# Radiogenic $^{40}$Ca in Seawater

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The sources and sinks of seawater Ca are of interest for understanding paleoseawater chemistry and the global carbon cycle. Radioactive $^{40}$K is concentrated in continental crust, and continental crustal rocks show enrichments in radiogenic $^{40}$Ca [1]. The composition of the oceans reflects competition between continental and seafloor weathering inputs.

Measurements of crustal rocks suggest that the modern oceans are likely to be enriched in $^{40}$Ca by 1.5 epsilon units ($\varepsilon_{Ca}$ = +1.5) relative to the mantle [1]. However, recent work [2] concluded that there were no differences between seawater, oceanic crust, and the reference material SRM915a, and that marine carbonates show no resolvable $\varepsilon_{Ca}$ variations through geologic time [2]. This latter result implies that seawater $^{40}$Ca is completely buffered by exchange with ocean floor rocks over all of Earth history, and is not consistent with other estimates of modern Ca fluxes [1].

We report $\varepsilon_{Ca}$ measurements in SRM915a, modern seawater (GEOTRACES seawater standard), a USGS carbonate standard (EN-1), USGS dolerite standards (DNC-1 and W2-a), and modern hydrothermal vent fluids, and find, by aggregating the results of ca. 10-15 analyses each, that seawater and SRM915a have $\varepsilon_{Ca}$ = +1.4 ±0.5 relative to the igneous rock standards ($\varepsilon_{Ca}$ = 0 ±0.3). Hydrothermal fluid from Lost City vent has $\varepsilon_{Ca}$ = -0.1 ±0.6 indicating almost all of its Ca is from ocean floor basalt as expected.

Our results indicate that SRM915a is a poor reference for evaluating excess $^{40}$Ca or estimating fluxes in the global Ca cycle [2]. The appropriate reference is bulk silicate Earth (BSE), and this can be defined by modern oceanic basalts and certain meteorites [1,3-5]. Riverine Ca inputs to the ocean are much larger than those from MOR hydrothermal systems, and the riverine input is probably augmented by marine carbonate diagenesis and continental groundwater [1]. These considerations, and estimates of upper crustal $\varepsilon_{Ca}$ values of about +2 to +3, are consistent with our measurement of modern seawater. Paleoseawater $\varepsilon_{Ca}$ may be sensitive to past changes in the Ca cycle.

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