

# New Insights into Groundwater Dating from Paired $^{14}\text{C}$ , $^4\text{He}$ , and High-precision $^{40}\text{Ar}$ Measurements in the Columbia River Basalt Aquifer System

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Sustainable groundwater use requires an understanding of groundwater recharge rates and transport pathways. Quantitative knowledge of the groundwater residence times (i.e., the time since a parcel of water was recharged) is critical in this regard for understanding these properties, and for calibrating groundwater flow models that are also helpful for evaluating the susceptibility wells to contamination. Much of the groundwater in the upper kilometer of the crust has a characteristic residence time on the order of 10,000 years. On this timescale, the most common tracer applied to estimate groundwater residence times is radiocarbon ( $^{14}\text{C}$ ) of dissolved inorganic carbon, which is prone to systematic biases, e.g., from carbonate dissolution. Noble gas isotopes, which either accumulate in the subsurface over time due to natural decay of U, Th, K (e.g.,  $^4\text{He}$ ,  $^{40}\text{Ar}$ ), or radioactively decay (e.g.,  $^{81}\text{Kr}$ ) once isolated from surface recharge, have also been applied to calculate residence times. Here, we compare  $^4\text{He}$ ,  $^{14}\text{C}$  and high-precision  $^{40}\text{Ar}$  measurements from fifteen groundwater samples from the regional aquifer system of the Columbia River Basalt Group in eastern Washington, to explore and refine models applied to groundwater dating and radiogenic volatile accumulation in groundwater. Isotopes of Ar are measured via a new analytical technique developed at Woods Hole Oceanographic Institution, involving high-volume samples and high-precision dynamic isotope-ratio mass spectrometric analyses of  $^{38}\text{Ar}/^{36}\text{Ar}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  [1,2,3]. Fractionation during dissolution and vadose zone transport are accounted for and corrected, enabling the resolution of excess  $^{40}\text{Ar}$ . We find a

correlation between excess  $^4\text{He}$  and  $^{40}\text{Ar}$  throughout the entire dataset, continuing into the deepest samples which have homogeneously low  $^{14}\text{C}$  (~1 pmC). Similar correlations are observed with excess  $^3\text{He}$  and we discuss implications for the possible sources and mechanisms by which excess  $^4\text{He}$  and  $^{40}\text{Ar}$  are added to groundwater over time. We will also share new results from application of this new technique to resolve excess  $^{40}\text{Ar}$  from multiple aquifers across the USA and Israel.

[1] Seltzer, A.M., et al., 2021. Chemical Geology.

[2] Ng, J., et al., 2023 Rapid communications in Mass Spectrometry.

[3] Seltzer, A.M. & Bekaert, D.V., 2022. International Journal of Mass Spectrometry.