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# Variations in the marine Ca cycle over the past 20 million years

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## Abstract

A 20 million year marine Ca isotope record is constructed based on measurements of 36 nanofossil ooze samples from DSDP Site 590. The Ca isotopic composition ( $\delta^{44}\text{Ca}$ , relative to our “bulk Earth” average) of carbonate ooze samples varies between  $-0.2$  and  $-0.9$ , and the inferred  $\delta^{44}\text{Ca}$  of seawater calcium varies between  $+1.1$  and  $+0.4$  (modern seawater value is  $+0.95$  on our scale). Fluctuations in the seawater Ca isotope ratio occur in 2 to 4 million year intervals and indicate that the supply and removal of Ca from the oceans are seldom in balance. The Ca isotope record is used to reconstruct past weathering fluxes and marine calcium concentrations. The inferred marine concentration of Ca fluctuates by about  $\pm 20\%$  on 2–4 million year time scales and by about  $\pm 50\%$  over the 20 million year record. These variations are presumably superimposed on the previously inferred 100 million year variations. The seawater Ca concentration was about 0.5 times present at 20 Ma and generally increased until 6 Ma (1.7 times present). Local maxima in seawater calcium concentrations occur at 6.4 and 4 Ma, preceding periods of enhanced marine productivity and high mass accumulation rates at Site 590. While the calculated calcium concentrations are sensitive to the assumed  $\delta^{44}\text{Ca}$  value for the weathering flux, the 2–4 million year features of the derived curves are not.

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## 1. Introduction

The chemical evolution of seawater over geologic time has been a topic of study for many years [1,2]. Proxies for the chemical composition of seawater,

such as fluid inclusions in evaporite minerals, indicate that the concentrations of major ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ) have changed significantly over the Phanerozoic [3–5]. Since measurements allowing estimates of seawater chemistry in the past are scarce, the resulting records have low temporal resolution and, as a result, only broad limits can be placed on seawater evolution.

Studies of fluid inclusions in halite and model simulations of seawater chemistry suggest that the

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seawater calcium concentration has decreased by a factor of 2–4 over the past 40 million years [3,6,4,7]. Since the concentration of calcium is controlled by the balance between input and output, this implies that Ca inputs have been lower than Ca outputs for significant periods during this time. Calcium fluxes to the ocean are determined by silicate and carbonate weathering on continents, the alteration of basalt by seawater, and the dolomitization of  $\text{CaCO}_3$  in marine sediments [8]. The output of Ca from the ocean is dominated by carbonate sedimentation and affected to a smaller degree by Ca–sulfate precipitation. In general, the data from fluid inclusions in evaporites implies that weathering has added less Ca to the ocean over the past 40 million years than carbonate sedimentation has removed.

This study reports Ca isotopic data on 36 samples of nanofossil ooze from DSDP Site 590B spanning the age range 0.1–20 Ma. The data are used to reconstruct past Ca isotopic compositions of the oceans and to interpret variations in the relative rates of Ca delivery to and removal from the oceans [9]. We suggest that the Ca isotope data may be used to estimate past variations in the Ca concentration of the oceans at a higher resolution than currently utilized methods. Our approach is based on the assumption that marine carbonates have Ca isotopic ratios that are systematically related to the Ca isotopic ratio of seawater. Since the residence time of Ca in the ocean is about  $10^6$  years and the mixing time of the ocean is about  $10^3$  years, the ocean is likely to be homogeneous with respect to Ca and the isotopic record at a particular site may be considered a global record.

Previous studies that address past variations in the Ca isotopic composition of the oceans [9,10] and aspects of the modern Ca cycle [11,12] are reviewed by DePaolo [13]. In this study, we present a higher resolution data set which more appropriately represents the Ca cycle.

## 2. Sample location and description

Carbonate sediments from Deep-Sea Drilling Project Site 590 (Hole 590B) were sampled on the Lord Howe Rise in the southwest Pacific Ocean ( $31^\circ 10.02'$  S,  $163^\circ 21.51'$  E; 1299 m water depth) [14,15]. Site

590 is situated on the subtropical divergence in the transitional zone between warm subtropical and temperate regions [14,15]. The sediment is primarily nanofossil ooze but contains foraminifera-rich intervals and thin volcanic ash layers [14,15]. The oldest sediments cored are earliest Miocene (~24 Ma). Mass accumulation rates (MAR) at Site 590 were low in Early to Middle Miocene time, but higher and fairly constant from 15 to 6 Ma at  $\sim 2000 \text{ g cm}^{-2} \text{ m.y.}^{-1}$  (<63  $\mu\text{m}$  fraction) [16]. Between 6 and 3 Ma, the bulk MAR reached a maximum value  $\sim 8000 \text{ g cm}^{-2} \text{ m.y.}^{-1}$  (<63  $\mu\text{m}$  fraction) while the carbonate MAR peaked at  $\sim 7000 \text{ g cm}^{-2} \text{ m.y.}^{-1}$  [17,16]. After 3 Ma, MARs at 590 decreased to the Holocene rate of  $\sim 1800 \text{ g cm}^{-2} \text{ m.y.}^{-1}$ .

## 3. Analytical methods

The procedures for the chemical separation and mass spectrometric analysis of Ca are modified from those previously described [18,19]. Because of the relative purity of the carbonate samples, and the fact that calcium carbonate can be preferentially dissolved when mixed with silicates, deep sea carbonate ooze with small amounts of silicate can be analyzed with minimal chemical preparation. Samples are dissolved in acetic acid and centrifuged; a mixed  $^{42}\text{Ca}$ – $^{48}\text{Ca}$  tracer ( $^{42}\text{Ca}/^{48}\text{Ca} \approx 0.7$ ) is added to an aliquot of the separated supernatant. The dissolved, spiked sample is loaded directly onto Ta filaments with phosphoric acid ( $\text{H}_3\text{PO}_4$ ) for mass spectrometric analysis.

Mass spectrometric analysis of  $\text{Ca}^+$  ions is performed on a single-collector mass spectrometer (modified VG354 design with one large Faraday bucket collector). Ion beam intensities, integration times, and sample sizes are the same as previously reported [9,20,21]. Double spike subtraction and recovery of the unspiked sample isotopic composition uses an iterative technique [9,20,21]. All but one of the samples were measured in replicate ( $n=2, 3$ , or 4) and the reported uncertainty is the external  $2\sigma$  error determined by replicate measurements. Most samples yield uncertainties close to 0.1‰, but a few samples did not reproduce well and have larger uncertainties.

All  $^{44}\text{Ca}/^{40}\text{Ca}$  ratios are expressed as  $\delta^{44}\text{Ca}$  values relative to our standard value of 0.0212116 [19,18],

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