

Stable water isotope signatures in porewaters of argillaceous rocks

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The distribution of stable water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) in ground- and porewaters provides insights into the hydrogeological evolution of aquifer - aquitard sequences and large scale transport processes [1]. In clay-rich lithologies, isotope data can be determined directly on samples extracted by high pressure squeezing (SQ) or advective displacement (AD) [2]. As the complexity of these extraction methods limits the amount of data, less laborious methods such as the isotope diffusive exchange technique (IDE) [3] are needed for profiles of high spatial resolution.

The negative charge of clay mineral surfaces interacts with the water molecule and with cations surrounded by hydration shells. Thus, in a simplified way free and bound porewater can be distinguished in clay-rich rocks. While the advective flow in SQ and AD targets the free water only, the IDE may tap both porewater fractions.

Within the framework of the Swiss deep drilling campaign for the site selection of a deep geological repository for radioactive waste, high resolution stable water isotope profiles were acquired using IDE, augmented by a smaller dataset from SQ and AD [1]. Systematic differences in the isotopic compositions obtained by AD/SQ versus IDE in the porewater profiles are discussed with respect to their implication for the isotopic signatures of porewater domains. The dataset is complemented with benchmarking studies, in which clay-rich rocks were equilibrated with an artificial porewater using AD or in-diffusion experiments and subsequently analysed by IDE.

While the observed differences in the isotopic composition obtained by the different methods are relevant for a mechanistic understanding of the distribution of water stable isotopes in clays, they are small compared to the natural range in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of porewater profiles and thus not significant for the interpretation of large-scale transport processes.

[1] Gimmi, Aschwanden, Waber, Gaucher, Ma & Traber (2023), Applied Geochemistry, 105846.

[2] Kiczka, Wersin, Mazurek, Zwahlen, Jenni, Mäder & Traber (2023), Applied Geochemistry, 105838.

[3] Aschwanden, Waber, Eichinger & Gimmi, (2023), Applied Geochemistry, 105844.