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A first investigation of the stable silicon isotopic composition of groundwaters in the UK

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Over the past decade, study of the silicon flux through groundwater to the oceans has gained momentum, and it has been estimated that dissolved silicon flux to the ocean via terrestrial submarine groundwater discharge is 0.7 ± 0.1 Tmol yr^{-1}.

For the first time, Si isotope analysis has been applied to groundwater samples from the UK, with 17 samples collected from boreholes, one from a spring and two comparative samples from surface waters.

Two study areas were chosen with contrasting geological settings. The first study area comprises a coastal, shallow (<30m) Quaternary Sand and Gravel aquifer and a bedrock sourced thermal spring (Cardiff, UK), whilst the second area comprises a mined sequence of Carboniferous Coal Measures strata (Glasgow, UK).

Contrary to the Glasgow groundwater samples, which have a relatively consistent Si isotopic composition ranging from 0.42‰ to 1.10‰, the Cardiff groundwater samples exhibit large variation from -0.28‰ to 1.68‰. The only negative Si isotope value found in the Cardiff groundwater comes from the sample from Taffs Well thermal spring, which has been shown to have a residence time of at least 5000 years with limited interaction with modern water. Thus, the negative Si isotope could be the result of long-time water-rock interaction. There is a relatively strong correlation between the ratio of DSi concentration to chlorine and $\delta^{30}Si$ in the Cardiff groundwater samples, which might indicate that preferential uptake of the lighter silicon isotopes during secondary clay formation has left the residual groundwater with a heavier silicon isotopic composition. Furthermore, whereas the Cardiff groundwater is enriched in major cations (Na^+, Mg^{2+}, Ca^{2+} and K^+) compared with the surface water, the ratios of these major cations to chlorine of the surface waters are higher than that of most of the Cardiff groundwater samples. This trend potentially reveals the removal of these cations in groundwater systems in active uptake processes such as secondary clay formation. Our results highlight the important roles of water-rock interaction and secondary clay formation on the groundwater Si isotopic composition, providing further insights into elemental cycles in groundwater.