

Insights into fluid sources and flow rates from lithium isotope composition of methane-seep carbonates

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Authigenic carbonates in marine sediments provide valuable insights into the element and isotopic composition of pore fluids. Pore fluids at methane seeps experience fluid–rock interactions over a broad range of temperatures during their ascent to the seafloor, which can be traced by the stable isotopes of lithium (Li) in the fluids. The Li isotope composition of authigenic carbonate precipitating at methane seeps is therefore a promising archive of the source and migration history of pore fluids, but remains largely unexamined to date. Here we analyzed the element geochemistry and isotopic composition of Li in methane-seep carbonates collected from the Black Sea and the Japan Sea. The Ca/Li ratios and $\delta^7\text{Li}$ values of the aragonite- and calcite-rich samples revealed a positive correlation, indicating a minor admixture of clay-bound Li. The $\delta^7\text{Li}$ values of the carbonates corrected for clay-bound Li were used to estimate the isotopic composition of the parent fluids, yielding values as low as ca. 17‰. The estimated $\delta^7\text{Li}$ values and Li/Ca ratios of the fluids cannot be explained by fluid mixing alone, suggested by the relationships between the Li/Ca ratios, $\delta^7\text{Li}$ values, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The low $\delta^7\text{Li}$ values of the fluids can be rather explained by isotopic fractionation between a deep fluid, sourced from >250 m below seafloor, and secondary minerals over a range of temperatures experienced during advective fluid transport. Advection rates of $\geq 10^{-2}$ cm yr⁻¹ would be necessary to explain the data, indicated by reaction-transport modeling. Variations in the Li/Ca and $\delta^7\text{Li}$ values recorded in the carbonates could then be explained by compositional evolution of the fluids during the advective transport. This study shows that the Li isotope composition of seep carbonates is an excellent indicator of fluid sources and flow rates at methane seeps through geological time, which may also help to understand the formation history of gas hydrates.

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