



Constraints on ocean acidification associated with rapid and massive carbon injections: The early Paleogene record at ocean drilling program site 1215, equatorial Pacific Ocean

Lizette Leon-Rodriguez ^{a,*}, Gerald R. Dickens ^{a,b}

^a Department of Earth Sciences, Rice University, MS-126 P.O. Box 1892, Houston TX, 77281-1892, USA

^b Institutionen för Geologiska Vetenskaper, Stockholms Universitet, 106 91 Stockholm, Sweden

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ABSTRACT

Massive amounts of ^{13}C -depleted carbon rapidly entered the ocean more than once during the Early Paleogene, providing a geological framework for understanding future perturbations in carbon cycling, including ocean acidification. To assess the number of events and their impact on deep-sea carbonate accumulation, we investigated a 42 m thick unit of Upper Paleocene–Lower Eocene carbonate ooze, which was deposited on a subsiding flank of the East Pacific Rise. Age control was established using calcareous nannofossils and planktonic foraminifera, as well as stable carbon isotopes of bulk carbonate. Carbonate content, foraminiferal test fragmentation, and planktonic/benthic foraminiferal ratio were measured to ascertain changes in carbonate dissolution. Based on these analyses, carbonate preservation generally increased from the late Paleocene (55.4 Ma) through the early Eocene (51.4 Ma), after which it became poor to negligible. This trend was punctuated by three (and probably four) short-term intervals characterized by carbonate dissolution and negative $\delta^{13}\text{C}$ excursions. These horizons almost assuredly correspond to the PETM (~55.5 Ma), H1/ETM-2 (~53.7 Ma), I1 (~53.2 Ma), and K/X (~52.5 Ma) events. Carbonate preservation also increased within 200 kyr after two and perhaps all four intervals. We suggest the lysocline and calcite compensation depth (CCD) generally deepened between 55.4 and 51.4 Ma but shoaled and subsequently overcompensated during and after three and likely four intervals of rapid and massive carbon injection. Oxygen isotope data further suggests these intervals were times of anomalous warmth.

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1. Introduction

It is “virtually certain” that current and future release of CO_2 by anthropogenic activities will decrease pH and calcium carbonate solubility in the ocean (Denman et al., 2007). This expected “ocean acidification” will reduce CO_2 uptake from the atmosphere to the ocean, may impact marine organisms that calcify, and should modify certain physical properties of seawater, such as sound and light propagation (Brewer and Hester, 2009; Doney et al., 2009; Feely et al., 2009). Basic responses of the ocean carbon cycle to future CO_2 inputs have been predicted (e.g., Caldeira and Wickett, 2003; Orr et al., 2005, 2009; Tans, 2009); Walker and Kasting, 1992. However, the magnitudes remain unconstrained because they depend on a multitude of factors (e.g., Kump et al., 2009; Tans, 2009; Zachos et al., 2008).

The Late Paleocene through Early Eocene, nominally 58 to 50 million years ago (Ma), is perhaps the best past time interval in

which to understand ocean acidification (Kump et al., 2009; Ridgwell and Schmidt, 2010; Zachos et al., 2008; Zeebe et al., 2009). Carbon isotope and seafloor carbonate records spanning this time strongly suggest long-term ($>10^5$ years) and short-term ($<10^5$ years) perturbations to ocean carbon chemistry (e.g., Dickens et al., 1997; Hilting et al., 2008; Zachos et al., 2008). Among these are profound changes across the Paleocene–Eocene Thermal Maximum (PETM) ca. 55 Ma, a geologically brief event characterized by a 5 to 9 °C rise in Earth surface temperatures and numerous biotic turnovers (e.g., Sluijs et al., 2007a), including those of calcifying marine organisms (Bralower, 2002; Kelly, 2002; Kump et al., 2009; Raffi et al., 2005; Thomas, 2007). The onset of the PETM is marked by a prominent negative carbon isotope excursion (CIE) in globally distributed marine and terrestrial sediment sequences, and by carbonate dissolution in widely separated deep-sea sediment sections (e.g., Kennett and Stott, 1991; Lu and Keller, 1993; Sluijs et al., 2007a; Zachos et al., 2005, 2007; Zeebe and Zachos, 2007). A tremendous and rapid ($<10^5$ years) addition of ^{13}C -depleted CO_2 into the ocean/atmosphere system produced these signals, although the source and mass of the input remain uncertain (e.g., Dickens et al., 1997; Kump et al., 2009; Ridgwell and Schmidt, 2010; Zachos et al., 2005, 2007, 2008; Zeebe et al., 2009).

* Corresponding author: Tel.: +1 713 702 0216; fax: +1 713 348 5214.
E-mail address: lizette@rice.edu (L. Leon-Rodriguez).

Carbonate dissolution in deep-sea sediment across the PETM almost certainly reflects ocean acidification, more specifically rises in the lysocline and calcite compensation depth (CCD) (Dickens, 2000; Dickens et al., 1997; Kump et al., 2009; Ridgwell and Schmidt, 2010; Zachos et al., 2005, 2008; Zeebe and Zachos, 2007; Zeebe et al., 2009). These are “depth horizons” in the ocean related to calcite accumulation (Bramlette, 1961; Broecker and Broecker, 1974; Peterson, 1966; Takahashi and Broecker, 1977): the former is where calcite dissolution begins to increase significantly, such that accumulation decreases markedly; the latter is where calcite dissolution balances calcite rain, such that accumulation effectively drops to zero (Boudreau et al., 2010). Basically, when massive amounts of CO₂ entered the ocean during the PETM, the pH and CO₃²⁻ concentration dropped, and depths of diminished carbonate accumulation shoaled.

Three open issues have emerged in recent discussions of the PETM and its associated ocean acidification. First, how does deep-sea carbonate dissolution across the PETM vary from one section to another? Cores recovered from several areas, such as in the central Atlantic (ODP Sites 999 and 1001 in the Caribbean Sea; ODP Sites 1262–1267 on Walvis Ridge) and the southern Indian (ODP Site 738) show pronounced dissolution across the event (e.g., Bralower et al., 1997; Lu and Keller, 1993; Zachos et al., 2005). This has been argued to represent major (>1 km) global rises in the lysocline and CCD (Sluijs et al., 2007a; Zachos et al., 2005). However, cores from other locations, such as in the Southern Atlantic (ODP Site 690 on Maud Rise), eastern Indian (DSDP Site 259 in Perth Basin) or Pacific (ODP Site 1209 on Shatsky Rise), exhibit limited dissolution (e.g., Hancock et al., 2007; Zeebe and Zachos, 2007; Zeebe et al., 2009). Second, was the PETM one of several similar events during the Early Paleogene? Some explanations for the carbon injection, for example impact of a carbonaceous comet (Kent et al., 2003) or rapid generation and release of thermogenic methane by intrusive sills (Svensen et al., 2004), have implicitly considered it a unique event. By contrast, recent papers (e.g., Agnini et al., 2009; Galeotti et al., 2010; Lourens et al., 2005; Nicolo et al., 2007; Sluijs et al., 2009; Stap et al., 2009, 2010) have suggested that the PETM was the most pronounced of a series of Early Paleogene “hyperthermals,” each characterized by massive injection of ¹³C depleted carbon. Other postulated events include short intervals centered at ~53.7 Ma (called H1 or ETM-2), at ~53.2 Ma (I1), and at ~52.5 Ma (K or X) (Appendix A). Third, what was the average depth of the CCD and lysocline before and after the PETM? Some reconstructions of the CCD through the late Paleocene and early Eocene (Rea and Lyle, 2005; Shipboard Scientific Party, 2002; van Andel, 1975) have it relatively shallow (~3200 m) and constant. However, others suggest it deepened through this interval (Hancock et al., 2007). The answers to these questions are uncertain but essential for understanding and modeling the impacts of massive carbon addition upon ocean carbon chemistry (Kump et al., 2009; Panchuk et al., 2008; Ridgwell and Schmidt, 2010; Zeebe et al., 2009).

To better understand Late Paleocene–Early Eocene carbon cycle variations, especially during the postulated carbon injection events, stable isotope and carbonate dissolution records across this time interval are needed from multiple sites of different ocean basins. Here we generate records at ODP Site 1215 in the Eastern Pacific Ocean (Fig. 1). This site was chosen because it should have been located near or below the lysocline between 58 and 50 Ma. We show that it has an important but complex history of carbonate accumulation. From the Late Paleocene through the Early Eocene, the site likely subsided as the lysocline and CCD deepened; superimposed on this long-term trend are major rises and falls in the lysocline and CCD during and after at least three (and possibly four) suspected hyperthermal events.

2. Site and samples

Site 1215 (Fig. 1) is located northeast of Hawaii in the central Pacific (26°01.77'N, 147°55.99'W) at 5396 m below sea level (Shipboard

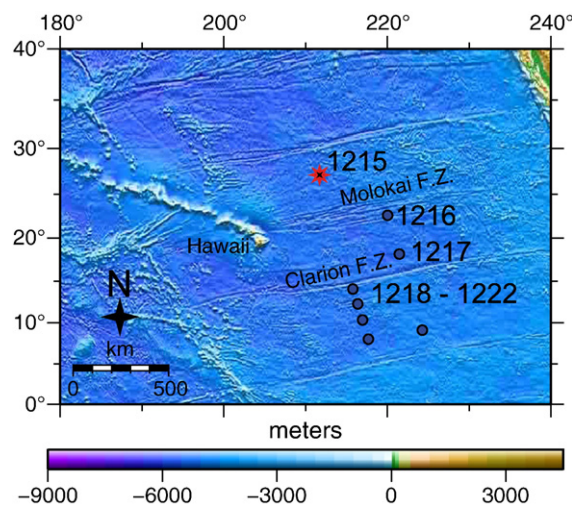


Fig. 1. Location of Site 1215 and other sites drilled by ODP Leg 199 (Shipboard Scientific Party Leg 199, 2002). Topography and bathymetry from Smith and Sandwell (1997).

Scientific Party, 2002). It lies on oceanic crust of the Pacific Plate formed during the youngest part of magnetic polarity C26r (Shipboard Scientific Party, 2002), which corresponds to 58 Ma (Cande and Kent, 1995).

Two holes (A and B) were drilled and cored at Site 1215. The recovered section (Fig. 2) comprises ~70 m of sediment, divided into three units, as well as underlying basalt pebbles (Shipboard Scientific Party, 2002). For the sediment, Unit I is red clay from the seafloor to 26 m below seafloor (mbsf), Unit II is clayey calcareous ooze to 68 mbsf, and Unit III is metalliferous oxide ooze to basalt at 70 mbsf. Biogenic silica is not a major component, although chert nodules and horizons are scattered throughout Unit II (Shipboard Scientific Party, 2002).

Shipboard stratigraphy indicates Late Paleocene to Holocene deposition for the sediment section. However, only depths within Units II and III could be assigned a reasonable (~1 Myr) chronology. This interval (26–70 mbsf) is upper Paleocene to lower Eocene (Fig. 2). The magnetostratigraphy for this unit includes several data gaps, and is not interpreted easily without additional constraints. Biostratigraphic zones were not defined very well in initial studies because of low sample resolution.

Magnetic susceptibility (MS) of sediment at Site 1215 varies significantly (Fig. 2). Unit I and Unit II are characterized generally by high and low MS, respectively. However, several short intervals of high MS lie between 26 and 60 mbsf. The MS of deep-marine sediment often correlates inversely to carbonate content (e.g., Ellwood et al., 2000; Lourens et al., 2005). Consequently, these MS “highs” in Unit II may represent carbonate dissolution horizons. A prominent MS high occurs at ~54.7 mbsf, which corresponds to the PETM according to shipboard biostratigraphy (Shipboard Scientific Party, 2002). Overlying MS peaks in Unit II might, therefore, correlate to suspected hyperthermals of the Early Eocene.

We collected 117 10-cc “tubes” of sediment between 20 and 60 mbsf from Hole 1215A. These were taken every 30 to 50 cm with increased resolution of every 5 to 10 cm across dark horizons with high MS. Samples were selected to avoid disturbed intervals caused by drilling and coring.

3. Methods

3.1. Sample processing

All samples were cleaned with 18 MΩ deionized water to eliminate salts that precipitated from interstitial water. After freeze-drying, three

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