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ScienceDirect
Earth and Planetary Science Letters 260 (2007) 505–515
EPSL
www.elsevier.com/locate/epsl

Calcium isotope fractionation in coccoliths of cultured *Calcidiscus leptoporus*, *Helicosphaera carteri*, *Syracosphaera pulchra* and *Umbilicosphaera foliosa*

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Received 22 December 2006; received in revised form 14 May 2007; accepted 1 June 2007
Available online 12 June 2007
Editor: H. Elderfield

Abstract

Four species of marine calcifying algae, the coccolithophores *Calcidiscus leptoporus*, *Helicosphaera carteri*, *Syracosphaera pulchra* and *Umbilicosphaera foliosa* were grown in laboratory cultures under temperatures varying between 14 and 23 °C, and one species, *C. leptoporus*, under varying [CO_3^{2-}], ranging from 105 to 219 μmol/kg. Calcium isotope compositions of the coccoliths resemble in both absolute fractionation and temperature sensitivity previous calibrations of marine calcifying species e.g. *Emiliania huxleyi* (coccolithophores) and *Orbulina universa* (planktonic foraminifera) as well as inorganically precipitated $CaCO_3$, but also reveal small species specific differences. In contrast to inorganically precipitated calcite, but similar to *E. huxleyi* and *O. universa*, the carbonate ion concentration of the medium has no statistically significant influence on the Ca isotope fractionation of *C. leptoporus* coccoliths; however, combined data of *E. huxleyi* and *C. leptoporus* indicate that the observed trends might be related to changes of the calcite saturation state of the medium. Since coccoliths constitute a significant portion of the global oceanic $CaCO_3$ export production, the Ca isotope fractionation in these biogenic structures is important for defining the isotopic composition of the Ca sink of the ocean, one of the key parameters for modelling changes to the marine Ca budget over time. For the present ocean our results are in general agreement with the previously postulated and applied mean value of the oceanic Ca sink (Δ_{sed}) of about −1.3‰, but the observed inter- and intra-species differences point to possible changes in Δ_{sed} through earth history, due to changing physico-chemical conditions of the ocean and shifts in floral and faunal assemblages.

Keywords: coccolithophores; calcium isotopes; *Calcidiscus leptoporus*; *Helicosphaera carteri*; *Syracosphaera pulchra*; *Umbilicosphaera foliosa*; $\delta^{44/40}Ca$; $\delta^{44}Ca$; $\delta^{mu}Ca$

1. Introduction

Coccolithophores are unicellular marine phytoplankton, belonging to the taxon Haptophyta and are

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doi:10.1016/j.epsl.2007.06.001

characterized by an exoskeleton composed of minute calcite platelets, the 'coccoliths'. Coccolithophores are important primary producers and contribute about half the total marine $CaCO_3$ export production (Milliman, 1993). As a consequence, they are an important link between global calcium (Ca) and carbon (C) cycling. Because they act as a major Ca sink, coccoliths play an important role in determining the isotopic Ca budget of the marine realm, and consequently their isotopic composition is an important parameter for reconstructing the Ca budget of the global ocean (De La Rocha and DePaolo, 2000; Schmitt et al., 2003; Soudry et al., 2004; Heuser et al., 2005; Fantle and DePaolo, 2005). However, previous studies on coccolith oozes have reported a disparate range of seemingly conflicting Ca isotope values. De La Rocha and DePaolo (2000) and Fantle and DePaolo (2005) reported Ca isotope values of coccolith oozes similar to cultured specimens of *Emiliania huxleyi* (16 °C: $1000 \cdot \ln\alpha = -1.3‰$; with $\alpha = ({}^{44}Ca/{}^{40}Ca)_{coccolith}/({}^{44}Ca/{}^{40}Ca)_{seawater}$) (De La Rocha and DePaolo, 2000). In contrast, Zhu and Macdougall (1998) observed considerably lighter Ca isotope values in Holocene coccolith oozes ($1000 \cdot \ln\alpha = -1.9$ to -2.6).

Detailed investigation of the Ca isotope response to changing environmental parameters such as salinity, pCO_2/pH, illumination, Ca^{2+} concentration and temperature, identified temperature, apart from the isotopic composition of the medium, as the main factor influencing the Ca isotope composition of *E. huxleyi* coccoliths (Gussone et al., 2006; Langer et al., 2007). The small but significant temperature dependence of 0.027±0.006‰/°C (7.3±1.6 ppm/amu/°C) found in *E. huxleyi* is too limited to be a possible explanation for the observed disparity in Ca isotope values between Quaternary coccolith oozes (Zhu and Macdougall, 1998; De La Rocha and DePaolo, 2000; DePaolo, 2004).

To investigate if species-specific vital effects might be responsible for the observed discrepancies in the Ca isotope composition of bulk marine carbonate oozes, we cultured four different coccolithophore species under varying temperature regimes, as well as one species under different pCO_2 levels. These parameters were chosen because previous studies revealed that temperature and carbonate chemistry can have a large effect on Ca isotope fractionation: Different species of foraminifera exhibit temperature dependent Ca isotope fractionation patterns, with temperature sensitivities differing by roughly an order of magnitude between taxa (Zhu and Macdougall, 1998; Nägler et al., 2000; Gussone et al., 2004), and Lemarchand et al. (2004) observed a large sensitivity of Ca isotope fractionation of inorganically precipitated calcite in response to changes in the carbonate ion concentration of the fluid.

2. Materials and methods

2.1. Coccolithophore culturing

We cultured coccolithophore species from the CODENET culture collection maintained in the ALGOBANK laboratory at the University de Basse Normandie in Caen, France. Four species, *Syracosphaera pulchra* (strain GK7, GK17), *Calcidiscus leptoporus* (strains NS10-2, ASM31), *Umbilicosphaera foliosa* (strain ESP 6MI) and *Helicosphaera carteri* (strains NS10-8, NS8-4) were grown in monoclonal cultures covering a temperature range from 14 to 23 °C (Table 2) at The Natural History Museum (NHM), London. In addition one *C. leptoporus* strain (AS31) was grown at different CO_2 levels at the Alfred Wegener Institute (AWI), Bremerhaven. SEM illustrations of the investigated coccolithophore species are displayed in Plate I. In the past *C. leptoporus* was informally divided into three size clusters, small, intermediate, and large. Recent life cycle and morphological research resulted in a division on the subspecies level (Geisen et al., 2002). Sáez et al. (2003) however raised the subspecies to species rank based on molecular data. The cultures used for this work

Table 1
Composition of K medium

Additions	Final concentration in medium (μM)	Comments
(1) KNO_3	884	Same as *f*/2
(2) NH_4Cl	10	Addition to *f*/2
(3) Na_2 ortho-PO_4	36	Same as *f*/2 (K uses organic form)
(4) Trace metals:		
FeEDTA [a]	11.7	*f*/2 uses $FeCl_3$
$MnCl_2 \cdot 4H_2O$	0.9	Same as *f*/2
$ZnSO_4 \cdot 7H_2O$	0.03	Same as *f*/2
$CoSO_4 \cdot 7H_2O$	0.05	Same as *f*/2
$Na_2MoO_4 \cdot 2H_2O$	0.08	Same as *f*/2
$CuSO_4 \cdot 5H_2O$	0.01	One half *f*/2 level
$Na_2EDTA \cdot 2H_2O$	100	Order of magnitude higher than *f*/2
Na_2SeO_3	0.01	Addition to *f*/2
(5) Vitamins		
Thiamin–HCl	0.3	Same as *f*/2
Biotin	0.0021	Same as *f*/2
B12	0.00037	Same as *f*/2
Seawater	To 1 l	

Stock solutions are numbered 1–5. Each stock is made such that the addition of 1 ml/l yields the final concentration in the medium.
1–5 made with reagent grade chemicals and HPLC grade water.
All solutions filter-sterilised through 0.2 μm membrane filters.
1–4 stored at 4 °C.
5 stored frozen at −20 °C.
[a] Ethylenediamine tetra-acetic acid.