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Research paper

Temporally variable diagenetic overgrowth on deep-sea nannofossil carbonates across Palaeogene hyperthermals and implications for isotopic analyses

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ABSTRACT

Calcareous nannofossil assemblages of deep-sea sediments were subjected to intensive diagenetic alterations during early Palaeogene hyperthermal events. These alterations may have significantly modified bulk isotopic and trace metal signals and nannofossil preservation, thus biassing palaeoceanographic and palaeoecological interpretation. We present a detailed characterisation of the temporal variation in degree of diagenetic overgrowth on nannoliths during the PETM and Early Eocene Thermal Maximum (ETM2) using scanning electron microscopy (SEM), and explore in detail the consequences of these changes in overgrowth for interpretation of nannofossil assemblages and geochemical records covering the ETM2 at ODP Site 1265 where the event is well recognised. Results show that the nannofossil genera *Discoaster* and *Zygrhablithus* are particularly receptive to significant amounts of diagenetic calcite overgrowth, which was confirmed by Sr/Ca variations within single discoasters. Overgrowths show a strong correlation with changes in sediment carbonate content across the hyperthermals, with notably less overgrowth in low carbonate intervals. This secondary calcite affects stable isotope, notably oxygen isotopes, and assemblage composition modifying the dissolution susceptibility of taxa. In particular, the size fraction with a high contribution of overgrown discoasters has heavier $\delta^{18}O$ values. Size fractions that are mainly composed of primary calcite give lighter $\delta^{18}O$ values, and reveal a conspicuous early warming trend across ETM2 that appears to be attenuated in fractions with a major contribution of secondary calcite. Hence, coccolith-based indices based on the degree of overgrowth may be used to evaluate the degree of diagenetic alteration, as to improve precision and accuracy of the interpretation of nannofossil-based stable isotope records and abundance data.

1. Introduction

Bulk carbonate geochemical records are widely used for palaeoceanographic reconstructions, especially in Palaeogene sediments where planktic foraminifera often comprise less than 5% of the bulk carbonate. These bulk carbonate geochemical records can be produced with little sample preparation, an advantage for generating long series at high temporal resolution. However, the scientific significance of bulk records has occasionally been questioned, as variable biogenic and abiogenic carbonate phases may impair palaeoclimatic interpretations (Schrag et al., 1995).

Most of the bulk carbonate consists of the fossil remains of coccolithophores and other calcareous nannoplankton, i.e. coccoliths are dominant biogenic carbonates in many deep-sea sediments (Baumann et al. 2004 and Hay, 2004). Reconstructing climatic trends using the isotopic composition of coccolith calcite is in general more complicated than for foraminifera, since culture studies of extant coccolithophores have shown a large span of vital effects (Dudley et al., 1986; Ziveri et al., 2003; Ziveri et al., 2012), and the potential of separation into mono-specific assemblages is limited for coccolith assemblages, given their small size, particularly when lith sizes of species overlap. Hence, shifts in nannofossil assemblage composition might

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significantly bias isotopic signals measured on mixed coccolith fractions. This difference in vital effects, however, may not be of great significance for Palaeogene sediments, as recent work on Early Palaeogene assemblages suggests a more limited array of vital effects (Stoll, 2005; Bolton et al., 2012). Of potentially greater importance in older sediments, isotopic signals, especially oxygen isotopic values, from carbonates may be influenced by diagenetic alteration (Schrag, 1999; Pearson et al., 2007). Although most studies recognise that some diagenetic alteration of bulk geochemical signals has taken place, numerical models of diagenesis assume that all sediments follow the same trajectory of decreasing rates of sediment dissolution and overgrowth with increasing depth in the sediment column, calibrated from modern pore water chemical profiles (Richter, 1993). As a result, diagenetic modification of oxygen isotopic values is modelled as a uniform shift in the composition of sediments, attenuating primary trends but without imparting any additional higher frequency variation (Schrag et al., 1995; 1999).

We suggest that these models of homogeneous overgrowth may not be applicable, however, for large and rapid shifts in the ocean carbonate system, such as during the Palaeocene Eocene Thermal Maximum (PETM, ~56 Ma) and Eocene Thermal Maximum (ETM2, ~53.7 Ma) (Zachos et al., 2005; Zachos et al., 2010). During these events, the calcite compensation depth (CCD) shoaled rapidly, due to massive injection of light carbon into the atmosphere and oceans, as indicated by the large carbon isotope excursion (CIE) to lighter values in both marine and terrestrial records (e.g. Zachos et al., 2005; Lourens et al., 2005; Sluijs et al., 2007). Temporal variability of the degree of secondary (abiogenic) calcite formation or overgrowth on nannofossils may have had a large impact on the isotopic and trace metal signals, thereby complicating the interpretation of the excursion values found during these hyperthermal events. Identifying temporal variations in abiogenic calcite contribution to bulk and fine carbonate will allow for the selection of the best preserved fraction for geochemical analysis.

In this study, we provide geochemical and morphological evidence, indicating that the degree of diagenetic calcite overgrowth on nannofossils varies on much shorter depth- and timescales than previously modelled (Richter, 1993; Schrag et al., 1995;1999). For this, we analysed the oxygen isotopic composition of different nannofossil size fractions, which may help distinguish between the primary isotopic signals and bias caused by secondary calcite.

Furthermore, we present here results of analyses on preservation and diagenetic overgrowth on nannofossils in carbonates covering the ETM2 (ODP Site 1265) and PETM interval at ODP Site 1263. Site 1263 is marked by a pronounced carbonate dissolution (Zachos et al., 2005) and is hence one of the most suitable locations to determine the degree of overgrowth changes during this event. In particular, we focus on two common taxa *Discoaster* and *Zygrhablithus*, which form nannofossils with structures rather different from the heterococcolith placoliths which dominate most assemblages. *Discoaster* is an extinct genus of nannoplankton represented by star-shaped nannofossils, called discoasters (Young et al., 1997). The rays of the discoasters are formed of single calcite crystals which are significantly larger than those of most coccoliths and other nannofossils. *Zygrhablithus* specimens by contrast are holococcoliths and so formed by an array of minute (ca 0.1 μm) equant crystallites. Pristine *Zygrhablithus* holococcoliths are delicate hollow structures (Bown et al., 2008) but with overgrowth they are transformed into robust structures formed primarily by four large blocks.

Discoasters and *Zygrhablithus* holococcoliths often show extensive overgrowth and in view of their volumetric importance to the carbonate budget, these overgrowths can distort climatic signals reconstructed from nannofossil assemblages significantly. Because the large crystals of discoasters serve as a nucleus for overgrowth, and these robust nannoliths are present throughout the section, we focus on quantifying how the degree of overgrowth responds to the changing carbonate saturation state in bottom waters. We describe the relationship between overgrowth and the preservation of robust vs fragile taxa in the sediments during the ETM2 interval. Fragile, dissolution susceptible taxa are preferentially lost during periods of more intense dissolution (Gibbs et al., 2004; Jiang and Wise, 2009), and conditions that promote dissolution generally discourage extensive overgrowth because they entail lower degrees of oversaturation with respect to $CaCO_3$. Finally, in our analysis of the combined trace metal (Sr/Ca) and stable isotope composition of nannofossil size fractions across ETM2 at ODP Site 1265A, we show how this variable secondary overgrowth likely influences the geochemical records of the nannofossil fractions in the sediments.

2 . Methods and materials

We focus on sediments from ETM2 at ODP Site 1265 and PETM interval at ODP Site 1263. The sediments preceding and following the PETM and ETM2 have high carbonate wt.% (~90%), which decreases in the dissolution interval to less than 1% during the PETM at Site 1263 (Zachos et al., 2005), and to ~50% in the dissolution interval (or Elmo horizon) at the peak of the CIE that marks ETM2 (Lourens et al., 2005; Stap et al., 2009). These decreases in $CaCO_3$ are inferred as a direct response to undersaturated bottom waters. In some locations, rapid decreases in bottom water saturation state may result in enhanced dissolution of sediments previously deposited during periods of higher saturation state. This phenomenon, known as burn-down, can cause $CaCO_3$ contents to be depressed stratigraphically below the onset of the CIE which marks the timing of lower saturation states in the water column. In the two intervals examined in detail in this study, there is not a strong signal of burn-down at the scale of sampling employed here, i.e. there is no interval of depressed $CaCO_3$ below the $\delta^{13}C$ excursion. Rather, during the ETM2 the interval of dissolution and minimum $CaCO_3$ at is constrained to the middle of the CIE, i.e. the Elmo horizon (Fig. 2). In the PETM, $CaCO_3$ content decreases synchronously with $\delta^{13}C$. Thus, in these two sample locations, at the scale of our sampling, the use of $CaCO_3$ is a reliable indicator of the timing of undersaturated bottom waters.

Samples for nannofossil abundance counts were taken every centimetre from 14 cm below (277.59 mcd) to 11 cm above (277.27 mcd) the Elmo horizon in ODP Hole 1265A and for every 5 cm outside this interval. Smear slides were prepared using standard techniques. The nannofossils were identified to genus level; about 300–400 specimens were counted per interval. Samples for SEM analyses of nannofossil preservation at Site 1263 were selected based on carbonate content and taken about every 5–10 cm.

Scanning Electron Microscope (SEM) analysis of nannofossil assemblages from various sites (Fig. 1) with different preservation states was used to characterise the amount of overgrowth during the PETM and ETM2, and was performed at the Free University Amsterdam (JEOL JSM 6301F scanning microscope) and at the Natural History Museum London (Philips XL-30 digital scanning field emission electron microscope). For the Walvis Ridge sites, we quantified the degree of overgrowth on discoasters and *Zygrhablithus* holococcoliths across the PETM and ETM2 events by selecting 40 to 50 specimens that were imaged by SEM in a certain number of fields of view and assessed their preservation subjectively using a reference scale of four categories of preservation: 1) minimally overgrown, 2) slightly overgrown, 3) moderately overgrown and 4) heavily overgrown (Figs. 2 and 3). Low overgrowth stages are characterised by thin specimens with biogenically sculpted surfaces whereas high overgrowth stages result in thick specimens with angular crystal faces. In addition to sediments from ODP 1263 and ODP 1265, we also examined nannofossils from coeval sediments at a few other locations to obtain a broader view of types of preservation typical in deep-sea sediments at this time (see Fig. 1).

We compare the stable isotope chemistry of the bulk fine sediment and separated fractions of nannofossils containing different proportions of overgrown calcite. The bulk fine fraction is defined here as the portion