Calcium isotope fractionation as a function of solution stoichiometry in groundwater

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While modeling predictions have suggested fluid calcium to carbonate ratio may influence the calcium isotope fractionaton factor as well as the net rate constant during calcite growth, field evidence of the macroscopic effects of solution stochiometry on precipitation rate and isotopic fractionation has been difficult to observe. Here we present some of the first evidence of solution stoichiometry influencing the fractionation in δ^{44}Ca of groundwater in a series of clogged well bores during organic carbon ammended uranium bioremediation of a contaminated aquifer in western Colorado. Secondary mineral formation induced by carbonate alkalinity generated during the bioremediation process lead to substantial permeability reduction in multiple electron-donor injection wells at the field site. These conditions resulted in removal of aqueous calcium from a backrgound concentration of 6mM to >1mM while δ^{44}Ca enrichment ranged from 1‰ to greater than 2.5‰ [Figure 1].

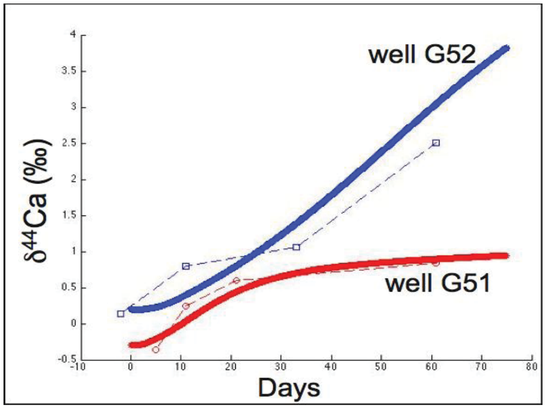

Figure 1: Data and models of δ^{44}Ca fractionation in clogged well bores as a function of time.

The variation observed in δ^{44}Ca between wells is attributed to the difference in carbonate alkalinity generated in each well bore, presenting some of the first field evidence supporting theoretical models of calcium isotope fractionation as a function of fluid Ca^{2+}:CO_3^{2-} ratio. Where the Ca^{2+}:CO_3^{2-} ratio remains >30 the δ^{44}Ca fractionation is accurately modeled by precipitating Ca-40 and Ca-44 as independent species in a TST-style model with carbonate formation calculated as a solid solution [Figure 1 red line]. However reproducing the observed δ^{44}Ca trend where Ca^{2+}:CO_3^{2-} <30 is only accomplished by utilizing a newly developed analytical model for calcium isotope fractionation as a function of solution stochiometry [Figure 1 blue line].

Constraining late Miocene seawater composition: a multiproxy approach

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The late Miocene (11.61–5.33 Ma) was one of the most climatically stable periods of the past 60 Myr. However, superimposed on the stable long-term trend, short-term, 40 kyr high-amplitude changes in δ^{18}O are observed that suggest Milankovitch forcing of seawater δ^{18}O composition, temperature, or both. Understanding seawater composition evolution during this time could offer insight into the natural variation of important climate parameters, such as ice volume and sea surface temperatures.

The goal of our study is to reconstruct seawater δ^{18}O composition at different levels in the water column across the late Miocene (3.50-8.50 Ma). The study site is located in the Eastern Equatorial Pacific (Site U1338), and samples were collected during IODP Expediton 321. Understanding temporal changes in Equatorial Pacific seawater temperature and compostion is critical due to the importance of the low-latitude regions for global ocean circulation. Reconstructing $\delta^{18}O_{seawater}$ will be achieved by combining multiple geochemical proxies on benthic and planktic foraminifera. Here we present preliminary δ^{18}O and δ^{13}C data from the benthic foraminifera *Cibicidoides mundulus*. The data's long-term trends reflect global patterns, which implies the site is suitable for a high-resolution seawater composition study. Our ultimate target resolution is 3-4 kyr, which allows resolution of ~20 kyr orbital cycles. As $\delta^{18}O_{calcite}$ from benthic foraminifera is a function of both $\delta^{18}O_{seawater}$ and calcification temperature, the $\delta^{18}O_{calcite}$ will be combined with Mg/Ca and Li/Ca measurements, both temperature proxies, to reconstruct $\delta^{18}O_{seawater}$.

A second component of future work is to reconstruct temporal changes in surface water δ^{18}O and Mg/Ca by combining traditional stable isotope and trace element measurements with a novel proxy called clumped isotopes. The 'clumped isotope themometer' Δ^{47} reflects the amount of rare, heavy stable isotopes ^{13}C and ^{18}O bound together in the carbonate crystal lattice. Δ^{47} shows an inverse relationship with temperature, as more ^{13}C-^{18}O bonding occurs at lower temperature. The initial T-Δ^{47} calibration was based on inorganic calcite, however a recent study has shown that foraminiferal and coccolithophore calcite shows the same T-Δ^{47} relationship and is not affected by 'vital effects'.

We will present initial data comparing Δ^{47} measurements on the fine fraction (predominantly consisting of coccolithophores) to Mg/Ca and δ^{18}O measurements on planktic foraminifera (*Globigerinoides sacculifer*). By measuring Δ^{47} on samples consisting mainly of planktic material, we will be able to deconvolve sea surface temperature from secular changes in Mg/Ca and δ^{18}O seawater values measured in planktic foraminiferal calcite.