

Groundwater and Subsurface Fluid Dynamics: Tracing Equilibrium and Fractionation with Noble Gases

SABRINA DINIZ¹, MAGALI PUJOL², GUILLAUME GALLIERO¹, DR. JAMES ALEXANDER SCOTT, PHD² AND ANNE BATTANI¹

¹Université de Pau et des Pays de L'Adour, E2S UPPA, CNRS, LFCR, Pau, France

²OneTech, TotalEnergies

The inertness and scarcity of noble gases in geological fluids make them ideal tracers of subsurface fluid origins and processes. The noble gas composition of subsurface water [1] and its equilibrium interaction with other fluids are well-established. However, non-equilibrium conditions in natural systems deeper than 1 km challenge our understanding of fluid behaviour. In particular, fluid density, temperature, and noble gas concentration influence molecular movement through kinetic diffusion, thermodiffusion, gravitational segregation [2] within layers, and solubility-driven fractionation at fluid interfaces [3].

This study bridges the gap between fractionation and equilibrium states by examining six gas, oil, and water samples from a 4 km deep reservoir. Results reveal unsteady conditions, with fractionation factors (F) for atmosphere-derived ($^{20}\text{Ne}/^{36}\text{Ar}$) and crustal-produced ($^4\text{He}/^{40}\text{Ar}$)* noble gases evolving differently and varying based on phase characteristics. The samples' vertical location and proximity to fluid interfaces affect the type and intensity of fractionation. By reviewing decades of noble gas data from subsurface gases and groundwater, we provide new insights into the physical constraints shaping fractionation. We show that gas phases reach equilibrium one or two orders of magnitude faster than water, revealing dualities in fractionation patterns, even within interconnected reservoirs. Natural gas systems often show covariation in $F(^4\text{He}/^{40}\text{Ar})^*$ and $F(^{20}\text{Ne}/^{36}\text{Ar})$, providing insight into mixing processes and timing [4]. This is less common in denser fluids. In deep groundwater, the fractionation of crustal noble gases correlates with salinity and residence time, varying according to in-reservoir or external processes. We also demonstrate how argon isotope fractionation [5] relates to fluid equilibrium states, specifically ^{40}Ar , ^{38}Ar and ^{36}Ar , and can be used to determine water contact depth.

This research emphasises the significance of aquifer characterisation in establishing baselines for subsurface fluid dynamics interpretation and CO_2 storage operations.

[1] Kipfer et al. (2002). Reviews in Mineralogy and Geochemistry, 47(1), 615-700.

[2] Severinghaus et al. (1996). Geochimica et Cosmochimica Acta, Vol.60, n°6, 1005-1018.

[3] Hoang et al. (2025). Geochimica et Cosmochimica Acta, 388, 127-142.

[4] Ballentine et al. (1991). Earth and Planetary Science Letters, 105, 229 – 246.

[5] Seltzer et al., (2019). Earth and Planetary Science Letters,