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Expanding the noble gas toolkit for hydrogeology - *F.G. Houtermans Award Lecture*

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Noble gases have long represented a powerful suite of physical tracers for groundwater studies. Owing to their lack of chemical and biological reactivity, dissolved noble gases in groundwater - inherited from atmospheric equilibration during recharge and/or produced within aquifers - provide fundamental insights into groundwater recharge and transport. Several recent advances have opened the door to new noble gas applications in hydrogeology, including high-frequency and in situ measurements, analysis of inert radionuclides via atom-trap trace analysis, and high-precision measurements of dissolved noble-gas isotopes via dynamic isotope-ratio mass spectrometry.

Here I focus primarily on the latter, providing an overview of high-precision Ar, Kr, and Xe isotope measurements in groundwater (on the order of 0.001‰/amu) and their emerging use to constrain water-table depth via vadose-zone gravitational fractionation, as well as excess radiogenic ^{40}Ar input to groundwater on 10^4-10^5 year residence timescales. Complementing existing noble gas abundance and helium isotope measurements, high-precision Kr and Xe isotopes now allow noble gases to constrain not only recharge temperature and excess air, but also water-table depth. Recent progress spans initial vadose-zone air measurements, laboratory determinations of solubility equilibrium isotope effects, and molecular dynamics simulations, culminating in over two hundred real-world groundwater measurements. Together, these advances are yielding a clearer picture of stable noble gas isotope dynamics in groundwater systems, including both validation of theoretical expectations and, crucially, shortcomings of theory that expose underappreciated processes. Recent measurements from groundwater systems in North America, Australia, France, and the Middle East demonstrate new potential for resolving past water-table depth changes and linking these changes with climatic and hydrogeologic drivers, attributing sources of geogenic noble gases in aquifers, and revealing new complexities in vadose-zone dynamics in fractured and arid recharge environments. Ultimately, by combining insights from stable isotopes, radioisotopes, and in situ measurements, these new additions to the noble gas toolkit offer an increasingly powerful framework for resolving groundwater recharge processes, flow pathways, and residence timescales.