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Late Archean-early Proterozoic evolution of seawater $^{40}Ca/^{44}Ca$ records the growth and emergence of felsic continental crust

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Studies of ancient siliciclastic sediments suggest that continental crust switched from a mafic to a more felsic composition between ~3-2.5 Ga [1]. However, siliciclastic sediments are influenced by regional variations in source rock composition, and may not provide a global picture of continental crust composition. Seawater composition is influenced by the balance between continental weathering and hydrothermal alteration of seafloor basalts, and is therefore sensitive to changes in continental crust composition. Because felsic rocks have much higher K/Ca than mafic/ultramafic rocks, weathering of felsic crust results in delivery of radiogenic ^{40}Ca to the oceans [2]. We have analyzed mass-independent variations in $^{40}Ca/^{44}Ca$ in a suite of carbonates ranging in age from modern to 2.8 Ga. Sr/Ca and $^{87}Sr/^{86}Sr$ in 2.8 Ga Steep Rock (Canada) carbonates are strongly correlated with $d^{44/40}Ca$, reflective of varying degrees of diagenetic alteration. Two samples that record the least alteration have $\varepsilon^{40}Ca$ (-0.9 and -0.7) close to mantle values (~-1). A third sample that has been dolomitized has elevated $\varepsilon^{40}Ca$ (-0.2) as well as elevated $^{87}Sr/^{86}Sr$ (0.7078 vs. 0.7018 in the non-dolomitized samples). In contrast, a carbonate sample from the 1.8 Ga Duck Creek formation, Australia, records an $\varepsilon^{40}Ca$ value of -0.4, close to the modern seawater value of -0.3. Finally, modern carbonate ooids from Little Ambergris have an $\varepsilon^{40}Ca$ value (-0.41) indistinguishable from modern seawater. Both the altered and unaltered carbonates define a broad positive correlation between $\varepsilon^{40}Ca$ and $^{87}Sr/^{86}Sr$. These preliminary data suggest that seawater $\varepsilon^{40}Ca$ at 2.8 Ga was close to mantle values, but that by 1.8 Ga seawater had evolved to a more radiogenic composition close to modern seawater. Because of the moderate half-life of ^{40}K (1.25 billion years), there is a lag between formation of felsic crust and the delivery of radiogenic ^{40}Ca to the oceans. The inferred increase in seawater $\varepsilon^{40}Ca$ between 2.8 and 1.8 Ga is thus consistent with the shift in crustal composition between 3-2.5 Ga inferred previously. This shift may mark the onset of modern-style plate tectonics.

[1] Tang et al., Science 251, 372-375, 2016. [2] Antonelli et al., ACS Earth Space Chem. 5, 2481-2492, 2021.