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

Elizabeth M. Griffith a,*, Matthew S. Fantle b, Anton Eisenhauer c, Adina Paytan d, Thomas D. Bulle n e

a Department of Earth and Environmental Sciences, University of Texas at Arlington, TX 76019, USA
b Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA
c GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1-3, 24148 Kiel, Germany
d Institute of Marine Sciences, University of California, Santa Cruz, CA 95064, USA
e Branch of Regional Research, Water Resources Division, U.S. Geological Survey, Menlo Park, CA 94025, USA

A R T I C L E   I N F O

Article history:
Received 8 August 2014
Received in revised form 11 February 2015
Accepted 5 March 2015
Editor: G.M. Henderson

Keywords:
calcium isotopes
diagenetic effects
Paleocene–Eocene Thermal Maximum
marine barite

A B S T R A C T

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 (δ44Ca) of carbonates are unclear. To shed light on this issue, bulk carbonate δ44Ca 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 δ44Ca 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 δ44Ca 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 δ44Ca 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.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The Ca isotopic composition (δ44Ca) 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; Heusser 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; Turcyn 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 δ44Ca of synchronous minerals at various locations in the ocean should record a value reflective of global seawater δ44Ca, and not local or regional δ44Ca. Recent work, however, suggests complications arising from the assumption of homogeneous oceanic δ44Ca, 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).
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 $\delta^{44}\text{Ca}$, however the effects of extreme dissolution events have not been considered (Fanti and DePaolo, 2007; Fanti, 2010; Fanti 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; $\sim$55 Ma) on deep-sea carbonate and marine barite $\delta^{44}\text{Ca}$ 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 timescales, and offers critical insights into the expression of diagenetic effects in the rock record.

Assuming that seawater $\delta^{44}\text{Ca}$ 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 $\delta^{44}\text{Ca}$ records may then be attributed to diagenetic effects, mineralogical variations, or changes in archive-specific isotopic fractionation factors (e.g., Fanti, 2010; Fanti and Tipper, 2014). By contrast, similar temporal trends at multiple locations suggest with greater confidence that measured $\delta^{44}\text{Ca}$ records reflect primary environmental signals that are globally interpretable.

The current study presents records of $\delta^{44}\text{Ca}$ derived from bulk carbonate and marine barite, $\delta^{87}\text{Sr}/\delta^{86}\text{Sr}$ from marine barite, carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) 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 $\delta^{44}\text{Ca}$ 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 lysolcine 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 $\delta^{44}\text{Ca}$ 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 $\sim$$2200$ m; Takeda and Kaho, 2007) and Site 1221C (paleowater depth $\sim$$2000$ 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 $\sim80\%$ (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 nmbf, 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 $\delta^{44}\text{Ca}$ 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 Fanti 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 ($^{44}\text{Ca}/^{40}\text{Ca}$) 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., $\delta^{44}\text{Ca}$ or $\delta^{40}\text{Ca}$, in permil, unit) 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$_3$ (Griffith et al., 2008b, 2008c). The Sr isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$) of barite was measured on a VG534-5 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 MΩcm) and 1 M NH$_4$OH (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 spectroscopy (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 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ 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.
All C and O isotope data are reported in delta notation relative to Vienna Pee Dee Belemnite (VPDB). External reproducibility, calculated as twice the standard deviation of replicate analyses of NBS-19 (n = 8), is 0.04‰ and 0.12‰ for δ^{13}C and δ^{18}O, respectively. Total inorganic carbon was measured at the University of Florida using a UIC Coulometrics 5011 CO₂ coulometer coupled with an AutoMate carbonate device.

Ages were determined relative to the carbon isotope excursion (CIE) by correlating the bulk carbonate δ^{13}C record at Site 1212B to Site 690 δ^{13}C (Röhl et al., 2007; Table 4). Using updated ³He ages for Site 690 (Murphy et al., 2010) results in 1212B sedimentation rates (between 0.15 and 0.22 cm/ka) that are within the range of previous estimates (Shipboard Scientific Party, 2002a). Site 1221 δ^{13}C record is significantly affected by dissolution and is not dated in the same manner. Instead, the previously identified benthic extinction event at Site 1221 (Nomura and Takata, 2005) and a ³He age model for Site 1221 (Ma et al., 2014) were used to assign age. The resulting Site 1221 age model indicates large variations in apparent sedimentation rate from 0.25 cm/ka within the CIE to 1.5 cm/ka at the end of the recovery phase, similar to patterns seen at other sites (e.g., Röhl et al., 2007).

3. Results

The CIE is well expressed at 1212B, with a pre-excursion average δ^{13}C value of 3.21‰, an approximate 3‰ decrease in bulk carbonate δ^{13}C ~ 50 ka after the identified onset of the excursion, and a minimum value of 0.30‰ (Fig. 2). Over the core section of 1212B analyzed, the average CaCO₃ content is 94% (2RSD = 8.5%, n = 30), although there is a brief drop to ~80 wt % at 79.92 mbsf (~15 ka after the onset of the CIE). The drop in CaCO₃ content is followed by the minimum δ^{18}O (~1.5%) at 79.90 mbsf (~15 ka later); pre-CIE δ^{18}O values are −0.86 ± 0.19‰ (2SD, n = 14) while the latter part of the recovery period has an average δ^{18}O of

---

**Fig. 1.** ODP Site 1221C core photograph and SEM of bulk sample (left) and barite residues in backscatter electron mode (right). Calcium carbonate weight percent of bulk samples from Murphy et al. (2006) and barite weight percent from Faul and Paytan (2005).
Table 1
Bulk carbonate Site 1212B and 1221C $\delta^{44}$Ca and trace elemental ratio data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (mbf)</th>
<th>Age from base CIE (ka)</th>
<th>$\delta^{44}$Ca CaCO$_3$ (rel sw)</th>
<th>$\delta^{44}$Ca CaCO$_3$ (rel NIST915a)</th>
<th>$2\sigma_{\text{mean}}$</th>
<th>n</th>
<th>Sr/Ca (mmol/mol)$^b$</th>
<th>Mg/Ca (mmol/mol)$^b$</th>
<th>Sr/Ca (mmol/mol)$^b$</th>
<th>Mg/Ca (mmol/mol)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 198</td>
<td>1212B, 9-5, 45–46</td>
<td>79.65</td>
<td>198</td>
<td>−0.85</td>
<td>1.03</td>
<td>0.05</td>
<td>2</td>
<td>1.0</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 48–52</td>
<td>79.68</td>
<td>179</td>
<td>−0.78</td>
<td>1.1</td>
<td>0.08</td>
<td>2</td>
<td>1.0</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 51–52</td>
<td>79.71</td>
<td>161</td>
<td>−0.83</td>
<td>1.05</td>
<td>0.18</td>
<td>2</td>
<td>0.9</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 54–55</td>
<td>79.74</td>
<td>139</td>
<td>−0.94</td>
<td>0.94</td>
<td>0.05</td>
<td>2</td>
<td>1.0</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 58–59</td>
<td>79.78</td>
<td>117</td>
<td>−0.97</td>
<td>0.91</td>
<td>0.28</td>
<td>2</td>
<td>0.9</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 62–64</td>
<td>79.82</td>
<td>90</td>
<td>−0.83</td>
<td>1.05</td>
<td></td>
<td>2</td>
<td>1.0</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 64–65</td>
<td>79.84</td>
<td>80</td>
<td>−0.69</td>
<td>1.19</td>
<td>0</td>
<td>2</td>
<td>1.0</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 66–67</td>
<td>79.86</td>
<td>70</td>
<td>−1.08</td>
<td>0.8</td>
<td>0.14</td>
<td>2</td>
<td>1.1</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 72–73</td>
<td>79.92</td>
<td>15</td>
<td>−0.94</td>
<td>0.94</td>
<td>0.14</td>
<td>2</td>
<td>1.5</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 76–77</td>
<td>79.96</td>
<td>−9</td>
<td>−1.17</td>
<td>0.71</td>
<td>0.05</td>
<td>2</td>
<td>1.4</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 83–84</td>
<td>80.03</td>
<td>−41</td>
<td>−1.04</td>
<td>0.84</td>
<td>0.05</td>
<td>2</td>
<td>1.3</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 87–88</td>
<td>80.07</td>
<td>−59</td>
<td>−0.97</td>
<td>0.91</td>
<td>0.18</td>
<td>2</td>
<td>1.3</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 93–94</td>
<td>80.13</td>
<td>−86</td>
<td>−1.27</td>
<td>0.61</td>
<td>0.23</td>
<td>2</td>
<td>1.3</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 95–97</td>
<td>80.16</td>
<td>−99</td>
<td>−0.92</td>
<td>0.96</td>
<td>0.09</td>
<td>2</td>
<td>1.3</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1212B, 9-5, 100–101</td>
<td>80.2</td>
<td>−117</td>
<td>−0.71</td>
<td>1.17</td>
<td>0.05</td>
<td>2</td>
<td>1.3</td>
<td>6.2</td>
<td></td>
</tr>
</tbody>
</table>

Note: all samples were measured for $\delta^{44}$Ca at USGS-Menlo Park (Bullen). $^a$ Conversion following Hippler et al. (2003). $^b$ 1 M acetic acid leach. $^c$ 1 M ammonium acetate–acetic acid buffer leach.

$−0.60 \pm 0.13\%$ (2SD, n = 6). Trace element data in the bulk carbonate show a pattern of decreasing Sr/Ca and increasing Mg/Ca beginning at 79.94 mbf and the initiation of the bulk carbonate in 1212B has an average $\delta^{44}$Ca of −0.93 ± 0.32% (2SD, n = 15) (Fig. 2).

The $\delta^{13}$C and $\delta^{18}$O bulk carbonate and species-specific benthic foraminiferal records previously published for 1221C (Fig. 3) do not exhibit the expected large CIE or decrease in $\delta^{18}$O (Nunes and Norris, 2005). Trace element data in the acetic acid leaches from 1221C show large but variable increases in Sr/Ca values from 1.2 to 4.6 mmol/mol (Fig. 3) opposite to that seen in 1212B. Analysis of the ammonium acetate–acetic acid buffer leach at 1221C also exhibit elevated Mg/Ca values from 5 to ~400 mmol/mol (Fig. 3).

Mean bulk carbonate $\delta^{44}$Ca at Site 1221C is identical to Site 1212B, but exhibits high variability considering the time scale of ~0.5 Ma over the interval studied (−0.96 ± 0.80% 2SD, n = 22; Fig. 3). Marine barite $\delta^{44}$Ca from Site 1221C has an average value of −1.99 ± 0.70% (2SD, n = 27) over the same time period. Site 1221C carbonate and barite exhibit different $\delta^{44}$Ca trends over the PETM; most notably, the records diverge during the CIE as CaCO$_3$ decreases from ~80% to a few w%. The barite $\delta^{44}$Ca record shows significant variations at the boundaries of the dissolution event, while the bulk carbonate $\delta^{44}$Ca record at 1221C increases systematically by up to 0.8%.

By comparison, while bulk carbonate $\delta^{44}$Ca changes abruptly and substantially over the PETM at 1221C, bulk carbonate $\delta^{44}$Ca at 1212B is relatively invariant during the CIE of the PETM but shows an apparent increase from −1.2 to −0.8% over the PETM (from just before the CIE to ~170 ka after the boundary).

4. Discussion

The lack of agreement in absolute values or trends in the bulk carbonate $\delta^{44}$Ca data from Sites 1221 and 1212 indicate that one or both of the Ca isotopic records are affected to some degree by diagenesis; the depth interval over which the records differ suggests that this effect is associated with carbonate dissolution induced by ocean acidification. The 1221C bulk carbonate $\delta^{44}$Ca record exhibits a large, abrupt, and relatively long-lasting positive excursion (on the order of +0.8% close to the onset of the CIE) that is markedly different from the 1221C barite and the 1212B bulk carbonate records (Fig. 3).

We contend that the shift to heavier $\delta^{44}$Ca values in 1221C is not an original environmental signal that reflects temperature or species dependent changes in isotopic fractionation or a real
Table 2
Marine barite Site 1221C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>Age from base CIE (ka)</th>
<th>δ²⁶⁶Ca barite (rel sw)</th>
<th>δ²⁶⁶Ca 'seawater' (rel sw)</th>
<th>δ¹⁴³Ca 'seawater' (rel NIST915a)</th>
<th>2σ mean</th>
<th>n</th>
<th>Sr/Ba (mmol/mol)</th>
<th>Sr/Sr²³⁸⁸Sr</th>
<th>2σ mean</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 199</td>
<td>1221C, 11-3, 0–3</td>
<td>153.40</td>
<td>195.9</td>
<td>−1.95</td>
<td>0.06</td>
<td>1.94</td>
<td>0.18</td>
<td>2</td>
<td>0.70776</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 25–28</td>
<td>153.65</td>
<td>179.4</td>
<td>−1.76</td>
<td>0.25</td>
<td>2.13</td>
<td>0.30</td>
<td>2</td>
<td>37.9</td>
<td>0.70776</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 35–38</td>
<td>153.75</td>
<td>172.7</td>
<td>−1.99</td>
<td>0.02</td>
<td>1.90</td>
<td>0.24</td>
<td>2</td>
<td>35.5</td>
<td>0.70776</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 45–48</td>
<td>153.85</td>
<td>166.1</td>
<td>−1.95</td>
<td>0.06</td>
<td>1.94</td>
<td>0.20</td>
<td>2</td>
<td>34.4</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 50–54</td>
<td>153.90</td>
<td>155.6</td>
<td>−1.84</td>
<td>0.17</td>
<td>2.05</td>
<td>0.18</td>
<td>2</td>
<td>37.4</td>
<td>0.70779</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 54–58</td>
<td>153.94</td>
<td>140.6</td>
<td>−1.09</td>
<td>0.92</td>
<td>2.80</td>
<td>0.20</td>
<td>2</td>
<td>36.7</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td>Repeat</td>
<td>1221C, 11-3, 130–133</td>
<td>153.94</td>
<td>140.6</td>
<td>−1.36</td>
<td>0.65</td>
<td>2.53</td>
<td>0.04</td>
<td>2</td>
<td>32.8</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 58–62</td>
<td>153.98</td>
<td>124.9</td>
<td>−2.25</td>
<td>−0.24</td>
<td>1.64</td>
<td>0.35</td>
<td>3</td>
<td>32.8</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 62–66</td>
<td>154.02</td>
<td>108.9</td>
<td>−1.37</td>
<td>0.64</td>
<td>2.52</td>
<td>0.71</td>
<td>2</td>
<td>38.4</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 66–70</td>
<td>154.06</td>
<td>93.37</td>
<td>−1.93</td>
<td>0.08</td>
<td>1.96</td>
<td>0.16</td>
<td>2</td>
<td>33.6</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 70–72</td>
<td>154.10</td>
<td>77.8</td>
<td>−1.95</td>
<td>0.06</td>
<td>1.94</td>
<td>0.18</td>
<td>3</td>
<td>41.2</td>
<td>0.70776</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 80–82</td>
<td>154.20</td>
<td>38.9</td>
<td>−2.07</td>
<td>−0.06</td>
<td>1.82</td>
<td>0.01</td>
<td>2</td>
<td>36.1</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 82–84</td>
<td>154.22</td>
<td>31.1</td>
<td>−2.03</td>
<td>−0.02</td>
<td>1.86</td>
<td>0.28</td>
<td>3</td>
<td>37.8</td>
<td>0.70775</td>
<td>0.00003</td>
</tr>
<tr>
<td>Repeat</td>
<td>1221C, 11-3, 88–90</td>
<td>154.22</td>
<td>31.1</td>
<td>−2.08</td>
<td>−0.07</td>
<td>1.81</td>
<td>0.18</td>
<td>2</td>
<td>38.4</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 88–90</td>
<td>154.24</td>
<td>23.3</td>
<td>−2.44</td>
<td>−0.43</td>
<td>1.45</td>
<td>0.20</td>
<td>2</td>
<td>37.8</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 88–90</td>
<td>154.24</td>
<td>23.3</td>
<td>−2.59</td>
<td>−0.38</td>
<td>1.30</td>
<td>0.18</td>
<td>3</td>
<td>37.8</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td>Repeat</td>
<td>1221C, 11-3, 86–88</td>
<td>154.26</td>
<td>15.5</td>
<td>−2.37</td>
<td>−0.36</td>
<td>1.52</td>
<td>0.02</td>
<td>3</td>
<td>37.8</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 88–90</td>
<td>154.26</td>
<td>15.5</td>
<td>−2.09</td>
<td>−0.08</td>
<td>1.80</td>
<td>0.18</td>
<td>1</td>
<td>37.8</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 92–94</td>
<td>154.32</td>
<td>−1.51</td>
<td>−2.35</td>
<td>−0.34</td>
<td>1.54</td>
<td>0.03</td>
<td>2</td>
<td>37.6</td>
<td>0.70776</td>
<td>0.00002</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 96–98</td>
<td>154.36</td>
<td>−4.29</td>
<td>−2.26</td>
<td>−0.25</td>
<td>1.63</td>
<td>0.16</td>
<td>3</td>
<td>34.3</td>
<td>0.70776</td>
<td>0.00004</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 105–108</td>
<td>154.45</td>
<td>−10.56</td>
<td>−1.89</td>
<td>0.12</td>
<td>2.00</td>
<td>0.03</td>
<td>2</td>
<td>39.3</td>
<td>0.70776</td>
<td>0.00003</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 110–113</td>
<td>154.50</td>
<td>−14.05</td>
<td>−2.03</td>
<td>−0.02</td>
<td>1.86</td>
<td>0.09</td>
<td>2</td>
<td>40.0</td>
<td>0.70776</td>
<td>0.00003</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 130–133</td>
<td>154.70</td>
<td>−30.25</td>
<td>−1.55</td>
<td>0.46</td>
<td>2.34</td>
<td>0.40</td>
<td>2</td>
<td>38.9</td>
<td>0.70776</td>
<td>0.00003</td>
</tr>
<tr>
<td></td>
<td>1221C, 11-3, 135–138</td>
<td>154.75</td>
<td>−33.95</td>
<td>−2.42</td>
<td>−0.41</td>
<td>1.47</td>
<td>0.17</td>
<td>2</td>
<td>35.4</td>
<td>0.70775</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1221C, 11c, 9–12</td>
<td>154.82</td>
<td>−39.14</td>
<td>−1.79</td>
<td>0.22</td>
<td>1.11</td>
<td>0.11</td>
<td>2</td>
<td>38.6</td>
<td>0.70777</td>
<td>0.00001</td>
</tr>
<tr>
<td></td>
<td>1221C, 11c, 9–12</td>
<td>154.91</td>
<td>−45.81</td>
<td>−2.03</td>
<td>−0.02</td>
<td>1.86</td>
<td>0.17</td>
<td>2</td>
<td>37.9</td>
<td>0.70773</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

a Conversion following Hippler et al. (2003).
b Samples in parentheses were measured at USGS-Menlo Park; others were analyzed in Kiel, Germany.

i Indicates samples with ages extrapolated from sedimentation rates established by He ages in samples further upcore (Ma et al., 2014).

Repeat Indicates samples that are considered outliers or had high errors.

Paytan et al. (2007).
change in seawater $\delta^{44}$Ca due to changes in input sources. If the observed shift is attributed to surface ocean warming this would imply an unlikely $40^\circ$C increase in temperature (e.g., Gussone et al., 2005). The time scale of the ocean acidification event suggests that the global ocean $\delta^{44}$Ca would not have changed significantly over the PETM (Komar and Zeebe, 2011); however, it is possible that local differences in the $\delta^{44}$Ca of surface waters could explain our observations. While attractive, there is no clear mechanism for explaining such a large shift to higher values, particularly in the open ocean. The signal clearly did not result from mixing of mineral sources with different isotopic compositions, as there are no source materials on Earth capable of increasing the $\delta^{44}$Ca of surface waters (Fante and Tipper, 2014). A local Ca isotopic distillation effect, on the other hand, due to rapid and significant uptake of Ca by marine calcifiers contradicts the widely held opinion that biological calcification in the surface ocean decreases during ocean acidification events (e.g., Hönisch et al., 2012 and references therein).

Accordingly, there is considerable evidence supporting the contention that the $\delta^{44}$Ca offset observed at 1221C reflects post burial diagenetic effects related to ocean acidification during the PETM. Site 1221 was below the CCD during the CIE (Zeebe et al., 2009), which is reflected in the rapid drop in carbonate content in the sedimentary section (Fig. 3). Benthic $\delta^{18}$O values at ~154 mbsf increase by about 1‰, inconsistent with calcification of benthic foraminifera in warming bottom waters and the inferred relationship between $\delta^{44}$Ca and temperature. Mineralogical analyses document the presence of diagenetic minerals such as dolomite and authigenic apatite over the PETM interval at Site 1221, which is consistent with the formation of authigenic minerals in the sedimentary section. Perhaps most convincingly, the sedimentary record at Site 1212 exhibits a minimal loss of carbonate over the PETM and no evidence of a comparable offset in $\delta^{44}$Ca. Because diagenetic alteration appears a feasible explanation for the observations at 1221, we explore this hypothesis in detail below.

4.1. Potential influence of carbonate dissolution on sedimentary $\delta^{44}$Ca

Carbonate dissolution alone is not a feasible mechanism for generating sizeable Ca isotopic effects in the solid phase. Partial dissolution of foraminiferal tests of G. sacculifer and N. pachyderma has demonstrated the relative insensitivity of foraminiferal $\delta^{44}$Ca to partial dissolution (Gussone et al., 2009). No Ca isotope measurements of partially dissolved coccoliths or nanofossil ooze
exist, but dissolution of carbonates has been hypothesized to impact Ca isotopes minimally (e.g., Langer, 2005; Fantle and DePaolo, 2007). It also stands to reason that if dissolution did fractionate Ca isotopically, any fractionated surface generated will be removed as the dissolution front advances into the particle. So while a dissolution effect on δ44Ca might be noticeable in small particles (highest surface area to volume) during minor dissolution events, such a signal is likely to be removed entirely from the record during the sort of aggressive dissolution associated with the PETM ocean acidification event.

Relatedly, though distinct from dissolution as a fractionating mechanism, it is feasible that carbonate dissolution preferentially accesses isotopically distinct, and differentially soluble, carbonates in the sediment column (i.e., selective dissolution). Such a hypothesis requires that there is substantial isotopic heterogeneity in foraminiferal and/or nanofossil carbonate, a result that is not consistent with currently available data. While some work suggests significant Ca isotopic differences between the outer (gametogenic) calcite layer and the inner (ontogenic) calcite layers of two planktomic foraminifers (G. truncatulinoides and G. tumida) of up to 3.7‰ (Kasemann et al., 2008), dissolution studies of planktonic foraminiferal tests indicate that partial dissolution does not necessarily access such heterogeneity, if it is widespread (Gussone et al., 2009). Thus, the bulk of published work to date does not support the expression of large Ca isotopic heterogeneity in carbonates due to partial dissolution (e.g., Gussone et al., 2003, 2007; Kisekure et al., 2011; Müller et al., 2011).

4.2. Potential influence of secondary carbonate precipitation on sedimentary δ44Ca

There is both mineralogical (e.g., authigenic minerals identified from smear slides including 'sugary coatings' noted on foraminiferal tests) and geochemical (e.g., carbonate δ18O and trace element composition) evidence at 1221C for secondary mineral precipitation in the sediment column over the PETM interval. Both authigenic apatite and dolomite occur in the depth intervals near the CIE (Lyle et al., 2002). Dolomite is most abundant outside of the CIE interval at 1221 (~15% in smear slides at 154.34 and 153.7 mbsf), yet is often absent or constitutes <5% of the particles found in smear slides within the clay layers associated with the PETM (Fig. 1). Apatite is present (~5% in smear slides) from 154.10 to 154.00 mbsf, which corresponds to the end of the CIE.

Diagenetic textures and overprinting of δ18O, noted previously (Nomura and Takata, 2005; Nunes and Norris, 2005), support the hypothesis of substantial recrystallization of, or secondary calcite precipitation associated with, foraminiferal tests. In addition, the bulk carbonate δ18O values at 1212, relative to 1221, indicate substantial diagenetic overprinting of δ18O to lower values at 1221 (Fig. 4). Both molar Sr/Ca and Mg/Ca ratios in the acetic–acid soluble fraction are high within the section of core affected by carbonate dissolution (i.e., chemical “burndown”; Fig. 3). At face value, these data imply recrystallization or precipitation of secondary carbonates in the presence of pore fluids with elevated Sr and Mg concentrations, perhaps influenced by both carbonate and clay dissolution. However, as there is no clear correlation between the trace metal ratios and δ44Ca values, we contend that while clays may have influenced pore water Sr/Ca and Mg/Ca they do not control the δ44Ca values of the carbonate.

We suggest that the high δ44Ca values in the acetic acid leach reflect either re-equilibration of existing carbonates with high δ44Ca pore fluids and/or precipitation of authigenic minerals (carbonates or other phases) from high δ44Ca pore fluids. The mass of authigenic mineral formed, in the latter case, would have to be comparable to the mass of pre-existing carbonate and the fractionation factor associated with authigenic precipitation assumed to be close to one to explain the δ44Ca data (i.e., Fantle and DePaolo, 2007; Fantle, 2015). There are two options for the timing of authigenic mineral precipitation: during and/or after the period of chemical burndown. If carbonates are the primary authigenic phase, then it is most likely that they formed after chemical burndown ceased, perhaps associated with the observed and modeled global overshoot of the CDD during the recovery phase (e.g., Zeebe et al., 2005; Zeebe and Sachs, 2013).

The geochemical composition of an authigenic mineral depends on the pore fluid composition and the partition coefficient or fractionation factor associated with precipitation (e.g., Fantle, 2010; Fantle et al., 2010; Fantle and Higgins, 2014). In general, the pore fluid composition is dictated by the mass fluxes into and out of the pore fluid (i.e., the rates of dissolution, ion exchange, and precipitation) balanced against the rates at which transport processes operate (i.e., diffusion and advection). When transport processes

---

Fig. 3. ODP Site 1221C (a) δ13C of bulk CaCO3 (b) δ18O of bulk CaCO3 (black) and benthic foraminifera (red and blue) relative to VPDB (Nunes and Norris, 2005). (c) Sr/Ca (mmol/mol) of bulk CaCO3 (open blue circles), Sr/Ca (mmol/mol) of calcite fraction (blue), Mg/Ca (mmol/mol) of calcite fraction (red triangles), and weight percent (wt%) CaCO3 in black (Murphy et al., 2006), and (d) barite δ44Ca relative to modern seawater (gray) and bulk carbonate δ44Ca (black). Error bars are plotted as in Fig. 1. δ44Ca curve is a cubic smoothing spline of data (Table 2). Dashed vertical line is average modern coretop barite (Griffith et al., 2008c). Solid vertical line is an average value of modern bulk carbonate (Fantle and DePaolo, 2005). See Fig. 2 for description of shading. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
are fast relative to reaction (i.e., in an open system), the system is said to have a large reactive length scale and the fluid can be maintain considerably out of equilibrium with respect to the solid. When reaction rate is fast compared to transport, then the system behaves more like a closed system and has a smaller reactive length scale. If there is isotopic fractionation or a strong elemental partitioning behavior during mineral precipitation, the fluid can be modified or distilled. Because pore fluid $^{44}$Ca ultimately determines the isotopic composition of authigenic minerals, it is critical to understand the evolution of pore fluid $^{44}$Ca during dissolution events similar to the one associated with the PETM.

In nannofossil ooze sections, there is a strong $^{44}$Ca gradient in the uppermost ten to fifteen meters of the sedimentary section (Fig. 5b ‘Pre-CIE Steady State’), which reflects the balance between diffusive communication with seawater (defined as $0\%$ in this study) and the dissolution/recrystallization of carbonates ($^{44}$Ca $\approx -1.3\%$ on the seawater scale; Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015). Such a boundary layer will al-
ways exist in the presence of recrystallizing sediments, though the depth range over which it extends can change to reflect (primarily) changes in the reactive flux of solute to the pore fluid. In a recrystallizing column, for instance, the boundary layer thickness (L_ca) can be approximated by L_ca = (D/RMK)^1/2, where D is the diffusion coefficient of Ca appropriate for the sedimentary column and RMK is a reactive term with units of inverse time (Fantle et al., 2010; Fantle and Higgins, 2014). Accordingly, during ocean acidification associated with the PETM, this gradient may have been compressed due to massive and rapid carbonate dissolution, shifting pore fluid δ^{44}Ca values in the upper meter of the sedimentary column towards (but not necessarily identical to) bulk carbonate values (Fig. 5b ‘Perturbation’). It should be clearly stated, however, that while burndown can compress the boundary layer, there will always be a δ^{44}Ca gradient in pore fluids at the top of the sedimentary section.

Given the corrosive nature of pore fluids during chemical burndown, it is unlikely that authigenic carbonates formed during the burndown. Instead, as the CCD deepened and dissolution in the sedimentary column slowed, pore fluid δ^{44}Ca evolved towards steady state, generating a transient pore fluid profile in the process (Fig. 5b ‘Return To Steady State’). During this interval, corrosive conditions would have diminished, making it possible to form secondary carbonates at various depths in the sedimentary column. Assuming a fractionation factor close to one for inorganic carbonate precipitation at slow rates (Fantle and DePaolo, 2007; Tang et al., 2008; Fantle, 2015), the resulting authigenic carbonates would have δ^{44}Ca values reflective of the pore fluid δ^{44}Ca. In the diffusive boundary layer near the top of the section, pore fluid δ^{44}Ca would have been seawater-like (Fig. 5b ‘Return To Steady State’). With increasing depth (and an increasing extent of equilibration between solid and pore fluid), pore fluid δ^{44}Ca values would transition to those of the bulk carbonate (Fantle and DePaolo, 2007; Fantle et al., 2010).

The Ca isotopic composition of 1221 sediments over the PETM, therefore, are most simply interpreted as reflecting precipitation of authigenic carbonate within the diffusive boundary layer after the cessation of chemical burndown. Assuming a typical meter-scale reactive boundary layer in the sedimentary column, this hypothesis requires authigenic precipitation of CaCO_3 to have occurred over a limited depth range (order 10 cm) at the percent level and not over the entire interval impacted by burndown. There is little evidence that other authigenic phases that may have formed during burndown, such as dolomite or apatite, control the observed trends in δ^{44}Ca.

Alternatively, the data can be explained by enhanced recrystallization rates in sediments affected by burndown, effectively decreasing the reactive length scale. If the latter scenario is considered, and the measured 1221 δ^{44}Ca values assumed to reflect accurately the depth over which the diffusive boundary layer extends (~30 cm; Fig. 3), then this would suggest recrystallization rates >10^{-4} a^{-1}, or more than 1000 times faster than “typical” recrystallization rates in bulk nanofossil ooze (Richter and DePaolo, 1987, 1988; Richter and Liang, 1993; Richter, 1996; Fantle and DePaolo, 2007; Fantle, 2015). Though this scenario seems improbable, such an interpretation is generally supported by the rather large increase in benthic δ^{18}O at ~154 mbsf.

Accordingly, the bulk carbonate δ^{44}Ca at Site 1221 can be interpreted in terms of a depth, and not time, variant signal related to the saturation state of ocean bottom waters that is not reflective of the global Ca cycle. Bulk carbonate δ^{44}Ca at the base of the PETM interval may be relatively unaltered, or the result of secondary carbonate formation from a pore fluid impacted by reaction (be it dissolution or recrystallization) with bulk carbonate. The transition to higher δ^{44}Ca would then reflect the formation of authigenic minerals in the diffusive boundary layer within ~10 cm of the seawater–sediment interface. This hypothesis does not require mineral formation during a transient state, though such a scenario is plausible. In either case, the measured bulk carbonate δ^{44}Ca values are consistent with secondary mineral formation, and possibly extensive recrystallization, in the sedimentary column after the cessation of carbonate burndown.

Above the clay-rich PETM interval, the return to typical carbonate δ^{44}Ca values reflects the reestablishment (and dominance) of the flux of surface ocean-derived carbonate particles. This hypothesis accounts for the entire apparent bulk carbonate δ^{44}Ca “excursion”, explains why the highest sedimentary δ^{44}Ca values are offset in the depth realm from the onset of the PETM, and even accounts for the few outlier barite samples, including both anomalously high and low δ^{44}Ca values in marine barites at either end of the CIE (see discussion below). Further, while it is unclear whether elevated Sr/Ca ratios represent a pure carbonate fraction, such a mechanism (in addition to increases in partition coefficients) can also explain high authigenic trace element ratios.

At 1221C, benthic foraminiferal δ^{18}O values increase by ~0.9‰, though this is not pervasive throughout the PETM interval. This signal is only clearly observed over a small depth interval coincident with the maximum bulk carbonate and marine barite δ^{44}Ca, and thus is inferred to have occurred close to the seawater–sediment interface. Benthic foraminiferal δ^{18}O values at 1221C are inconsistent with δ^{18}O values predicted for tests that formed, or underwent diagenesis, at temperatures that were warmer than those during initial formation (i.e., “typical diagenesis”; Schrag et al., 1995). Taken at face value, benthic foraminiferal δ^{18}O suggest diagenesis under colder conditions than those of formation, a scenario not consistent with deep water warming associated with the PETM.

An alternative explanation is that the benthic foraminifera δ^{18}O reflects interaction with pore fluids with δ^{18}O values slightly higher than those of the bottom waters, or either increased bottom water δ^{18}O or lower pH at the end of the PETM. While an alteration of pore fluid δ^{18}O can technically occur due to carbonate dissolution, mass balance suggests that it is highly unlikely that carbonate dissolution could impact pore fluid δ^{18}O on the order of a permil. This constraint, plus the inferred proximity to the seawater–sediment interface, suggests that it is most likely that an increase in fractionation factor associated with a decrease in pH (Zeebe, 2007) or an increase in bottom water δ^{18}O are responsible for the benthic foraminiferal δ^{18}O trend. While it is also possible that the benthic fraction analyzed contained dolomite, which has a larger fractionation factor than calcite at a given temperature (Horita, 2014), no dolomite rhombs were observed in the benthic fraction analyzed (Nunes and Norris, 2005).

In contrast to the benthic foraminiferal tests, bulk carbonate δ^{18}O values within the recovery interval at 1221 are isotopically lighter than contemporaneous carbonates at 1212 (Fig. 4). This suggests that bulk sediments at 1221 are likely also impacted by diagenetic alteration at temperatures warmer than those associated with formation (e.g., Schrag et al., 1995). Regardless of the timing, both bulk carbonate and benthic foraminiferal calcite are clearly affected by secondary calcite precipitation, in contrast to bulk carbonates at 1212. This supports the contention that the δ^{44}Ca values observed at 1221 reflect secondary carbonate precipitation and not a primary signal.

4.3. Implications for Ca isotope proxy development

The large differences in δ^{44}Ca measured in the bulk carbonate records from 1212 and 1221 suggest that a δ^{44}Ca carbonate record from a single site may not be suitable for global reconstructions, especially during climatic or environmental perturbations such as ocean acidification events. Certainly, as suggested previ-
ously (Fantle, 2010), this issue should be resolved by measuring $\delta^{44}$Ca records from multiple sites and proxy archives in order to reconstruct the past accurately.

In a similar fashion, the data presented demonstrate how the analysis of coeval minerals (e.g., carbonate and barite from the same sample) can be used to identify diagenetically altered samples. Given that barite is less susceptible to post depositional diagenesis in the absence of sulfate reduction (Paytan et al., 1993) and is more similar to the 1212B carbonate record, we conclude that the bulk carbonate $\delta^{44}$Ca at 1221C cannot represent a global signal and is therefore impacted significantly by diagenesis.

Likewise, the increase of 0.4‰ in bulk carbonate $\delta^{44}$Ca at 1212 cannot represent a global seawater signal, as the magnitude is too large and the time scale too short relative to the residence time of Ca in the Paleogene ocean to represent the evolution of global seawater. If, as suggested for Site 1221, an increase in $\delta^{44}$Ca of bulk carbonate over time scales much less than the residence time of Ca in the oceans is indicative of diagenesis, then $\delta^{44}$Ca at 1212 is also likely impacted by diagenesis. The implication of this observation is that even those records that appear pristine, based on % CaCO$_3$, can be significantly overprinted by authigenic mineral precipitation associated with ocean acidification.

Relatedly, the data presented beg the question of whether or not marine barite is a robust archive of seawater $\delta^{44}$Ca over the entire PETM event. Before and after the CIE, the calculated $\delta^{44}$Ca of Paleogene seawater (0.10±0.20‰; 2SD, n = 9) is statistically indistinguishable from Holocene seawater values (Fig. 3d). This value is determined assuming a constant isotopic offset between barite and seawater of −2.01‰ (Griffith et al., 2008c), after removing the outliers identified in Table 2. At the boundaries of the CIE at 1221, however, there appear to be two populations of barites with $\delta^{44}$Ca significantly different from the barite before and after the CIE. The first occurs at the base of the CIE, close to the depth at which bulk carbonate $\delta^{44}$Ca begins to increase strongly. These marine barites have substantially lower $\delta^{44}$Ca values (up to −0.6‰) than barites before and after (and within) the CIE. The second population of barites that differ from the pre CIE values occurs at the beginning of the recovery phase of the bulk carbonate record (and end of the CIE), at the same depth horizon in which benthic $\delta^{18}$O increases by ~1‰ and bulk carbonate $\delta^{44}$Ca peaks.

While these barite samples could be primary and reflective of changes in ocean chemistry, or changes in isotopic fractionation such as those related to changes in the saturation state of barite and thus barite precipitation rates, the rather consistent Sr/Ba in these samples (Table 2; 36.6±5.9 mmol/mol, average ± 2SD, n = 22) suggest a constant barite saturation state across the PETM (Paytan et al., 2007). In addition, the average $^{87}$Sr/$^{86}$Sr of these outlier barites (0.70776±0.00003 2SD) is similar to that expected for contemporaneous seawater (Hodell et al., 2007). However this does not negate the possibility of an authigenic origin for these outlier barites. This is due to the fact that the $^{87}$Sr/$^{86}$Sr of pore fluids from which authigenic barite would have precipitated would have been isotopically identical to seawater within the upper tens to hundreds of centimeters of the sedimentary column (e.g., Fantle and DePaolo, 2006). In such a case, there is little isotopic leverage to produce authigenic barite with substantially different $^{87}$Sr/$^{86}$Sr than seawater in the upper part of the sedimentary column, even in the presence of rapidly dissolving carbonate (e.g., Fantle, 2015).

Consequently, we propose that both intervals of outlier barites include a proportion of authigenic barite affected by the evolution of pore fluid $\delta^{44}$Ca over the course of the PETM. It should be noted that outside of the extreme dissolution event of the PETM, authigenic barite records seawater chemistry if it precipitates within the upper sediment mixed layer (Paytan et al., 1996). Interestingly, the two populations of outlier barite exhibit completely opposite Ca isotopic effects, suggesting that they reflect the evolution of pore fluid $\delta^{44}$Ca over the course of the PETM. Such an interpretation agrees with the explanation of a depth, and not time, variant signal recorded in the bulk carbonate $\delta^{44}$Ca put forth above. At the base of the CIE, assuming an equilibrium fractionation factor of −2.01‰ (Griffith et al., 2008c), authigenic barite appear to reflect isotopically light pore fluid $\delta^{44}$Ca values, which have been influenced by the dissolution of (or isotopic equilibration with) bulk carbonate.

The relatively high $\delta^{44}$Ca values in the barites at ~154.0 mbsf are somewhat more difficult to explain. We hypothesize that these barites precipitated in the sedimentary column from pore fluids that were isotopically similar to seawater (i.e., within the diffusive boundary layer), following the interpretation of bulk carbonate $\delta^{44}$Ca discussed above. If a fractionation factor of −2.01‰ is assumed, this implies that the fluids from which the barites formed were at least +1‰ relative to seawater. Such a high value for pore fluid and/or seawater $\delta^{44}$Ca seems improbable. Thus, the data appear to require a fractionation factor significantly less than the core top-derived −2.01‰. The observation that barite $\delta^{44}$Ca is significantly affected by the variations in pore fluid chemistry over the PETM while Sr/Ba is not can be explained by the relative sensitivity of Ca and Sr to alteration. Calcium concentrations in barite are more than ten times lower than Sr (~2.4 mmol Ca/mol Ba; Averett and Paytan, 2003), and Ca concentrations in seawater about 100 times higher than Sr concentrations, such that Ca is potentially more easily perturbed in barite than Sr during diagenesis.

Ultimately, identification of two populations of authigenically-influenced barite $\delta^{44}$Ca is important, as the data suggest that the barite Ca isotopic fractionation factor during diagenesis can vary in the sedimentary column. Not only has this not been observed previously, but it has the potential to complicate the use of marine barite as a paleo-seawater Ca isotope proxy over intervals of abrupt and extreme change in ocean chemistry. More work has to be done to confirm these interpretations by using barite from other sections or time intervals.

5. Conclusions

Previous modeling results of global changes in Ca input to the oceans due to enhanced weathering and carbonate dissolution during the PETM (Komar and Zeebe, 2011) suggest that these processes will result in little change to the global seawater Ca isotope ratio (~0.05‰); much less than the changes measured in carbonate and marine barite $\delta^{44}$Ca records from two sites in the Pacific with vastly different dissolution histories. The lack of agreement among synchronous carbonate records indicate that dissolution, recrystallization and secondary precipitation (i.e., post burial diagenetic effects) affected the bulk carbonate $\delta^{44}$Ca record at 1221, which was below the CCD during the core interval of the PETM; 1212 was likely affected to a lesser extent. The high values of the bulk carbonate $\delta^{44}$Ca at 1221 reflect either re-equilibration of existing carbonates with high $\delta^{44}$Ca pore fluids or precipitation of authigenic carbonate from high $\delta^{44}$Ca pore fluids. High $\delta^{44}$Ca pore fluids recorded in carbonates at the top of the clay-rich PETM interval are reflecting their proximity to the sediment–seawater interface during secondary mineral formation after the cessation of carbonate burndown. Thus the secondary minerals record a depth dependent (not time dependent) signal. Above the clay-rich PETM interval, the return to typical carbonate $\delta^{44}$Ca values reflects the re-establishment of the flux of carbonate particles derived from the surface ocean. This hypothesis is in agreement with bulk carbonate and benthic foraminiferal oxygen isotopes and trace metal ratios (Sr/Ca and Mg/Ca) at 1221. Marine barite $\delta^{44}$Ca is mostly unaffected by post burial diagenetic effects seen in the bulk carbonate record at 1221 within the core of the event but may be affected at the base of the event due to short-lived perturbations to the pore
fluid Ca isotopic composition which should be better preserved in the barite record which is thought to behave as a closed system below the sediment mixed layer (Paytan et al., 1996). The barite record, where not affected by changes in pore fluid chemistry at the sediment-seawater interface, suggests seawater values at the PETM were generally similar to present day values. A coherent reconstruction of seawater Ca isotope values over extreme climatic events such as the PETM requires careful consideration of many varied effects on stable isotopic fractionation of Ca in the recording phases. Multiple sites and sedimentary phases are necessary to reconstruct global changes in seawater Ca reliably and give credence to modeling efforts of the paleoceanographic data.

Acknowledgements

The authors acknowledge samples and data provided by the Integrated Ocean Drilling Program. This work was supported in part by NSF CAREER Grant OCE-0449732 (A.P.). This is a contribution to EUROClimate project 04 ECLIM FP08 CASIOPEIA (DFG EI272/29-1). The authors thank Joe Street for helpful comments on an earlier version of this manuscript, and are grateful to P. Pogge von Strandmann and two anonymous reviewers for constructive comments on the initial submission.

References


