



Impact of dissolution on the sedimentary record of the Paleocene–Eocene thermal maximum



Timothy J. Bralower^{a,b,*}, D. Clay Kelly^c, Samantha Gibbs^d, Kenneth Farley^e,
Laurie Eccles^a, T. Logan Lindemann^a, Gregory J. Smith^a

^a Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA

^b Climate Change Research Centre, University of New South Wales, Sydney, 2052, Australia

^c Department of Geoscience, University of Wisconsin, Madison, WI 53706, USA

^d Ocean and Earth Science, National Oceanography Centre, Southampton, University of Southampton, Southampton, SO14 3ZH, UK

^e Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA

ARTICLE INFO

Article history:

Received 23 October 2013

Received in revised form 10 May 2014

Accepted 27 May 2014

Available online 19 June 2014

Editor: G.M. Henderson

Keywords:

dissolution

chemical erosion

nannofossils

planktonic foraminifera

Paleocene Eocene thermal maximum

ABSTRACT

The input of massive amounts of carbon to the atmosphere and ocean at the Paleocene–Eocene Thermal Maximum (PETM; ~55.53 Ma) resulted in pervasive carbonate dissolution at the seafloor. At many sites this dissolution also penetrated into the underlying sediment column. The magnitude of dissolution at and below the seafloor, a process known as chemical erosion, and its effect on the stratigraphy of the PETM, are notoriously difficult to constrain. Here, we illuminate the impact of dissolution by analyzing the complete spectrum of sedimentological grain sizes across the PETM at three deep-sea sites characterized by a range of bottom water dissolution intensity. We show that the grain size spectrum provides a measure of the sediment fraction lost during dissolution. We compare these data with dissolution and other proxy records, electron micrograph observations of samples and lithology. The complete data set indicates that the two sites with slower carbonate accumulation, and less active bioturbation, are characterized by significant chemical erosion. At the third site, higher carbonate accumulation rates, more active bioturbation, and possibly winnowing have limited the impacts of dissolution. However, grain size data suggest that bioturbation and winnowing were not sufficiently intense to diminish the fidelity of isotopic and microfossil assemblage records.

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1. Introduction

Unabated anthropogenic carbon emission looms as an increasingly significant threat to the ocean and its inhabitants. It has been estimated that the ocean has absorbed roughly a third of the carbon emitted, which is causing a decrease in carbonate ion content and pH (e.g., Broecker and Takahashi, 1977; Caldeira and Wickert, 2005), a response known as ocean acidification (e.g., Feely et al., 2004; Orr et al., 2005; Doney et al., 2009). However, the long-term impact of increased CO₂ emission on the marine carbon cycle is not clear, nor is it resolved how the system will respond once emission levels decrease. Acidification poses a substantial threat to organisms that form shells of the minerals aragonite and calcite and plays an important role in carbon drawdown. Thus intensive investigations of the modern ocean, its biogeochemical cy-

cles and ecosystems are underway (e.g., Kleypas and Yates, 2009; Beaufort et al., 2011; Pandolfi et al., 2011; Lohbeck et al., 2012).

Ancient abrupt warming events, such as the Paleocene–Eocene thermal maximum (PETM; ~55.53 million years before present; Westerhold et al., 2008), provide an opportunity to constrain the impact of massive carbon input on the oceans and their ecosystems over millennial time scales (e.g., Dickens et al., 1997; Zeebe and Zachos, 2007). Consequently, marine environments, chemical cycles, and the fossil record of the PETM have been studied in detail (e.g., Thomas and Shackleton, 1996; Thomas et al., 2002; Wing et al., 2005; Zachos et al., 2005, 2007; Sluijs et al., 2007a, 2007b; Foster et al., 2013; Zeebe and Zachos, 2013; Penman et al., 2014).

The onset of the PETM involved the introduction of vast quantities of carbon to the ocean–atmosphere system as signified by the abrupt ~3–4‰ carbon isotope excursion (CIE) at the base of the event. Estimates for the mass and rate of carbon input vary substantially, ranging from ~2000 Pg to as high as 6800 Pg over approximately 1 kyr to 50 kyr (Dickens et al., 1995; Panchuk et al., 2008; Zeebe et al., 2009; Cui et al., 2011; Dickens, 2011;

* Corresponding author. Tel.: +1 814 863 1240.

E-mail address: bralower@psu.edu (T.J. Bralower).

Sluijs and Dickens, 2012). The greenhouse effect of the carbon addition, in conjunction with positive feedback mechanisms, was sufficient to induce warming of ocean surface and deep waters by 6–8 °C (e.g., Zachos et al., 2001, 2003; Zeebe et al., 2009), increase stratification in some locations, and likely alter ocean circulation patterns (e.g., Thomas et al., 2003; Nunes and Norris, 2006; Zeebe and Zachos, 2007; Lunt et al., 2010). The combined effects of warming and changing circulation conspired to lower oxygen levels and alter patterns of primary productivity, thereby modifying habitats from the surface ocean (e.g., Kelly et al., 1998; Crouch et al., 2001; Bralower, 2002; Kelly, 2002; Gibbs et al., 2006a; Agnini et al., 2007; Sluijs et al., 2007a; Raffi et al., 2009; Nicolo et al., 2010; Winguth et al., 2012; Norris et al., 2013) down to its depths where the PETM corresponds to the largest extinction of deep sea benthic foraminifera in the last 93 million years (e.g., Thomas, 1990, 1998, 2003, 2007).

Many of the expected changes in carbon cycling predicted for the future occurred during the PETM (e.g., Ridgwell and Schmidt, 2010; Hönisch et al., 2012; Zeebe and Zachos, 2013). The base of deep-sea PETM records show an abrupt decrease in CaCO₃ content, a deterioration in microfossil preservation, a sharp drop in sedimentation rate, and a discrete claystone layer (e.g., Thomas, 1998; Zachos et al., 2005; Bralower et al., 2006; Colosimo et al., 2006). These changes indicate major decreases in the carbonate saturation of intermediate- and deep-ocean waters leading to substantial shoaling of two key surfaces: the lysocline, which is the level at which the rate of dissolution of carbonate particles sinking through the water column increases (e.g., Berger and Winterer, 1974), and the calcite compensation depth (CCD), which is the depth at which all of the settling calcite is removed via dissolution (Zachos et al., 2005).

Corrosive PETM bottom waters dissolve carbonate particles settling to the sea floor as well as those in the actively burrowed uppermost 10 cm of the sediment column (e.g. Walker and Kastling, 1992; Archer et al., 1997, 1998; Dickens et al., 1997; Dickens, 2000). In cases where all of the carbonate is removed in the bioturbated zone, dissolution had the potential to remove previously deposited carbonate layers (Zachos et al., 2005; Colosimo et al., 2006; Kelly et al., 2010, 2012). Terminology for these processes varies between authors; hence to accurately represent the location of dissolution, we use the term *syn-depositional dissolution* for dissolution of newly deposited carbonate in the bioturbated benthic transition layer to distinguish it from *burndown dissolution*—which refers to dissolution of previously deposited layers below this interval. We use the term *chemical erosion* to refer collectively to syn-depositional and burndown dissolution.

Understanding chemical erosion is critical because of its potential to remove key stratigraphic horizons from the onset of PETM records and the interval immediately proceeding it. However, because dissolution removes carbonate materials, it is a notoriously difficult process to detect in the sedimentary record. For this reason, much of our understanding of chemical erosion derives from geochemical models designed to simulate the response of the marine carbonate system to carbon input (e.g., Dickens et al., 1997; Ridgwell, 2007; Ridgwell and Hargreaves, 2007; Zeebe and Zachos, 2007; Panchuk et al., 2008). Because the onset of the PETM occurs over centimeters in deep-sea sediment records, chemical erosion is recognized as complicating the interpretation of the stratigraphy of the earliest stages of the event (e.g., Murphy et al., 2010), but how it has obscured isotopic and other proxy records has not been determined. Without this information, the magnitude of environmental changes can only be estimated with any accuracy in sections from above the lysocline, most of which lie on continental shelves. Still, the PETM represents a great opportunity to understand the impact of dissolution on the stratigraphic record because of the existence of numerous calcareous sections arrayed over a broad range

of ocean depths, including depth transects (e.g., Zachos et al., 2005; Bralower et al., 2006).

Foraminiferal fragmentation is generally considered the most reliable indicator of dissolution in deep-sea sediments (e.g., Arrhenius, 1952; Thunell, 1976; Haug and Tiedemann, 1998; Le and Shackleton, 1992; Howard and Prell, 1994; Hancock and Dickens, 2006). Dissolution during the PETM indeed led to an increase in fragmentation, the proportion of foraminiferal shells that are fragments or broken (e.g., Kelly et al., 2005, 2010; Colosimo et al., 2006), and complete dissolution of carbonate at sites below the CCD produced fragmentation levels approaching infinity (e.g., Kelly et al., 2010; Leon-Rodriguez and Dickens, 2010). Considerably less is known about the effect of dissolution on nannoplankton, the dominant component of many deep-sea sediments, including those that record the PETM. For reasons not fully understood, it is thought that the calcite crystal arrangement or the higher surface areas of some nannofossils tends to make them more resistant to dissolution than most planktic and calcareous benthic foraminifera (e.g., Schlanger and Douglas, 1974; Broecker and Clark, 1999; Chiu and Broecker, 2008). The PETM at all open-ocean sites corresponds to an increase in dissolution-resistant nannofossil species (Raffi and De Bernardi, 2008; Gibbs et al., 2010; Dedert et al., 2014), in part an ecological response to changes in surface environments. However, changes in the volumetric abundance of nannofossils in the PETM has never been determined largely because these fossils are roughly two orders of magnitude smaller than their foraminiferal counterparts, making them difficult to analyze with the same grain-size technique.

Because of their size, foraminifera and especially nannofossils are susceptible to redistribution by processes such as bioturbation (mixing by burrowing infauna) and winnowing through the resuspension of fine-grained material by bottom currents on the deep-sea floor (e.g., Stow et al., 2002). Thus both processes are a key part of interpreting data from high-resolution (cm-scale) PETM studies (e.g., Thomas, 2003; Stoll, 2005; Zachos et al., 2007). Also, models indicate that bioturbation impacts chemical erosion (e.g., Archer et al., 1997; Zeebe and Zachos, 2007; Panchuk et al., 2008), but this hypothesis has not been tested with data. Burrows are readily observed in sediments and their density and diversity provide a measure of the degree of bioturbation (e.g., Savrda et al., 1984). The occurrence of winnowing can be interpreted from grain size distributions (e.g., McCave et al., 1995; Kranck et al., 1996).

Here we focus on the impact of dissolution on nannoplankton and planktic foraminifera in sediments that record the PETM. We combine grain size analyses and electron microscopy of sediments from three sites that were affected to varying degrees by dissolution during the event. These data shed light on the mechanics of dissolution during the event, the identification of syn-depositional and burndown dissolution in PETM sections, and the impact of dissolution, bioturbation and winnowing on the stratigraphy of the event. Ultimately, this knowledge allows us to identify sections where the full suite of acidification responses can be investigated.

2. Material and methods

Sediment samples were obtained from across the PETM at Ocean Drilling Program (ODP) Site 1209 (Shatsky Rise, Central Pacific; 32°39.1'N, 158°30.4'E; 2387 m water depth; 1900 m paleodepth, Takeda and Kaiho, 2007), ODP Site 1262 (Walvis Ridge, South Atlantic; 27°11.2'S, 1°34.6'E; 4755 m water depth; 3600 m paleodepth, Zachos et al., 2005), and from the lower part of the PETM at ODP Site 690 (Maud Rise, Weddell Sea; 65°9.6'S, 1°12.3'E; 2925 m water depth; 1900–2000 m paleodepth, Thomas, 1990), (Fig. 1). At Site 690 the PETM corresponds to a ~2.5 m interval of cyclically alternating white to pale brown calcareous ooze (Fig. 2).

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