Reconstructing the $\delta^{44/40}Ca$ of seawater: insights from modern and ancient elasmobranch teeth

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Reconstructions of the $\delta^{44/40}Ca$ of seawater are a vital aspect in deciphering the global Ca cycle through Earth history. Measurements of non-traditional stable isotopes, including $\delta^{44/40}Ca$, in bioapatite such as elasmobranch enamel, have the potential to be a robust proxy for geochemical, environmental and ecological reconstructions of seawater. In particular, the utility of this archive is strenghtened by the large temporal range occupied by elasmobranchs (Devonian to modern day), abundance in the rock record due to high replacement rates of teeth in sharks, and resistance to mineralogical and geochemical overprinting via diagenetic alteration.

Here we present isotope (e.g. $\delta^{44/40}Ca$, $\delta^{26}Mg$, $^{87}Sr/^{86}Sr$) and trace element (e.g. Sr/Ca, Mg/Ca) data for modern and fossil shark teeh, as well as synthetic apatite precipitates. Modern teeth have an average $\delta^{44/40}Ca$ value of -2.07±0.48 ‰ (2σ, n = 80) and Sr/Ca ratio of 2.30±0.24 mmol/mol (2σ, n = 40), both offset from present day seawater (0 ‰ and 8.6 mmol/mol, respectively). These samples spanned a range of feeding ecologies, from primary to tertiary piscivores, though trophic level appears to impart a nominal influence on the chemical offset from seawater. Instead, we hypothesize that the modern signal is related to a combination of inorganic (as observed via apatite precipitation experiments) and biological (e.g. metabolic and ionic regulation) effects.

We also present a near-continuous record of seawater chemistry derived from ~300 teeth for the last 200 Myr. Corrected $\delta^{44/40}Ca$ and Sr/Ca values based on calibrations from modern samples broadly agree with previously published compilations, with a ~0.5 ‰ increase in $\delta^{44/40}Ca$ observed over the Neogene. The observed enrichment in the isotopic compostion of seawater suggests a change in the fractal partitioning of the global Ca sink (platform vs. pelagic carbonates) and may be attributed to a decrease in global areal shelf extent.