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Modeling the marine aragonite cycle: changes under rising carbon dioxide and its role in shallow water CaCO_3 dissolution

R. Gangstø^{1,2}, M. Gehlen¹, B. Schneider^{1,*}, L. Bopp¹, O. Aumont³, and F. Joos^{2,4}

¹LSCE/IPSL, Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ,
Orme des Merisiers, Bât. 712, CEA/Saclay, 91198 Gif-sur-Yvette Cedex, France

²Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstr. 5, 3012
Bern, Switzerland

³LOCEAN/IPSL, Centre IRD de Bretagne, BP 70, 29280 Plouzané, France

⁴Oeschger Centre for Climate Change Research, University of Bern, Erlachstrasse 9a, 3012
Bern, Switzerland

*now at: Inst. of Geosciences, University of Kiel, Luedwig-Meyn-Str. 10, 24098 Kiel, Germany

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Correspondence to: R. Gangstø (gangsto@climate.unibe.ch)

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Abstract

The marine aragonite cycle has been included in the global biogeochemical model PISCES to study the role of aragonite in shallow water CaCO_3 dissolution. Aragonite production is parameterized as a function of mesozooplankton biomass and aragonite saturation state of ambient waters. Observation-based estimates of marine carbonate production and dissolution are well reproduced by the model and about 60% of the combined CaCO_3 water column dissolution from aragonite and calcite is simulated above 2000 m. In contrast, a calcite-only version yields a much smaller fraction. This suggests that the aragonite cycle should be included in models for a realistic representation of CaCO_3 dissolution and alkalinity. For the SRES A2 CO_2 scenario, production rates of aragonite are projected to notably decrease after 2050. By the end of this century, global aragonite production is reduced by almost one third and total CaCO_3 production by 19% relative to pre-industrial. Geographically, the effect from increasing atmospheric CO_2 , and the subsequent reduction in saturation state, is largest in the subpolar and polar areas where the modeled aragonite production is projected to decrease by 65% until 2100.

1 Introduction

The ocean calcium carbonate (CaCO_3) budget is a topic of long standing interest in marine geochemical research (e.g. Berger, 1978; Milliman, 1993; Milliman and Droxler, 1996; Milliman et al., 1999; Iglesias-Rodriguez et al., 2002; Berelson et al., 2007). The growing awareness of the impacts of rising atmospheric CO_2 concentrations on the chemistry of the ocean and related consequences on marine biota in general and calcifying organisms in particular has recently revived this area of study (e.g. Caldeira and Wickett, 2003; Feely et al., 2004; Orr et al., 2005; Royal Society, 2005, Kleypas et al., 2006). In a recent review of the marine CaCO_3 cycle, Iglesias-Rodriguez et al. (2002) highlight the lack of fundamental understanding of controls of CaCO_3 for-

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mation, dissolution and burial. This lack of fundamental understanding hampers our capability for assessing the present state of the carbonate system and forecasting its evolution under increasing atmospheric CO₂ and global warming.

The present study focuses on one striking and yet not well explained feature of past and recent estimates of the global ocean CaCO₃ budget, namely the reported loss (60–80%) of pelagic CaCO₃ production in the upper 500 to 1000 m of the water column (e.g. Milliman and Droxler, 1996; Berelson et al., 2007). This contradicts the general paradigm of the conservative nature of pelagic CaCO₃ at shallow depths (Sverdrup et al., 1942). The latter is directly derived from the evolution with depth of the saturation product for CaCO₃ minerals which increases with decreasing temperature and increasing pressure/depth (Zeebe and Wolf-Gladrow, 2001). As a consequence surface ocean waters are at present oversaturated with respect to CaCO₃ (e.g. Orr et al., 2005) precluding dissolution from a thermodynamic point of view.

Mechanisms proposed to explain the occurrence of CaCO₃ dissolution above the saturation horizon invoke biological mediation. It was proposed that CaCO₃ particles would dissolve after ingestion by pelagic grazers during gut passage (Harris, 1994). Until recently, dissolution during gut passage had, however, not been unequivocally demonstrated (Honjo and Roman, 1978; Pond et al., 1995). Antia et al. (2008) have shown that microzooplankton grazing may explain the reported amplitude of dissolution fluxes, while its exact quantitative contribution to shallow-water dissolution remains uncertain. Alternatively, the oxic remineralization of particulate organic C in aggregates could be at the origin of undersaturated microenvironments triggering the dissolution of CaCO₃ particles associated to POC within the same aggregate (Milliman et al., 1999). However, Jansen et al. (2002) concluded from a modeling study that CaCO₃ dissolution in marine aggregates in response to CO₂ production by POC remineralisation is unlikely to be at the origin of observed shallow-water dissolution fluxes.

In the absence of a clear identification of processes driving shallow water CaCO₃ dissolution, we might address the topic from the side of methods used to infer the order of magnitude of dissolution fluxes. On one hand, we have the evolution of CaCO₃

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fluxes recorded in sediment traps in comparison to upper ocean CaCO_3 production estimates (e.g. Milliman et al., 1999; Feely et al., 2004; Wollast and Chou, 1998). This approach has its own set of caveats (e.g. Milliman et al., 1999; Berelson et al., 2007) the complete discussion of which is beyond the scope of this paper. On the other hand, we have tracer based approaches, in particular the alkalinity based approach TA^* (Feely et al., 2002; Sabine et al., 2002; Chung et al., 2003). Conceptually, it relays on the breakdown of total alkalinity (TA) into three components: the preformed alkalinity TA^0 , the alkalinity of the water parcel as it leaves the surface ocean; the contribution from organic matter remineralization at depth, TA^{AOU} , and the contribution from CaCO_3 dissolution at depth, TA^* . Friis et al. (2006) conclude from a model based assessment of the TA^* method, that this method probably overestimates the magnitude of CaCO_3 dissolution at shallow water depth because this approach does not take into account the influence of water mass transport.

In the pelagic realm CaCO_3 is produced mainly as two polymorphs of differing solubility: calcite (coccolithophores, foraminifera) and aragonite (mostly pteropods), the latter being 50% more soluble than calcite. The contribution of aragonite to shallow water CaCO_3 dissolution is mentioned by several authors (e.g. Milliman et al., 1999; Berelson et al., 2007), but judged to be insignificant on the basis of its supposed only minor contribution to total pelagic CaCO_3 production (10% according to Fabry, 1990). Estimates of aragonite production and fluxes in the modern ocean are however scarce. Moreover these estimates cover a wide range, spreading from 10 to 50% of the total global CaCO_3 flux (Berner, 1977; Berger, 1978; Berner and Honjo, 1981; Fabry and Deuser, 1991). A significant contribution of aragonite to the reported shallow water dissolution can thus not be ruled out a priori. Our study explores the potential contribution of aragonite to shallow water CaCO_3 dissolution by means of a model study. As a follow-up of Gehlen et al. (2007), we implemented aragonite production and dissolution to the global biogeochemical ocean model PISCES. In the first section of this paper, we present a global open ocean CaCO_3 budget for calcite and for aragonite. Model improvements are discussed with reference to the study by Gehlen et al. (2007)

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which was also based on PISCES, but did only consider calcite. In the second section, we assess potential changes to the global CaCO_3 budget in response to increasing atmospheric CO_2 levels following the IPCC SRES A2 scenario.

2 The PISCES model

2.1 General model description

The model used in the current study is the PISCES global ocean biogeochemical model (Aumont et al., 2003; Aumont and Bopp, 2006; Gehlen et al., 2006) which simulates the biogeochemical cycle of oxygen, carbon and the main nutrients controlling marine biological productivity: nitrate, ammonium, phosphate, silicate and iron. Biological productivity is limited by the external availability of nutrients. The phosphorus and nitrogen cycles in the model are decoupled by nitrogen fixation and denitrification.

The model distinguishes two phytoplankton size classes (nanophytoplankton and diatoms) and two zooplankton size classes (microzooplankton and mesozooplankton). The C/N/P ratios are assumed constant for all species and fixed to the Redfield ratios. For phytoplankton, the prognostic variables are total biomass, iron, chlorophyll and silicon contents. The internal ratios of Fe/C, Chl/C and Si/C are predicted by the model. The only prognostic variable for zooplankton is total biomass. The bacterial pool is not modeled explicitly.

There are three non-living compartments for organic carbon in PISCES: small particulate organic carbon (POC_s), big particulate organic carbon (POC_b) and semi-labile dissolved organic carbon (DOC). The C/N/P composition of dissolved and particulate matter is also coupled to Redfield stoichiometry. However, the iron, silicon and calcite pools of the particles are fully simulated and their ratios relative to organic carbon are allowed to vary. The production of calcite is assigned to nanophytoplankton as a function of temperature, saturation state, nutrient and light availability. The particulate detrital pools (POC_s , POC_b , biogenic silica and calcite) are fuelled by mortality,

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aggregation from nanophytoplankton and diatoms, fecal pellet production and grazing.

The model simulates dissolved inorganic carbon and total alkalinity. The carbon chemistry follows the OCMIP protocol (<http://www.ipsl.jussieu.fr/OCMIP>). A description of the model including model equations and parameters can be found as auxiliary material in Aumont and Bopp (2006).

2.2 Calcium carbonate geochemistry

The two-fold objective of this paper is (1) exploring the potential for aragonite dissolution to significantly contribute to shallow water CaCO_3 dissolution and producing a first evaluation of the impact of future rising atmospheric CO_2 levels on aragonite production and dissolution. We adopt a geochemical approach to the question. This is justified by the limited observations available on aragonite production and dissolution in the ocean. Aragonite production and dissolution was implemented to PISCES in line with the general model structure and previous developments around the CaCO_3 geochemistry in the model (Gehlen et al., 2007). This choice allows a straight-forward comparison between the model results of this study and output of PISCES in its calcite-only version (referred to as PISC/CAL) (Gehlen et al., 2007).

2.2.1 Aragonite production

In the modern ocean pelagos, cosmopolitan shelled pteropods are the main producers of aragonite (Lalli and Gilmer, 1989). Information on pteropod biogeography and ecology is scarce and largely summarized in Lalli and Gilmer (1989). Pteropods are mostly found in near-surface waters down to depths of about 200 m. Only a few species are restricted to deeper waters. We did not implement pteropods as a distinct functional type in the model, but assigned aragonite production to the corresponding zooplankton size class, mesozooplankton. Orr et al. (2005) report dissolution of pteropod aragonite shells in living organisms during exposure to water undersaturated with respect to aragonite. We might thus assume that the vertical distribution of pteropods across

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the water column is controlled by carbonate chemistry, e.g. that the organisms, and thus aragonite production, are restricted the water masses oversaturated with respect to aragonite.

We are unaware of published data on the response of calcification in pteropods to the saturation state. Previous studies on the effect of carbonate chemistry on the calcification in marine calcifiers focused on coccolithophores (e.g. Sciandra et al., 2003, Riebesell et al., 2000; Zondervan et al., 2001, 2002; Delille et al., 2005), foraminifera (e.g. Wolf-Gladrow et al., 1999; Bijma et al., 1999) and corals (e.g. Gattuso et al., 1998; Kleypas et al., 1999; Langdon et al., 2003, 2005). All these studies report a decrease in calcification with increasing $p\text{CO}_2$ or decreasing saturation state. We expect that the calcification response will display a tolerance over a range of oversaturation typical of the natural variability experienced by the organism until a critical threshold is reached. Passing the threshold value, calcification is expected to decrease rapidly. The mathematical expression corresponds to a saturation curve, such as the Michaelis Menten equation derived for calcite production in Gehlen et al. (2007) from a compilation of experimental results for *E. huxleyi*.

Aragonite production is expressed as the ratio of particulate inorganic C in the form of aragonite (PIC_A) to particulate organic C (POC), as a function of the saturation state of seawater and mesozooplankton biomass:

$$\frac{\text{PIC}_A}{\text{POC}} \approx \text{MESO} \times \left(\frac{\text{PIC}_A}{\text{POC}} \right)_{\max} \times \frac{(\Omega_A - 1)}{K_{\max} + (\Omega_A - 1)} \text{ for } (\Omega_A - 1) > 0 \quad (1)$$

where: MESO, mesozooplankton biomass (mole C l^{-1});

$(\text{PIC}_A/\text{POC})_{\max}=0.8$, maximum ratio reached under optimal growth conditions;

$K_{\max}=0.4$, with analogy to the half saturation constant;

The saturation index $\Omega_A=[\text{Ca}^{2+}]\times([\text{CO}_3^{2-}]/K_{sp,A})$ and $K_{sp,A}$ corresponds to the stoichiometric ion concentration product for aragonite after Mucci (1983). The pool of sinking aragonite particles is fuelled by mortality. The sum of calcite and aragonite production routed to the sinking particles is referred to as net CaCO_3 production.

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The particles sink with a prescribed sinking speed according to:

$$w = w_{\min} + (w_{\max} - w_{\min}) \times \max \left(0, \frac{z - z_m}{2000} \right) \quad (2)$$

where: $w_{\min}$, minimum sinking speed of 50 m d⁻¹;

$w_{\max}$, maximum sinking speed at 2000 m below the mixed layer of 200 m d⁻¹;

z , depth (m);

z_m , mixed layer depth (m).

The *export flux* is defined as the amount of sinking CaCO₃ particles that falls through the depth horizon of 100 m. There is no ocean-sediment interaction included in our model version. From the flux of CaCO₃ reaching the deepest model boxes (=lower boundary) an alkalinity equivalent of totally 0.18 PgC y⁻¹ corresponding to river input is removed (burial flux). The rest is re-dissolved instantaneously in the deepest grid cells. The model is strictly mass conserving.

2.2.2 Aragonite dissolution

Compared to the numerous studies addressing the dissolution kinetics of calcite (e.g. Morse and Berner, 1972; Berner and Morse, 1974; Morse, 1978; Honjo and Erez, 1978; Plummer et al., 1978; Keir, 1980; Walter and Morse, 1985; Arakaki and Mucci, 1995; Morse and Arvidson, 2002; Gehlen et al., 2005a, b; Morse et al., 2007), only a modest number of investigations focused on the dissolution behavior of aragonite (e.g. Morse et al., 1979; Keir, 1980; Busenberg and Plummer, 1986; Morse et al., 2007). These studies converge to assign a similar rate law to aragonite and calcite dissolution. The corresponding rate expression, R , for CaCO₃ dissolution writes:

$$R = k \times (1 - \Omega_A)^n \quad \text{for } (\Omega_A - 1) < 0 \quad (3)$$

where: k , dissolution rate parameter, d⁻¹; n , dimensionless reaction rate constant.

The dissolution of CaCO₃ is in general described as a higher order reaction with estimates of n ranging from 2.3 to 4.5 (e.g. Morse and Arvidson, 2002). Due to the limited

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information available specifically on aragonite dissolution, we adopted the same rate description and reaction rate constant as for calcite in Gehlen et al. (2007). Aragonite dissolution is thus described as a first order reaction ($n=1$) with respect to undersaturation with a dissolution rate constant of 10.9 d^{-1} . The latter was derived from the evolution with depth of CaCO_3 fluxes recorded in traps deployed below 1000 m (Gehlen et al., 2007).

The quantity of CaCO_3 particles that re-dissolves in the deepest grid cells of the model is not included in our definition of pelagic CaCO_3 dissolution. The ratio between pelagic dissolution and net production is here denoted as relative CaCO_3 dissolution.

3 Model simulations

The physical fields that are used to force PISCES are based on a climatological simulation with the ORCA2 global ocean model configuration of OPA version 8.2 (Madec et al., 1998). The mean horizontal resolution of the model is approximately 2° by 2° cos latitude and the meridional resolution is enhanced to 0.5° at the equator. The model has 30 vertical levels; with an increment that increases from 10 m at the surface to 500 m at depth (12 levels are located in the first 125 m). The physical/dynamical simulation with OPA employs climatological atmospheric forcing from various data sets. These include NCEP/NCAR 2m atmospheric temperature (averaged between 1948 and 2003) and relative humidity, ISCCP total cloudiness (averaged between 1983 and 2001), precipitation (averaged between 1979 and 2001), weekly wind stress based on ERS and TAO observations and creates a representation of ocean circulation/mixing that is forced by observational climatologies. Please see Aumont and Bopp (2006) for more details and the associated references.

Model alkalinity field was initialized with the global mean alkalinity value from Goyet et al. (2000). The new parameterizations of aragonite production and dissolution were implemented with aragonite production accounting for 1/3 of the total net CaCO_3 production. This is in the upper end of the range of most estimates and permits the identi-

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cation of an approximate upper limit of which aragonite may contribute to the estimated shallow depth CaCO_3 dissolution. The consequent changes in the CaCO_3 cycle call for a long spin-up; hence the model was integrated over 5000 years using the degradation-integration tool DEGINT (Aumont et al., 1998) to reach quasi-equilibrium. The tracer output was used to re-initialize the PISCES model at the original resolution ($2 \times 2^\circ \cos$ (latitude), 31 vertical levels) and the model was then integrated over 300 years using a constant climatological ocean circulation field without interannual variability before reaching final equilibrium. Atmospheric CO_2 was all the time kept constant and equal to 278 parts per million (ppm).

To study the effect of rising $p\text{CO}_2$ on the carbonate cycle, a model experiment with two different atmospheric CO_2 -scenarios were performed: one with constant pre-industrial CO_2 concentrations and one with prescribed increasing atmospheric CO_2 concentrations. The prescribed increase of atmospheric CO_2 starts with a pre-industrial value of 286.2 ppm and follows the historical development (IPCC SRES 20C3M) for the period from 1861–1999 and the A2 scenario (IPCC SRES A2) from 2000–2100. The resulting atmospheric $p\text{CO}_2$ values for the years 2000 and 2100 are 367 ppm and 827 ppm, respectively. For all simulations the model was forced with a constant climatological ocean circulation field without interannual variability.

4 Results and discussion

4.1 Model initial state

4.1.1 Aragonite saturation state

Simulated aragonite saturation horizons are compared to the pre-industrial saturation depth values from the Global Ocean Data Analysis Project (GLODAP) (Key et al., 2004), and presented in Fig 1. Except from the North Atlantic, where the modeled aragonite saturation horizon is located slightly deeper than the GLODAP saturation

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horizon, there is a very good match between model and observations. The modeled aragonite saturation horizon follows the estimated saturation depth characteristics: it is deepest in the Atlantic, and shoals through the Indian to the Pacific Oceans following the water circulation along the deep conveyor belt, where the water masses get more and more enriched in DIC the older they get due to the remineralization of organic matter.

4.1.2 CaCO_3 sources and sinks

Table 1 compares global pelagic pre-industrial CaCO_3 production, export and dissolution obtained from the present model study, from a similar study (PISC/CAL) which only considered calcite (Gehlen et al., 2007) and from observation-based estimates. The final total net calcification in the present study at the end of the spin-up (0.87 PgC y^{-1}) is slightly higher than the one in PISC/CAL (0.79 PgC y^{-1}). Both values lay at the lower end of the range of estimates. The total pelagic CaCO_3 dissolution predicted by the model is 0.55 PgC y^{-1} , whereas the value obtained with the model version PISC/CAL was 0.48 PgC y^{-1} . The results from both model versions closely match the estimate of $0.5 \pm 0.2 \text{ PgC y}^{-1}$ published by Feely et al. (2004). They are lower than the best estimate from Berelson et al. (2007), but still consistent with their uncertainty range (Table 1). Finally the budget is closed by the sinking CaCO_3 particles that reach the model lower boundary. This flux does not correspond to the burial flux reported in literature and may not be directly compared to observations.

The modeled CaCO_3 export from the upper 100 m matches well the result by Sarmiento et al. (2002) of 0.6 PgC y^{-1} . The export is smaller than the net production due to a quantity of CaCO_3 production below, and a small amount of dissolution above, 100 m.

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4.1.3 Calcite and aragonite production

The different environmental controls on calcite and aragonite production in the model lead to different global distributions of calcite and aragonite production (Fig. 2). For the calcite production (Fig. 2a), the spatial variability is well reproduced by the model: low values in central ocean gyres, high values in upwelling zones of the eastern boundary currents, the Arabian Sea and the equatorial Pacific and Atlantic. Consistent with Milliman (1993), the model also predicts increased rates of calcite productivity in sub-polar waters. Vertically integrated rates of calcite production range between $0.02 \text{ mgC m}^{-2} \text{ d}^{-1}$ in central ocean gyres to $78 \text{ mgC m}^{-2} \text{ d}^{-1}$ reached in localized hot spots as the Gulf of Thailand and south of the Gulf of Guinea. Milliman (1993) reports typical values for open ocean CaCO_3 production spanning from 0.4 to $20 \text{ mgC m}^{-2} \text{ d}^{-1}$, where the contribution of aragonite is explicitly excluded. A total open ocean CaCO_3 production of $6.9\text{--}7.9 \text{ mgC m}^{-2} \text{ d}^{-1}$ was calculated by Morse and MacKenzie (1990). The model yields an average total CaCO_3 production of $6.7 \text{ mgC m}^{-2} \text{ d}^{-1}$.

The distribution of aragonite production in the model follows ocean productivity with maximum values in areas where the latter is high (e.g. upwelling zones, subpolar waters) (Fig. 2b). This pattern reflects the occurrence of mesozooplankton which is tightly coupled to the availability of food. The model simulates an average aragonite production of $2.4 \text{ mgC m}^{-2} \text{ d}^{-1}$. Fabry (1989, 1990) reports estimates ranging from $0.25 \text{ mgC m}^{-2} \text{ d}^{-1}$ in the Central Pacific to $0.83 \text{ mgC m}^{-2} \text{ d}^{-1}$ in the equatorial Pacific. Betzer et al. (1984) observed an aragonite flux of $2.3\text{--}4.9 \text{ mgC m}^{-2} \text{ d}^{-1}$ at 100 m in the North Pacific, where the samples were taken above the aragonite saturation horizon and living pteropods were excluded (Betzer et al., 1984). Of the total net CaCO_3 production, aragonite production in the model (0.30 PgC y^{-1}) amounts to 35%.

While the model predicts aragonite production in high latitudes of the right order of magnitude, it overestimates the production in equatorial areas. About 40% of the modeled total aragonite production takes place between 0° and 20° while only 10% occurs at latitudes greater than 40° . While the calcification rates in equatorial upwelling ar-

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5 eas are considered high, most of the aragonite production is assumed to take place in subpolar and polar areas (Lalli and Gilmer, 1989). This indicates a general overestimation by our model of the aragonite production in the equatorial areas, possibly in combination with an underestimation in higher latitudes. The latter is supported by an
10 underestimation of the modeled mesozooplankton biomass in ocean gyres and subpolar areas compared to observations compiled by Buitenhuis et al. (2006), especially in the north Pacific. The low mesozooplankton biomass in ocean gyres in turn reflects the tendency of the model to underpredict ocean productivity in these regions (Gehlen et al., 2006). However, in agreement with observations, the model presents higher arago-
15 nite production in the western North and eastern equatorial Pacific and lower values in the Central Pacific, which is consistent with the mesozooplankton distribution in these areas (Fabry, 1990; Buitenhuis et al., 2006).

4.1.4 Calcite and aragonite dissolution

15 Although total CaCO_3 dissolution in both the present model version and in PISC/CAL match literature estimates, we see an essential difference between the two model versions when studying the vertical distribution of the CaCO_3 dissolution in the water column. The profiles of CaCO_3 water column dissolution for the Atlantic, Pacific and Indian Ocean (Fig. 3) show how the water column dissolution of aragonite (Fig. 3b) starts at distinctly shallower depths than dissolution of calcite (Fig. 3a), which is di-
20 rectly related to the shallower location of the aragonite saturation horizon compared to the calcite saturation horizon in the three oceans (e.g. Broecker and Takahashi, 1978; Feely and Chen, 1982; Feely et al. 2004). It results in shallow depth CaCO_3 dissolution in the Pacific Ocean, mid-depth water dissolution in the Indian Ocean and deep water dissolution in the Atlantic Ocean basin (Fig. 3c). Maxima in open water aragonite
25 dissolution are at 400 m, 1000 m, and 3200 m depth in the Pacific, Indian and Atlantic, respectively, while the basin-mean peak rates for water column calcite dissolution are simulated at 1000 m, 2300 m, and 4200 m.

The simulated total amount of CaCO_3 that dissolves in the upper 1000 m of the

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pelagic ocean equals 0.12 PgC y^{-1} , whereas 0.32 PgC y^{-1} dissolves in the upper 2000 m (Table 1). Milliman and Droxler (1996) compared the dissolution in the upper 1000 m to the total CaCO_3 production and reported that between 60–80% of the total production dissolved at shallow depths. Feely et al. used the 2000 m horizon to separate the upper and lower part of the water column and compared the dissolution in the upper part to the total water column dissolution. Combining the sediment trap flux of CaCO_3 at 2000 m (0.41 PgC y^{-1}) and the CaCO_3 accumulation in continental shelf sediments ($0.13\text{--}0.17 \text{ PgC y}^{-1}$), they conclude that up to 60% or more of the total dissolution occurs in the water column or sediments in the upper 2000 m, with most of the CaCO_3 dissolving before it reaches the sediment-water interface. Whereas our model yields a dissolution flux in the upper 1000 m accounting for only 14% of the total CaCO_3 produced, it simulates a dissolution flux above 2000 m corresponding to 58% of the total pelagic water column CaCO_3 dissolution, comparable to the findings of Feely et al. (2004). In contrast, the equivalent percentages for the model version PISC/CAL which only considered calcite are no more than 2.5 and 38%, respectively.

Our modeled aragonite contribution to the shallow depth CaCO_3 dissolution represents an upper limit estimate. Thus, the discrepancy between model output and estimates (Milliman and Droxler, 1996) in the upper 1000 m supports the findings that additional mechanisms (e.g. Friis et al., 2007, Antja et al., 2008) are needed in order to explain the overall estimated loss of CaCO_3 or excess of alkalinity in the upper part of the water column. However, our results maintain that the underestimation of the modeled CaCO_3 dissolution in the upper 0–2000 m in PISC/CAL may to a great extent result from an exclusion of aragonite in the PISCES model as proposed by Gehlen et al. (2007). The increased shallow depth dissolution obtained by implementing aragonite yields support to the hypothesis that high dissolution fluxes at depths above 2000 m may largely be attributed to more soluble CaCO_3 phases like aragonite (Iglesias-Rodriguez et al., 2002; Kleypas et al., 2006). Furthermore, the vertical distribution of the CaCO_3 dissolution fluxes in the present model version is considerably improved compared to the PISC/CAL version.

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4.2 Transient simulation

Projections of future changes of the CaCO_3 budget with increasing atmospheric CO_2 will next be presented and discussed. Figure 4 presents a) timeseries of the mean saturation state of surface waters with respect to aragonite and corresponding maps for year b) 1861, c) 2000, d) 2050, e) 2075 and f) 2100 for the SRES A2 scenario. In addition to the Global Ocean, results are shown for two critical areas: 1) the high latitudes or polar and subpolar regions (here defined as the area $>40^\circ \text{S}$ and $>40^\circ \text{N}$) where the largest change in saturation state occurs, and 2) the equatorial area (here restricted within 20°S – 20°N) which include important upwelling areas with high calcification rates. Time series of a) and b) net calcite and aragonite production, c) and d) calcite and aragonite dissolution and e) and f) relative calcite and aragonite dissolution are shown in Fig. 5. Model results for CaCO_3 production, export, sinking fluxes, dissolution and relative dissolution for year 1861, 2000 and 2100 are summarized in Table 2.

The mean global saturation state of surface ocean waters (0–100 m) with respect to aragonite decreases from $\Omega_a > 3.5$ in year 1861 to less than 2 in year 2100 (Fig. 4a). In the equatorial area the mean saturation state decreases rapidly from $\Omega_a > 4$ to $\Omega_a = 2$ at the end of the scenario, whereas at high latitudes where the saturation state is already very low, it reaches values below 1 before year 2100. According to our parameterization, calcification may occur everywhere where $\Omega_a > 1$. Maps of Ω_a averaged over the top 100 m of the water column (Fig. 4b–f) show that in year 1861 the criteria for aragonite production is met everywhere across the global surface ocean. In year 2000 the areas of $\Omega_a > 4$ are somewhat reduced, while in year 2050 such areas do no longer exist and small regions of the surface water in the Arctic Ocean are now already projected to be undersaturated with respect to aragonite for the SRES A2 scenario. Following the decreasing saturation values, in year 2075 large areas of both the Arctic and the Southern Ocean are undersaturated with respect to aragonite, whereas in year 2100, compared to pre-industrial times, the conditions for calcification have altered dra-

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matically. Most of the Southern and the Arctic Ocean experience at this time $\Omega_a < 1$, indicating unfavorable conditions for aragonite production and matching results of Orr et al. (2005) for the Southern Ocean and of Steinacher (2007) for the Arctic.

The change in saturation state with respect to calcite follows a similar pattern (see Gehlen et al., 2007), however as the saturation horizon of aragonite is located shallower in the water column than the one of calcite (e.g., Broecker and Takahashi, 1978; Feely and Chen, 1982) the surface waters get undersaturated with respect to aragonite at a much earlier stage.

The predicted reduction in saturation state is further reflected in the modeled production and dissolution rates of CaCO_3 (Fig. 5 and Table 2). Both calcite and aragonite calcification rates have decreased considerably at the end of the SRES A2 scenario (Fig. 5a). While the reduction in production rates is insignificant during the historical period up to year 2000, it is large after year 2050. For calcite the total global production rate per year has decreased by 13% at the end of the scenario, from 0.57 (pre-industrial times.) to 0.49 PgC y^{-1} (year 2100). For aragonite the corresponding reduction in global production rate is of considerably 29%, i.e. of almost 1/3 since pre-industrial times, with global aragonite production decreasing from 0.31 to 0.22 PgC y^{-1} . The modeled decrease in total CaCO_3 production is 19%. The calcite and aragonite export flux at 100 m decreases by 13 and 41%, respectively, providing a decrease in total CaCO_3 export of 23%.

Gehlen et al. (2007) simulates a decrease in CaCO_3 production of 27% at the end of their scenario, where the initial production was 0.8 PgC y^{-1} . The export was reduced by 29%. Their final atmospheric CO_2 concentration was however 4 times the pre-industrial concentration, while with the SRES A2 scenario used in the present study the atmospheric value of CO_2 in year 2100 is closer to 3 times the pre-industrial value. On the other hand, the duration of their scenario was shorter and the annual rate of $p\text{CO}_2$ was higher. At 3 times the pre-industrial value a reduction in calcification of approximately 15% was predicted with PISC/CAL, not far from our predicted reduction in calcite production of 13% with the present model version.

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In addition to the decrease in carbonate production with increasing CO₂ concentrations, the modeled amount of water column calcite and aragonite dissolution decreases (Fig. 5b). The fact that this occurs, although one might expect higher dissolution in more acidic waters, can be explained by the reduced abundance of particulate CaCO₃ due to lower CaCO₃ productivity. The relative amount of pelagic CaCO₃ dissolution, however, expressed as the ratio of calcite and aragonite dissolution versus the respective rate of production (dissolution/production) in percent, is increasing. A slight increase from 67 to 71% of calcite material is dissolved in the water column, whereas for aragonite the ratio increases by 12%, from 60 to 72%, i.e. 3 times more than for calcite. This leads to a total increase in relative CaCO₃ dissolution from 64 to 71%. Due to the gradually lower saturation state value in surface waters, the predicted increase in relative calcite and especially aragonite dissolution is highest in the upper part of the water column. In the upper 2000 m the relative dissolution of calcite, aragonite and total CaCO₃ increase by 10, 16 and 11%, respectively (Table 2).

As the waters within year 2100 mainly become undersaturated with respect to calcite and aragonite in the high latitudes, we would expect the largest effects on CaCO₃ production in this area. In fact, the calcite production in the high latitudes is reduced by as much as 24%, while the aragonite production is reduced dramatically by 65% (from 0.03 to 0.009 PgC y⁻¹). The relative calcite dissolution has increased by 4%, whereas the relative aragonite dissolution has experienced a drastic increase of 72%, from 41 to 113%. The latter value implies that in the end of the SRES A2 scenario, more aragonite is actually dissolved than produced in this area, indicating transport of some aragonite particles from lower to higher latitudes. The changes in aragonite production and dissolution suggest the potential for detrimental impacts of acidification on pteropods in the high latitudes, where shells of pteropods dominate the flux of CaCO₃ (Collier et al., 2000; Honjo et al., 2000; Urban-Rich; 2001; Accornero et al., 2003; Tsurumi et al., 2005; Manno et al., 2007).

In the equatorial area, the calcite and aragonite production is reduced by 9.5 and 18%, whereas the relative dissolution has increased by 4% and 5%, respectively. This

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change is small compared to the percentages presented for the high latitudes, however the quantitative impacts on calcite and aragonite producers may be large due to the moderate to high calcification rates observed in equatorial regions (e.g. Deuser and Ross, 1989; Fabry and Deuser, 1991; Kalberer et al., 1993; Fischer et al., 1996). In year 2100 the model still predicts a large area with aragonite saturation values above 2 in the gyres (Fig. 4). However, near the coast and in the equatorial upwelling area the saturation state is already close to 1 in year 2100. In areas with upwelling of DIC enriched deep-water the saturation state may decrease rapidly with increasing CO₂ concentrations. We would thus expect that shortly after year 2100 the surface waters in the equatorial and especially upwelling areas would become undersaturated, which would probably prevent large amounts of aragonite from being produced in this area.

5 Conclusions

The work presented here is intended as a first step towards understanding the role of aragonite production and dissolution in the global CaCO₃ budget and its evolution with increasing atmospheric pCO₂. Aragonite was included in the global biogeochemical model PISCES, where the parameterized production and dissolution were implemented with analogy to the corresponding terms for calcite. The production was assigned to mesozooplankton as a function of mesozooplankton biomass and aragonite saturation state of ambient waters. The marine carbonate cycle is well reproduced by the model with net global carbonate production rates corresponding to recent data-based estimates. Except from an overestimation by the model of produced aragonite in the equatorial zones, the model predicts a global spatial variability in aragonite production and dissolution consistent with literature.

With aragonite included in the model, the total CaCO₃ water column dissolution above 2000 m constitutes 58% of the modeled dissolution corresponding to estimates. In contrast, the corresponding value for the calcite-only version is 38%. The model provides less CaCO₃ dissolution in the upper 1000 m than reported, indicating that other

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mechanisms in addition to aragonite dissolution are needed to explain the entire loss of CaCO_3 in the upper part of the water column. Compared to the calcite-only model version however, taking into account production and dissolution of aragonite in addition to calcite in PISCES significantly improves the vertical distribution of dissolution rates and fluxes by allowing water column CaCO_3 dissolution above the calcite saturation horizon. Our results support the hypothesis that high dissolution fluxes in the upper part of the water column may largely be attributed to aragonite.

Effects of increasing atmospheric CO_2 on the CaCO_3 production and dissolution were studied using the SRES A2 scenario. Following the increasing values of atmospheric CO_2 , year 2050 appears to be a critical threshold moment; at this time already the entire ocean surface is predicted to have suboptimal conditions for aragonite production and some surface water areas in the Arctic are undersaturated with respect to aragonite. As a result of the decreasing saturation state, the global modeled aragonite production is reduced by almost one third in year 2100 compared to pre-industrial times. The global relative aragonite dissolution (dissolution/production) has increased by 12%. At latitudes above 40° , where production rates of aragonite are assumed to be highest, a decrease in aragonite production of substantially 65% is projected. Here the relative aragonite dissolution increases by 72%. Total global modeled CaCO_3 production has decreased by 19% by the end of the SRES A2 scenario, compared to approximately 15% for the model version without aragonite. Most of the increase in relative dissolution takes place in the upper part of the water column. While the feedback to atmospheric CO_2 of reduced CaCO_3 production and increased relative dissolution is assumed to be small (Gehlen et al., 2007), the predicted changes in aragonite production and dissolution highlight potential impacts of changing carbonate chemistry on aragonite producing organisms and the surrounding ecosystem of the pelagic ocean, especially in subpolar and polar areas.

The inclusion of 1/3 aragonite is in the upper range of most estimates, leading to a probable overestimation of the quantitative changes in aragonite production and dissolution with increasing atmospheric $p\text{CO}_2$. Alternatively, if the decrease in production

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of pteropod aragonite follows a linear parameterization as found by Langdon (2005) for corals instead of the curve fitted to experiments with coccolithophores, a faster response to the increasing CO₂ is expected. This would point towards an underestimation of the quantitative reduction in aragonite production suggested by our model.

- 5 Thus further exploration is needed to quantify the contribution of aragonite to the total CaCO₃ budget and the evolution of aragonite production and dissolution in the future ocean.

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Table 1. The carbonate cycle in PISCES: Comparison between model output and data in Pg $\text{CaCO}_3\text{-C y}^{-1}$. PISC/CAL=results from an equivalent model study without aragonite (Gehlen et al., 2007).

Process	Present study	PISC /CAL	Data	Data references
Source				
Net CaCO_3 production	0.9	0.8	0.8–1.6	Iglesias-Rodriguez et al. (2002), Lee (2001), Jin et al. (2006), Berelson et al. (2007)
Sinks				
Total pelagic CaCO_3 dissolution	0.5	0.5	0.5 ± 0.2 1.0 ± 0.5 ($>1500\text{ m}$)	Feely et al. (2004), Berelson et al. (2007)
CaCO_3 flux at lower boundary	0.3	0.3	–	–
CaCO_3 burial flux	–	–	0.3	Feely et al. (2004)
Related fluxes				
Export flux 100 m	0.6	0.6	0.6	Sarmiento et al. (2002), Berelson et al. (2007)
CaCO_3 dissolution 0–1000 m (% of tot. CaCO_3 production)	0.1 (14%)	0.02 (2.5%)	– (60–80%)	– (Milliman and Droxler, 1996)
CaCO_3 dissolution 0–2000 m (% of tot. CaCO_3 dissolution)	0.3 (58%)	0.2 (34%)	– ($\geq 60\%$)	– (Feely et al., 2004)

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Table 2. Summary of pelagic calcite and aragonite production, sinking fluxes, dissolution and relative dissolution for the years 1861, 2000 and 2100 (averaged over 10 years and drift corrected) in PgC y⁻¹. Changes between pre-industrial times and at the end of the scenario are given in %.

Process	Pre-ind (1861–1870)	Today (1996–2005)	Future (2091–2100)	Changes between Pre-ind and Future (%)
Production				
Net calcite production	0.57	0.56	0.49	–13
Net aragonite production	0.31	0.30	0.22	–29
Net CaCO ₃ production	0.87	0.85	0.71	–19
Export (100 m)				
Calcite export	0.41	0.41	0.36	–13
Aragonite export	0.22	0.21	0.13	–41
CaCO ₃ export	0.63	0.62	0.49	–23
Dissolution, total				
Calcite dissolution	0.38	0.37	0.35	–7
Aragonite dissolution	0.18	0.18	0.16	–15
CaCO ₃ dissolution	0.56	0.55	0.50	–10
Relative dissolution, total				
Calcite dissolution/net prod. (%)	67	67	71	4
Aragonite dissolution/net prod. (%)	60	62	72	12
CaCO ₃ dissolution/net prod. (%)	64	65	71	7
Dissolution, 0–2000 m				
Calcite dissolution	0.18	0.18	0.20	12
Aragonite dissolution	0.15	0.15	0.14	–6
CaCO ₃ dissolution	0.34	0.34	0.35	4
Relative dissolution, 0–2000 m				
Relative calcite dissolution (%)	32	33	42	10
Relative aragonite dissolution (%)	50	53	66	16
Relative CaCO ₃ dissolution (%)	38	40	49	11

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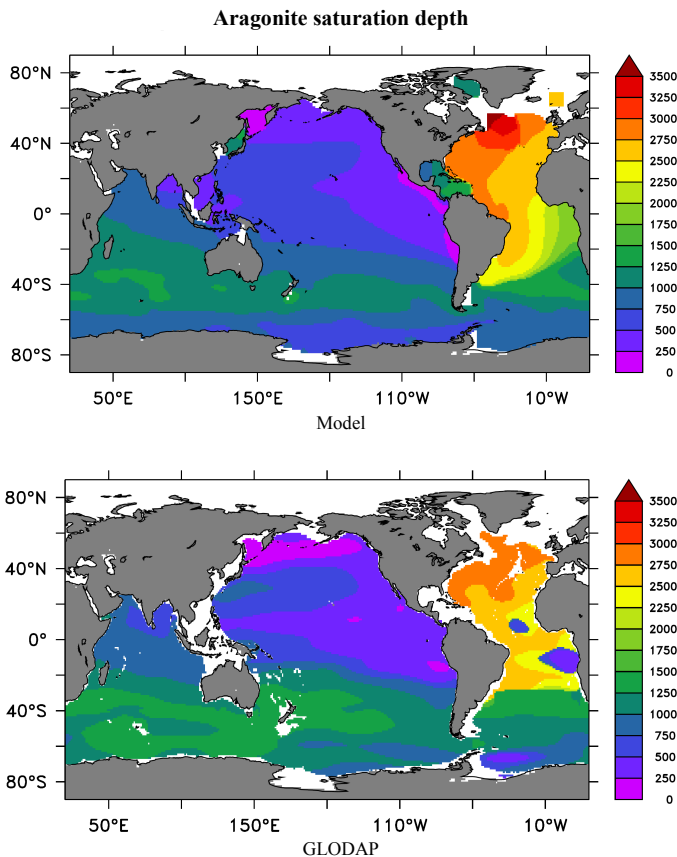


Fig. 1. Depth of aragonite saturation horizon: **(a)** model output, **(b)** recalculated from GLODAP (Key et al., 2004).

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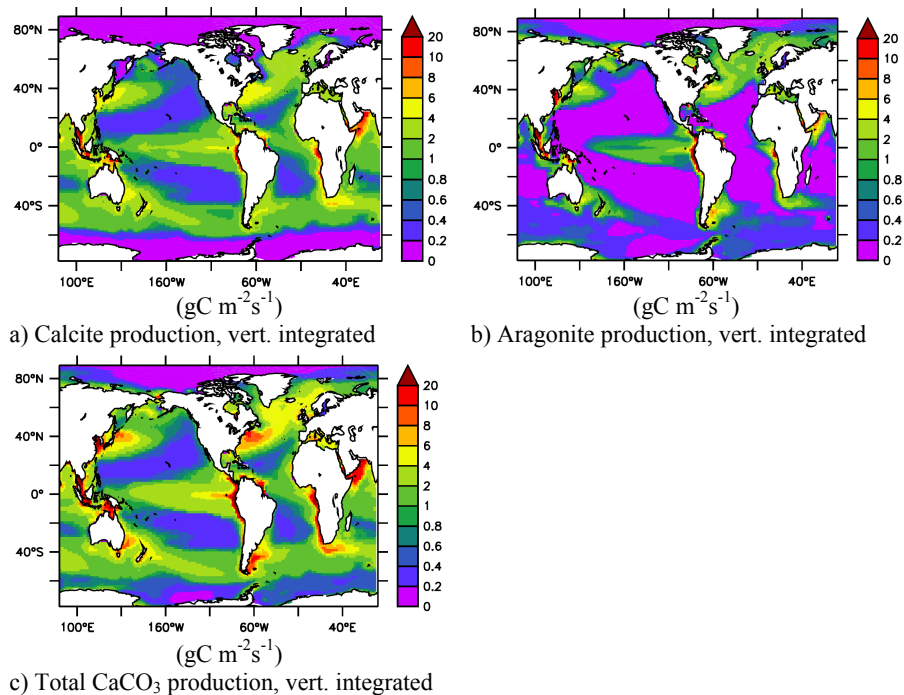


Fig. 2. Production of **(a)** calcite, **(b)** aragonite and **(c)** total CaCO_3 in $\text{gC m}^{-2} \text{s}^{-1}$, integrated over depth.

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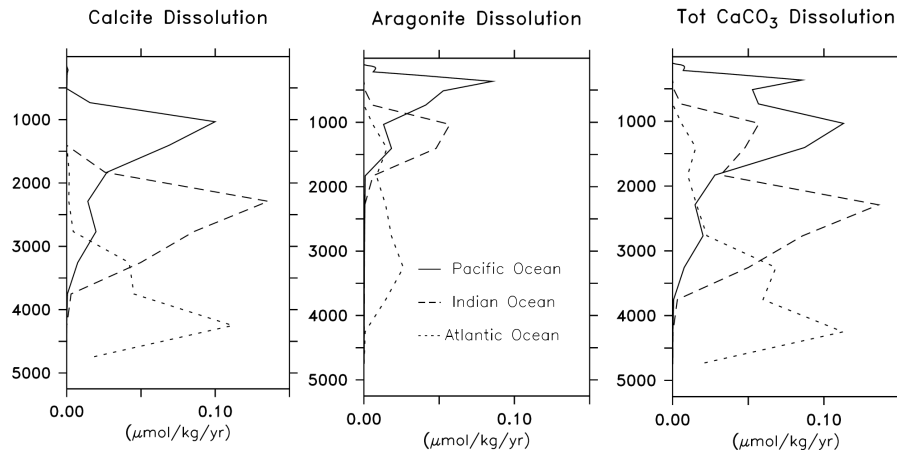


Fig. 3. Average (a) calcite, (b) aragonite and (c) total CaCO_3 dissolution rates in the Atlantic, Pacific and Indian Ocean basin.

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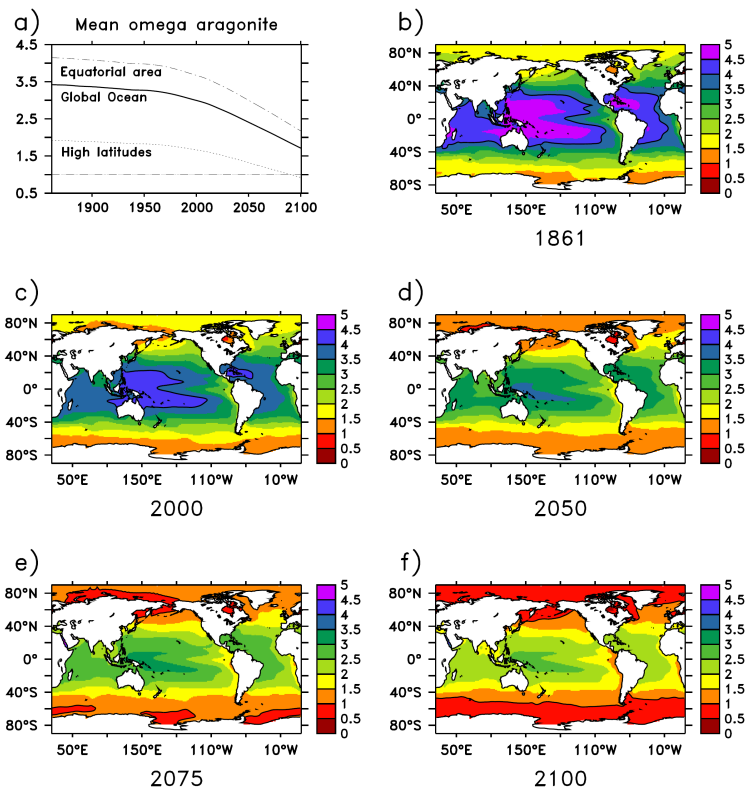


Fig. 4. Saturation state with respect to aragonite of surface waters (0–100 m): **(a)** timeseries of mean Ω_a for the global ocean, the equatorial area and for high latitudes, and maps in year **(b)** 1861, **(c)** 2000, **(d)** 2050, **(e)** 2075 and **(f)** 2100. Solid curves indicate $\Omega_a=4$ for year 1861 and 2000 and $\Omega_a=1$ for year 2050, 2075 and 2100.

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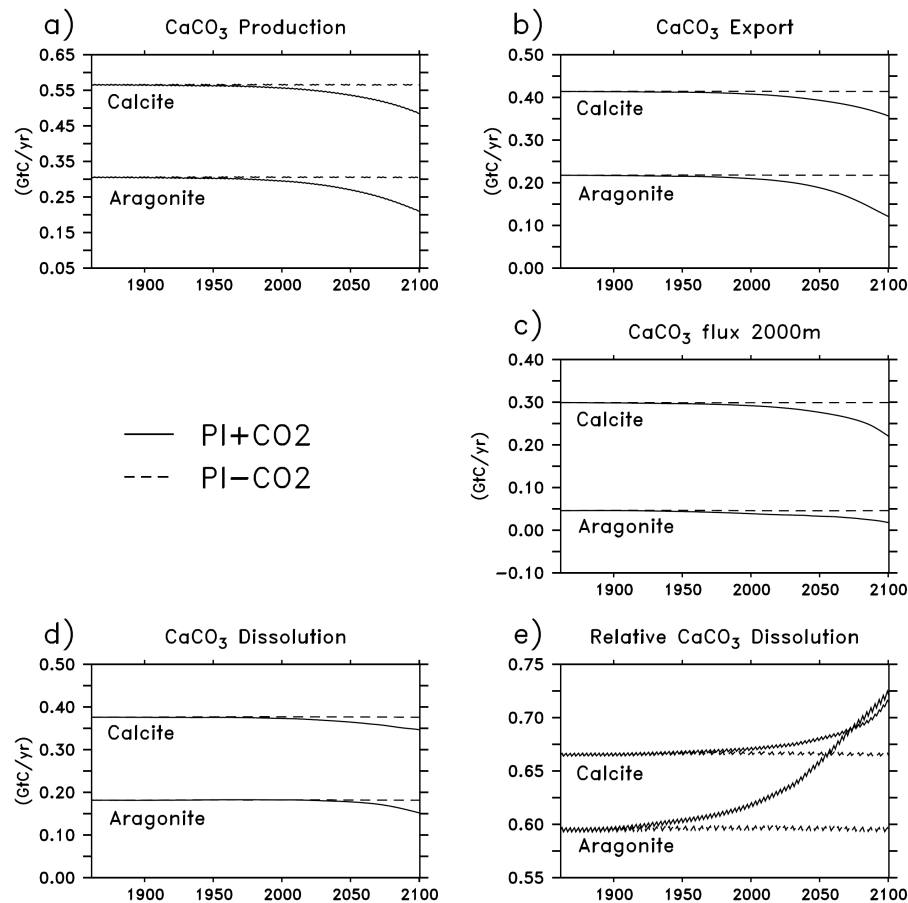


Fig. 5. Time series of global calcite and aragonite: **(a)** net production, **(b)** export, **(c)** sinking flux at 2000 m, **(d)** dissolution and **(e)** total pelagic dissolution/net production. PI+CO₂ represents model simulations with increasing CO₂ while PI-CO₂ is the control run.