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The Role of Calcium Isotopes ($\delta^{44/40}Ca$) in Tracing Cation Exchange Processes

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Cation exchange, a critical water-rock interaction in clay-rich systems (e.g., $Ca^{2+} + Na_2X \rightleftharpoons CaX + 2Na^+$), plays a pivotal role in regulating geochemical cycles, influencing water quality, and distinguishing carbonate versus silicate weathering contributions. Recent advancements in calcium isotope analysis ($\delta^{44/40}Ca$) have expanded its application as a tracer for processes such as mineral dissolution, carbonate precipitation, and cation exchange. However, existing methodologies for quantifying Ca isotope fractionation coefficients during cation exchange remain limited by inconsistent experimental conditions and insufficient precision. To address these limitations, this study introduces an optimized experimental protocol and applies in a natural groundwater system. Our findings reveal preferential adsorption of light Ca isotopes onto clay surfaces, with fractionation magnitudes following the sequence: montmorillonite > illite > kaolinite. This hierarchy correlates with mineral-specific properties, including exchange site typology (permanent vs. variable charge), site density, ionic double-layer thickness, and exchange kinetics. Furthermore, enhanced fractionation was observed under conditions of smaller clay particle sizes and lower initial Ca^{2+} concentrations. To demonstrate practical applications, we employed a multi-tracer approach ($\delta^{44/40}Ca$, $^{87}Sr/^{86}Sr$, $\delta^{13}C$, ^3H, and ^{14}C) to investigate groundwater evolution in the Dongzhi Tableland loess aquifer (NW China), a system characterized by simplified hydrogeology. Results indicate that Ca^{2+} and Mg^{2+} derive predominantly from carbonate dissolution, while Na^+ originates from two sources: cation exchange (71% mean contribution) and atmospheric precipitation (29% mean contribution). A positive correlation between $\delta^{44/40}Ca$ values and groundwater age reflects progressive isotope enrichment during prolonged cation exchange. Notably, silicate weathering contributions to aqueous Na^+ were negligible, underscoring the limited silicate weathering impact in this arid-zone aquifer. This work advances the application of Ca isotopes in geochemical tracing by (1) refining experimental methods for cation exchange studies and (2) establishing $\delta^{44/40}Ca$ as a sensitive indicator of water-rock interaction timescales. The methodology provides a novel framework for hydrogeological investigations and related fields requiring precise quantification of subsurface cation exchange processes. This study was supported by the National Natural Science Foundation of China (Grants 42172277, 42141009) and National S&T Major Project (2024ZD1000404).