



Multi-isotope tracing of CO₂ leakage and water-rock interaction in a natural CCS analogue.

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Natural analogues of CO₂ accumulation and, potentially, leakage, provide a highly valuable opportunity to study (1) geochemical processes within a CO₂-reservoir and the overlying aquifers or aquicludes, i.e. gas-water-rock interactions, (2) geology and tightness of reservoirs over geological timescales, (3) potential or real leakage pathways, (3) impact of leakage on shallow groundwater resources quality, and (4) direct and indirect geochemical indicators of gas leakage (Lions *et al.*, 2014, Humez *et al.*, 2014). The Florina Basin in NW Macedonia, Greece, contains a deep CO₂-rich aquifer within a graben structure. The graben filling consists of highly heterogeneous Neogene clastic sediments constituted by components from the adjacent massifs including carbonates, schists, gneiss as well as some ultramafic volcanic rocks. Clay layers are observed that isolate hydraulically the deep, partly artesian aquifer. Organic matter, in form of lignite accumulations, is abundant in the Neogene series. The underlying bedrocks are metamorphic carbonates and silicate rocks. The origin of the CO₂ accumulation is controversial (deep, partially mantle-derived D'Allessandro *et al.*, 2008 or resulting from thermal decomposition of carbonates, Hatziyannis and Arvanitis, 2011). Groundwaters have been sampled from springs and borewells over 3 years at different depths. First results on major, minor and trace elements give evidence of water-rock interaction, mainly with carbonates but also with ultramafic components but do not indicate that CO₂-seepage is the principal driver of those processes (Gemeni *et al.*, submitted).

Here we present isotope data on a selection of groundwaters ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}_{TDIC}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{11}\text{B}$, $\delta^7\text{Li}$). Stable isotopes of water indicate paleo-recharge for some of the groundwaters, limited exchange with gaseous CO₂ and, in one case, possibly thermal exchange processes with silicates. Sr isotope ratios vary between marine ratios and radiogenic values indicating interaction with carbonates and silicates. Both $\delta^{11}\text{B}$ and $\delta^7\text{Li}$ show a very large range of variation and fairly good correlation, between -29.7 ‰ and +24‰ vs. NBS951 for boron and -11‰ and +20.4‰ vs. L-SVEC for lithium. The negative $\delta^{11}\text{B}$ and $\delta^7\text{Li}$ values are among the lowest reported in literature for groundwaters, comparable only to values observed for boron in case of geothermal fluids interaction with clay minerals (Pennisi *et al.*, 2009) or in some amphiboles (e.g. Gillis *et al.*, 2003) or lithium in ultramafic rocks (Nishio *et al.*, 2004). Those variations reflect water-rock interaction with the silicate fraction of the highly heterogeneous graben filling but no clear indication of enhanced reactions due to CO₂ intrusion has been found. The $\delta^{13}\text{C}$ values of TDIC are also strongly variable (-10.5 to +15 ‰ vs. PDB), reflecting biogenic inputs (e.g. from lignite layers), dissolution of carbonates and, potentially, methanogenesis through CO₂ reduction.

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