APPENDIX A: DETERMINATION OF ^{3}HE$_{TRIT}$ USING NE CONCENTRATIONS

In this Appendix we describe calculations and assumptions for determining ^{3}He$_{trit}$ when (1) assuming ^{3}He$_{terr}$ is negligible and (2) using only Ne and He data (i.e., "Ne-only" model). Readers may also find it helpful to review different formulations in SCHLOSSER et al. (1989) and JURGENS et al. (2020; their equation 23 and related text).

If the only source of excess helium is from air trapped at recharge, and that air was in equilibrium with the atmosphere, then ^{3}He$_{terr}$ in equation 3.3 (main text) would be equal to zero and tritiogenic helium (in TU) can be calculated as

$$^3He_{trit} = 4.021 * 10^{14}\left[\frac{^4He_{tot}(R_{tot}-R_{atm}) + {}^4He_{sol}(1-\alpha)}{(1-S/1000)}\right] \tag{A1}$$

where, R_{tot} is the measured ^{3}He/^{4}He ratio, R_{atm} is the atmospheric ^{3}He/^{4}He ratio (1.384 x 10^{-6}, CLARKE et al. 1976), α is the solubility isotope effect at temperature (ex. 0.983 at 0° C, from BENSON and KRAUSE 1980; or 0.988 at 0° C from WEISS 1970), *S* is the salinity of the sample ^{4}He$_{tot}$ (‰), is the measured ^{4}He concentration in cm^{3}STP/g H_2O for the water sample, and ^{4}He$_{sol}$ is the calculated ^{4}He concentration (cm^{3}STP/g H_2O) in solubility equilibrium with the atmosphere (SCHLOSSER et al. 1988). Solubility of He for a range of temperature and salinity is found in WEISS (1971). Solubility isotope effect data for ^{3}He and ^{4}He for different temperatures are found in WEISS (1970) or BENSON and KRAUSE (1980).

In the case where nucleogenic helium or mantle helium is a potential source of helium, equation A1 may not provide an accurate estimate of tritiogenic helium. If the concentration of neon gas is also measured in the water samples (SCHLOSSER et al. 1988; SCHLOSSER et al. 1989) it provides an additional useful ratio, ^{4}He/Ne, which can be compared to the known ratio in the atmosphere to assess for production of ^{4}He in the subsurface.

By measuring neon in water samples and assuming that the atmosphere is the only source of Ne (WEISE and MOSER 1987; SCHLOSSER et al. 1989) the contribution of terrigenic ^{3}H can be calculated.

Equation A2 shows the calculation of ^{3}He in solubility equilibrium with the atmosphere, based on ^{4}He concentration in solubility equilibrium with the atmosphere (^{4}He$_{sol}$) and where R_{sol} is the ratio of ^{3}He to ^{4}He for water in isotopic equilibrium with the atmosphere (1.37 x 10^{-6}, SOLOMON et al. 1993).

$$^3He_{sol} = R_{sol}{}^4He_{sol} \tag{A2}$$

^{3}He$_e$ is then determined using measured Ne concentration and ^{4}He in the groundwater sample

$$^3He_e = R_{sol}\left[(Ne_{tot} - Ne_{sol})\alpha'\left(\frac{^4He}{Ne}\right)_{atm}\right] \tag{A3}$$

where the ratio of ^{4}He/Ne in the atmosphere is known to be 0.288 (SCHLOSSER et al. 1989). Ne$_{tot}$ and Ne$_{sol}$ are the total neon concentration (measured in groundwater sample) and calculated neon concentration at solubility equilibrium with the atmosphere (WEISS 1971), respectively. The air-water fractionation term, α′, in equation A3 is defined as R_{gas}/R_{water} and equal to 1.012 at 10° C (SOLOMON et al. 1993; based on isotopic fractionation value of -1.2% from WEISS 1970).

Assuming mantle-derived helium is negligible and given equations A1 through A3 to account for atmospheric sources of helium, only the nucleogenic helium (^{3}He$_{nuc}$) remains to be determined before solving equation 3.1 for tritiogenic helium. Nucleogenic helium is calculated

$$^3He_{nuc} = R_{rad}\left[{}^4He_{tot} - {}^4He_{sol} - (Ne_{tot} - Ne_{sol})\left(\frac{^4He}{Ne}\right)_{atm}\right] \tag{A4}$$

where R_{rad} is the known ratio of radiogenic ^{4}He to nucleogenic ^{3}He (2 x 10^{-8}; SCHLOSSER et al. 1989; SOLOMON et al. 1993) and all other variables are as previously defined.

Solving equation 3.3 for tritiogenic helium and substituting equations A1 through A4 yields equation A5, which is ultimately used to determine tritiogenic ^{3}He in the groundwater sample (SOLOMON & COOK 2000). Note that typical units for the variables in equation A5 are cm^{3}STP/g H_2O, which requires that ^{3}He$_{trit}$ be converted to TU before applying the age equation (equation 2.3, main text).

$$\begin{aligned} ^3He_{trit} = {} & {}^3He_{tot} - R_{sol}{}^4He_{sol} - R_{sol}\left[(Ne_{tot} - Ne_{sol})\alpha'\left(\frac{^4He}{Ne}\right)_{atm}\right] \\ & - R_{rad}\left[{}^4He_{tot} - {}^4He_{sol} - (Ne_{tot} - Ne_{sol})\left(\frac{^4He}{Ne}\right)_{atm}\right] \end{aligned} \tag{A5}$$