



## An explanation for the $^{18}\text{O}$ excess in Noelaerhabdaceae coccolith calcite

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### Abstract

Coccoliths have dominated the sedimentary archive in the pelagic environment since the Jurassic. The biominerals produced by the coccolithophores are ideally placed to infer sea surface temperatures from their oxygen isotopic composition, as calcification in this photosynthetic algal group only occurs in the sunlit surface waters. In the present study, we dissect the isotopic mechanisms contributing to the “vital effect”, which overprints the oceanic temperatures recorded in coccolith calcite. Applying the passive diffusion model of carbon acquisition by the marine phytoplankton widely used in biogeochemical and palaeoceanographic studies, our results suggest that the oxygen isotope offsets from inorganic calcite in fast dividing species *Emiliania huxleyi* and *Gephyrocapsa oceanica* originates from the legacy of assimilated  $^{18}\text{O}$ -rich  $\text{CO}_2$  that induces transient isotopic disequilibrium to the internal dissolved inorganic carbon (DIC) pool. The extent to which this intracellular isotopic disequilibrium is recorded in coccolith calcite (1.5 to +3‰ over a 10 to 25 °C temperature range) is set by the degree of isotopic re-equilibration between  $\text{CO}_2$  and water molecules before intracellular mineralisation. We show that the extent of re-equilibration is, in turn, set by temperature through both physiological (dynamics of the utilisation of the DIC pool) and thermodynamic (completeness of the re-equilibration of the relative  $^{18}\text{O}$ -rich  $\text{CO}_2$  influx) processes. At the highest temperature, less ambient aqueous  $\text{CO}_2$  is present for algal growth, and the consequence of carbon limitation is exacerbation of the oxygen isotope vital effect, obliterating the temperature signal. This culture dataset further demonstrates that the vital effect is variable for a given species/morphotype, and depends on the intricate relationship between the environment and the physiology of biomineralising algae.

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**Keywords:** Biomineralisation; *Emiliania huxleyi*; *Gephyrocapsa oceanica*; Oxygen isotope fractionation; Temperature proxy; Vital effect; Carbon ( $\text{CO}_2$ ) limitation

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## 1. INTRODUCTION

Understanding how the physiology of marine organisms affects the fractionation of stable isotopes in biogenic carbonates has geological and biogeochemical importance. Firstly, such a goal would help the development and validation of geological proxies. Secondly, the stable isotope signatures determined from studies of fractionations then may be used to constrain present (and past) physiology, particularly with regard to carbon utilisation. In the case of the coccolithophores with the dual ability to fix carbon to produce organic matter and to calcify, the cells accumulate an internal carbon pool ( $C_i$ ) to serve the carbon requirements both for photosynthetic carbon fixation in the chloroplast and mineralisation in the coccolith vesicle with large isotopic consequences (Sekino and Shiraiwa, 1996; Benthien et al., 2007; Rickaby et al., 2010; Rokitta and Rost, 2012; Bolton and Stoll, 2013; Hermoso, 2014, 2015; Hermoso et al., 2014; Holtz et al., 2015). Previous culture studies have suggested a control of stable isotope composition (hence a vital effect) in coccolith calcite by algal growth rate (Ziveri et al., 2003). The vital effect is here defined as the species-specific offset in  $\delta^{18}\text{O}$  values between biogenic calcite and inorganic calcite grown under the same conditions (temperature, pH, etc. . .). The aim of the present study is to deepen our knowledge of the mechanism of oxygen isotope fractionation in coccolith calcite by isolating the vital effect component and determining how its magnitude varies with growth rate, cell size, carbon availability and temperature. Carbon isotope data from cultured coccoliths are not presented in the present study, as they will be published in a subsequent contribution.

The early works by Anderson and Steinmetz (1981) and Paull and Thierstein (1987) documented a large modulation of the isotopic offset in Noelaerhabdaceae coccolith from the foraminiferal record through glacial/interglacial cycles in the Pleistocene. A recent reappraisal of the data identified a  $p\text{CO}_2$ -driver for such a modulation of the oxygen and carbon vital effects in coccoliths with maximum values during glacial (relatively low  $p\text{CO}_2$ ) stades (Hermoso, 2016). Other sedimentary records suggest that the vital effect for reticulofenestrated coccoliths (extinct taxa of the Noelaerhabdaceae) was insignificant in the Pliocene (Bolton et al., 2012). During this period,  $p\text{CO}_2$  values were similar to or higher than Pleistocene interglacial concentrations (Badger et al., 2013), hence representing a coherent  $\text{CO}_2$  availability/palaeo-vital effect framework. Taken together, these results from the natural environment, however, challenge the constancy of the vital effect deduced from laboratory culture experiments on Noelaerhabdaceae coccoliths (Dudley et al., 1986; Hermoso et al., 2015).

Here, we investigate how this vital effect varies using laboratory experiments. Our working hypothesis is that the vital effect derives from the isotopic disequilibrium of the  $C_i$  pool with regulating mechanisms such as cell geometry, temperature and  $\text{CO}_2$  supply-to-demand ratio, as is the case for carbon isotopic fractionation in organic matter (Bidigare et al., 1997). We grew six strains of Noelaerhabdaceae coccolithophores with very distinct cell sizes and over a range of temperatures (Figs. 1 and 2). Changing

temperature has a direct impact on the solubility of aqueous  $\text{CO}_2$ , on the isotopic equilibrium between the DIC species, DIC and water (Zeebe and Wolf-Gladrow, 2001). In addition, the physiology of algae also changes with temperature, in particular with regards to the carbon demand by the cells (Sett et al., 2014; Rickaby et al., 2016). Hence, by changing the ambient temperature of the culture medium, we test the consistency of temperature dependence of the magnitude of disequilibrium in the oxygen isotope system compared to equilibrium conditions, elucidate a component of the vital effect, and examine the reliability of the coccolith-derived  $\delta^{18}\text{O}$  proxy for reconstructing sea surface temperatures (SSTs) in the past.

## 2. MATERIAL AND METHODS

### 2.1. Medium

We used growth medium consisting of natural seawater from the English Channel sampled by the Marine Biology Association, Plymouth (UK). This seawater was aged at 4 °C for at least 6 months. Air was bubbled through each of the aged seawater batches at distinct temperatures (10, 15, 20, and 25 °C) overnight and prior to medium preparation. The  $p\text{CO}_2$  of the laboratory air used to aerate the culture media was measured at 400 ppmV using a Licor LI-840A infrared analyser at 400 ppmV. Each batch was subsequently amended with nitrate (288  $\mu\text{M}$ ), phosphate (18  $\mu\text{M}$ ), EDTA, trace metals and vitamins following the  $K/2$  recipe by Keller et al. (2007) and the pH adjusted to 8.2 (total scale) by addition of 1 N NaOH. Prior to inoculation, medium was sterilised by microfiltration (Millipore 0.22  $\mu\text{m}$  Stericup device) and transferred into sterile 0.25 L polystyrene culture flasks.

The initial concentration of aqueous  $\text{CO}_2$  in each medium was calculated for each temperature using the software  $\text{CO}_2\text{CALC}$  (Robbins et al., 2010) with temperature, salinity, alkalinity and pH as input parameters. A total alkalinity of  $2600 \pm 39 \mu\text{mol kg}_{\text{sw}}^{-1}$  was measured in the initial batch solution using a 916 Ti Touch automatic titrator (Metrohm) and a 0.25 M HCl titrant standardised using a  $\text{Na}_2\text{CO}_3$  solution. The method was adapted from Bradshaw et al. (1981) for the determination of total alkalinity in seawater. Calculated concentrations of aqueous  $\text{CO}_2$  in the medium ranged linearly from 13.5  $\mu\text{mol C kg}_{\text{sw}}^{-1}$  at 10 °C to 8.3  $\mu\text{M}$  at 25 °C (Fig. 2).

### 2.2. Cells and growth

Coccolithophore strains *Emiliania huxleyi* (RCC 1256; RCC 1216; RCC 1212) and *Gephyrocapsa oceanica* (RCC 1211; RCC 1318; RCC 1314) were supplied by the Roscoff Culture Collection, France. The assignment to a morphotype for *E. huxleyi* and typical coccosphere size are given in Fig. 1. These algal clones were selected to cover a large range of cell size within the Noelaerhabdaceae coccolithophores, ranging from 3.7 to 7.2  $\mu\text{m}$  in diameter (Fig. 1). More information, including the origin and previous names of each strain can be found at: <http://roscoff-culture-collection.org>.

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