The isotopic mass balance of calcium

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Carbonate minerals constitute a fundamental part of the sedimentary geological record and have yielded canonical stable isotope datasets ($\delta^{13}C$ and $\delta^{18}O$, e.g. [1]), but questions remain about how to interpret this valuable archive. We suggest that additional information about the nature of these datasets can be obtained by examining the record of calcium isotopes ($\delta^{44/40}Ca$) of sedimentary carbonates through time and considering the calcium cycle and isotopic mass balance. Calcium is the major complementary cation accompanying carbon and oxygen in this geological archive and has high preservation potential. In an attempt to define a representative sample set of carbonates through the Precambrian, we present a record of >500 calcium-isotope analyses in bulk limestones and dolomites, including a variety of sedimentary environments and textures. By characterizing the dominant sink for oceanic calcium, this new dataset constrains the isotopic mass balance of calcium in the surface environment over billions of years of Earth history.

Variability in this $\delta^{44/40}Ca$ dataset indicates the influence of carbonate mineralogy (i.e. aragonite vs calcite) in the carbonate calcium-isotope record and suggests that calcium isotopes can be useful in identifying the former presence of aragonite, even in rocks with a history of neomorphism and recrystallization.

Although carbonates are the dominant sink for calcium and are largely recycled within the sedimentary reservoir, a small fraction of calcium in the surface environment is removed via metamorphism or subduction. We also present data characterizing the minor subducted sink of calcium, as represented by carbonate veins in oceanic crust. The distinct isotopic signature of this sink relative to sedimentary carbonates allows us to place limits on the importance of subduction relative to sedimentary recycling and to model the isotopic evolution of the crustal calcium reservoir over time.

[1] Shields & Veizer (2002) *Geochem. Geophys. Geosyst.* **3**, 1–12.