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Influence of temperature and CO₂ on the strontium and magnesium composition of coccolithophore calcite

M. N. Müller^{1,2,*}, M. Lebrato^{2,3,*}, U. Riebesell², J. Barcelos e Ramos⁴,
K. G. Schulz^{2,5}, S. Blanco-Ameijeiras^{6,**}, S. Sett², A. Eisenhauer², and
H. M. Stoll⁷

¹Institute for Marine and Antarctic Studies (IMAS), Private Bag 129, Hobart, TAS 7001, Australia

²GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1–3, 24148 Kiel, Germany

³Scripps Institution of Oceanography, UCSD, Hubbs Hall Room 2265, 8750 Biological Grade, San Diego, USA

⁴Centre of Climate, Meteorology and Global Change (CMMG), University of Azores, Rua do Capitão d'Ávila, Pico da Urze 970-0042 Angra do Heroísmo, Açores, Portugal

⁵Centre for Coastal Biogeochemistry, School of Environmental Science and Management, Southern Cross University, P.O. Box 157, Lismore, NSW 2480, Australia

⁶National Oceanography Centre, University of Southampton, European Way, SO14 3ZH Southampton, UK

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⁷Department of Geology, University of Oviedo, Arias de Velasco, s/n 30005, Oviedo, Asturias, Spain

*Both authors contributed equally to this work.

**now at: Institute F.-A. Forel, Faculty of Sciences, University of Geneva, 10 Route de Suisse, 1290 Versoix, Switzerland

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Correspondence to: M. N. Müller (marius.muller@utas.edu.au)

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Abstract

Marine calcareous sediments provide a fundamental basis for paleoceanographic studies aiming to reconstruct past oceanic conditions and understand key biogeochemical element cycles. Calcifying unicellular phytoplankton (coccolithophores) are a major contributor to both carbon and calcium cycling by photosynthesis and the production of calcite (coccoliths) in the euphotic zone and the subsequent long-term deposition and burial into marine sediments. Here we present data from controlled laboratory experiments on four coccolithophore species and elucidate the relation between the divalent cation (Sr, Mg and Ca) partitioning in coccoliths and cellular physiology (growth, calcification and photosynthesis). Coccolithophores were cultured under different seawater temperature and carbonate chemistry conditions. The partition coefficient of strontium (D_{Sr}) was positively correlated with both carbon dioxide (pCO_2) and temperature but displayed no coherent relation to particulate organic and inorganic carbon production rates. Furthermore, D_{Sr} correlated positively with cellular growth rates when driven by temperature but no correlation was present when changes in growth rates were pCO_2 -induced. The results demonstrate the complex interaction between environmental forcing and physiological control on the strontium partitioning in coccolithophore calcite. The partition coefficient of magnesium (D_{Mg}) displayed species-specific differences and elevated values under nutrient limitation. No conclusive correlation between coccolith D_{Mg} and temperature was observed but pCO_2 induced a rising trend in coccolith D_{Mg} . Interestingly, the best correlation was found between coccolith D_{Mg} and chlorophyll *a* production suggesting that chlorophyll *a* and calcite associated Mg originate from the same intracellular pool. These results give an extended insight into the driving factors that lead to variations in the coccolith Mg/Ca ratio and can be used for Sr/Ca and Mg/Ca paleoproxy calibration.

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1 Introduction

Coccolithophores, a key functional phytoplankton group, evolved about 225 million years ago and their calcitic plates (coccoliths) that cover the cell are found in the sediment record since then (Bown et al., 2004). The geochemical composition of their intracellularly produced coccoliths has been the focus of numerous studies reconstructing past oceanographic and environmental conditions (Stoll and Ziveri, 2004; Erba, 2006; Ziveri et al., 2012). Since the industrial revolution, coccolithophores are exposed to a rapidly changing environment including an increase in sea-surface temperature and shifting seawater carbonate chemistry speciation due to anthropogenically released carbon dioxide (Boyd and Hutchins, 2012). The ability of coccolithophores to both fix carbon via photosynthesis and calcification makes them an important contributor to the strength of the biological carbon pump. Assessing the response of coccolithophores following projected changes in seawater temperature and carbonate chemistry speciation (increasing CO₂ availability and decreasing pH) is of key interest to estimate potential impacts on oceanic carbon sequestration. The physiological response of coccolithophores to changing carbonate chemistry speciation and temperature is relatively well described (see Riebesell and Tortell, 2011 and Raven and Crawford, 2012), however, associated changes in coccolith elemental partitioning and composition (e.g. Sr/Ca and Mg/Ca) are less well studied (Stoll and Ziveri, 2004; Stoll et al., 2012).

The distribution and partitioning of divalent cations, replacing the calcium ion in the calcite lattice, are driven by a combination of thermodynamic precipitation kinetics and cellular physiology (Langer et al., 2006; Müller et al., 2011; Stoll et al., 2012). The latter has been summarized under the term “vital effects” and controlled laboratory experiments are inevitable to understand and validate the underlying mechanisms in order to reliably apply coccolithophore-based paleoproxies (Ziveri et al., 2012).

Coccolithophore productivity and growth has been hypothesized to primarily control coccolith Sr/Ca ratios with a secondary influence of temperature and seawater Sr/Ca ratio (Stoll and Schrag, 2000; Stoll and Ziveri, 2004; Stoll et al., 2007). Cellular con-

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cepts were developed to model and describe the Sr partitioning in coccolithophore calcite (Langer et al., 2006, 2009), based on the assumption that Ca and Sr are transported via the same pathways which is supported by experimental evidence (Müller et al., 2011). The effect of carbonate chemistry speciation on coccolith Sr/Ca ratio is unknown as well as the associated influence of coccolithophore growth affected by seawater pH and CO₂ availability.

Coccolithophores precipitate low-Mg calcite (< 1 % mol) despite that magnesium is the most abundant divalent cation in plant cells and its concentration in the cytosol is about 20 000 times higher than cytosolic free-Ca concentration (Brownlee et al., 1995; Bose et al., 2011). The transport of Mg in coccolithophores presumably differs distinctly from Sr and Ca and is likely associated with specific ion transporters and channels (Mackinder et al., 2010; Holtz et al., 2013) as in bacteria and higher plants (Legong et al., 2001). A relation between the coccolithophore Mg/Ca ratio and temperature is still under discussion and complicated by the nontrivial removal of organically bound Mg (Blanco-Ameijeiras et al., 2012).

Potential changes in the partitioning of Sr and Mg and thus in the Sr/Ca and Mg/Ca ratio of calcareous sediments may alter their biogeochemical cycling over geological time scales because biogenic calcification and the subsequent burial of calcium carbonate represents a major elemental export process from the ocean to the lithosphere. Furthermore, the dissolution dynamics of carbonate-rich sediments are, to a certain degree, controlled by their Mg/Ca ratio (Andersson et al., 2008; Morse et al., 2006).

Here we present the partitioning coefficients for Sr and Mg and the related coccolith Sr/Ca and Mg/Ca ratios from laboratory culture experiments in which temperature and carbonate chemistry of the growth medium were tightly controlled and monitored. Calcite samples were cleaned with a newly developed organic matter removal procedure (Blanco-Ameijeiras et al., 2012). The results provide the most comprehensive laboratory study to date on the response of coccolith elemental ratios to changing environmental conditions (e.g. ocean acidification and warming) and should be considered when applying paleoproxies based on Sr/Ca and Mg/Ca coccolith ratios.

2 Methods

The present study combines results from four independent culture experiments conducted with *Emiliana huxleyi* (Exp. 1 and 2), *Coccolithus braarudii* (Exp. 1 and 3), *Gephyrocapsa oceanica* (Exp. 4) and *Calcidiscus quadriperforatus* (Exp. 1).

5 All experiments were conducted within a temperature range from 10 to 25°C. The carbonate system was manipulated with the goal to either keeping $p\text{CO}_2$ constant (Exp. 1) or establishing a $p\text{CO}_2$ gradient ranging from ≈ 25 to 3520 μatm (Exp. 2, 3 and 4). A summary of the seawater conditions (temperature and carbonate system) and abiotic parameters (light intensity and day length) are given in the Supplement.
10 Additional information on Exp. 3 and 4 is provided in Krug et al. (2011) and Sett et al. (2013), respectively.

2.1 Culture conditions

15 *Coccolithus braarudii* RCC-1200, *Calcidiscus quadriperforatus* RCC-1135 and *Gephyrocapsa oceanica* RCC-1303 were obtained from the Roscoff Culture Collection. *Emiliana huxleyi* was isolated in 2005 during the PeECE III mesocosm study in the Raune Fjord (Norway) by M. N. Müller. Cultures were maintained in 0.20 μm filtered North Sea water (NSW) with a salinity of 34 except *G. oceanica* which was cultured in artificial sea water (ASW) with a salinity of 35. Macro- and micro-nutrients were added according
20 to a modified f/2 media (Guillard, 1975) with final concentrations assuring nutrient replete conditions in all experiments (nitrate $\geq 64 \mu\text{mol L}^{-1}$, phosphate $\geq 3.6 \mu\text{mol L}^{-1}$ and trace metals and vitamins \geq f/20 media concentration). Cultures received a daily illumination between 130 and 180 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ under a light : dark cycle of 14 : 10 h (Exp. 1 and 2) or 16 : 8 h (Exp. 3 and 4).

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2.2 Experimental set-up

Temperature was controlled in growth cabinets (Rumed, series 1000, deviation of $\pm 0.5^\circ\text{C}$) and $p\text{CO}_2$ was adjusted in the NSW experiments (Exp. 1, 2 and 3) by addition of HCl or NaOH, keeping the dissolved inorganic carbon concentration (DIC) constant (Exp. 1: $2273 \pm 42 \mu\text{mol kg}^{-1}$, $n = 6$; Exp. 2: $2157 \pm 18 \mu\text{mol kg}^{-1}$, $n = 10$; Exp. 3: $2105 \pm 20 \mu\text{mol kg}^{-1}$, $n = 15$) while changing the total alkalinity (TA). The carbonate system of the ASW in Exp. 4 was adjusted by keeping TA constant ($2311 \pm 56 \mu\text{mol kg}^{-1}$, $n = 24$) and varying DIC (addition of HCl and Na_2CO_3). Precultures were kept in exponential growth and acclimated to the experimental conditions over 7 to 20 generations. Acclimated experimental cultures were incubated in triplicates (Exp. 1 and 3), duplicates (Exp. 2) or without replicates (Exp. 4) in acid cleaned (10% HCl) and autoclaved polycarbonate bottles at target conditions. In all experiments, cultures were inoculated to low cell densities and allowed to grow exponentially for about 7–10 generations, corresponding to a maximum DIC consumption of 12% (Exp. 1 and 3) or 7% (Exp. 2 and 4). Growth media (adjusted to the target condition) was sampled for DIC, TA and seawater ion composition. At the termination of the experiment (2–3 h after the onset of light), samples were taken for DIC, TA, seawater ion composition, cell number, total particulate carbon and nitrogen (TPC and TPN), particulate organic carbon (POC), chlorophyll *a* (Chl *a*) and coccolith elemental composition. Sample pellets for coccolith calcite of *G. oceanica* (Exp. 4) were sampled 2–4 days after samples for physiological parameters were taken. Thus, the coccolith geochemistry data of *G. oceanica* is not directly related to the measured seawater chemistry and physiological parameters. This issue will be considered and discussed later on (Sect. 4.1).

2.3 Carbonate chemistry

The carbonate system was monitored by DIC and TA measurements at the start and the end of the experiments. DIC was analysed after Stoll et al. (2001), using an automated segmented-flow analyser (Quattro) equipped with an auto-sampler

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(10 $\mu\text{mol kg}^{-1}$ accuracy and 5 $\mu\text{mol kg}^{-1}$ precision). Total alkalinity was measured by the potentiometric titration method after Dickson et al. (2003) with an accuracy and precision of 24 and 3.5 $\mu\text{mol kg}^{-1}$, respectively. DIC and TA were calibrated and measured against certified reference material supplied by A. Dickson (Scripps, La Jolla, USA). Carbonate system parameters were calculated from temperature, salinity, DIC and TA (mean values from the start and end of experiments) using CO2SYS (version 1.05 by E. Lewis and D. W. R. Wallace), with the stoichiometric equilibrium constants for carbonic acid given in Roy et al. (1993).

2.4 Physiological parameters

2.4.1 Cellular growth rates

Cell densities were determined with a Coulter Counter (Z Series). Samples were measured three times and the mean was used to calculate the growth rate μ (d^{-1}) as

$$\mu = \frac{(\ln c_1 - \ln c_0)}{t_1 - t_0} \quad (1)$$

where c_0 and c_1 denote the number of cells at the start (t_0) and end (t_1) of the incubation period (expressed in days).

2.4.2 Production rates of particulate organic and inorganic carbon, total nitrogen and chlorophyll *a*

Three sub-samples were taken for TPC/TPN, POC and Chl *a* from each treatment bottle (Chl *a* was not sampled in Exp. 3), filtrated onto precombusted GF/F filters (500 °C for 6 h) and stored frozen at -20 °C. For POC analysis filters were fumed over 37 % HCl for 2 h to remove all inorganic carbon and dried overnight at 60 °C. Filters for TPC/TPN and POC were measured on an Euro EA Elemental Analyser (Sharp, 1974). Particulate inorganic carbon was calculated from the difference of TPC and POC. Until analysis,

Chl *a* filters were kept in the dark to avoid photo-oxidation and measurements were performed using a fluorimetric method after Welschmeyer (1994). Production rates of particulate material (PM) were calculated as

$$PM_{\text{prod}} = \text{cell quota (pg cell}^{-1}) \times \mu(\text{d}^{-1}) \quad (2)$$

where PM can be POC, PIC, TPN or Chl *a*.

2.5 Coccolith geochemistry

After samples for the physiological parameters were taken (Sect. 2.2), the remaining culture medium (replicates of each experiment were pooled; Exp. 1–3) was centrifuged at 14 000 rpm for 10 min. The supernatant was discarded and the sample pellet was dried at 60 °C for 48 h and stored at room temperature. Dried pellets from Exp. 1–3 were cleaned with NaClO after Müller et al. (2011) and additionally oxidised with H₂O₂ as outlined in Blanco-Ameijeiras et al. (2012). This method removes organic material with an efficiency of above 99 % and minimises the contamination of coccolith Mg/Ca analyses by organic Mg. Pellets of Exp. 4 received a reduction step with hydroxylamine-hydrochloride prior to oxidising with H₂O₂ (Blanco-Ameijeiras et al., 2012).

2.5.1 Elemental analyses

Mg/Ca and Sr/Ca ratios of the coccoliths and of the ASW (Exp. 4) were analysed using matrix-matched standards on a simultaneous dual ICP-AES (Thermo ICAP DUO 6300 at the University of Oviedo). Standards were prepared from single element ICP standards (CPI Corporation) diluted in the same acid matrix as the samples. The calibration standards covered the Mg/Ca and Sr/Ca range in the calcite samples. Elemental ratios are reported from measurements made in radial detection mode for Sr at 421 nm, Mg at 279.5 nm, Fe at 259 nm, Ca at 315 nm and P at 177 nm. Calibration was conducted off-line using the intensity ratio method described by de Villiers et al. (2002). In this case, three standards were prepared with constant Ca concen-

trations and variable Sr/Ca and Mg/Ca ratios of 0.75 to 4 mmol mol⁻¹. Aliquots from this set of standards were uniformly diluted to provide curves for various Ca concentrations to match sample concentrations. Sr/Ca internal reproducibility was better than 0.02 mmol mol⁻¹, based on replicate analyses of the same sample dilutions. Mg/Ca internal reproducibility was better than 0.8 % of the measured ratio.

Coccolith P/Ca and Fe/Ca ratios are presented along with the Mg/Ca ratios as an indicator for Mg cleaning efficiency. Outlier detection, using the interquartile range (IQR), was performed on P/Ca and Fe/Ca ratios to determine non-sufficient Mg removal and the corresponding Mg/Ca ratios were removed from the data set. Sr/Ca ratio measurements were not excluded from the data set because Sr contamination from seawater and organic matter represents a minor issue for coccolith Sr/Ca ratio measurements (Blanco-Ameijeiras et al., 2012). Average values for P/Ca and Fe/Ca ratios (excluding outliers) were 1.36 ± 0.73 and 0.82 ± 1.19 mmol mol⁻¹ (±1 SD), respectively.

Elemental composition of the NSW (Exp. 1–3) was determined via Jobin Yvon JY 170 Ultratrace series ICP-OES at GEOMAR. The internal error for each analysis is typically < 1.2 % (±2 RSD) and the external reproducibility determined by repeat analysis of IAPSO seawater standard is ±1.5 %, ±0.7 % and ±0.3 % (±2 RSD, *n* = 3) for Ca, Mg and Sr, respectively. The partition coefficient of the trace metal (Sr and Mg), D_{Tr} , between calcite (c) and seawater (s) was calculated as:

$$D_{Tr} = \frac{(Tr/Ca)_c}{(Tr/Ca)_s} \quad (3)$$

3 Results

Seawater carbonate chemistry speciation and physiological parameters of all experiments are listed in the Supplement Tables 1 and 2, respectively.

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At ambient $p\text{CO}_2$ levels, elevated temperature enhanced growth and PIC_{prod} in all tested coccolithophore species. The POC_{prod} was positively affected by temperature except for *E. huxleyi*, decreasing from 10 to 20 °C in Exp. 1. Cellular ratios of PIC : POC increased or did not change with temperature.

Under changing carbonate chemistry speciation, *C. braarudii*, *G. oceanica* and *E. huxleyi* were negatively affected in growth rate, PIC_{prod} and PIC : POC ratio when $p\text{CO}_2$ was raised from ambient to high levels with species-specific sensitivities depending on temperature (detailed information regarding the physiological response of *C. braarudii* and *G. oceanica* can be found in Krug et al. (2011) and Sett et al. (2013), respectively). The POC_{prod} , on the other hand, followed an optimum-curve behaviour in response to $p\text{CO}_2$ peaking between 400 and 1150 μatm . The C : N ratio in all tested coccolithophore species was insensitive to changes in $p\text{CO}_2$.

In general, Chl a_{prod} followed similar trends as described for POC_{prod} and lowest Chl a_{prod} rates were observed in *E. huxleyi* (Exp. 2) at 10 °C.

The coccolith Sr/Ca ratio and the strontium partition coefficient (D_{Sr}) ranged from 2.40 to 4.38 mmol mol^{-1} and from 0.28 to 0.45, respectively, with highest values found in calcite produced at 25 °C by *E. huxleyi* and *G. oceanica* (Fig. 1, Table 1). Elevating seawater temperature at constant $p\text{CO}_2$ conditions ($370 \pm 70 \mu\text{atm}$) resulted in a positive relationship between temperature and the coccolith strontium partition coefficient (when combining all species, Fig. 1a). Species-specific D_{Sr} was positively correlated with $p\text{CO}_2$ with the steepest slopes detected for *E. huxleyi* (Fig. 1b, data points of *G. oceanica* at 25 °C were influenced by nutrient limitation which is discussed in

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Sect. 4.1):

$$10^{\circ}\text{C} (E. huxleyi) : D_{\text{Sr}} = 6.19 \times 10^{-5} p\text{CO}_2 + 0.299 (r^2 = 0.853, p = 0.025), \quad (4)$$

$$17^{\circ}\text{C} (C. braarudii) : D_{\text{Sr}} = 1.16 \times 10^{-5} p\text{CO}_2 + 0.386 (r^2 = 0.792, p = 0.043), \quad (5)$$

$$20^{\circ}\text{C} (E. huxleyi) : D_{\text{Sr}} = 7.88 \times 10^{-5} p\text{CO}_2 + 0.355 (r^2 = 0.758, p = 0.027), \quad (6)$$

$$20^{\circ}\text{C} (G. oceanica) : D_{\text{Sr}} = 3.89 \times 10^{-5} p\text{CO}_2 + 0.347 (r^2 = 0.885, p < 0.001), \quad (7)$$

$$25^{\circ}\text{C} (G. oceanica) : D_{\text{Sr}} = -8.30 \times 10^{-7} p\text{CO}_2 + 0.437 (r^2 = 0.083, p > 0.05). \quad (8)$$

The Mg/Ca ratio and magnesium partition coefficient (D_{Mg}) ranged from 0.066 to 98.6 mmol mol⁻¹ and 0.01×10^{-3} to 18.7×10^{-3} , respectively, depending on treatment and coccolithophore species (Fig. 2, Table 1). Highest D_{Mg} was measured in *E. huxleyi* (Exp. 2) at 10°C and lowest in *G. oceanica* (Exp. 4). No consistent correlation with temperature could be detected within the tested range (when combining all species, Fig. 2a). Within the applied $p\text{CO}_2$ range, an increasing trend was apparent in D_{Mg} of *G. oceanica*, *C. braarudii* and *E. huxleyi* (Fig. 2b).

4 Discussion

4.1 Experimental approaches and procedures

The $p\text{CO}_2$ conditions in Exp. 1 were not as constant as desired and varied from ≈ 280 to 500 μatm (average of $370 \pm 70 \mu\text{atm}$). Within this $p\text{CO}_2$ range, however, expected changes in coccolithophore physiology are below the detection limit of the applied measurements (Krug et al., 2011; Bach et al., 2011). Therefore, all changes in physiological rates of Exp. 1 can be attributed to variations in seawater temperature as all other experimental parameters were constant.

In Exp. 2, 3 and 4 the seawater carbonate system was manipulated by applying two different methods. First, seawater TA was changed while keeping DIC concentration

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constant by the addition of HCl or NaOH (Exp. 2 and 3) and second, adjusting DIC and TA by the addition of Na₂CO₃ and HCl to artificial seawater (Exp. 4). The advantages and disadvantages of these two methods have been presented and discussed in Riebesell et al. (2010) and Schulz et al. (2009). The second method correctly mimics ocean acidification but both methods are comparable when applying pCO₂ levels within a range from ≈ 180 to 1100 μatm (Schulz et al., 2009). Therefore, physiological and geochemical measurements derived from pCO₂ conditions above 1100 μatm (Exp. 2 and 3) or below 180 μatm (Exp. 4) should be considered with caution when relating to the process of ocean acidification.

Calcite pellets of *G. oceanica* were obtained 2 to 4 days after samples were taken for physiological determinations and seawater carbonate chemistry. This approach was preferred to ensure sufficient material for elemental Mg analysis. However, the exponential growth of *G. oceanica* and increasing cell density induces a fast consumption of available nutrients (including DIC) and, depending on growth rate and time of calcite sampling, might have caused nutrient limitation and major changes in the seawater carbonate chemistry speciation and hence in cell physiology. In this regard, the theoretical total drawdown of DIC and dissolved inorganic nitrogen was calculated from growth rate, carbon and nitrogen cell quotas and the time of calcite pellet sampling. For the experiment with *G. oceanica* conducted at 20 °C, this resulted in an average drawdown of DIC and nitrogen of 18 and 33 %, respectively, indicating no nutrient limitation at the time of calcite pellet sampling. At 25 °C, however, calcite pellets were sampled for when cells had already consumed all available nitrogen, probably being in limitation for more than 2 days. Nitrogen and phosphorus were initially added to the growth media in a Redfield ratio of 16 : 1 and thereby a combined limitation of nitrogen and phosphorus is plausible for *G. oceanica* at 25 °C. Consequently, the calcite geochemistry data of *G. oceanica* at 25 °C cannot be related to physiological parameters or the seawater carbonate chemistry speciation but rather indicates the response to nutrient limitation.

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4.2 Calcite geochemistry and physiological influence

The partition coefficient of strontium (D_{Sr}) for each tested coccolithophore species increased with seawater temperature (Fig. 1a) and is well within the range of reported values from culture experiments (Rickaby et al., 2002; Stoll et al., 2002; Langer et al., 2006). Species-specific D_{Sr} was significantly correlated to pCO_2 at 10, 17 and 20 °C (Fig. 1b) but a correlation was not present at 25 °C. The correlation between D_{Sr} and pCO_2 in *G. oceanica* at 25 °C is presumably biased by the effect of nutrient limitation (see above) and therefore not comparable to the regressions found at 10, 17 and 20 °C.

No general relation could be found between D_{Sr} and a specific physiological parameter (growth, POC_{prod} , PIC_{prod} , TPN_{prod} and $Chl\ a_{prod}$) when using combined data from temperature and carbonate chemistry manipulations. A significant correlation for all tested coccolithophore species was found between D_{Sr} and temperature induced variations in growth rate at ambient pCO_2 ($370 \pm 70\ \mu atm$) levels (Fig. 3a). This correlation is likely induced by physiological control rather than temperature itself because Sr incorporation during inorganic calcite precipitation is reported to be negatively correlated with temperature (Tang et al., 2008). In this sense, it seems that coccolith D_{Sr} is applicable as an appropriate indicator for coccolithophore productivity (in terms of growth rate) and a similar relation between D_{Sr} and growth rate would be expected when changes in growth rate are induced by pCO_2 (or carbonate chemistry speciation). Whereas pCO_2 was positively correlated with D_{Sr} in all tested coccolithophore species (Fig. 1b and see equations in Sect. 4), no species-specific correlation was found between pCO_2 induced variations in growth rate and D_{Sr} (Fig. 3b). Coccolithophore growth rate and POC_{prod} have been shown to follow a species-specific optimum-curve behaviour peaking at pCO_2 values between ≈ 400 and $1100\ \mu atm$ (Krug et al., 2011; Sett et al., 2013; Bach et al., 2011). Here we demonstrate that over an extended range of pCO_2 from 25 to $3500\ \mu atm$ the D_{Sr} follows a linear regression depending on temperature and species (Fig. 1b). This suggests that seawater carbonate chemistry speciation has a significant influence on coccolithophore D_{Sr} independent of cellular productivity (growth and

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POC_{prod}). It remains an open question which carbonate chemistry parameter is responsible for the observed change in coccolith D_{Sr} and thus the Sr/Ca ratio. These results should be taken into account when applying coccolith Sr/Ca ratios as productivity proxy on fossil coccoliths from times that experienced changing carbonate chemistry speciation (e.g. Paleocene–Eocene Thermal Maximum). Furthermore, it should be noted that the effect of pCO_2 on D_{Sr} is minor compared to changes induced by nutrient limitation (Rickaby et al., 2002).

The Mg/Ca ratio of biogenic carbonates of foraminifera and corals has been positively correlated with sea surface temperature (Mitsuguchi et al., 1996; Marr et al., 2011). This relationship, however, was not found in calcite samples of in this study (Fig. 2a) neither in the majority of coccolithophore field samples (Stoll et al., 2007). Values for D_{Mg} of *G. oceanica* were about one to two orders of magnitude lower than values measured of *C. braarudii*, *C. quadriperforatus* and *E. huxleyi* (Table 1). An offset because of the additional reductive cleaning step, used for calcite pellets of *G. oceanica* (see Sect. 2.5), can be ruled out because no similar offset was detected in the P/Ca and Fe/Ca ratios (Table 1) that were used as indicators for the cleaning efficiency. *Gephyrocapsa oceanica* was cultured in artificial seawater media whereas all other species were grown in natural seawater. An effect of the different culture media is unlikely as all other physiological and coccolith chemistry parameters display comparable values (Table 1 and Supplement Table 2). Therefore, we assume the observed offset in D_{Mg} of *G. oceanica* is species-specific.

A consistent increase in D_{Mg} with elevated pCO_2 was detected in *C. braarudii*, *G. oceanica* and *E. huxleyi*. This rising trend was statistically significant for *G. oceanica* at 20 °C ($y = 5.40 \times 10^{-6}x + 0.0134$; $r^2 = 0.899$, $p < 0.001$) but the small sample size for *C. braarudii* and *E. huxleyi* precluded a statistic analyses for the latter two species. At 25 °C, values for D_{Mg} of *G. oceanica* were up to 7 times higher and displayed a greater variability than at 20 °C which was presumably triggered by the experienced nutrient limitation before the calcite pellets were sampled. Nutrient limitation is commonly experienced by coccolithophores in the open ocean and during bloom events (Van Oos-

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tende et al., 2012) and our data indicate that this effect has the potential to greatly influence the Mg/Ca signature of fossil coccoliths.

The relatively high intraspecific variability in D_{Mg} values from the presented culture experiments and from sediment samples (Stoll et al., 2007) compared to D_{Sr} let us suggest that the control mechanisms and pathways for Mg and Sr partitioning in coccoliths are likely to be distinctively different. Magnesium plays a crucial role in all energy demanding processes by activating ATP in a number of enzymatic reactions as well as in DNA and RNA synthesis. In plants, Mg is furthermore essential for photosynthesis and the production of chlorophyll. The influx of Mg into the cell is presumably managed through unique membrane channels (Legong et al., 2001) and regarding the numerous processes involving Mg, the distribution of free Mg in the cytosol is likely to be under tight physiological control involving Mg-binding proteins. A disturbance or change in the physiological control/utilisation of the cytosolic free-Mg might have a secondary effect on the calcite magnesium partitioning. Indeed, a relationship between coccolith Mg chemistry and chlorophyll *a* was suggested earlier (Ra et al., 2010; Müller et al., 2011). This notion is supported by plotting the D_{Mg} as a function of Chl a_{prod} rate (Fig. 4a), resulting in a significant negative correlation for *G. oceanica*. The values for Chl a_{prod} and D_{Mg} of *E. huxleyi*, *C. quadriperforatus* and *C. braarudii* displayed a wide range from 0.06 to 5.43 pgChl *a* cell⁻¹ day⁻¹ (Supplement Table 2) and from 0.12 to 18.7 × 10⁻³ (Table 1), respectively. A correlation, combining the latter three species, became visible when analysing log-transformed data whereby the correlation for *G. oceanica* remained significant (Fig. 4b).

The apparent relation between Chl a_{prod} and the coccolith D_{Mg} under both temperature and pCO_2 variations suggests a physiological control over the cytosolic free-Mg available for incorporation into the calcite lattice. We suggest that Mg bound to the calcite lattice originates from the same pool as organically associated Mg, resulting in the observed correlation of coccolith D_{Mg} and Chl a_{prod} . As Ca antagonist, Mg can alter the morphological structure and dissolution kinetics of calcium carbonate precipitates (Loste et al., 2003) and, indeed, laboratory studies indicate drastic malformation of

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coccolith at high Mg concentration ($> 80 \text{ mmol L}^{-1}$) in the external growth media (Herfort et al., 2004). The pathway of Mg to the site of calcification (coccolith vesicle) is unknown for coccolithophores but previous results (Langer et al., 2006; Müller et al., 2011) and the current study indicate that Mg is transported into the cell and to the site of calcification on a distinct different pathway than Ca and Sr. Therefore, the Mg/Ca ratio of extant and fossil coccoliths should be influenced by the individual concentrations of Mg and Ca in seawater rather than the seawater Mg/Ca ratio.

5 Conclusions

The D_{Sr} and Sr/Ca ratio of coccolithophore calcite has been subject to numerous paleoceanographic studies and the application as proxy for coccolithophore productivity (in terms of growth rate) is widely applied. Our laboratory results indicate that this relationship is not valid when coccolithophore growth is influenced by variations in the seawater carbonate chemistry speciation as opposed to temperature. Furthermore, we found that carbonate chemistry speciation has a distinct effect on the D_{Sr} independent of coccolithophore physiology. Strontium and magnesium partitioning in coccolithophore calcite seems to follow different cellular control mechanisms. Whereas no overall correlation was present between D_{Sr} and one of the physiological parameters measured, coccolith D_{Mg} was correlated to chlorophyll *a* production (both under temperature and carbonate chemistry variations), suggesting a tight link between coccolith Mg partitioning and Mg-associated physiological processes. These findings provide a useful contribution for the calibration of paleoproxies based on coccolith Sr/Ca and Mg/Ca ratios and give further insights into the underlying cellular mechanisms that lead to coccolith Sr and Mg partitioning.

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Table 1. Coccolith calcite chemistry of the four individual experiments with corresponding experimental conditions. P/Ca and Fe/Ca ratios (averages of 1.36 ± 0.73 and 0.82 ± 1.19 , respectively) were used as an indicator for Mg cleaning efficiency. Detected outliers indicated non-sufficient Mg removal (indicated with *) and corresponding Mg/Ca ratios were removed from the data set.

Experiment 1: North Sea water, salinity = 34, light = $180 \mu\text{mol photons m}^{-2} \text{s}^{-1}$, light : dark = 14 : 10 h, replicates = 3. Seawater Sr/Ca = $8.42 \pm 0.30 \text{ mmol mol}^{-1}$, Mg/Ca = $5.29 \pm 0.15 \text{ mol mol}^{-1}$.								
Species	T (°C)	pCO ₂ (µatm)	Sr/Ca (mmol mol ⁻¹)	D _{Sr}	Mg/Ca (mmol mol ⁻¹)	D _{Mg} × 10 ⁻³	P/Ca (mmol mol ⁻¹)	Fe/Ca (mmol mol ⁻¹)
<i>C. braarudii</i>	10	417 ± 15	2.40	0.28	1.44	0.27	1.65	1.92
<i>C. braarudii</i>	15	320 ± 17	3.00	0.36	0.74	0.14	0.32	0.17
<i>C. braarudii</i>	18	501 ± 30	2.86	0.34	1.04	0.20	0.46	0.93
<i>C. quadriperforatus</i>	15	308 ± 2	2.67	0.32	1.54	0.29	2.48	2.33
<i>C. quadriperforatus</i>	18	451 ± 45	2.79	0.33	1.70	0.32	0.39	0.54
<i>C. quadriperforatus</i>	20	316 ± 46	3.10	0.37	0.62	0.12	3.41	0.22
<i>E. huxleyi</i>	10	276 ± 6	2.64	0.31	–	–	1.37	5.68*
<i>E. huxleyi</i>	15	306 ± 5	2.93	0.35	1.61	0.30	1.32	0.93
<i>E. huxleyi</i>	20	400 ± 41	3.21	0.38	1.97	0.37	1.27	0.79
<i>E. huxleyi</i>	25	427 ± 30	3.34	0.40	4.59	0.87	1.03	3.52
Experiment 2: North Sea water, salinity = 34, light = $130 \mu\text{mol photons m}^{-2} \text{s}^{-1}$, light : dark = 14 : 10 h, replicates = 2. Seawater Sr/Ca = $8.42 \pm 0.30 \text{ mmol mol}^{-1}$, Mg/Ca = $5.29 \pm 0.15 \text{ mol mol}^{-1}$.								
Species	T (°C)	pCO ₂ (µatm)	Sr/Ca (mmol mol ⁻¹)	D _{Sr}	Mg/Ca (mmol mol ⁻¹)	D _{Mg} × 10 ⁻³	P/Ca (mmol mol ⁻¹)	Fe/Ca (mmol mol ⁻¹)
<i>E. huxleyi</i>	10	193 ± 3	2.60	0.31	–	–	2.04	22.3*
<i>E. huxleyi</i>	10	467 ± 9	2.82	0.33	12.3	2.33	0.91	0.87
<i>E. huxleyi</i>	10	699 ± 5	2.75	0.33	13.1	2.50	1.90	2.61
<i>E. huxleyi</i>	10	898 ± 24	3.13	0.37	98.6	18.7	2.12	2.76
<i>E. huxleyi</i>	10	1238 ± 23	3.12	0.37	–	–	4.55*	14.8*
<i>E. huxleyi</i>	20	175 ± 1	–	–	–	–	–	–
<i>E. huxleyi</i>	20	365 ± 4	3.35	0.40	–	–	–	–
<i>E. huxleyi</i>	20	690 ± 12	3.26	0.39	–	–	–	–
<i>E. huxleyi</i>	20	812 ± 20	3.53	0.42	–	–	–	–
<i>E. huxleyi</i>	20	1106 ± 12	3.80	0.45	–	–	–	–

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Table 1. Continued.

Experiment 3: North Sea water, salinity = 34, light = 130 $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$, light : dark = 16 : 08 h, replicates = 3. Seawater Sr/Ca = $8.42 \pm 0.30 \text{ mmol mol}^{-1}$, Mg/Ca = $5.29 \pm 0.15 \text{ mol mol}^{-1}$.								
Species	T (°C)	pCO ₂ (μatm)	Sr/Ca (mmol mol^{-1})	D _{Sr}	Mg/Ca (mmol mol^{-1})	D _{Mg} × 10 ⁻³	P/Ca (mmol mol^{-1})	Fe/Ca (mmol mol^{-1})
<i>C. braarudii</i>	17	524 ± 27	3.26	0.39	8.49	1.61	0.43	4.66
<i>C. braarudii</i>	17	1151 ± 130	3.42	0.41	7.02	1.33	1.26	3.60
<i>C. braarudii</i>	17	1799 ± 257	3.40	0.40	15.6	2.96	0.11	0.53
<i>C. braarudii</i>	17	2311 ± 122	3.47	0.41	–	–	–	–
<i>C. braarudii</i>	17	3508 ± 172	3.63	0.43	–	–	9.71*	127*
Experiment 4: Artificial sea water, salinity = 35, light = 150 $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$, light : dark = 16 : 08 h, replicates = 1. Seawater Sr/Ca = $9.66 \pm 0.22 \text{ mmol mol}^{-1}$, Mg/Ca = $5.43 \pm 0.14 \text{ mol mol}^{-1}$.								
Species	T (°C)	pCO ₂ (μatm)	Sr/Ca (mmol mol^{-1})	D _{Sr}	Mg/Ca (mmol mol^{-1})	D _{Mg} × 10 ⁻³	P/Ca (mmol mol^{-1})	Fe/Ca (mmol mol^{-1})
<i>G. oceanica</i>	20	25	–	–	–	–	–	–
<i>G. oceanica</i>	20	59	3.28	0.34	0.086	0.016	0.50	0.87
<i>G. oceanica</i>	20	108	3.38	0.35	0.066	0.012	0.73	0.01
<i>G. oceanica</i>	20	280	3.47	0.36	0.079	0.015	0.66	0.05
<i>G. oceanica</i>	20	413	3.51	0.36	0.080	0.015	1.01	0
<i>G. oceanica</i>	20	574	3.56	0.37	0.087	0.016	0.87	0
<i>G. oceanica</i>	20	764	3.64	0.38	0.091	0.017	1.22	0
<i>G. oceanica</i>	20	940	3.65	0.38	0.099	0.018	1.12	0
<i>G. oceanica</i>	20	1216	3.93	0.41	0.121	0.022	1.36	0
<i>G. oceanica</i>	20	1476	3.91	0.40	0.116	0.021	1.46	0
<i>G. oceanica</i>	20	1781	4.14	0.43	0.124	0.023	1.60	0
<i>G. oceanica</i>	20	2104	3.97	0.41	0.130	0.024	1.04	0
<i>G. oceanica</i>	25	26	–	–	–	–	–	–
<i>G. oceanica</i>	25	58	4.08	0.42	0.279	0.051	1.70	0.30
<i>G. oceanica</i>	25	288	4.12	0.43	0.172	0.032	1.57	0.08
<i>G. oceanica</i>	25	318	4.23	0.44	0.211	0.039	1.60	0.07
<i>G. oceanica</i>	25	447	4.27	0.44	0.330	0.061	1.95	0.08
<i>G. oceanica</i>	25	612	4.33	0.45	0.276	0.051	2.27	0.76
<i>G. oceanica</i>	25	771	4.34	0.45	0.341	0.063	2.62	0.21
<i>G. oceanica</i>	25	980	4.16	0.43	–	–	4.62*	0.29
<i>G. oceanica</i>	25	1284	4.27	0.44	–	–	6.69*	0.40
<i>G. oceanica</i>	25	1731	4.18	0.43	–	–	7.47*	0.35
<i>G. oceanica</i>	25	2067	4.28	0.44	0.946	0.174	2.01	0.15
<i>G. oceanica</i>	25	3517	4.12	0.43	–	–	12.43*	0.46

Coccolith Sr/Ca and Mg/Ca ratios

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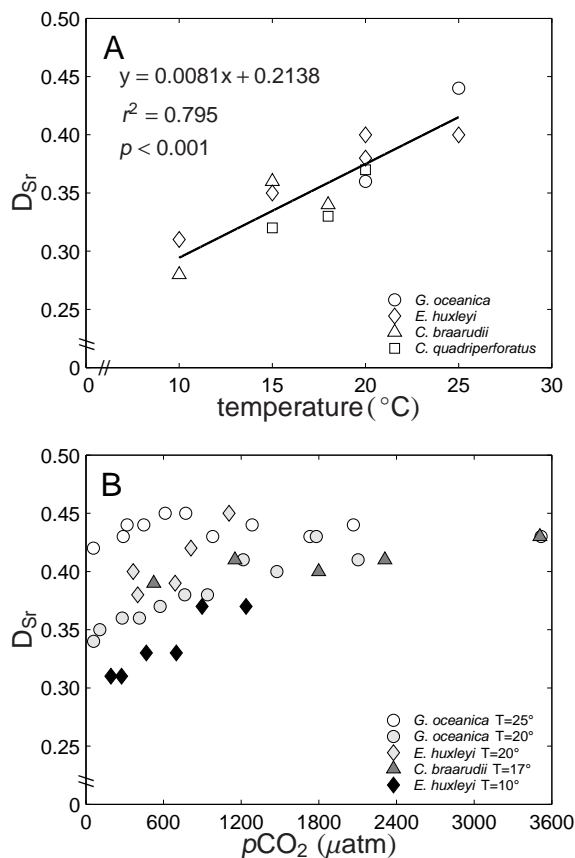


Fig. 1. Strontium partition coefficient (D_{Sr}) as a function of **(A)** temperature ($pCO_2 = 370 \pm 70 \mu atm$) and **(B)** pCO_2 (temperature as indicated). Black line in **(A)** represents a linear regression through all data points. Please note that *G. oceanica* experienced nutrient limitation at 25 $^{\circ}C$ (see text for details).

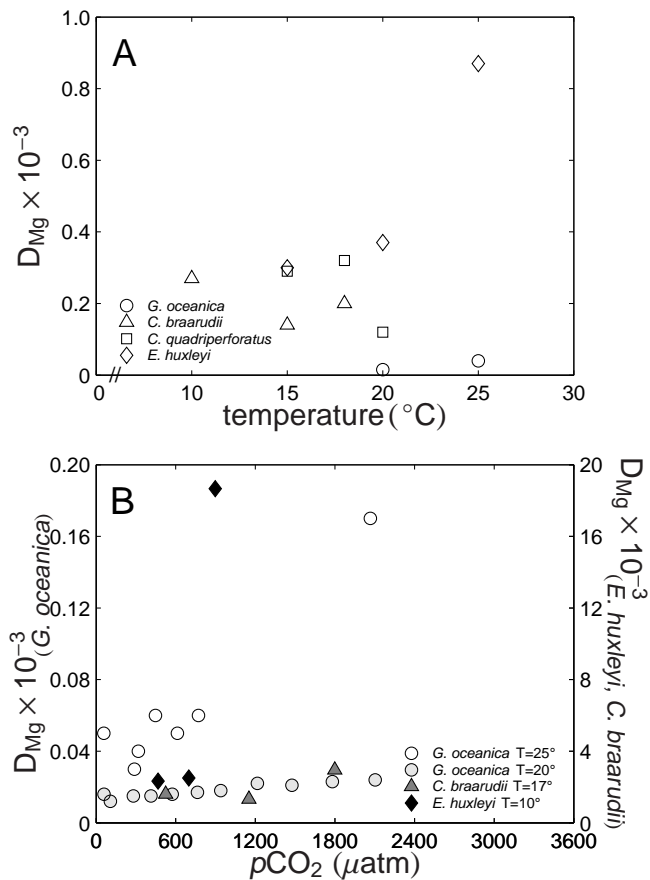


Fig. 2. Magnesium partition coefficient (D_{Mg}) as a function of **(A)** temperature ($pCO_2 = 370 \pm 70 \mu atm$) and **(B)** pCO_2 (temperature as indicated). In **(B)** markers of *E. huxleyi* and *C. braarudii* are related to the right y-axis. Please note that *G. oceanica* experienced nutrient limitation at $25^{\circ}C$ (see text for details).

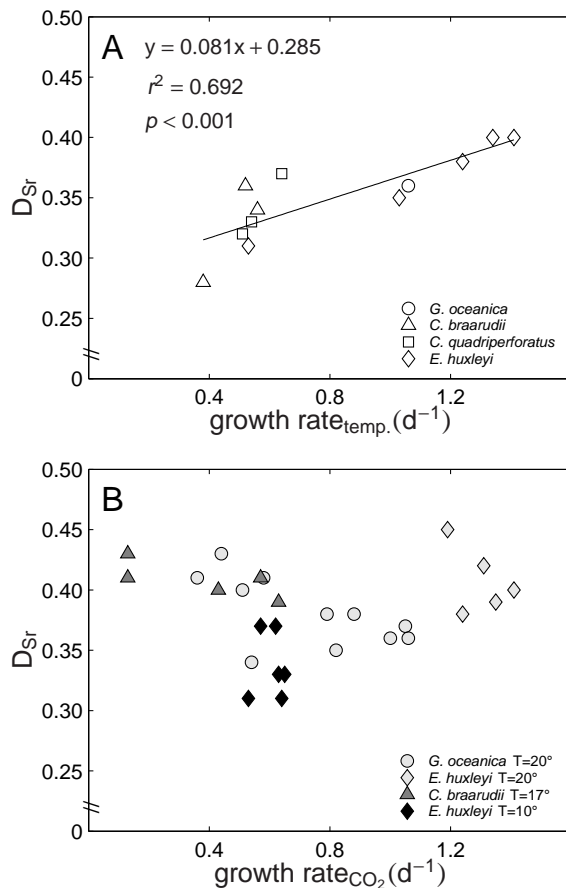


Fig. 3. Strontium partition coefficient (D_{Sr}) as a function of growth rate (excluding the data from *G. oceanica* at 25 °C). **(A)** Growth rate driven by changes in temperature ranging from 10 to 25 °C ($pCO_2 = 370 \pm 70 \mu\text{atm}$); black line indicates linear regression through all points. **(B)** Growth rate driven by pCO_2 ranging from ≈ 25 to 3520 μatm (temperatures as indicated).

Coccolith Sr/Ca and Mg/Ca ratios

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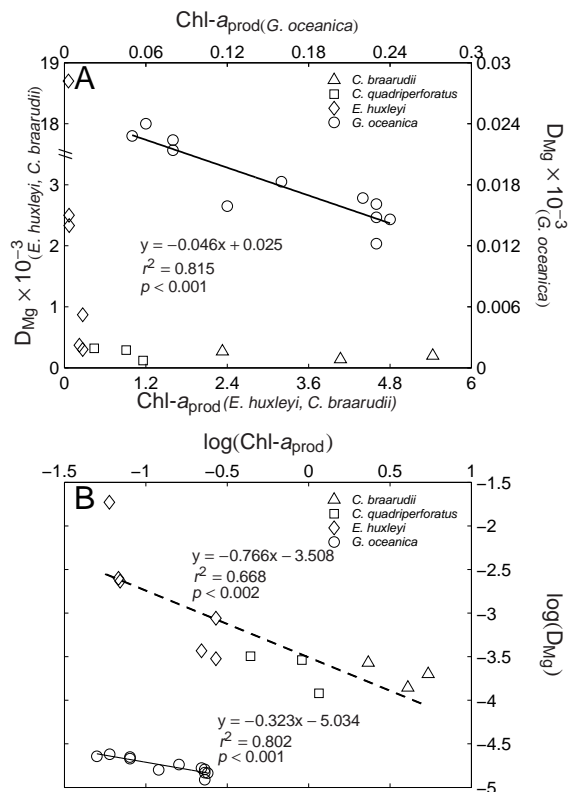


Fig. 4. Magnesium partition coefficient (D_{Mg}) as a function of chlorophyll a production rates **(A)**, black line indicates linear regression through data points of *G. oceanica* at 20 °C. **(B)** The log-transformed data of **(A)** to illustrate the linear correlation in the combined data of *E. huxleyi*, *C. braarudii* and *C. quadriperforatus* (dashed line). The solid line in **(B)** indicates the linear correlation through data points of *G. oceanica* at 20 °C.