On the radiogenic ^{40}Ca anomaly in seawater and limestone

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Caro *et al.* [1] estimate that the silicate upper continental crust has a radiogenic ^{40}Ca anomaly of 2.5 epsilon units from ^{40}K decay. Surprisingly, Caro *et al.* show that epsilon ^{40}Ca of seawater and limestone is indistinguishable from the mantle value (epsilon ^{40}Ca~0, since the mantle has low K/Ca), with an uncertainty of about ± 0.3 units. To balance the modern oceanic ^{40}Ca budget, they suggest that the riverine flux of radiogenic crustal Ca is balanced by a small nonradiogenic flux from high-temperature hydrothermal processes at mid-ocean ridges, and a larger flux of nonradiogenic calcium from low-temperature hydrothermal systems on ridge flanks. If correct, waters in ridge flank hydrothermal systems must play a major role in the chemical mass balance of the oceans.

We discuss 3 factors that, without invoking ridge flank exchange, help explain the enigma that limestone and seawater Ca are much less radiogenic than the silicate crust. First, radiogenic ^{40}Ca is diluted into the large mass of limestone. Second, the time-averaged hydrothermal flux would be twice the present value if it scaled with past heat production. Third, nonradiogenic hydrothermal Ca would have been retained in the limestone and (via metamorphism) in the silicate crust; it would be recycled by subsequent weathering, thereby lowering epsilon ^{40}Ca in rivers. These three factors together can account for about two-thirds of the difference between the estimated ^{40}Ca anomaly of the silicate continental crust and the nonradiogenic Ca composition of seawater and limestone.

[1] Caro, Papanastastassiou & Wasserburg (2010), *Earth and Planetary Science Letters* **296**, 124-132.

Limited early continents from the chemistry of Eoarchean rocks

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Continuing and fundamental questions in Earth history focus on the timing and mechanisms of early continent formation. These questions take on additional significance in consideration of potential early life habitats and early tectonic regimes. Key approaches used to argue for, and against, massive early continents, have centered on the signatures of long-lived isotopic systems, i.e. initial εNd and εHf, preserved in the oldest rocks. For example, positive deviations from bulk silicate Earth compositions have been equated with massive early crust formation. Such interpretations contain the assumption that continental crust has been the primary complement to the depleted mantle throughout Earth history. However, using an expanded ^{142}Nd,^{143}Nd,^{176}Hf database derived from Eoarchean rocks worldwide we demonstrate that Nd and Hf isotopic data do not record the distinctive correlations observed in younger granitic terranes; these correlations are generated in the mantle by long term crust extraction. Furthermore, positive ^{142}Nd anomalies (relative to modern terrestrial compositions) measured in some Eoarchean rocks require extremely early (4.53 Ga - 4.4 Ga) Sm/Nd fractionation. Overall, neither Sm-Nd or Lu-Hf fractionation in the >3.7 Ga mantle can be linked to continental crust extraction.

Other types of observations from ancient rocks further support the case for limited crustal volumes. Eoarchean rocks are now recognised in 8 gneiss complexes worldwide. In each area, the oldest felsic rocks (ca. 3.7-4.0 Ga) are typically tonalites, with no evidence of pre-existing crust in the form of inherited zircon grains with older U-Pb ages. Where data are available, the initial εNd and εHf values range from chondritic to positive and δ^{18}O isotopic compositions are mantle-like; thus there is no chemical evidence for reworking of older components. In contrast, younger (≤3.65 Ga) granites (*sensu stricto)* often contain inherited zircons whose U-Pb ages match the oldest crust in each region; initial εNd and εHf values become more negative with decreasing rock age, reflecting incorporation of older felsic components. We consider that, at present, there is no compelling evidence for the existence of extensive early continents, prior to ~3.65 Ga.