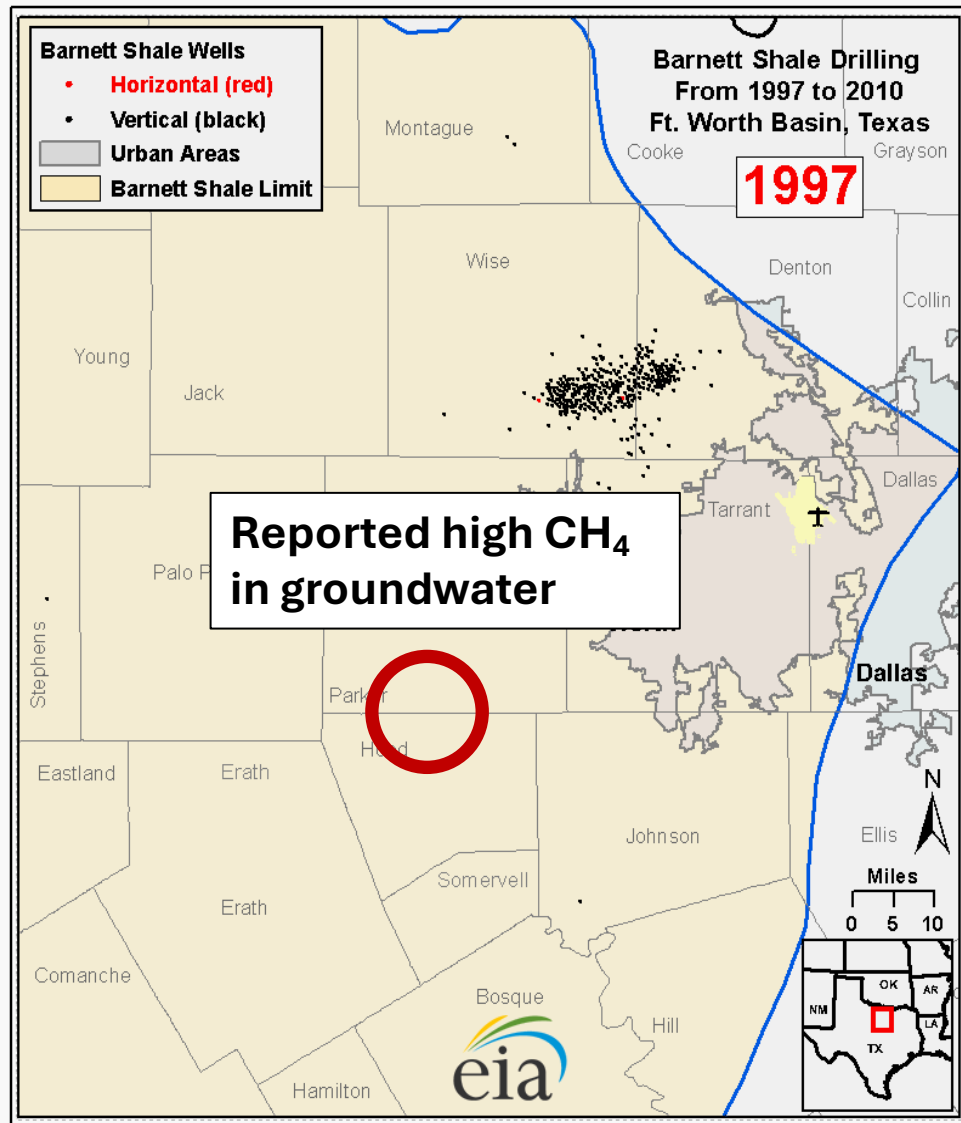
- ${}^{20}\text{Ne}/{}^{22}\text{Ne} = 13.8$ is the most “pure” Ne mantle component. It represents the most ancient Ne component in the Earth. We refer to it as being a “primordial or solar” component.

- Ar: Not well known... we can simply say that
 ${}^{40}\text{Ar}/{}^{36}\text{Ar} > 295.5$

Take-away messages

- ^{36}Ar and ^{38}Ar are almost entirely atmospheric; thus, their concentrations in groundwater as well as $^{38}\text{Ar}/^{36}\text{Ar}$ 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
- ^4He is by far, the most massively produced isotope in the crust by contrast, production of ^3He in the crust is negligible with respect to that of ^4He
- Remember also that there is about 1 million times more ^4He than ^3He in the atmosphere ($R_a = 1.384 \times 10^{-6}$), while there is much more ^3He in the mantle than in the crust.

Case study 4: environmental impacts of shale gas drilling



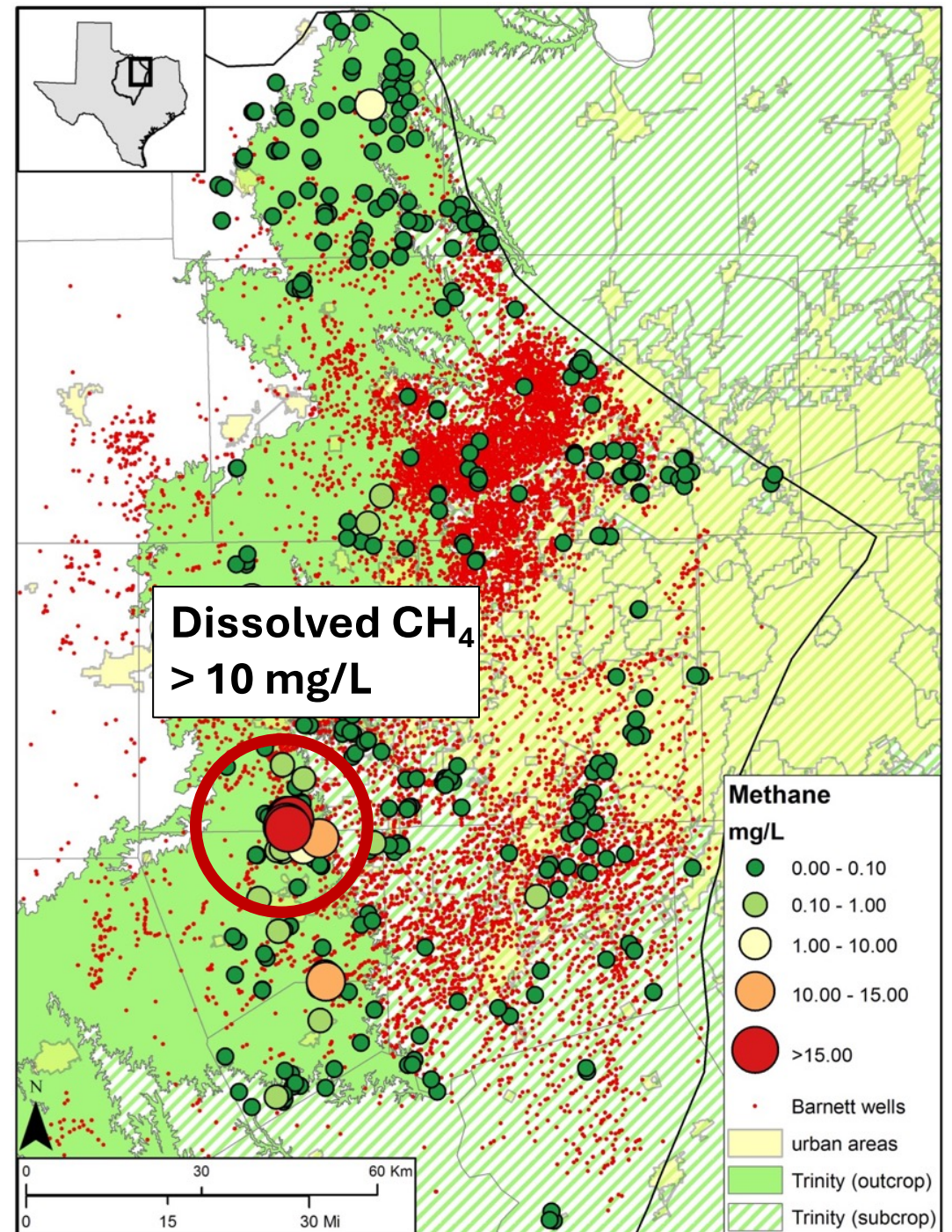
SYSTEM	STAGE	GROUP or FORMATION	AGE	DEPTH	
CRET.	LOWER	TRINITY AQUIFER	145 Ma	~120 m	
	MIDDLE	STRAWN GROUP	310 Ma		
	PENNSYLVANIAN	LOWER	Caddo	315 Ma	~260 m
MORROWAN		BEND GROUP	Marble Falls		~1590 m
		ATOKAN			
ORD. MISS.		M-UPPER	Barnett		325 Ma
IBEXIAN	LOWER	ELLENBERGER GROUP	475 Ma	~1830 m	

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

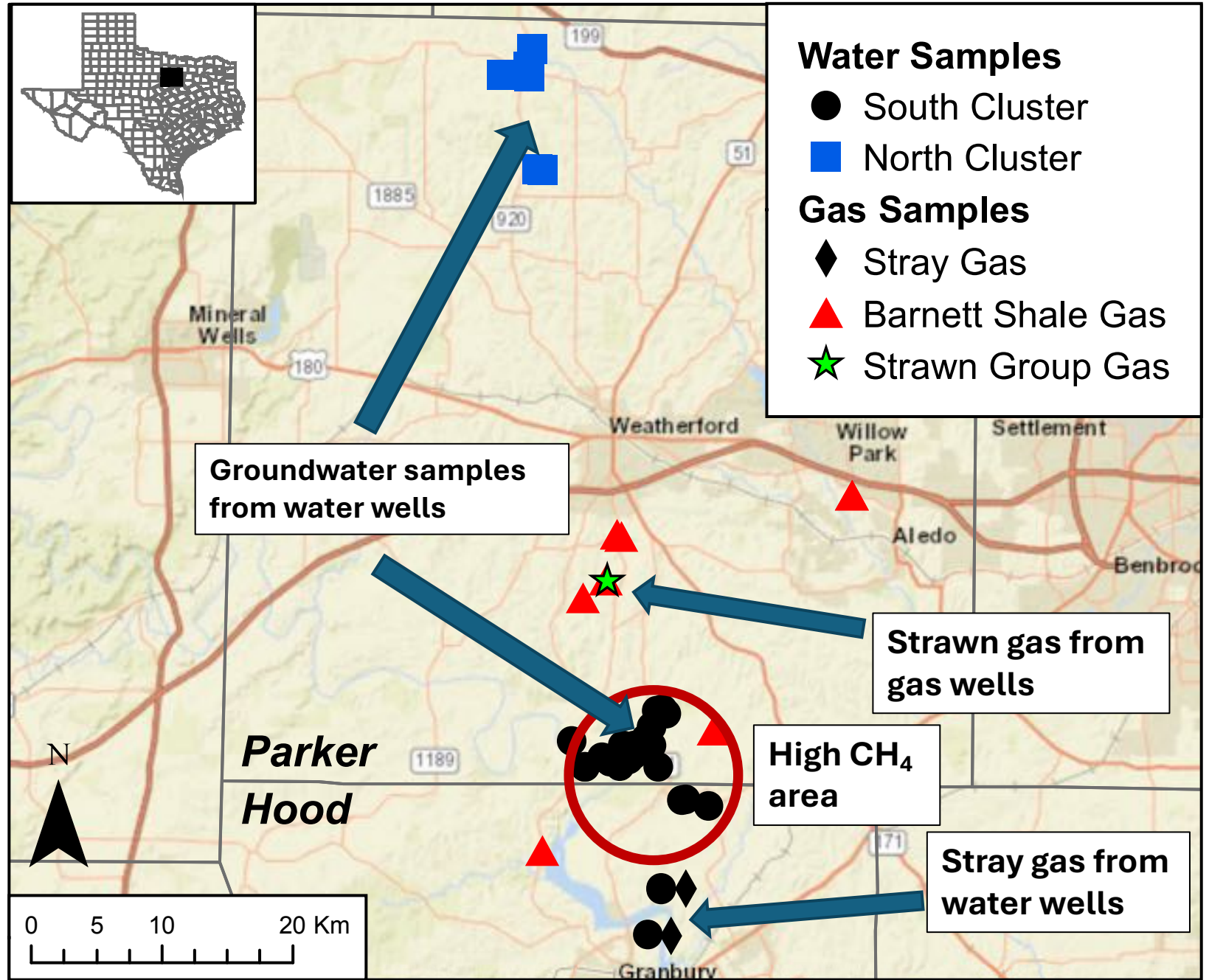
500+ groundwater samples collected and analyzed for dissolved stray gas (methane) in 2013 and 2014

The source of stray gas?

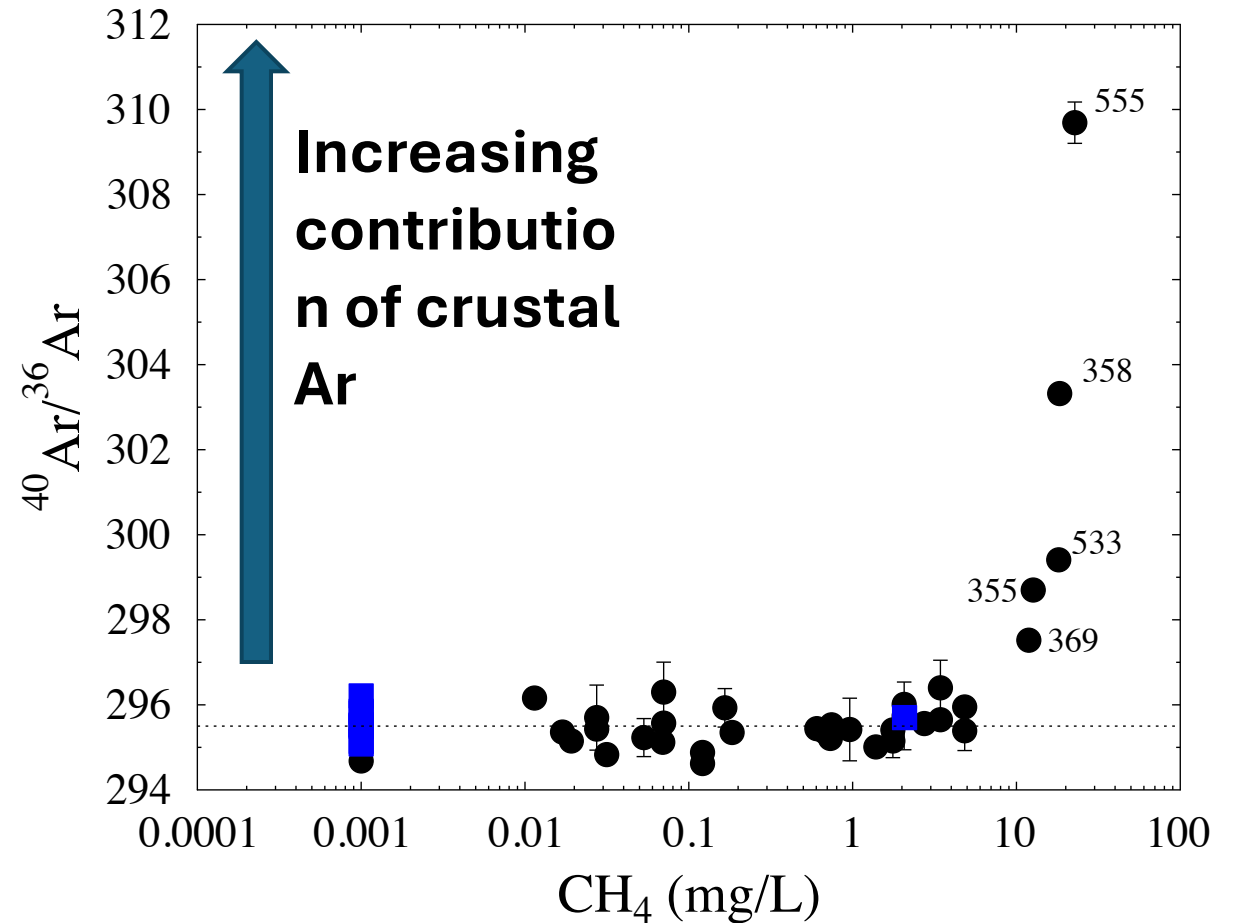
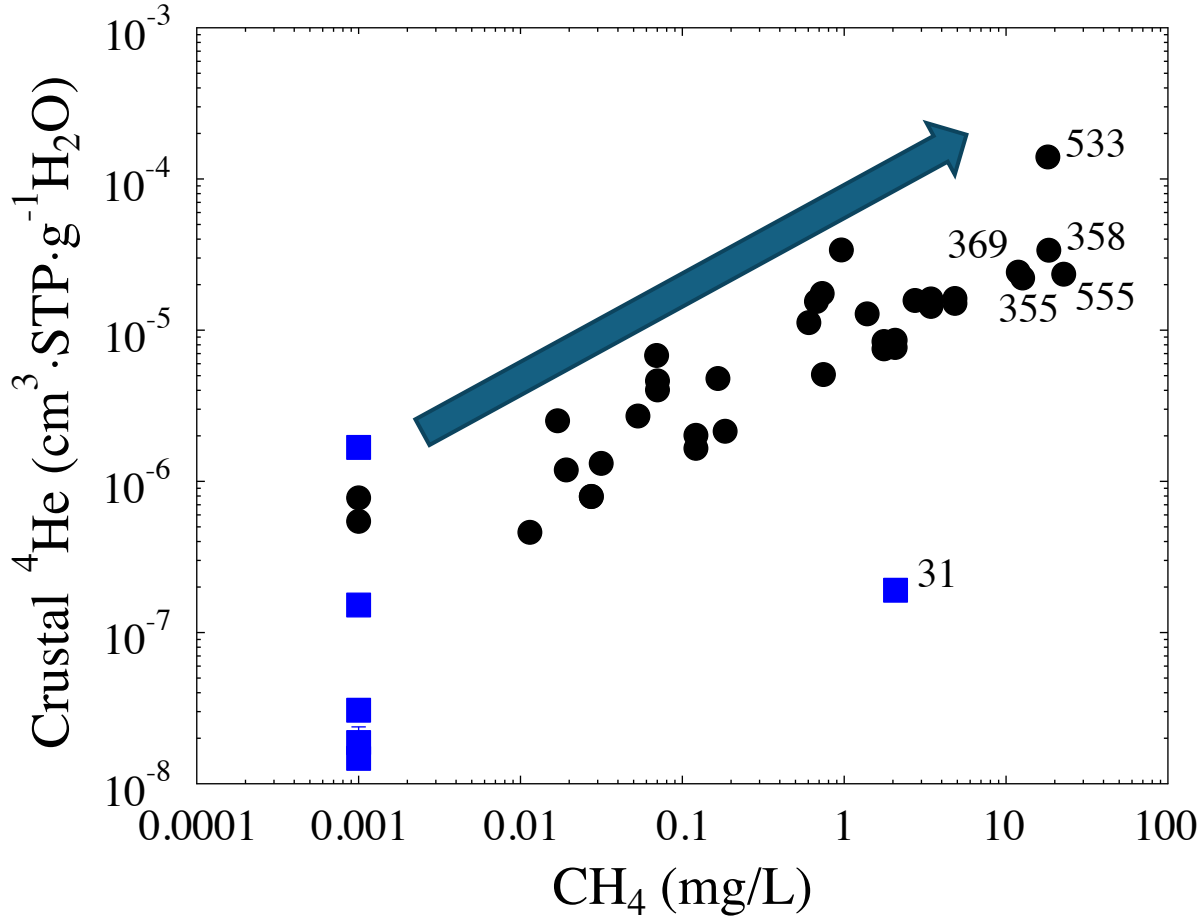
- The deep **Barnett Shale** vs. the shallow **Strawn Group**?
- Naturally-occurring or migrating from nearby gas wells?



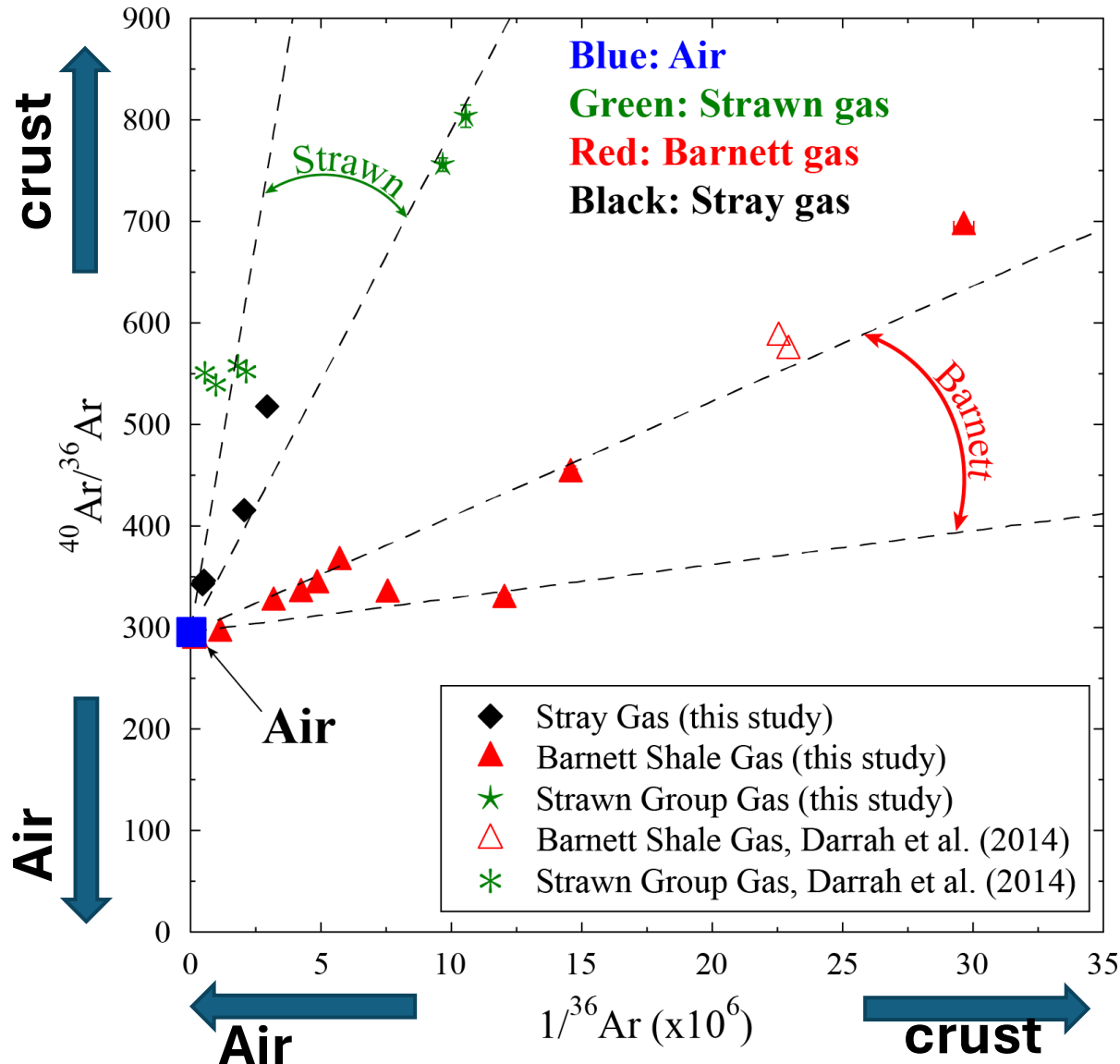
Collecting groundwater and gas samples for noble gas analyses



Correlated noble gases and CH₄ concentrations in water



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

