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Calibration of marine Ca and Sr isotope proxies against 'salinity' in fresh-to-hypersaline coastal lagoon-estuarine settings of South Australia

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The application of marine Ca and Sr isotope proxies for paleo-seawater studies requires their precise calibration in modern coastal and marine environments. Here we investigate the variability of $\delta^{44/40}$Ca and ^{87}Sr/^{86}Sr proxies (as a function of *salinity*) in natural waters collected from the lagoon-estuarine environments of the Coorong Lagoon and Murray Mouth (CLMM) hydrological system, in South Australia. The latter represents a unique 'natural laboratory' for proxy calibration studies, as the salinity in the CLMM system ranges from *fresh* (~0 psu; near the River Murray Mouth), through *normal marine* (~35 psu; in Coorong North Lagoon), to *hypersaline* (up to ~130 psu; in South Lagoon). Our results confirmed that both $\delta^{44/40}$Ca and ^{87}Sr/^{86}Sr proxies in coastal/lagoon waters are sensitve to *salinity* changes due to (i) seawater-freshwater mixing of isotopically distinct waters, and (ii) the input of local groundwaters into the lagoon. In addition, and unlike the radiogenic ^{87}Sr/^{86}Sr tracer, the $\delta^{44/40}$Ca is also sensitive to local carbonate ($CaCO_3$) precipitation and deposition in the *hypersaline* South Lagoon, where the lagoon waters are highly oversaturated with respect to $CaCO_3$ minerals. The degree of mineral saturation (i.e., calcite, aragonite, gypsum) across the Coorong Lagoon was quantified using PHREEQC modelling, and the calculated mineral saturation indices (SI) are evaluated with respect to variations in the $\delta^{44/40}$Ca of lagoon waters and their salinities.

Specifically, a progressive seawater evaporation in South Lagoon leads to *hypersalinity* and a local oversaturation with respect to main Ca-bearing minerals (i.e., calcite and aragonite, but not gypsum), which in turn impacts the Ca isotope composition of local waters, as these have systematically higher $\delta^{44/40}$Ca signatures (compared to *normal seawater*) due to preferential removal of light Ca into $CaCO_3$. A simple Rayleight modelling approach (and also PHREEQC calculations) suggest that about 40 to 55% of the dissolved Ca^{2+} in the South Lagoon was removed as $CaCO_3$, which has also implications for a better understanding of the local carbon cycling and C burial fluxes within the lagoon.