Quaternary Science Reviews 137 (2016) 69–78

Contents lists available at ScienceDirect

Quaternary Science Reviews

journal homepage: www.elsevier.com/locate/quascirev

Isotopic record of Pleistocene glacial/interglacial cycles in pelagic carbonates: Revisiting historical data from the Caribbean Sea

Michaël Hermoso

University of Oxford, Department of Earth Sciences, South Parks Road, Oxford OX1 3AN, United Kingdom

A R T I C L E I N F O

Article history:
Received 28 October 2015
Received in revised form
3 February 2016
Accepted 5 February 2016
Available online xxx

Keywords:
Coccoliths
Foraminifera
Stable isotopes
Vital effect
Pleistocene
Glacials/interglacials
Surface water chemistry
Low latitude realm

A B S T R A C T

The glacial/interglacial cycles of the Pleistocene were first recognised by variations in the oxygen isotopic composition of planktonic foraminifera from cores in the Caribbean Sea. Since this pioneering work by Emiliani, this proxy has been extensively applied to a variety of carbonate biominerals over the entirety of the Meso-Cenozoic. However, palaeoceanographic studies have overwhelmingly focused on foraminifera compared to other calcifying microorganism fossils, such as the coccoliths. In this study, I revisit coccolith stable isotopic data obtained from the classic P6304-4 core in light of recent developments in the biogeochemistry of coccolithophores. In particular, I show that the coccolith stable isotope record of the last 13 Marine Isotope Stages (~480 kyrs) is significantly biased by large vital effects. The magnitude of coccolith carbon and oxygen isotope vital effects is not uniform, but shows remarkable co-variance with the Vostok CO_2 ice record. During periods of relatively elevated CO_2 (interstadials), the expression of the vital effect is relatively small, whereas it can as high as +3‰ for the oxygen isotopes during glacial stadials, which I argue is a result of enhanced CO_2 limitation of coccolithophores. Using this paradigm, I propose that coccolithophore vital effects are not a complicating factor, but rather the signal of interest. As the magnitude of the coccolith vital effect is shown to scale with pCO_2, coccolith carbon and oxygen isotopes may be used in conjunction with foraminifera data to reconstruct and refine aqueous CO_2 concentrations in the past.

1. Introduction

Sixty years after Harold Urey and Cesare Emiliani demonstrated the potential of oxygen isotope composition of marine carbonate as a proxy for ocean temperatures (Urey, 1947; Emiliani, 1955), we are still working on refining this geochemical tool. Aside from the phenomenal gain of knowledge of the palaeoclimates that this proxy has permitted, it is laudable that we are continuously developing this isotopic tool to generate more reliable SST estimates (Zeebe et al., 2008; Arbuszewski et al., 2010; Watkins et al., 2013; Minoletti et al., 2014; Prentice et al., 2014; Reghellin et al., 2015; Tripati et al., 2015). It is now possible to isotopically measure individual foraminifera specimens thanks to analytical progress in mass spectrometry, but the interpretation of such high-precision results and how they can be translated into robust SST estimates remains a much larger source of uncertainty. Marine sediments formed in the pelagic environment predominantly originate from the accumulation of foraminifera shells and coccoliths, and their biogenic nature suggests that they are compositionally distinct from theoretical inorganic calcite (vital effect).

Multidisciplinary approaches bridging traditional geosciences, and biological techniques and concepts have greatly contributed to increasing our understanding of stable isotope fractionation in biologically-precipitated calcite. In particular, laboratory cultures of living calcifying organisms have enabled a mechanistic understanding of the vital effect, as well as the development of the alkenone temperature proxy (Dudley et al., 1986; Spero et al., 1997; Grimalt et al., 2000; Ziveri et al., 2003; Hermoso et al., 2014; Hermoso et al., 2016). On one hand, planktonic foraminifera are relatively easy to separate from the sediment by handpicking. Towed plankton net and core top studies both enabled calibration of the oxygen isotopic composition with the environment (not only temperature) in which the foraminifera are thought to have lived (Bouvier-Soumagnac and Duplessy, 1985; Mulitza et al., 1998). On the other hand, the coccolithophores are relatively easy to culture, but it is more complicated to isolate their fossil remains, the coccoliths, from other carbonate constituents of the sediments due to

E-mail address: Michael.Hermoso@earth.ox.ac.uk.

http://dx.doi.org/10.1016/j.quascirev.2016.02.003
0277-3791/

their microscopic size. Relatively recent techniques based on decanting, settling, microsieving and microseparation of sediment fine fractions allow obtention of near-monotaxic coccolith assemblages (Stoll and Ziveri, 2002; Minoletti et al., 2009).

A series of piston cores (P6304) from the Caribbean Sea have particular historical significance in the development of the $\delta^{18}O$ proxy since it is from this core material that the pioneering work by Emiliani was conducted (Emiliani, 1966; 1972). Species-specific isotopic analyses of the foraminifera *Globigerinoides sacculifer* led Emiliani to recognise glacial and interglacial periods in the Late Pleistocene. Subsequent work on isotopic analyses performed on the fine fraction in the P6304-4 site investigated the response of another prominent calcium carbonate, perhaps dominant, fraction of pelagic sediments, the coccoliths (Steinmetz and Anderson, 1984).

The present study follows on from the historical work in the Caribbean Sea, and aims to establish how the coccoliths have isotopically recorded a suite of environmental change (temperature, pCO_2, pH, alkalinity) through the last 13 glacial stages in the Pleistocene. If coccolith $\delta^{18}O$ strictly follows the trends seen in foraminiferal record in the P6304-4 site, the reason(s) for which the magnitude of the isotopic cycles is much larger and more highly variable in coccolith calcite than in foraminifera remain unexplained thirty years on.

2. Material and methods

2.1. The classic P6304-4 core and available isotopic measurements

The P6304-4 site (15°27′N; 70°43′W) is part of a series of piston cores from the Caribbean Sea in 1963 (Fig. 1). Correlations with the other P6304 cores and various other historical sites (A172-6 and V12-122) were obtained by oxygen stratigraphy, but to date, the age model for P6304-4 has not been attempted.

The isotopic ($\delta^{18}O$ only) data from the foraminifera *Globigerinoides sacculifer* during the last 450 kyrs used in the present study originate from the work by Emiliani (1972). *G. sacculifer* is a key foraminifera species used to retrieve surface water conditions in low latitude realms. The depth habitat of *G. sacculifer* is very shallow, commonly assigned to a range comprised between 20 and 30 m (Multiza et al., 1998; Farmer et al., 2007), hence reflecting the physico-chemical evolution of surface waters.

Coccolith assemblages from the P6304-4 core sediments were purified from the same samples used by Emiliani (Anderson and Steinmetz, 1981). A settling/centrifuging technique has allowed concentrating assemblages consisting "*almost exclusively of well-preserved coccoliths*" after Anderson and Steinmetz (1981). These microfractions were taxonomically and isotopically analysed (Anderson and Steinmetz, 1981; Steinmetz and Anderson, 1984). Over the entire range of the studied interval, the coccolith assemblages have revealed to be largely dominated by *Gephyrocapsa* spp. (Fig. A.1). Notably, it was argued that the applied microseparation technique has excluded *Emiliania huxleyi* from the microfractions owing to the small size (<3 μm) of this coccolith species. The preservation of coccoliths was very good, albeit with some evidence of dissolution in samples predating MIS 10 (Fig. 2), as originally reported by Emiliani (1972) and Steinmetz and Anderson (1984).

2.2. Age model and the ODP 999A site

ODP Site 999A (12°45′N, 78°44′W) was drilled during the Leg 165 (Fig. 1). The Pleistocene portion of the core has been extensively studied in recent years (Schmidt et al., 2006; Foster, 2008; Bolton et al., 2012). Available data are abundant, and especially those from *G. ruber* analyses ($\delta^{18}O$; $\delta^{13}C$; $\delta^{11}B$, and B/Ca and Mg/Ca elemental ratios), offering a well-constrained chemostratigraphic and palaeoenvironmental framework in the Caribbean region (Schmidt et al., 2006; Foster, 2008). It is thus possible to utilise the current age model of the Late Pleistocene of the core ODP 999A and the LR04 $\delta^{18}O$ stack record (Lisiecki and Raymo, 2005; Schmidt et al., 2006) to constrain the age model for site P6304-4, applying

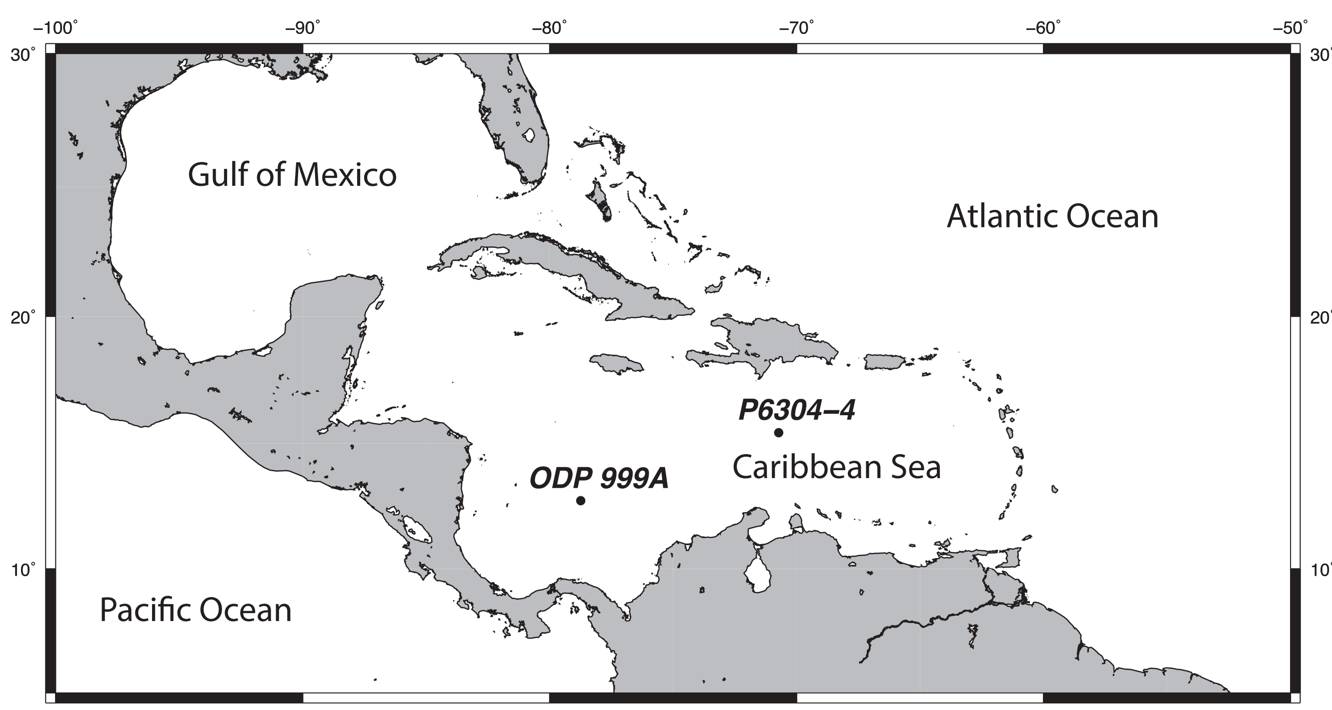

Fig. 1. Map showing the location of the P6304-4 and ODP 999A sites in the Caribbean Sea. The map layout was generated using the GMT software (Wessel et al., 2013).