

Noble gas accumulation in deep aquifers: Insights into ^{40}Ar accompanied by He isotopes

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Noble gas isotopes, such as the radioactive ^{81}Kr and radiogenic ^4He [1] and ^{40}Ar [2], are useful tracers for old (10^4 – 10^5 -yr-order) groundwater, providing possible insights into groundwater residence time, water rock interaction and mixing processes. Together, they can help to deconvolute complex groundwater systems. These tracers undergo distinct processes enabling age estimation. ^{81}Kr can be utilized to date groundwater on timescales between approximately 50–1000 ka due to its radioactive decay, while the stable isotopes ^{40}Ar and ^4He accumulate from the radioactive decay in rocks and subsequent release into the liquid phase. Furthermore, while excess ^4He ($^4\text{He}_{\text{ex}}$) in old groundwater can be quantified using ‘traditional’ mass spectrometry [1], excess ^{40}Ar ($^{40}\text{Ar}_{\text{ex}}$) is largely masked by the atmospheric input and difficult to detect. This study builds upon recent developments in measurement techniques [2,3], which enable quantification of $^{40}\text{Ar}_{\text{ex}}$ in old (^{81}Kr -depleted) groundwater from the northern tip of the Red Sea.

High $^4\text{He}_{\text{ex}}$, combined with $^{40}\text{Ar}_{\text{ex}}$ of up to ~6‰ relative to the atmospheric-derived background, were identified in the hundreds-of-meters deep Nubian Sandstone Aquifer. Furthermore, ^3He and ^4He supported by Ne measurements allow the differentiation of crustal and mantle influence. All samples are dominated by terrigenous He, with mantle He contributing to up to 3.5% of this component. While $^{40}\text{Ar}_{\text{ex}}$ shows no clear correlation with ^{81}Kr , it strongly correlates with $^3\text{He}_{\text{ex}}$. This suggests that $^{40}\text{Ar}_{\text{ex}}$ largely reflects mantle input rather than in-situ accumulation from potassium decay in aquifer minerals. This hypothesis is corroborated and expanded upon by several new, unpublished datasets from other parts of the world [4-6], which show a tight coupling between $^3\text{He}_{\text{ex}}$ and $^{40}\text{Ar}_{\text{ex}}$. We hypothesize that radiogenic ^{40}Ar is readily released from minerals at high temperatures, such as in the mantle, but is largely unreleased from colder crustal minerals.

[1] Purtschert et al. (2023), *Science of The Total Environment*

859, 159886.

[2] Seltzer et al. (2021), *Chemical Geology* 583, 120458.

[3] Seltzer & Bekaert (2022), *International Journal of Mass Spectrometry* 478, 116873.

[4] Noyes et al. (in review), *Water Resources Research*.

[5] Tyne et al. (in review), *Nature Geoscience*.

[6] Kulongoski et al. (2003), *Chemical Geology* 202, 95-113.