



# Testing Urey's carbonate–silicate cycle using the calcium isotopic composition of sedimentary carbonates



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## ABSTRACT

Carbonate minerals constitute a major component of the sedimentary geological record and an archive of a fraction of the carbon and calcium cycled through the Earth's surface reservoirs for over three billion years. For calcium, carbonate minerals constitute the ultimate sink for almost all calcium liberated during continental and submarine weathering of silicate minerals. This study presents >500 stable isotope ratios of calcium in Precambrian carbonate sediments, both limestones and dolomites, in an attempt to characterize the isotope mass balance of the sedimentary carbonate reservoir through time. The mean of the dataset is indistinguishable from estimates of the calcium isotope ratio of bulk silicate Earth, consistent with the Urey cycle being the dominant mechanism exchanging calcium among surface reservoirs. The variability in bulk sediment calcium isotope ratios within each geological unit does not reflect changes in the global calcium cycle, but rather highlights the importance of local mineralogical and/or diagenetic effects in the carbonate record. This dataset demonstrates the potential for calcium isotope ratios to help assess these local effects, such as the former presence of aragonite, even in rocks with a history of neomorphism and recrystallization. Additionally, 29 calcium isotope measurements are presented from ODP (Ocean Drilling Program) Site 801 that contribute to the characterization of altered oceanic crust as an additional sink for calcium, and whose distinct isotopic signature places a limit on the importance of this subduction flux over Earth history.

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## 1. Introduction

The carbonate–silicate cycle, also known as the Urey reactions (Urey, 1952), describes the interactions between the solid and fluid Earth that control the global carbon cycle and Earth's climate on million-year timescales (Berner et al., 1983). Carbon dioxide degassed from Earth's interior eventually cycles back to the solid Earth as carbonate minerals and some organic matter. Calcium (and to a lesser extent, magnesium) is the major cation that accompanies this return flux. Exactly how carbon and calcium return from the Earth's surface to its interior over Earth history remains uncertain, owing to the difficulty of quantifying the fluxes associated with alteration of oceanic crust, metamorphism, and subduction. Model reconstructions of the history of the global carbon cycle (e.g. Sleep and Zahnle, 2001) suggest that recycling of carbonate back into Earth's interior is vigorous, particularly on early Earth, but empirical evidence to test these models is lacking.

In addition to participating in carbon cycling on geological timescales, the accumulation of limestone (and dolomite) sediments in the crust also provides one of the most important archives of Earth's surface environment. The chemical composition of marine carbonate sediments has been used to reconstruct the history of the global oxygen and carbon cycles and important steps in biotic evolution (e.g. Schidlowski, 1988; Des Marais et al., 1992). A critical and untested assumption in the interpretation of many chemical and isotopic records in ancient carbonates is that they are a good approximation of the global sink of carbon in contemporaneous carbonate sediments. However, carbonate sediments preserved in the geological record reflect only a fraction of the mass initially deposited (Wilkinson and Walker, 1989); exactly what fraction, and whether it is chemically and isotopically representative of the global carbonate sink, is not well known.

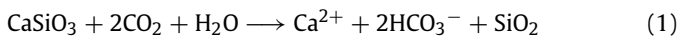
### 1.1. A simple model of calcium mass balance

The special role played by calcium in the cycling of carbon between its fluid and solid reservoirs means that the calcium mass balance carries information about the magnitude of fluxes between

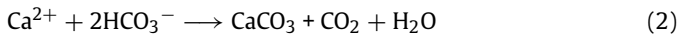
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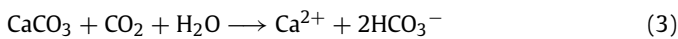
these reservoirs. A simplified version of this cycle begins with a silicate weathering reaction:



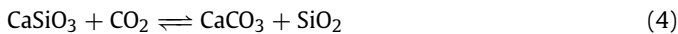
where carbon dioxide (carbonic acid) dissolves an idealized calcium silicate, wollastonite, to yield calcium, bicarbonate, and silica. The weathering of igneous minerals is the original source of all calcium to the surface (i.e. fluid and sedimentary) reservoirs. These aqueous products are then removed by calcium carbonate precipitation:



which accumulates in environments such as continental shelves, pelagic sediments, or within oceanic crust. Some fraction of sedimentary carbonates resulting from equation (2) will eventually be recycled by carbonate weathering:



(the reverse of equation (2)) whose products may mix with those of primary silicate weathering in the oceans. The balance of equation (1) relative to equation (3) therefore represents the ‘new’ calcium added to the surface system and mixed into the sedimentary reservoir, with subduction and metamorphism closing the cycle. The sum of equations (1) and (2) is the forward reaction of the classic Urey cycle/Urey reactions:



with the reverse representing carbonate metamorphism in subduction and orogenic zones.

If the Urey reactions are an accurate description of net surface processes, a prediction for the global calcium cycle is that, on average, the calcium isotopic composition of carbonate sediments through time should equal that of bulk silicate Earth (i.e. what goes in must come out). This prediction is independent of carbonate weathering, which merely recycles calcium within Earth’s surface reservoir, but does depend on 1) the calcium isotopic composition of exposed igneous minerals, and 2) fluxes of calcium associated with subduction and their isotopic composition. Implicit in studying the Urey cycle is that the  $\text{CaCO}_3$  produced, preserved, and sampled represents the global calcium (and hence inorganic carbon) sink from the ocean at the time of sedimentation. The simplicity of the calcium cycle compared to carbon–calcium has only a single major sink compared to carbon, which can be removed in both oxidized ( $\text{CaCO}_3$ ) and reduced (organic C) forms—means that reconstructions of calcium isotopes in carbonate sediments can also be used to test whether the geological record is representative of the long history of calcium and carbon fluxes between Earth’s surface and its interior.

This study presents a large ( $n = 505$ ) dataset of calcium isotope ratios ( $\delta^{44/40}\text{Ca}$ ) in carbonate sediments over 2.5 billion years of Earth history to test the hypotheses that: 1) the calcium isotopic composition of carbonate sediments, on average and over  $10^8$  yr timescales, equals that of bulk silicate Earth, and 2) the geological record of carbonate sediments is representative of the average sink of calcium (and therefore carbon). This approach does not track the composition of seawater through time (e.g. Farkaš et al., 2007), but characterizes the average calcium isotopic sink in carbonate sediments. This study provides a test of traditional interpretations of carbonate geochemical proxies (e.g.  $\delta^{13}\text{C}$ ) and of the suitability of the Urey cycle for describing the evolution of the carbonate reservoir and the Earth system.

## 2. Materials and methods

### 2.1. Samples

Sample selection for this study reflects an attempt to gather a representative segment of the geological record of carbonates and altered oceanic crust. Further discussion, including potential biases involved, is presented in section 4.1.

#### 2.1.1. Carbonate sediments

Carbonate rocks were selected from geological units of various ages spanning much of the Precambrian (3.0–0.54 Ga). Sample ages and descriptions are taken from published sources and a single age (often approximated and rounded to the nearest 0.1 Ga, with some formations very poorly constrained) is assigned to each formation. The temporal resolution of sampled formations is  $\sim 0.2$ – $0.3$  Gyr. Samples include both limestones and dolomites and generally reflect materials and/or formations considered representative for their age with respect to  $\delta^{13}\text{C}$  chemostratigraphy (Shields and Veizer, 2002). Ranges for published  $\delta^{13}\text{C}$  values of each formation or the same hand samples, where available, as well as references providing lithology, facies, and paleoenvironment are provided in the supplementary materials. Within a single section, samples were chosen indiscriminately at the desired stratigraphic resolution with the goal of obtaining representative materials deposited under the prevailing environmental conditions.

Complementary to the sampling strategy described above, designed to minimize bias within sedimentary sections, a handful of specific petrographic phases were also targeted to assess the influence of carbonate mineralogy on the carbonate record (see section 4.2 and Fig. 6). Petrographically identified aragonite crystals were sampled from the Steep Rock Group, Carawine Dolomite, Campbellrand Platform, and Atar Formation. Herringbone calcite cements (Sumner and Grotzinger, 1996) were targeted from the Campbellrand Platform.

#### 2.1.2. Altered oceanic crust

The alteration of oceanic crust in both high-temperature ( $\sim 350^\circ\text{C}$ ) and low-temperature ( $< 60^\circ\text{C}$ ) hydrothermal systems affects the calcium subduction flux in two main ways. At high temperatures, anhydrite precipitation and exchange reactions with igneous minerals occur (see section 4.3.2). At low temperatures, the formation of calcium carbonate veins results in carbon and calcium uptake from seawater (Alt and Teagle, 1999). To constrain the characteristics of these low-temperature alteration materials, samples were obtained from some of the oldest existing oceanic crust, at ODP Site 801 (170 Ma, western Pacific). Calcium carbonate veins were sampled from Hole 801C, targeting documented veins greater than 2 mm wide and with a majority  $\text{CaCO}_3$  composition (Plank et al., 2000). This site has been used to establish a composite reference material for altered oceanic crust (Kelley et al., 2003), representing an estimate of the bulk chemical composition of subduction.

### 2.2. Sample preparation

Bulk carbonate powders were obtained by drilling or crushing carbonate rock samples. For drilled powders, site selection criteria mimic those used for standard  $\delta^{13}\text{C}$  analyses, i.e. examining polished slab faces and avoiding obvious veins and fractures. Selective dissolution of carbonate phases was conducted with approximately 1 mL of buffered 0.1 M acetic acid–ammonium hydroxide solution per mg of sample, typically for 5 mg samples. Samples were ultrasonicated for four hours, then centrifuged for 30 min at 2500 rpm. The dissolved phase was removed into a clean vial, and the insoluble residue discarded.

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