

## When does the $^{39}\text{Ar}$ groundwater dating clock start?

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Groundwater dating by radioactive cosmogenic tracers such as  $^{39}\text{Ar}$  relies on the activity concentration decrease in dissolved gas, starting from a known atmospheric activity. It is commonly accepted that  $^{39}\text{Ar}$  concentration of fresh recharge deviates only marginally from the 100%modern value ( $1.8 \text{ mBq/L}_{\text{Ar}}$ ) [1]. The simple decay dating assumes that cosmogenic  $^{39}\text{Ar}$  production in the underground is negligible at depths below the water table. Here we present  $^{39}\text{Ar}$  data from quaternary glacial sediments as well as cretaceous chalk and tertiary limestone aquifers in Denmark, which clearly show that this is not always the case. Over modern  $^{39}\text{Ar}$  values in relatively shallow groundwater depths are observed in non-radiogenic rocks. Therefore, the point in time and space where the radioactive clock starts in the underground depends on the hydrological situation (recharge rate and vertical velocity distribution), the production rate and the release mechanism of the radioisotope from the rock to the groundwater. Underground production, that keeps supplying the dissolved activity concentration, is then not only delaying the clock start time, but also slowing down the clock rate resulting in too young groundwater age distributions if not corrected for.

The analytical results from Denmark are interpreted using depth-dependent residence time information determined by flow modelling and particle tracking [2] and compared with the isotopic data ( $^{39}\text{Ar}$ ,  $^{37}\text{Ar}$ ,  $^4\text{He}$ ,  $^{85}\text{Kr}$ ). We also reviewed and re-evaluated the various  $^{39}\text{Ar}$  and  $^{37}\text{Ar}$  production channels by neutron and muon interactions with the sediments as a function of depth, allowing for the calculation of the integrated cosmogenic  $^{39}\text{Ar}$  production along the groundwater flow path. We propose a  $^{39}\text{Ar}$  input activity correction scheme based on local hydrological and  $^{37}\text{Ar}/^{39}\text{Ar}$  ratio constraints.

[1] Gu et al. (2021), Chem. Geol. 583 [2] Trolldborg et al. (2008), J. Hydrol. Eng. 13.