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Effects of ocean acidification on the marine calcium isotope record at the Paleocene–Eocene Thermal Maximum

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ABSTRACT

Carbonates are used extensively to reconstruct paleoclimate and paleoceanographic conditions over geologic time scales. However, these archives are susceptible to diagenetic alteration via dissolution, recrystallization and secondary precipitation, particularly during ocean acidification events when intense dissolution can occur. Despite the possible effects of diagenesis on proxy fidelity, the impacts of diagenesis on the calcium isotopic composition (δ^{44}Ca) of carbonates are unclear. To shed light on this issue, bulk carbonate δ^{44}Ca was measured at high resolution in two Pacific deep sea sediment cores (ODP Sites 1212 and 1221) with considerably different dissolution histories over the Paleocene–Eocene Thermal Maximum (PETM, ∼55 Ma). The δ^{44}Ca of marine barite was also measured at the deeper Site 1221, which experienced severe carbonate dissolution during the PETM. Large variations (∼0.8‰) in bulk carbonate δ^{44}Ca occur in the deeper of the two sites at depths corresponding to the peak carbon isotope excursion, which correlate with a large drop in carbonate weight percent. Such an effect is not observed in either the 1221 barite record or the bulk carbonate record at the shallower Site 1212, which is also less affected by dissolution. We contend that ocean chemical changes associated with abrupt and massive carbon release into the ocean–atmosphere system and subsequent ocean acidification at the PETM affected the bulk carbonate δ^{44}Ca record via diagenesis in the sedimentary column. Such effects are considerable, and need to be taken into account when interpreting Ca isotope data and, potentially, other geochemical proxies over extreme climatic events that drive sediment dissolution.

1. Introduction

The Ca isotopic composition (δ^{44}Ca) of marine sediments offers the potential to reconstruct the global cycle of Ca over geologic time scales. Previous Ca isotope work has provided insight into seawater chemical evolution over million-year time scales (De la Rocha and DePaolo, 2000; Fantle and DePaolo, 2005; Heuser et al., 2005; Farkas et al., 2007; Griffith et al., 2008a, 2011; Fantle, 2010), the triggers of mass extinctions (Payne et al., 2010; Hinojosa et al., 2012), the behavior of the Earth system during Ocean Anoxic Events (Blättler et al., 2011) and Neoproterozoic glaciations (Kasemann et al., 2005, 2014). Calcium isotopes can also shed light on recrystallization rates during marine burial diagenesis (Fantle and DePaolo, 2007; Fantle et al., 2010; Turchyn and DePaolo, 2011; Fantle, 2015).

One advantage of using Ca isotopes to reconstruct the past is the long residence time of Ca (∼1 Ma; Berner and Berner, 1996), relative to the ocean mixing time, in the global ocean. The resulting assumption of a homogeneous oceanic Ca reservoir suggests that the δ^{44}Ca of synchronous minerals at various locations in the ocean should record a value reflective of global seawater δ^{44}Ca, and not local or regional δ^{44}Ca. Recent work, however, suggests complications arising from the assumption of homogeneous oceanic δ^{44}Ca, primarily in terms of spatial heterogeneities in nearshore settings (Holmden et al., 2012) and the impact of spatially variable fractionation factors associated with Ca removal in carbonates that precipitate in different marine settings (Fantle, 2010; Kasemann et al., 2014).

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Carbonate minerals are ubiquitous in Phanerozoic marine sediments and thus are often used as the archive for various paleoclimatic and paleoceanographic proxies. While it has long been recognized that carbonates are susceptible to post-depositional alteration (e.g., Epstein et al., 1951; Urey et al., 1951), the diagenetic effects on Ca isotopes are unclear. It has previously been suggested that carbonate-rich sections are generally well buffered against diagenetic alteration of δ^{44}Ca, however the effects of extreme dissolution events have not been considered (Fantle and DePaolo, 2007; Fantle, 2010; Fantle et al., 2010). It is imperative that any isotopic effects associated with such events are elucidated, and their genesis understood, as such events are often the foci of isotopic proxy studies (Payne et al., 2010; Blättler et al., 2011).

The current study investigates the effects of large-scale carbonate dissolution during the Paleocene–Eocene Thermal Maximum (PETM; ~55 Ma) on deep-sea carbonate and marine barite δ^{44}Ca records. The PETM event was caused by a massive carbon release into the ocean–atmosphere system, resulting in ocean acidification and consequent widespread dissolution of marine calcium carbonate (e.g., Zachos et al., 2005). The understanding of diagenetic effects on proxy records during the PETM has a broader relevance to similar episodes in Earth history over a range of time scales, and offers critical insight into the expression of diagenetic effects in the rock record.

Assuming that seawater δ^{44}Ca does not change as a result of perturbations that persist over time scales substantially less than the residence time of Ca (Komar and Zeebe, 2011), comparing synchronous Ca isotope records at different open ocean locations (or derived from different minerals at the same locations and depth interval) can elucidate the effects of post-depositional alteration on the proxy archives of interest. Differences in contemporaneous δ^{44}Ca records may then be attributed to diagenetic effects, mineralogical variations, or changes in archive-specific isotopic fractionation factors (e.g., Fantle, 2010; Fantle and Tipper, 2014). By contrast, similar temporal trends at multiple locations suggest with greater confidence that measured δ^{44}Ca records reflect primary environmental signals that are globally interpretable.

The current study presents records of δ^{44}Ca derived from bulk carbonate and marine barite, ^{87}Sr/^{86}Sr from marine barite, carbon (δ^{13}C) and oxygen (δ^{18}O) isotopic composition of bulk carbonate, trace element composition and weight percent (wt%) $CaCO_3$ from two Pacific Ocean locations – Ocean Drilling Program (ODP) Leg 198 Site 1212B (Shatsky Rise) and Leg 199 Site 1221C (Mahi Mahi Fracture Zone) – that are used to shed light on the role of diagenesis in influencing sedimentary δ^{44}Ca values. The ODP sites investigated have considerably different dissolution histories over the PETM: Site 1212B remained above the calcite compensation depth (CCD) throughout the event and Site 1221C was within the lysocline before, below the CCD during, and above the CCD after the PETM (Zeebe et al., 2009). The data suggest that the dissolution history over the PETM systematically (and predictably) influences the δ^{44}Ca of deep-sea carbonates and, possibly, marine barite.

2. Methods

Bulk carbonate and marine barite were sampled from ODP sediment cores at Site 1212B (paleowater depth ~2200 m; Takeda and Kaiho, 2007) and Site 1221C (paleowater depth ~3200 m; Murphy et al., 2006). The Leg 198 Site 1212B Paleocene–Eocene boundary interval consists predominantly of pale yellowish brown nannofossil ooze with clay alternating with pale orange to grayish orange nannofossil ooze (Shipboard Scientific Party, 2002a). An abrupt contact at the base of the PETM event is thought to be an unconformity, however, "the significance… is currently not understood" (Shipboard Scientific Party, 2002a).

The calcareous nannofossil chalk with clay recovered from Leg 199 Site 1221C abruptly transitions to zeolitic clay with dramatic color variations at the Paleocene–Eocene boundary (Shipboard Scientific Party, 2002b; Fig. 1). Very pale brown to brown strongly bioturbated chalk occurs at the base of the sampled interval. The last occurrence of Paleocene benthic foraminifers is at the base of the zeolitic clay layer (1221C-11X-3 90 cm), where the chalk below gradually grades into zeolitic clay over a span of several centimeters. The first occurrence of Eocene benthic foraminifers is found at 1221C-11X-3 50 cm, within the chalk where $CaCO_3$ weight percent reaches ~80% (Shipboard Scientific Party, 2002b).

Nannofossils are present in some samples from Site 1221 in the interval between the last and first occurrences of Paleocene and Eocene benthic foraminifers (154.3 to 153.9 mbsf, respectively; Lyle et al., 2002). Dolomite is interspersed throughout the core, but never constitutes >15% of those particles documented in smear slides (Lyle et al., 2002). Dolomite is generally more abundant outside the carbon isotope excursion (CIE) than within the CIE.

High-resolution δ^{44}Ca records derived from bulk $CaCO_3$ (both sites) and coeval barite (Site 1221C only) were determined for the PETM (Tables 1 and 2). Bulk carbonate samples were dissolved using weak (1 M) acetic acid, as previously described by Fantle and DePaolo (2005). Barite was extracted using a sequential leaching process (Paytan et al., 1993), screened for purity using a scanning electron microscope with energy dispersive X-ray spectroscopy, and prepared for isotopic analysis following Griffith et al. (2008c). Calcium isotopic composition (^{44}Ca/^{40}Ca) was measured by thermal ionization mass spectrometry (TIMS) at the U.S.G.S. (Menlo Park) and the Helmholtz Centre for Ocean Research (Kiel, Germany) using double-spike techniques on a Finnigan MAT 261 adjustable collector instrument and Thermo Scientific TRITON, respectively. All data are reported in delta notation (i.e., δ^{44}Ca or $\delta^{44/40}$Ca, in permil, ‰, units) relative to modern seawater (Griffith et al., 2008c). External reproducibility, determined as the average $2\sigma_{\text{mean}}$ of replicate analyses of individual samples is 0.15‰ and 0.17‰ for Menlo Park and Kiel, respectively. External precision was determined using reference materials measured over several years including seawater, NIST SRM 915a, La Jolla Ca, and CaF_2 (Griffith et al., 2008b, 2008c). The Sr isotopic composition (^{87}Sr/^{86}Sr) of barite was measured on a VG354-S TIMS at the University of California-Santa Cruz. External reproducibility, expressed as $2\sigma_{\text{mean}}$, on duplicate runs is <0.00006 and measurement of NIST SRM 987 yielded 0.710741 ± 7 (within run standard error).

Trace elemental ratios were determined on both a 1 M acetic acid leach (Sites 1212 and 1221) and a 0.1 M ammonium acetate–acetic acid buffer leach (Site 1221) (Table 1), following previously published methods (Apitz, 1991; Delaney and Linn, 1993). Site 1221 sediments were sequentially leached by ultra-pure water (18.2 MΩ cm) and 1 M NH_4OH (ion exchange step), and subsequently dissolved in the buffer. Both Sr/Ca and Mg/Ca ratios were determined on the 1 M acetic acid and 0.1 M ammonium acetate–acetic acid buffer leaches of sediments from Site 1221, which represent the carbonate component. All leaches were analyzed by inductively coupled plasma–atomic emission spectrometry (ICP-AES) at either the University of California-Santa Cruz (1221C 1 M acetic acid leach) or University of Texas at Arlington (1212B 1 M acetic acid leach and 1221C 0.1 M ammonium acetate–acetic acid buffer leach). External precision of the Sr/Ca and Mg/Ca ratios determined by duplicate dissolutions of samples in the 1 M acetic acid leach is <3% (RSD). External precision of the 0.1 M ammonium acetate–acetic acid buffer trace metal ratios determined by duplicate sample analyses were within 8% (RSD) for Sr/Ca, but were poorly replicated for Mg/Ca.

The δ^{18}O and δ^{13}C values of Site 1212B bulk carbonates (Table 3) were measured using a Finnigan-MAT 252 mass spectrometer with a Kiel III carbonate device at the University of Florida.