

Clay, brine, or both? What do lithium isotopes tell us about deeply buried Cretaceous alkaline lake rocks and how producing hydrocarbon fields may help in the energy transition

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Lithium is a valued commodity for modern battery technologies and offers a potential pathway towards greater electrification and away from fossil fuel dependence. Beyond its economic significance, lithium isotopes are also a powerful tool in geochemistry. They are used to trace present-day rates of primary silicate dissolution and secondary mineral formation, to reconstruct crustal rocks' palaeo-weathering trends, and mass transfer budgets. Whilst widely applied to marine and crustal systems, they can be a useful tool to investigate continental ("terrestrial") settings, such as sedimentary basins formed in palaeoenvironments strictly confined to the continents. The Lower Cretaceous carbonate rocks and associated silicate deposits of the Barra Velha Formation, in the Santos Basin, presently offshore Brazil, are such an example. They were primarily formed during the rifting and pre-break-up of western Gondwana. This setting sustained a prolific carbonate factory along with authigenic Mg-silicate clay formation, all of which speak to considerably arid conditions and alkaline waters in those lakes from which they precipitated. Progressive subsidence and burial diagenesis likely triggered dissolution and (re)precipitation of later phases, partially obscuring the primary, *syn*-sedimentary geochemical signals and original textures. But lithium and its isotopes may be important in helping to disentangle some of these processes too. For instance, lithium isotopes analysed in the carbonate and silicate components separately reveal minimal isotopic fractionation between these two materials. Interestingly, the carbonate $d^7\text{Li}$ is considerably lower than that of coeval marine carbonates. Lithium concentrations ($[\text{Li}^+]$) measured in both rock/mineral and aqueous fluid samples suggest authigenic clays, such as Mg-smectites, concentrated lithium as they were forming from alkaline waters, in their *syn*-sedimentary environment of deposition. Additionally, the silicate fraction $d^7\text{Li}$ and $[\text{Li}^+]$ values indicate two silicate end-members: fine detrital silicate grains (e.g., K-feldspar and mica-group minerals), with low $d^7\text{Li}$ and comparatively lower $[\text{Li}^+]$, and authigenic Mg-silicate clays, with progressively higher $d^7\text{Li}$ and high $[\text{Li}^+]$.

Because this formation is an important hydrocarbon reservoir rock in active production, lithium and lithium isotopes can also inform us of on-going fluid-rock interaction processes. And, perhaps, represent a new resource itself, with relatively low environmental footprint and low production costs associated with less energy-intensive extraction.