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**CO<sub>2</sub> transfer from  
surface ocean to  
atmosphere**

A. Lerman and  
F. T. Mackenzie

# CO<sub>2</sub> air-sea exchange due to calcium carbonate and organic matter storage: pre-industrial and Last Glacial Maximum estimates

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## Abstract

Release of CO<sub>2</sub> from surface ocean water owing to precipitation of CaCO<sub>3</sub> and the imbalance between biological production of organic matter and its respiration, and their net removal from surface water to sedimentary storage was studied by means of a model that gives the quotient  $\theta = (\text{CO}_2 \text{ released to the atmosphere}) / (\text{CaCO}_3 \text{ precipitated})$ . The surface ocean layer is approximated by a euphotic zone, 50 m thick, that includes the shallower coastal area and open ocean.  $\theta$  depends on water temperature, CaCO<sub>3</sub> and organic carbon mass formed, and atmospheric CO<sub>2</sub> concentration. At temperatures between 5 and 25°C, and three atmospheric CO<sub>2</sub> pressures – 195 ppmv corresponding to the Last Glacial Maximum, 280 ppmv for the end of pre-industrial time, and 375 ppmv for the present –  $\theta$  varies from a fraction of 0.38 to 0.79, increasing with decreasing temperature, increasing atmospheric CO<sub>2</sub> content, and increasing CaCO<sub>3</sub> precipitated mass (up to 45% of the DIC concentration in surface water). For a surface ocean layer that receives input of inorganic and organic carbon from land, the calculated CO<sub>2</sub> flux to the atmosphere at the Last Glacial Maximum is 20 to 22 × 10<sup>12</sup> mol/yr and in pre-industrial time it is 45 to 49 × 10<sup>12</sup> mol/yr. In addition to the environmental factors mentioned above, flux to the atmosphere and increase of atmospheric CO<sub>2</sub> depend on the thickness of the surface ocean layer. The significance of these fluxes and comparisons with the estimates of other investigators are discussed. Within the imbalanced global carbon cycle, our estimates are in agreement with the conclusions of others that the global ocean prior to anthropogenic emissions of CO<sub>2</sub> to the atmosphere was losing carbon, calcium, and total alkalinity owing to precipitation of CaCO<sub>3</sub> and consequent emission of CO<sub>2</sub>. Other pathways of CO<sub>2</sub> exchange between the atmosphere and land organic reservoir and rock weathering may reduce the imbalances in the carbon cycle on millennial time scales.

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## 1. Introduction

Precipitation of  $\text{CaCO}_3$  mineral phases in the surface water of the coastal zone and open ocean results in removal of dissolved inorganic carbon (DIC), redistribution of the concentrations of dissolved carbonate species, and increase in the relative concentration of  $\text{CO}_2$  in solution. Such changes in  $\text{CO}_2$  concentration affect its exchange with the atmosphere: an increase in dissolved  $\text{CO}_2$  may result in a greater flux to the atmosphere and changes in the  $\text{CO}_2$  concentrations in each reservoir. In a global ocean, release of  $\text{CO}_2$  due to precipitation of inorganic or biogenic  $\text{CaCO}_3$  must be compensated by restoration of dissolved inorganic carbon and calcium in water, although there might have been variations in the carbon content and alkalinity of ocean water through time (e.g. Hardie, 1996; Milliman, 1993; Broecker, 2002; Tyrrell and Zeebe, 2004).  $\text{CO}_2$  exchange between the atmosphere and the coastal and open surface ocean is only in part controlled by carbonate mineral precipitation. Other major mechanisms in the system are the storage and release of carbon from the biomass and humus on land that affect atmospheric  $\text{CO}_2$  levels and hence  $\text{CO}_2$  exchange across the air-sea interface; physical processes, for example oceanic circulation that generally removes  $\text{CO}_2$  from the atmosphere in the downwelling zones and returns it in the upwelling regions; production, respiration, remineralization, and net sedimentary storage of organic matter in the ocean; carbonate mineral storage in shallow-water ocean sediments, such as in coastal zone ecosystems; and the cycle of carbonate mineral settling from the euphotic zone, dissolution, deposition, and accumulation in the deep ocean (e.g. Broecker and Peng, 1982; Maier-Reimer and Hasselmann, 1987; Morse and Mackenzie, 1990; Maier-Reimer, 1993; Woodwell, 1995; Broecker and Henderson, 1998; Milliman et al., 1999; Sigman and Boyle, 2000).

In this paper we address the following issues:

(1) Production and release of  $\text{CO}_2$  from surface water in the shallow coastal and open ocean due to formation and net storage of  $\text{CaCO}_3$ . We extend the treatment of

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this problem beyond the original work of Smith (1985) and Frankignoulle et al. (1994) for a model 50-m-thick euphotic zone that receives inputs of inorganic and organic carbon from land, and for a range of CaCO<sub>3</sub> and organic carbon production and storage rates, temperatures, and atmospheric CO<sub>2</sub> concentrations. Furthermore, we generalize the CO<sub>2</sub> release rates both at a (i) constant atmospheric CO<sub>2</sub> and (ii) rising atmospheric CO<sub>2</sub> due to emissions from the surface ocean.

(2) We apply our CO<sub>2</sub> release parameters to the global conditions characteristic of the end of pre-industrial time, near the year 1700, and those at the Last Glacial Maximum (LGM), about 18000 yr ago. The results show that the CO<sub>2</sub> fluxes from the surface ocean to the atmosphere are affected by changes in temperature, atmospheric CO<sub>2</sub> concentration, and the carbonate and organic carbon sequestration rates in sediments. From our results we also estimate the fractions of the atmospheric CO<sub>2</sub> increase from about 195 ppmv at the LGM to 280 ppmv at the end of pre-industrial time that could have been contributed by global CaCO<sub>3</sub> and organic carbon (C<sub>org</sub>) production rates, and we compare the calculated CO<sub>2</sub> flux for modern time with the results of others.

(3) Estimates of the major fluxes in the global carbon cycle at time scales of 10<sup>2</sup> to 10<sup>4</sup> years, from the LGM to pre-industrial time, indicate significant imbalances in the atmospheric, terrestrial, and oceanic reservoirs. We address the possible reasons behind these imbalances and propose alternative pathways of carbon flows between the land organic reservoir, atmosphere, and carbonate and silicate rocks that reduce some of these imbalances.

We begin with a discussion of the background and the physical setting of the system, followed by a description of a more general CO<sub>2</sub> transfer model between a surface layer of the coastal and open ocean and the atmosphere. Three specific cases of CO<sub>2</sub> generation and emission from a surface layer without external inputs are given as basic and limiting cases of the general model: CO<sub>2</sub> release due to CaCO<sub>3</sub> precipitation to an atmosphere of constant P<sub>CO<sub>2</sub></sub>, release that causes an increase in atmospheric P<sub>CO<sub>2</sub></sub>, and a combined effect of both CaCO<sub>3</sub> and biological C<sub>org</sub> production on CO<sub>2</sub>

release. We apply the general model to estimate the pre-industrial and LGM sea-to-air CO<sub>2</sub> fluxes and discuss their bearing on the global carbon cycle up to the end of pre-industrial time. In this paper, we do not address the historical rise of atmospheric CO<sub>2</sub> since the LGM nor the industrial and agricultural CO<sub>2</sub> increase in the last 300 years.

5 In the varying practice of the units used for carbon fluxes and reservoir sizes, gigatons (Gt), petagrams (Pg), and moles, the conversion factors are: 1 Gt C = 1 Pg C =  $1 \times 10^{15}$  g C =  $83.3 \times 10^{12}$  mol C.

## 2. Model discussion

### 2.1. Background

10 A number of experimental studies have shown that precipitation of CaCO<sub>3</sub> minerals from supersaturated seawater is accompanied by a decrease in total alkalinity and an increase of dissolved CO<sub>2</sub> and H<sup>+</sup>-ion concentrations or a lowering of the solution pH (e.g. Wollast et al., 1980; Schoonmaker, 1981; Tribble and Mackenzie, 1998). Theoretical analysis of this process has been advanced by several investigators using different  
15 approaches. Smith (1985) analyzed the air-water interface CO<sub>2</sub> flux at the ambient atmospheric  $P_{\text{CO}_2}$  of 340 ppmv as a gas diffusional process across a boundary layer, in response to CaCO<sub>3</sub> deposition at the rate equivalent to global precipitation of about  $1.3 \times 10^{12}$  mol C/yr, which is significantly lower than CaCO<sub>3</sub> production or net storage rates in the ocean as a whole. Smith's (1985) results for ocean water of normal salinity  
20 at 25°C, in a model layer about 1 m thick, showed an increase in dissolved CO<sub>2</sub> during precipitation in a closed system and subsequent transfer of dissolved inorganic carbon as CO<sub>2</sub> to the atmosphere. Frankignoulle et al. (1994) estimated release of CO<sub>2</sub> from ocean water in response to CaCO<sub>3</sub> precipitation by means of an analytic function  $\Psi = (\text{released CO}_2)/(\text{precipitated CO}_3^{2-})$ . Their results show an increase in the CO<sub>2</sub>  
25 fraction released with increasing atmospheric  $P_{\text{CO}_2}$  in the range from 290 to 1000 ppmv and with decreasing temperature from 25 to 5°C. Because the study of Frankignoulle

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et al. (1994) deals with an atmosphere of constant CO<sub>2</sub> and gives no data on the mass or rate of CaCO<sub>3</sub> precipitation, we are able to compare our results with theirs only to a limited extent in a later section of this paper. In an attempt to make our analysis of the relationships between CO<sub>2</sub> release and CaCO<sub>3</sub> and C<sub>org</sub> deposition clear and reproducible, we outline in the Appendix the essential equations and computational steps leading to the results, even though the basic equations are well known.

The precipitation reaction of CaCO<sub>3</sub>, as usually written, removes 1 mol C from solution and produces 1 mol CO<sub>2</sub>, while dissolution consumes CO<sub>2</sub> and produces HCO<sub>3</sub><sup>-</sup>:

Precipitation



Dissolution

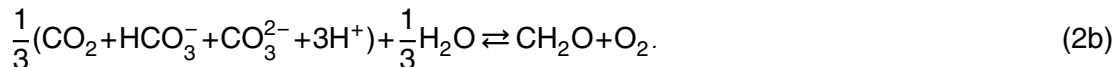
Primary production or net primary production (NPP = GPP - R<sub>auto</sub>, Fig. 1) consumes CO<sub>2</sub> and respiration or remineralization of organic matter produces CO<sub>2</sub> that may also drive Reaction (1) in the direction of carbonate mineral dissolution in surface waters and the deep ocean (Emerson and Bender, 1981; Moulin et al., 1985; Morse and Mackenzie, 1990; Archer and Maier-Reimer, 1994):

Gross Primary Production



Respiration

However, if biological production uses the bicarbonate and carbonate ions in addition to CO<sub>2</sub> then such a process may be written as a variant of Reaction (2a), if all the carbonate species are consumed in the same proportions as they occur in ocean water:



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Smith (1985) treated primary production as consuming DIC rather than CO<sub>2</sub> only. Studies by Raven (1994), Raven and Johnston (1994), and Sikes and Fabry (1994) provide justification for organic production in some marine species as affecting all the DIC chemical species rather than only CO<sub>2</sub> in ocean water.

5 Net primary production in the euphotic zone, removing dissolved CO<sub>2</sub>, essentially competes with the carbonate precipitation generating CO<sub>2</sub> that can be emitted to the atmosphere, as follows from the sum of Reactions (1) and (2a):



10 Some of the calcium carbonate produced in surface coastal and open ocean water, perhaps as much as 60%, dissolves in the water column and in sediments driven to a significant extent by remineralization of sinking organic matter in the ocean or organic matter deposited in sediments that produces CO<sub>2</sub> (Milliman, 1993; Wollast, 1994; Milliman et al., 1999; Mackenzie et al., 2004). These processes result in return of some of the carbon taken up in CaCO<sub>3</sub> and organic matter production back to ocean water.

15 A measure of the CaCO<sub>3</sub> and organic carbon production is often taken as the ratio of their proportions in sediments. In the geologically long-term sedimentary record, the ratio of carbon in carbonate rocks to carbon in organic matter ranges from about 5/1 to 2.5/1 (Garrels et al., 1973; Holland, 1978, p. 215, with a review of older literature; Turekian, 1996; Hayes et al., 1999; Li, 2001). It is about 2/1 in recent sediments that

20 include C<sub>org</sub> brought in from land or 4/1 if only the in situ produced organic matter is counted (Wollast and Mackenzie, 1989; Mackenzie et al., 2004). Significantly, riverine input to the ocean in pre-industrial time supplied only about 25% more inorganic than organic carbon (ratio 1.23/1; Mackenzie et al., 1993; Ver et al., 1999): 32 × 10<sup>12</sup> mol/yr of dissolved inorganic carbon and 26 × 10<sup>12</sup> mol/yr of reactive organic carbon, consisting of dissolved organic carbon (DOC, 18 × 10<sup>12</sup> mol/yr) and a 50%-fraction or 8 × 10<sup>12</sup>

25 mol/yr of total particulate carbon input (Smith and Hollibaugh, 1993). The remaining fraction of particulate carbon (POC), 8 × 10<sup>12</sup> mol/yr, is considered refractory and stored in coastal zone and continental slope sediments. The preceding numbers on the input

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and storage ratios in sediments show that a large fraction of reactive organic carbon brought to the ocean undergoes remineralization.

## 2.2. Physical setting

Our model of a surface water layer in the coastal zone and open ocean is a two-box ocean model shown in Fig. 1 (e.g. Chester, 2002). Refinement of this basic model is discussed in the sections below. The surface ocean layer is approximated by a euphotic zone of 50 m average thickness, where incident solar radiation declines to 0.1–1% of its surface irradiance value, although this zone in some areas of the ocean may be as thick as 150–200 m (e.g. Ketchum, 1969; Krom et al., 2003; Yentsch, 1966).

We take an average 50-m-thick euphotic zone over the global ocean surface area of  $3.61 \times 10^{14} \text{ m}^2$ ; its mass is  $1.854 \times 10^{19} \text{ kg}$  at a mean ocean water density of  $1027 \text{ kg/m}^3$ , and we disregard the density difference of about  $4 \text{ kg/m}^3$  between 5 and  $25^\circ\text{C}$ . We also do not consider the increase in salinity and individual dissolved species concentrations due to a 120-m lowering of sea level at the LGM (Fairbanks, 1989) that would have resulted in a 3% increase of the modern values. The volume of the euphotic zone is assumed constant: the ocean surface area covered by ice at the LGM might have been 10 to 15% of the total area; such a change in the area of the model surface ocean layer would be compensated by a change of 5 to 10 m in its thickness.

The euphotic zone is where the major groups of organisms producing  $\text{CaCO}_3$  as their skeletal material thrive, such as benthic corals, coralline and other calcareous algae, foraminifera and molluscs in the coastal zone and on banks and reefs; and in the pelagic open ocean, Coccolithophoridae, planktonic foraminifera, and pteropods. Most  $\text{CaCO}_3$  produced in the more recent geological past is primarily biogenic in origin, and lesser quantities of  $\text{CaCO}_3$  in the modern oceans and for part of the geologic past have been produced as cements in sediments and as whittings and ooids (e.g. Bathurst, 1974; Morse and Mackenzie, 1990). It is important to bear in mind that net storage of  $\text{CaCO}_3$  and  $C_{\text{org}}$  in sediments is the difference between their production rates and dissolution or remineralization rates, and sequestration in sediments repre-

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sents net removal of carbonate and organic carbon from the euphotic zone. Although the dissolution of  $\text{CaCO}_3$  and remineralization of biologically produced  $\text{C}_{\text{org}}$  are shown in Fig. 1 as occurring in the surface ocean layer, the location of the dissolution and remineralization processes is not germane to our computation of the  $\text{CO}_2$  release from the surface ocean that depends in the model only on the net removal of  $\text{CaCO}_3$  and organic carbon from the surface layer and its thickness. If the net removal of carbon into sediment storage is not matched by its input from land and oceanic crustal sources, then the oceanic reservoir is out of balance, and its inorganic and organic carbon content changes with time.

### 2.3. Basic relationships

An answer to the question – how much  $\text{CO}_2$  can be released from surface ocean water by precipitation of  $\text{CaCO}_3$ ? – depends not only on such obvious factors as dissolved carbonate concentration in ocean water, the acid-base balance, and temperature, but also on inputs of carbon from land and whether the atmospheric  $\text{CO}_2$  concentration is constant or rises due to emissions from the surface ocean. Computations of the  $\text{CO}_2$  transfer in the present time had been based on gas transfer velocity (e.g. Smith, 1985; Takahashi et al., 2002) that depends on such parameters as the degree of mixing of the water layer, properties of the diffusive boundary layer at the air-water interface, and wind velocity. To reduce some of the uncertainties associated with the past environmental conditions, we adopt a different approach to estimating the  $\text{CO}_2$  releases that are based on material balances and gas-solution partitioning of the generated  $\text{CO}_2$ . Equation (4) shows that on an annual basis, riverine input adds per 1 kg of surface layer water  $v$  mol  $\text{HCO}_3^-$  and  $w$  mol  $\text{C}_{\text{org}}$ . At this stage, DIC and total alkalinity ( $A_T$ ) are increased by  $v$  mol/kg. Organic carbon is remineralized and respired, producing  $\text{CO}_2$  according to Reaction (2a) and adding  $w$  mol  $\text{CO}_2$  to DIC. Precipitation of  $\text{CaCO}_3$  is a net removal of  $y$  mol  $\text{CaCO}_3$  from surface ocean water and  $z$  mol C are removed in primary production by the formation and storage of organic matter. When  $y$  mol  $\text{CaCO}_3/\text{kg}$  are removed from solution, ocean-water initial  $\text{DIC}_0$  decreases by  $y$  mol

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C/kg, initial  $\text{Ca}^{2+}$  concentration also decreases by  $y$  mol  $\text{Ca}^{2+}$ /kg, and the initial total alkalinity ( $A_{T,0}$ ) decreases by  $2y$  mol-equivalent/kg. In a system that is temporarily closed to  $\text{CO}_2$  exchange with the atmosphere, the sum of the individual input, precipitation, and respiration processes usually increases the initial dissolved  $\text{CO}_2$  because of the net removal of  $\text{CaCO}_3$  ( $y$ ) and oxidation of organic matter ( $w$ ). This  $\text{DIC}_{cl}$  in a temporarily closed system containing newly produced  $\text{CO}_2$  would equilibrate with atmospheric  $\text{CO}_2$  when the system is opened. Thus the balance in a temporarily closed stage is:

$$\text{DIC}_{cl} = \text{DIC}_0 + v + w - y - z \quad (4)$$

$$[\text{Ca}^{2+}] = [\text{Ca}^{2+}]_0 - y \quad (5)$$

$$A_T = A_{T,0} + v - 2y - z. \quad (6)$$

In Eq. (6), net storage of organic carbon ( $z$ ) would have no effect on total alkalinity if organic carbon formed only from  $\text{CO}_2$  and then the term  $z$  would be 0:

$$A_T = A_{T,0} + v - 2y. \quad (7)$$

General relationships between the changes in DIC and alkalinity at different  $\text{CaCO}_3$  and  $C_{\text{org}}$  input and removal rates have been given by Zeebe and Wolf-Gladrow (2001) and Sigman and Boyle (2000). An example of a change in DIC under pre-industrial conditions due to inputs and internal processes in a model surface ocean layer is from Eq. (4) (at the pre-industrial conditions of 280 ppmv atmospheric  $\text{CO}_2$  and  $5^\circ\text{C}$ ; data in Tables 3 and 4; the number of significant digits is retained for computational consistency):

$$\text{DIC}_{cl} = (2332.3 + 1.726 + 1.403 - 1.731 - 0.448) \times 10^{-6} = 2333.25 \times 10^{-6} \text{ mol/kg}.$$

The DIC concentration at equilibrium with atmospheric  $\text{CO}_2$  ( $\text{DIC}_{eq}$ ) is smaller than  $\text{DIC}_{cl}$  and this difference is the mass of inorganic carbon transferred to the atmosphere

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as CO<sub>2</sub>. It is important to reiterate that the CO<sub>2</sub> mass transferred to the atmosphere is not only a function of the DIC change but also of the change in total alkalinity (A<sub>T</sub>) and atmospheric CO<sub>2</sub> concentration that may be either constant or increasing due to the CO<sub>2</sub> emission from the surface water layer. The change in DIC due to CO<sub>2</sub> transfer across the air-sea interface is, from the preceding data:

$$\begin{aligned}\Delta[\text{DIC}] &= [\text{DIC}]_{cl} - [\text{DIC}]_{eq} \\ &= (2333.25 - 2330.99) \times 10^{-6} = 2.26 \times 10^{-6} \text{ mol/kg.}\end{aligned}\quad (8)$$

Details of the computation of the CO<sub>2</sub> release from Eq. (8) are given in the Appendix. A positive Δ[DIC] indicates CO<sub>2</sub> transfer from surface ocean water to the atmosphere. A negative Δ[DIC] would indicate uptake of atmospheric CO<sub>2</sub> by surface water under combinations of such processes as, for example, a low calcification rate, low inputs of inorganic and organic carbon from land, low rate of remineralization of organic matter or incomplete remineralization of the organic carbon input from land, and a rising atmospheric CO<sub>2</sub> concentration.

Quotient  $\theta$  is a measure of the CO<sub>2</sub> emission per unit of CaCO<sub>3</sub> mass precipitated,  $y$  mol CaCO<sub>3</sub>/kg:

$$\begin{aligned}\theta &= \Delta[\text{DIC}]/y \\ &= 2.26/1.731 = 1.3 \text{ mol/mol.}\end{aligned}\quad (9)$$

The value of  $\theta > 1$  indicates that the CO<sub>2</sub> amount released is greater than the CaCO<sub>3</sub> mass precipitated because of the additional inputs of bicarbonate ( $v$ ) and reactive organic matter that is converted to CO<sub>2</sub> ( $w$ ). In the absence of such external inputs,  $\theta$  is usually a fraction,  $\theta < 1$ , as is shown later in this section.

CO<sub>2</sub> emission from the surface ocean, as given in Eqs. (4) and (8), can be simplified for computational convenience. Because precipitation and net removal of CaCO<sub>3</sub> ( $y$ ) and addition of remineralizable organic carbon ( $w$ ) are the two main processes that generate dissolved CO<sub>2</sub>, they give a reasonable approximation to the computed CO<sub>2</sub>

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flux by the following relationship:

$$\Delta[\text{DIC}] \approx \theta y + w \quad (\text{mol kg}^{-1} \text{ or mol kg}^{-1} \text{ yr}^{-1}), \quad (10)$$

where  $\theta < 1$  is the value of  $\theta$  for  $\text{CaCO}_3$  precipitation at the specific environmental conditions (Table 2). The approximation to the  $\text{CO}_2$  flux in Eq. (10) is compared with the results of the complete computation in Table 5.

In pre-industrial time, the ocean was a source of atmospheric  $\text{CO}_2$  owing to heterotrophic respiration of organic matter brought by rivers from land and produced in situ, as well as owing to biological calcification in the coastal zone (Smith and Hollibaugh, 1983; Mackenzie et al., 2004, with references to earlier work). Equations (4), (8), and (10) are in agreement with this view of the direction of  $\text{CO}_2$  transfer and they combine these processes in a general balance of inorganic and organic carbon inputs from land, and calcium carbonate and organic matter production and sequestration in sediments.

#### 2.4. Possible effects of biological production on alkalinity

If biological production consumes the bicarbonate and carbonate ions in addition to  $\text{CO}_2$ , as in Reaction (2b), then total alkalinity would decrease along with the decrease in DIC. Total alkalinity of ocean water ( $A_T$ , mol-equivalent/kg) is the difference between the sum of the conservative or  $\text{H}^+$ -independent cation mol-equivalent concentrations and the sum of the conservative anions. In the simplest definition of total alkalinity, this difference is made up of the carbonate, borate, and water alkalinity terms that are defined in the Appendix (e.g. Morse and Mackenzie, 1990; Zeebe and Wolf-Gladrow, 2001):

$$A_T = A_C + A_B + A_W \quad (\text{mol-equivalent/kg}). \quad (11)$$

Carbonate alkalinity ( $A_C$ ) of an average ocean water accounts for 94 to 97% of total alkalinity ( $A_T$ ), within the range of atmospheric  $\text{CO}_2$  from 195 to 375 ppmv and temperature from 5 to 25°C. More detailed definitions of total alkalinity include such less abun-

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dant dissolved species as phosphate, nitrate, and silica. The relationships between  $A_T$ ,  $P_{CO_2}$ , total concentrations of dissolved species, and the  $H^+$ -ion concentration make it possible to calculate all the parameters in the marine inorganic carbon system when only two are known (Bacastow and Keeling, 1973; Morse and Mackenzie, 1990; DOE, 1994; Frankignoulle, 1994; Lewis and Wallace, 1998; Zeebe and Wolf-Gladrow, 2001; Proye and Gattuso, 2003).

Reduction in total alkalinity due to consumption of DIC in primary production and net removal of  $C_{org}$  from ocean water to sediments can be written as a ratio of the change in each parameter:  $\Delta A_T / \Delta [DIC]$ . This ratio varies from 1.05 to 1.2 depending on the conditions: it increases with an increasing temperature and decreases slightly with an increasing  $P_{CO_2}$  and initial DIC concentration. This relationship holds within the range of conditions (at normal seawater salinity) that cover the period since the Last Glacial Maximum to the present: that is, at the pH from about 8.08 to 8.35, total alkalinity between  $2.4$  and  $2.8 \times 10^{-3}$  mol-equivalent/kg, and atmospheric  $CO_2$  varying from 195 ppmv through the pre-industrial concentration of 280 ppmv to the present-day value of 375 ppmv.

## 2.5. Carbonate precipitation at a fixed atmospheric $CO_2$

In any model of  $CO_2$  emissions to an atmosphere of a constant  $P_{CO_2}$ , the emissions do not increase the atmospheric content, as if they were either removed from the carbon balance or taken up by other reservoirs.

In a system with no external inputs and no biological production, only  $CaCO_3$  precipitation produces  $CO_2$ , and Eqs. (4)–(6) are then simplified to the following form:

$$DIC_{cl} = DIC_0 - y \quad (12)$$

$$[Ca^{2+}] = [Ca^{2+}]_0 - y \quad (13)$$

$$A_T = A_{T,0} - 2y. \quad (14)$$

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The losses of CO<sub>2</sub> from the surface water layer as a result of CaCO<sub>3</sub> precipitation were calculated for the conditions shown in Table 1: ocean water of a constant salinity of 35 (a dimensionless number 35 on the UNESCO practical salinity scale, also called psu or practical salinity units, close to 35 g/kg); temperatures of 5, 15, and 25°C; and three values of atmospheric P<sub>CO<sub>2</sub></sub> – 195 ppmv, representative of the Last Glacial Maximum (Petit et al., 1999), 280 ppmv for the end of pre-industrial time at the year 1700 (Siegenthaler and Oeschger, 1987), and 375 ppmv for the present (Keeling and Whorf, 2003). Although this paper does not address the industrial atmospheric CO<sub>2</sub> rise, the value of 375 ppmv is included in the calculation of the CO<sub>2</sub> flux for a comparison with the lower concentrations. In addition to the surface ocean water pH ≈ 8.35 near the Last Glacial Maximum, Sanyal et al. (1995) also reported a higher pH for the deep ocean. However, Anderson and Archer (2002) found no increase in the deeper-ocean water pH between the depths of 1600 and 4200 m on the basis of restored carbonate-ion concentrations. A somewhat lower pH of 8.17 to 8.30 of the surface water in the Equatorial Pacific between about 20 and 16 ka b.p. was reported by Palmer and Pearson (2003). For internal consistency of the results in this paper that addresses the surface water layer of the coastal zone and open ocean, the initial total alkalinity (A<sub>T</sub>) was taken to be the same at all CO<sub>2</sub> partial pressures, from which new pH, DIC, and other H<sup>+</sup>-dependent parameters at other temperatures and CO<sub>2</sub> partial pressures were calculated. Total alkalinity is lower at lower temperatures where there is relatively more dissolved [CO<sub>2</sub>] that reduces carbonate alkalinity (A<sub>C</sub>). It should be noted that present-day total alkalinity and DIC of the surface ocean are lower than the values in Table 1: A<sub>T</sub> = 2.29 to 2.38 × 10<sup>-3</sup> mol-equivalent/kg and DIC = 1.90 to 2.12 × 10<sup>-3</sup> mol/kg (Takahashi, 1989). If the present-day surface ocean water were at equilibrium with atmospheric CO<sub>2</sub> of about 340 ppmv (1975–1985 range is about 330 to 345 ppmv; Keeling and Whorf, 2003), its total alkalinity would correspond to the pH of 8.11 to 8.12, about 0.2 pH units lower than the value taken for the surface ocean near the Last Glacial Maximum (Sanyal et al., 1995).

At a constant atmospheric P<sub>CO<sub>2</sub></sub>, dissolved [CO<sub>2</sub>] is also constant. In this case,

Eqs. (8) and (9) become:

$$\Delta[\text{DIC}] = [\text{DIC}_0 - y] - [\text{DIC}]_{eq} \quad (\text{mol/kg}) \quad (15)$$

and

$$\theta = \frac{\Delta[\text{DIC}]}{y} = \frac{(1-f)[\text{DIC}_0] - [\text{DIC}]_{eq}}{f[\text{DIC}_0]}, \quad (16)$$

5 where  $f$  is a fraction of the initial DIC concentration removed as  $\text{CaCO}_3$ .

The values of  $\theta$  for three atmospheric  $\text{CO}_2$  partial pressures and temperatures, 195 to 375 ppmv and 5 to 25°C, are shown in Fig. 2. The  $\text{CO}_2$  release to the atmosphere depends on the temperature – it is greater at a lower temperature; it increases with increasing atmospheric  $\text{CO}_2$  and the  $\text{CaCO}_3$  mass precipitated that corresponds to a larger fraction of DIC removed. The effect of temperature is due to the distribution of the dissolved species  $[\text{CO}_2]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{2-}]$ : at a lower temperature, the relative abundance of  $[\text{CO}_2]$  increases such that there is more dissolved  $\text{CO}_2$  at the start. In a normal ocean water within the pH range from 7.7 to 8.4, dissolved  $\text{CO}_2$  concentration at 5°C is 1.6 to 2.0 times greater than at 25°C:  $[\text{CO}_2]_{5^\circ} / [\text{CO}_2]_{25^\circ} \approx 1.6$  to 2.0. At a higher atmospheric  $P_{\text{CO}_2}$  at equilibrium with ocean water, there is also more dissolved  $\text{CO}_2$  and its internal increase due to carbonate precipitation is greater than at lower  $\text{CO}_2$  atmospheric pressures. This accounts for a greater release to the atmosphere and, consequently, a higher value of the ratio  $\theta$ . The  $\text{CaCO}_3$  mass precipitated that is shown in Fig. 2 corresponds to increasing fractions of initial DIC, from  $\leq 0.1$  to 45%, constrained by the condition that the final supersaturation with respect to calcite does not fall below 1,  $\Omega \geq 1$ . The results indicate that depending on the temperature, atmospheric  $\text{CO}_2$  concentration, and the carbonate amount precipitated, the fractions of  $\text{CO}_2$  released to the atmosphere per 1 mol  $\text{CaCO}_3$  are in the range from  $\theta = 0.44$  to 0.79.

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## 2.6. Rising atmospheric CO<sub>2</sub> due to carbonate precipitation

A balance between the CO<sub>2</sub> released from surface ocean and added to the atmosphere requires knowledge of the water volume from which the release takes place. First, we consider an average 50-m-thick euphotic zone, as described in Sect. 2.2. The increase in atmospheric CO<sub>2</sub> is computed by a numerical iteration routine because neither the final atmospheric CO<sub>2</sub> concentration nor the DIC concentration in surface ocean water is known. The computational procedure is detailed in the Appendix.

For the rising atmospheric CO<sub>2</sub> scenario, the changes in the pH, degree of saturation with respect to calcite ( $\Omega$ ), and carbonate alkalinity ( $A_C$ ) are shown in Fig. 3. The pH of the closed system declines by up to about 2 pH units at the higher end of CaCO<sub>3</sub> precipitation. Upon reequilibration with the atmosphere, the pH in an open system rises, and it is 0.35 to 0.47 pH units lower than the starting value of pH = 8.35. Pronounced differences in the degree of calcite saturation are evident at the different temperatures,  $\Omega$  decreasing from 25 to 5°C owing to the fact that the carbonate ion concentration, [CO<sub>3</sub><sup>2-</sup>], is lower at a lower temperature, other factors being equal. Initial total alkalinity ( $A_T$ ) is slightly different at the three temperatures because of the choice of a fixed initial pH = 8.35. The total alkalinity differences have a much smaller effect on  $\Omega$  than the temperature.

A little noticed, if at all, feature of the calcite solubility expression may be mentioned here: while in nearly pure water the apparent solubility product of calcite,  $K'_{cal}$ , increases steadily with a decreasing temperature (it increases by a factor of 1.25 or 25% from 25 to 5°C), in ocean water of salinity 35 in the same temperature range  $K'_{cal}$  increases very slightly, by a factor of 1.004 or 0.4%. Furthermore,  $K'_{cal}$  shows a solubility maximum near 12.5°C that is by a factor of 1.01 or 1% higher than the solubility at 25°C, then declining from 12.5 to 5°C (calcite solubility equations in Mucci, 1983, and Zeebe and Wolf-Gladrow, 2001).

The loss of CO<sub>2</sub> due to CaCO<sub>3</sub> precipitation, starting at an atmospheric CO<sub>2</sub> of 195 ppmv is shown in Fig. 4a and Table 2. If the surface layer volume is doubled,

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the precipitated carbonate mass also doubles, but the  $\text{CO}_2$  mass emitted to the atmosphere is somewhat less than double because the rising  $\text{CO}_2$  in the atmosphere exerts back-pressure on ocean water, thereby increasing its DIC. This relationship is reflected in the slightly lower values of  $\theta$  for the thicker model surface layers (50, 100, and 300 m, Table 2).

If primary production removes  $\text{CO}_2$  while  $\text{CaCO}_3$  precipitates, this reduces the  $\text{CO}_2$  amount releasable to the atmosphere and lowers the fraction released  $\theta$  to 0.17 to 0.35, at the conditions as shown in Fig. 4b:

$$\text{DIC}_{c/l} = \text{DIC}_0 - y - z \quad (17)$$

$$A_T = A_{T,0} - 2y, \quad (18)$$

where the ratio of carbonate to organic carbon removal is  $y/z = 4/1$ .

In fact, it is conceivable that in a strongly autotrophic ecosystem,  $\text{CO}_2$  production by carbonate precipitation may be completely compensated for by uptake of the  $\text{CO}_2$  generated by organic productivity, resulting in no transfer of  $\text{CO}_2$  from water to the atmosphere or in a transfer in the opposite direction, as shown in Reactions (1)–(3). Removal of DIC by primary production also lowers the supersaturation of ocean water with respect to carbonate minerals, which may have a kinetic effect and lead to a slower rate of carbonate precipitation. The rise in atmospheric  $\text{CO}_2$  in industrial time is believed to cause lower production of  $\text{CaCO}_3$  by calcifying organisms because of the consequent lowering of the saturation state of surface ocean waters, both in the shallow coastal and open ocean euphotic zone where calcareous organisms thrive (e.g. Agegian, 1985; Mackenzie and Agegian, 1989; Gattuso et al., 1993, 1999; Leclercq et al., 2002; Andersson et al., 2003; Buddemeier et al., 2004). This process is a weak negative feedback to the release of  $\text{CO}_2$  to the atmosphere from  $\text{CaCO}_3$  precipitation that increases with an increasing atmospheric  $\text{CO}_2$ .

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### 3. Results and discussion

Values of  $\theta$  at different conditions, atmospheric  $\text{CO}_2$  concentrations, and temperatures are summarized in Table 2 and Figs. 2 and 4. Factor  $\Psi$  of Frankignoulle et al. (1994), possibly analogous to  $\theta$  as mentioned in Sect. 2.1, has at  $15^\circ\text{C}$  a value of 0.55 for the time of glaciation and 0.67 for the present. Although  $\Psi$  and  $\theta$  are not directly comparable, the value of 0.55 agrees at the same temperature with  $\theta$  for calcification at constant atmospheric  $P_{\text{CO}_2}$  and for the case of a rising atmospheric  $\text{CO}_2$ . However, 0.55 in the constant  $P_{\text{CO}_2}$  case reflects a smaller amount of  $\text{CaCO}_3$  precipitated, 7 to 10% of DIC (Fig. 2), and in the open system case (Fig. 4a), it corresponds to precipitation of about 30% of DIC. Nevertheless, our results are in agreement with those of Frankignoulle et al. (1994) as to the direction of change of  $\theta$ : it increases with increasing atmospheric  $\text{CO}_2$  and with decreasing temperature.

The  $\text{CaCO}_3$  production and removal rates in the surface ocean layer account for only small fractions of the DIC mass in surface water: at the DIC concentration of about  $2.2 \times 10^{-3}$  mol/kg, annual  $\text{CaCO}_3$  production in a 50-m-thick euphotic zone is a fraction 0.0013 to 0.0023 of the total DIC mass and the net  $\text{CaCO}_3$  storage in sediments is even a smaller fraction.

The calculated rise in atmospheric  $\text{CO}_2$  due to increasing calcite precipitation is shown in Fig. 5. It should be reiterated that in this case the  $\text{CaCO}_3$  amounts that are shown on the  $x$ -axis of Fig. 5 are one-step precipitation without replenishment of carbon and alkalinity lost, and no time length is assigned to each precipitation step. Near the high end, the precipitated amounts of  $0.65$  to  $0.90 \times 10^{-3}$  mol  $\text{CaCO}_3/\text{kg}$  correspond to fractions of 34 to 45% of the DIC content of the surface ocean layer, depending on the temperature, where the  $\text{CaCO}_3$  precipitation reduces the ocean water saturation with respect to calcite to  $\Omega \approx 1.2$ . An increase of 85 ppmv  $\text{CO}_2$ , from 195 ppmv that mimics the Last Glacial Maximum to 280 ppmv at the end of pre-industrial time, could be met by  $\text{CO}_2$  emission from the surface ocean layer  $\sim 100$  m thick where 34 to 45% of DIC was removed as carbonate. A 50-m-thick model layer does not provide enough

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CO<sub>2</sub>, adding not more than 45 ppmv CO<sub>2</sub> or about one-half of the CO<sub>2</sub> rise from the LGM to pre-industrial time. An increase of 85 ppmv over a period of 18 ka translates into a mean increase rate of  $0.84 \times 10^{12}$  mol C/yr or 0.01 Gt C/yr, although the increase has been neither steady nor linear with time (Petit et al., 1999). This mean flux amounts to only about 1/50 to 1/10 of the other major interreservoir fluxes in the carbon cycle, including the calculated ocean-to-atmosphere fluxes (Tables 3, 4, Fig. 6). The land organic reservoir contained more than 1000 Gt C at the LGM and 3000 Gt C at preindustrial time, and the atmosphere and surface ocean contain each hundreds of Gt C; the individual fluxes are 0.1 to 0.6 Gt C/yr and the imbalances between the inputs and outflows in these reservoirs are between 0.12 and 0.35 Gt C/yr. With the data available at present, it is difficult to estimate the fluxes with such a degree of accuracy at millennial to dekamillennial<sup>1</sup> ( $10^3$  to  $10^4$  years) time scales that would give a reliable net rate of change in the atmosphere of the order of 0.01 Gt C/yr or  $0.84 \times 10^{12}$  mol C/yr. Although we demonstrate in Sect. 5 that the imbalances of the pre-industrial atmosphere and land organic reservoir may be reduced to  $\pm 0.02$  to  $\pm 0.04$  Gt C/yr ( $2$  to  $3.5 \times 10^{12}$  mol C/yr), we consider these values as tentative because of the uncertainties in the flux estimates both in pre-industrial and Last Glacial times. The magnitude of the differences between the fluxes mentioned above suggests that other powerful mechanisms of CO<sub>2</sub> removal from the atmosphere, such as uptake by the land reservoirs and CO<sub>2</sub> consumption in crustal rock weathering, must operate in the global carbon cycle at these time scales to prevent rapid and strong increases of atmospheric CO<sub>2</sub> from the oceanic source. However, our results also indicate that relatively small changes in the rate of CaCO<sub>3</sub> production in the ocean may have strong transient effects on the balance of atmospheric CO<sub>2</sub>.

<sup>1</sup>A compound from Greek ΔΕΚΑ for 10 (Smith, 1964) and millennial for 1000.

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## 4. CO<sub>2</sub> fluxes in pre-industrial and LGM times

Estimation of the CO<sub>2</sub> fluxes under the different conditions of the LGM and pre-industrial time is important to the understanding of the ocean-atmosphere CO<sub>2</sub> transfer within the global carbon cycle on centurial to dekamillennial (10<sup>2</sup> to 10<sup>4</sup> years) time scales. The departures of the global cycle from an idealized balanced state are controlled by the major fluxes between the atmosphere, land organic reservoir, crustal and carbonate rocks, and the oceanic system. We evaluate the CO<sub>2</sub> emissions from the surface ocean at the end of pre-industrial time and near the LGM from an open-system model of a surface layer that receives inputs of inorganic and organic carbon, and loses CaCO<sub>3</sub> and organic carbon by net storage in sediments (Sects. 2.3, 2.6). The basic data that we use to calculate the CO<sub>2</sub> fluxes are given in Table 3 and their sources and derivation are discussed below. A diagram of the global carbon cycle for Last Glacial Maximum and pre-industrial times is shown in Fig. 6.

### 4.1. Pre-industrial system

#### 4.1.1. Inorganic carbon in rivers

The pre-industrial inorganic carbon import by rivers to the ocean is based on the mean HCO<sub>3</sub><sup>-</sup> concentration in river water of 52 mg/kg or 0.852×10<sup>-3</sup> mol/kg (Drever, 1988, with references to earlier estimates) and riverine inflow of 3.74×10<sup>16</sup> kg/yr (Baumgartner and Reichel, 1975; Meybeck, 1979, 1984; Gleick, 1993), giving a rounded input of 32×10<sup>12</sup> mol C/yr. This is currently the best-known estimate of inorganic carbon input from land to the ocean in pre-industrial or pre-pollution time that we are aware of. The mean DIC concentration in rivers, based on the bicarbonate-ion concentration of [HCO<sub>3</sub><sup>-</sup>] = 0.852×10<sup>-3</sup> mol/kg, would of course be slightly higher, depending on the river water pH or internal P<sub>CO<sub>2</sub></sub> that are not as well documented as world average dissolved solid concentrations. For an average world river of composition as given by Meybeck (1979; Drever, 1988), a mean DIC concentration may be calculated

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as  $0.9$  to  $1.3 \times 10^{-3}$  mol C/kg. This estimate is based on a river-water internal  $P_{\text{CO}_2}$  range of 1,000 to 10,000 ppmv, approximated for the major world rivers by Garrels and Mackenzie (1971) and supported by numerous later studies showing river internal  $P_{\text{CO}_2}$  considerably higher than atmospheric. From the mean  $\text{HCO}_3^-$  concentration, internal  $P_{\text{CO}_2}$ , and the ionic strength based on dissolved ionic constituent concentrations (total 89 mg/kg; total dissolved solids are 100 mg/kg if  $\text{SiO}_2$  is included; Drever, 1988), at  $15^\circ\text{C}$ , the average river pH is between 6.7 and 7.7, giving the above calculated DIC concentration. A pH = 7.7 was given by Millero (2001) for an average world river from an older database. A range of the pH values in individual rivers of varying length, flow volume, and lithology of the drainage basins is exemplified by the major rivers and their tributaries in Northwestern Canada, the Amazon, Niger, Congo, and Mount Cameroon rivers that have pH values from 6.0 to 7.24 (Wu, 2004<sup>2</sup>), and seven major rivers originating in China and Southern Siberia, where the pH values of the headwaters are mostly above 8, ranging from 7.84 to 8.62 (Huh, 2004<sup>3</sup>). In view of the uncertainties in the DIC concentration, we use the riverine input of inorganic carbon as that of the bicarbonate ion,  $\text{HCO}_3^-$ .

#### 4.1.2. Other fluxes

The pre-industrial uptake rate of atmospheric or soil  $\text{CO}_2$  by silicate and carbonate mineral weathering has been estimated by a number of investigators as about 67% of the inorganic carbon transported by rivers (Mackenzie, 1992, with references to earlier results; Berner and Berner, 1996), giving  $21 \times 10^{12}$  mol C/yr, as shown in Fig. 6. Pre-industrial contribution of silicates to riverine  $\text{HCO}_3^-$  is about 37% and carbonates contribute about 61%. This translates into an atmospheric  $\text{CO}_2$  demand in weathering of  $(37+61/2) = 67\%$  and the remaining 33% comes from the  $\text{CO}_3^{2-}$  in carbonate rocks. A lower estimate of the mean  $\text{HCO}_3^-$  fraction as coming from the weathering of silicates,

<sup>2</sup>Wu, personal communication, 2004.

<sup>3</sup>Huh, personal communication, 2004.

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26%, was given by Gaillardet et al. (1999).

The CO<sub>2</sub> biological storage rate on land is the difference between net primary production and return of CO<sub>2</sub> from remineralization of soil organic matter (humus) to the atmosphere. For pre-industrial time, this is the difference between NPP of  $5,250 \times 10^{12}$  and volatilization of  $5,200 \times 10^{12}$  mol C/yr, giving a net storage rate on land of  $50 \times 10^{12}$  mol/yr. Organic carbon in rivers includes reactive organic carbon (DOC,  $18 \times 10^{12}$  mol/yr, and reactive POC,  $8 \times 10^{12}$  mol/yr) and refractory POC,  $8 \times 10^{12}$  mol/yr, that is transported to the sediments and represents a drain on atmospheric CO<sub>2</sub> (Sect. 2.1; Ver et al., 1999; Mackenzie et al., 2001).

The CaCO<sub>3</sub> net sediment storage rate of  $32.1 \times 10^{12}$  mol/yr (Milliman, 1993; Mackenzie et al., 2004) is the difference between CaCO<sub>3</sub> production in the surface ocean ( $53$  to  $94 \times 10^{12}$  mol/yr) and dissolution in the water column and sediments (Figs. 1, 6). The net organic carbon storage rate of  $8.3 \times 10^{12}$  mol/yr is the difference between net primary production and remineralization in the water column and surface sediments.

CO<sub>2</sub> input to the atmosphere from volcanic emissions and deep metamorphism of limestones,  $\lesssim 10 \times 10^{12}$  mol/yr, is near the upper limit of the range of estimates from 1 to about  $10 \times 10^{12}$  mol/yr (Des Marais, 1985; Mackenzie, 1992, with earlier data; Mackenzie et al., 1993).

#### 4.1.3. LGM system

The lower global mean temperature and a smaller land area at the Last Glacial Maximum were likely to affect at least some of the major carbon fluxes. The estimates of the LGM fluxes that are given below are approximations to global average conditions.

The CaCO<sub>3</sub> net storage rate at Last Glacial time was given by Milliman (1993) as between  $18$  and  $32 \times 10^{12}$  mol/yr (Table 3, Fig. 6). Primary production and net storage rate of organic carbon in oceanic sediments at and near the LGM have been estimated by a number of investigators as mostly higher than in pre-industrial and industrial times. From the C<sub>org</sub> accumulation rates that are based on the C<sub>org</sub> content of sediment cores

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at individual locations in the Equatorial Atlantic and Pacific and in the continental margins of the Atlantic, Pacific, and Indian Oceans, the LGM storage rates of  $C_{\text{org}}$  are between 0.5 to about 4 times the present storage rate (Rich, 1998; Ganersham et al., 1995; Holmes et al., 1997; Lyle et al., 1992; McCorkle et al., 1994; Pedersen, 1983; Verardo and McIntyre, 1994). A global estimate of  $C_{\text{org}}$  storage in oceanic sediments as 1.3 to 5 times higher than that at present has been given by Sarnheim et al. (1988). Because of the wide range of these estimates, we use two rates: the lower rate of  $6.5 \times 10^{12}$  mol/yr, for internal consistency of the scaled-down LGM fluxes, as explained below, and a higher rate of  $18 \times 10^{12}$  mol/yr that is more than double the pre-industrial rate (Table 3).

Ice-free continental area at present is  $132.8 \times 10^6$  km<sup>2</sup> and about  $16 \times 10^6$  km<sup>2</sup> is ice-covered land surface. At the LGM, the sealevel was 120 m below the present, exposing about 60% of the continental shelf area of  $29 \times 10^6$  km<sup>2</sup> and making the total land area  $165.6 \times 10^6$  km<sup>2</sup>. Of this surface,  $44 \times 10^6$  km<sup>2</sup> (Crowley, 1995) or  $40.8 \times 10^6$  km<sup>2</sup> (Emiliani, 1992) have been estimated as ice covered. Thus the land area factor for LGM time is:

$$f_L = \frac{121.6 \text{ km}^2}{132.8 \text{ km}^2} = 0.916. \quad (19)$$

River flow is a function of atmospheric precipitation and its dependence on temperature, as derived by Berner et al. (1983), indicates a decrease in water discharge with a decrease in temperature from some reference temperature  $T_0$ . For a temperature decrease of about 6°C, the present-day river flow decreases by the factor  $f_{\text{TR}}$ :

$$f_{\text{TR}} = 1 + 0.038 \times (T - T_0) = 1 + 0.038 \times (-6) = 0.772, \quad (20)$$

where  $T_0$  is the initial temperature (we take it as 15°C at pre-industrial time) and  $T$  is the LGM temperature of 9°C. For this temperature decrease, river flow decreases 23%.

The rate of atmospheric CO<sub>2</sub> consumption by weathering of crustal silicate rocks,  $21 \times 10^{12}$  mol/yr in pre-industrial time (Sect. 4.1.2), might have been lower at the LGM



because of the smaller land area and lower temperature. Temperature dependence of the weathering rate can be modeled as an Arrhenius-type reaction-rate relationship (Berner, 1994):

$$\ln f_{\text{TW}} = \frac{\Delta E}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) = \frac{15}{1.987 \times 10^{-3}} \left( \frac{1}{288} - \frac{1}{282} \right) = -0.557, \quad (21)$$

5 where  $f_{\text{TW}}$  is the temperature of weathering factor,  $R = 1.987 \times 10^{-3}$  kcal mol<sup>-1</sup> K<sup>-1</sup> is the gas constant,  $T_0$  (K) is the pre-industrial temperature and  $T$  is that at LGM time.  $\Delta E$  is activation energy of weathering reactions, taken at a representative value of 15 kcal/mol for silicate weathering at Earth surface temperatures (Brady, 1991; Berner, 1994; Lasaga, 1998). The weathering temperature factor for a 6°C temperature decrease is from the preceding:

$$f_{\text{TW}} = 0.573. \quad (22)$$

It should be noted that at the small temperature change of 6K, in a range of  $\Delta E = 15 \pm 5$  kcal/mol, the reaction rate factor  $f_{\text{TW}}$  changes by about  $\mp 19\%$  of its mean value 0.573, as given above. Lasaga (1998) discussed the strong effect of activation energy on geochemical reaction rates at different temperatures.

Biological processes, such as primary production and decomposition of organic matter in soils and sediments are also temperature dependent. This dependence is often described by an empirical  $Q_{10}$  factor that relates a change in the process rate to a temperature change of 10K. A value of  $Q_{10} = 2$  indicates that the process rate would be doubled for a 10°C temperature rise and halved for a 10°C decline. This value of  $Q_{10} = 2$  is consistent with the atmospheric CO<sub>2</sub> rise in industrial time, since the year 1700, and its projection into the 21st century (Ver et al., 1999; Mackenzie et al., 2001). The factor  $f_{\text{TB}}$  that relates the rate of a biologically-mediated process to temperature is:

$$f_{\text{TB}} = Q_{10}^{(T-T_0)/10} = 2^{(T-T_0)/10}. \quad (23)$$

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For a temperature decrease of 6°C, the factor is:

$$f_{TB} = 2^{-0.6} = 0.66. \quad (24)$$

The LGM parameters given in Table 3 were calculated with the use of the factors  $f_j$  as shown below. River flow, corrected for land area and temperature decrease by  $f_L$  from Eq. (19) and  $f_{TR}$  from Eq. (20), is:

$$\text{River flow} = 3.74 \times 10^{16} \times f_L \times f_{TR} = 2.64 \times 10^{16} \text{ kg/yr.}$$

Weathering uptake of CO<sub>2</sub>, taking into account land-area reduction and temperature effect  $f_{TW}$  from Eq. (22), is:

$$\text{Weathering rate} = 21 \times 10^{12} \times f_L \times f_{TW} = 11 \times 10^{12} \text{ mol/yr.}$$

Net land storage of CO<sub>2</sub> is affected by the reduced land area and biological temperature factor  $f_{TB}$  from Eq. (23):

$$\text{CO}_2 \text{ land storage} = 50 \times 10^{12} \times f_L \times f_{TB} = 30 \times 10^{12} \text{ mol/yr.}$$

Riverine transport of inorganic carbon to the ocean, taken as dissolved HCO<sub>3</sub><sup>-</sup>, is affected by the reduced runoff:

$$C_{\text{inorg}} \text{ input} = 32 \times 10^{12} \times f_L \times f_{TR} = 22.6 \times 10^{12} \text{ mol/yr.}$$

The preceding estimate might be lower if the relationships between the weathering rates of carbonate and silicate rocks, and CO<sub>2</sub> concentrations in the atmosphere and soil pore space, where CO<sub>2</sub> forms from decomposition of organic matter, were better known at the time scales of 10<sup>2</sup> to 10<sup>4</sup> years. It should be noted that the CO<sub>2</sub> source in weathering considered so far is the atmosphere, without a possible contribution from remineralization of soil humus. We shall address this issue in Sect. 5. Here, we use the value of 23 × 10<sup>12</sup> mol/yr derived above. If the silicate and carbonate mineral fractions in the weathering of the lithosphere were the same in Last Glacial time then the estimate of 11 × 10<sup>12</sup> mol/yr for CO<sub>2</sub> consumption in weathering, given above, would represent

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0.67 of HCO<sub>3</sub><sup>-</sup> in rivers, making the total flux from the silicates and carbonates 16×10<sup>12</sup> mol/yr. The difference between the C<sub>inorg</sub> input fluxes to the surface ocean of 23 and 16×10<sup>12</sup> mol/yr has only a small effect on the computed CO<sub>2</sub> emission rate, other conditions being equal: it results in a flux reduction of about 5% at the LGM conditions (from 22 to 21×10<sup>12</sup> mol/yr at 5°C, Table 4) that is a small number when all the other uncertainties are considered, and this flux reduction is primarily due to the fact that the CaCO<sub>3</sub> removal rate from the surface ocean in the model is not a function of the riverine input of inorganic carbon.

Transport of reactive organic carbon by rivers, both of DOC and POC (Sect. 2.1, Table 3), are first-order fluxes that are controlled by the size of the humus reservoir, river flow, and temperature dependence of the humus decomposition rate that produces dissolved organic carbon (Ver et al., 1999; Mackenzie et al., 2001). Particulate organic carbon transport is considered as an erosional process that depends on river flow, although there are indications that DOC and POC concentrations in rivers are somewhat negatively correlated (Meybeck, 1982, 1988). The mass of organic carbon in humus and litter in soils at LGM time was smaller than at present: 8.30×10<sup>16</sup> mol C (Friedlingstein et al., 1995), as compared to 12.95 to 18.50×10<sup>16</sup> mol C at pre-industrial time or at present (Friedlingstein et al., 1995; Ajtay et al., 1979; Ver, 1998). Thus the carbon mass in the soil humus reservoir at the LGM ( $H_{\text{LGM}}$ ) was the following fraction of the pre-industrial reservoir ( $H_{\text{pi}}$ ):

$$\frac{H_{\text{LGM}}}{H_{\text{pi}}} = \frac{8.30}{12.95 \text{ to } 18.5} = 0.64 \text{ to } 0.45.$$

Consequently, the LGM input of reactive organic carbon to the surface ocean by rivers is:

$$\begin{aligned} \text{Reactive } C_{\text{org}} \text{ input} &= [18 \times 10^{12} \times (H_{\text{LGM}}/H_{\text{pi}}) \times f_{\text{TB}} + 8 \times 10^{12}] \times f_{\text{L}} \times f_{\text{TR}} \\ &= 9.4 \text{ to } 11 \times 10^{12} \text{ mol/yr} \end{aligned}$$

and we use here a mean value of  $10.2 \times 10^{12}$  mol/yr.

Refractory organic carbon transported by rivers does not enter in the calculation of the ocean-atmosphere CO<sub>2</sub> transfer. However, it is part of the organic carbon balance of the land reservoir and its value at the LGM is reduced by the land drainage area and river flow:

$$\text{Refractory } C_{\text{org}} \text{ input} = 8 \times 10^{12} \times f_L \times f_{\text{TR}} = 5.7 \times 10^{12} \text{ mol/yr.}$$

The preceding flux estimates are given in Table 3 and Fig. 6.

#### 4.2. CO<sub>2</sub> fluxes with input from land and CaCO<sub>3</sub> and C<sub>org</sub> formation

The calculated CO<sub>2</sub> emission fluxes from the surface layer with input from land and in situ production of CaCO<sub>3</sub> and C<sub>org</sub> depend on both the temperature and atmospheric CO<sub>2</sub> concentration, as is also the case under the more restricted conditions of no inputs (Table 2). The effect of temperature alone on the CO<sub>2</sub> flux is shown by the values at 25 to 5°C for the pre-industrial conditions in Table 4: at the lower temperature, the flux is about 11% greater. Primary production consuming either only CO<sub>2</sub> or DIC has a somewhat greater effect on the calculated CO<sub>2</sub> flux: it is about 15 to 25% greater if total alkalinity is reduced along with DIC by production and net removal of organic carbon from water.

The CO<sub>2</sub> fluxes computed by the approximation of  $\theta$  in Eq. (10) are compared with the results of the complete method in Table 5. The agreement as a whole is satisfactory for the range of temperatures and atmospheric CO<sub>2</sub> pressures and other parameters that are addressed in this paper, and it provides a much simpler method of estimating the CO<sub>2</sub> flux using the given values of  $\theta$ .

Although this paper deals only with global average CO<sub>2</sub> transfers between a surface ocean layer and atmosphere and it does not address the perturbations of the Industrial Age nor the climatic latitudinal variations over the ocean surface, we may compare our results with the modern CO<sub>2</sub> evasion flux. The equatorial area of the global oceans, between 15°N and 15°S that accounts for 28% of total ocean surface area, emits CO<sub>2</sub>

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to the atmosphere at the rates of  $135 \times 10^{12}$  mol/yr (1.62 Gt C/yr; Tans et al., 1990) to  $89 \times 10^{12}$  mol/yr (1.07 Gt C/yr; Takahashi et al., 2002). At the atmospheric CO<sub>2</sub> concentration of 340 ppmv near the time of those measurements (Sect. 2.5), the CO<sub>2</sub> flux out of the model 50-m-thick surface layer is bracketed between 53 and  $80 \times 10^{12}$  mol/yr (0.64 to 0.97 Gt C/yr); a thicker surface layer would make the flux larger. These bracketing values are derived from Eq. (4), with the riverine DIC and organic carbon inputs to the ocean in the year 1980 increased by 21 to 23% of the pre-industrial values (Table 3; Mackenzie et al., 2001); the lower flux estimate of  $53 \times 10^{12}$  mol/yr is based on the pre-industrial net removal rates of CaCO<sub>3</sub> and biologically produced C<sub>org</sub> in the euphotic zone ( $40.4 \times 10^{12}$  mol/yr, Table 3), and the higher estimate of  $80 \times 10^{12}$  mol/yr is based on the CaCO<sub>3</sub> gross production rate of  $94 \times 10^{12}$  mol/yr.

**5. Implications for the global carbon cycle**

5.1. Pre-industrial reservoir imbalances

The broader features of the carbon cycle represented by the major reservoirs of the three domains – atmosphere, land, and ocean – are shown in Fig. 6. Somewhat different values of the reservoir masses and fluxes in the Holocene carbon cycle are given by Holmen (1992) and Sigman and Boyle (2000). Our results show that for both LGM and pre-industrial times the carbon input and removal rates produce a slight annual decrease in DIC and total alkalinity (A<sub>T</sub>) of the surface ocean layer. The algebraic sum of inputs, removal into net storage, and CO<sub>2</sub> emissions is slightly negative, from Eq. (4) and model results for the LGM fluxes at 5°C (Tables 3–5):

$$\frac{(\text{DIC}_0 + v + w - y - z) - \text{Emissions}}{\text{DIC}_0} - 1 = \frac{41808 + 23 + 10.2 - 18 - (6.56 \text{ to } 18) - (22.1 \text{ to } 20.2)}{41808} - 1 = -3.2 \times 10^{-4} \text{ to } -5.5 \times 10^{-4}. \quad (25)$$

DIC in surface ocean water decreases by 0.032 to 0.055% per year. Total alkalinity also decreases under the different model scenarios:  $A_T$  changes by  $-0.7 \times 10^{-6}$  to  $-2 \times 10^{-6}$  mol-equivalent/kg or by about  $-0.03$  to  $-0.08\%$  of the initial value.

Pre-industrial input of  $Ca^{2+}$  by rivers to the ocean has been estimated as  $12.5 \times 10^{12}$  mol/yr (Meybeck, 1979; Drever, 1988). Net removal of  $Ca^{2+}$  as  $CaCO_3$  from ocean water at the rate of 18 to  $32 \times 10^{12}$  mol/yr (Milliman, 1993) creates an imbalance. Both the decrease in total alkalinity and calcium concentration are in qualitative agreement with the conclusions of Milliman (1993) about a decrease in total alkalinity since the LGM, and of Berner and Berner (1996) concerning a greater removal of  $Ca^{2+}$  in  $CaCO_3$  than its total input to the ocean from rivers, basalt-seawater reactions, and cation exchange (their removal rate of  $23 \times 10^{12}$  mol/yr against input of  $19.5 \times 10^{12}$  mol/yr).

The interreservoir fluxes in the carbon cycle are estimates from many sources based on different time scales (Sects. 4.1, 4.2). Riverine input to the surface ocean, and uptake and release of carbon by the land organic reservoir (phytomass and soil humus) are usually estimated on decadal to centurial ( $10^1$  to  $10^2$  years) time scales. Net removal of  $CaCO_3$  and organic matter to oceanic sediments are processes on millennial to dekamillennial ( $10^3$  to  $10^4$  years) scales. Such geologic fluxes as  $CO_2$  input to the atmosphere by volcanism and deep metamorphism of limestones, and  $CO_2$  consumption in weathering of the crustal silicate rocks and sedimentary silicates and carbonates are estimates for chilimillennial to myrimillennial<sup>4</sup> ( $10^6$  to  $10^7$  years) time scales or even longer. Although on a geologically longer-term time scale the carbon cycle should vary about a secular balance or the atmosphere would be depleted of  $CO_2$ , the net imbalances of the atmosphere, land, and surface ocean in pre-industrial time are significant relative to the reservoir sizes: atmosphere  $-14 \times 10^{12}$  mol/yr, land organic reservoir  $+16 \times 10^{12}$  mol/yr, and surface ocean  $-29 \times 10^{12}$  mol/yr. The land organic reservoir is gaining carbon, and the ocean and atmosphere are losing it in pre-industrial time as well as at the LGM. At both periods, net storage of carbon in oceanic sediments and its

<sup>4</sup>Compounds from Greek ΧΙΛΙΟΙ for 1000 or ΜΥΡΙΑΙΟΙ for 10 000 (Woodhouse, 1910; Smith, 1964) and millennial.

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transfer to the atmosphere exceed the riverine input. The upwelling flux of DIC from the deep ocean, shown in Fig. 6, although not part of our CO<sub>2</sub> release calculation, is based on the DIC concentration difference of  $0.22 \times 10^{-3}$  mol/kg between the deep and surface ocean (Broecker and Peng, 1982), the upwelling velocity of 2.2 m/yr (Munk, 1966; Broecker, 1974; Stumm and Morgan, 1981; Albarède, 1995), the ocean surface area of  $3.6 \times 10^{14}$  m<sup>2</sup>, and mean ocean water density of 1027 kg/m<sup>3</sup>. This flux of  $179 \times 10^{12}$  mol/yr is very large in comparison to most of the other fluxes in the cycle.

The large imbalances of the individual reservoirs relative to their sizes are reflected in the instantaneous residence times of carbon in the atmosphere, land organic reservoir, and surface ocean that are measurable mostly in thousands of years (Table 6). However, more significant are the material imbalances of the individual reservoirs that translate into millennial time scales to “complete depletion”, as for the atmosphere and surface ocean, and a dekamillennial time scale for the doubling of the carbon content of the land organic reservoir.

## 5.2. Alternative pathways

The imbalances at pre-industrial and LGM times that indicate either depletion or doubling of the reservoir size on a scale of  $10^3$  to  $10^4$  years may be reduced if the accuracy of some of the fluxes shown in Fig. 6 is considered. If the net CO<sub>2</sub> storage on land,  $50 \times 10^{12}$  mol/yr in pre-industrial time, were lower by 25 to 33%, making it about  $37$  to  $33 \times 10^{12}$  mol/yr, the atmosphere and land organic reservoir would be close to balance, with the other fluxes unchanged: the imbalance of the atmosphere would be reduced to  $1.5 \pm 3.5 \times 10^{12}$  mol/yr and that of the land organic reservoir to  $1 \pm 2 \times 10^{12}$  mol/yr. Net carbon storage on land is a small difference (Sect. 4.1.2), about 1% of the much larger NPP ( $5250 \times 10^{12}$  mol/yr) and humus decomposition rates ( $5200 \times 10^{12}$  mol/yr), and a reduction of this small difference between them by about 25% to 33% would be well within the range of such estimates. As the pre-industrial carbon masses are  $5 \times 10^{16}$  mol in the atmosphere and 18 to  $26 \times 10^{16}$  mol on land (phytomass and humus), the

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characteristic times for the smaller imbalances lengthen by a factor of 10, to  $10^4$  yr for the atmosphere and  $10^5$  yr for the land (compare Table 6), making the rates of change slower.

Another aspect of the atmospheric imbalance may be the pathway of the weathering flux of  $21 \times 10^{12}$  mol C/yr (Sects. 4.1.2, 4.2, Fig. 6). On the basis of carbon isotopic evidence, Mook and Tan (1991) concluded that the main source of DIC in rivers is “CO<sub>2</sub> derived from the decay of organic matter in continental soils and from the dissolution of carbonate, while in general the contribution of atmospheric CO<sub>2</sub> is negligibly small.” From their data on the present-day  $\delta^{13}\text{C}$  of soil CO<sub>2</sub> (−26‰) and HCO<sub>3</sub><sup>−</sup> in rivers (−12‰), the Phanerozoic sedimentary carbonates (+1.5‰), and fractionation factors between HCO<sub>3</sub><sup>−</sup>(aq) and CO<sub>2</sub>(g), it is possible to estimate the fraction of soil organic matter that contributes to the dissolved HCO<sub>3</sub><sup>−</sup> in rivers. The fractionation of <sup>13</sup>C/<sup>12</sup>C in a gas-solution system makes HCO<sub>3</sub><sup>−</sup>(aq) heavier than CO<sub>2</sub>(g) by 9.6‰ at 5°C and 7.9‰ at 25°C (Mook et al., 1974; Friedman and O’Neil, 1977). The following balance equation gives fraction  $x$  of soil CO<sub>2</sub> in rivers:

$$[-26 + (9.6 \text{ to } 7.9)]x + 1.5(1 - x) = -12; \quad x = 0.69 \text{ to } 0.75. \quad (26)$$

Thus 69 to 75% of HCO<sub>3</sub><sup>−</sup> is derived from soil CO<sub>2</sub> that reacted with the silicates and carbonates and the remaining 31 to 25% from the weathering and dissolution of carbonates. These proportions are similar to other investigators’ values of about 67% for atmospheric CO<sub>2</sub> and 33% for carbonate rocks, as mentioned earlier.

If the CO<sub>2</sub> drawdown in weathering,  $21 \times 10^{12}$  mol C/yr (or a slightly larger value of 22 to  $24 \times 10^{12}$  mol/yr, corresponding to a fraction of 69 to 75% of riverine HCO<sub>3</sub><sup>−</sup>), comes from soil where CO<sub>2</sub> forms by remineralization of organic matter (e.g. Berner and Berner, 1996) rather than directly from the atmosphere, it would have significant consequences to the global carbon balance (Fig. 6). On land, decomposition and erosion of humus remove to rivers  $34 \times 10^{12}$  mol C/yr and rock weathering flux from soil CO<sub>2</sub> consumes 21 to  $24 \times 10^{12}$  mol C/yr, making a total removal of 55 to  $58 \times 10^{12}$  mol/yr against net storage from the atmosphere of  $50 \times 10^{12}$  mol/yr (Fig. 6). In this case the

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outflow from the atmosphere would be only to the land organic reservoir: a net outflow to the land of  $55$  to  $58 \times 10^{12}$  mol/yr against input to the atmosphere of about  $57 \times 10^{12}$  mol/yr ( $45$  to  $49 \times 10^{12}$  from the surface ocean and  $\leq 10 \times 10^{12}$  mol/yr from volcanic and metamorphic emissions) would make the atmosphere and land organic reservoir nearly balanced, within about  $\pm 2 \times 10^{12}$  mol/yr or between  $\pm 0.02$  to  $\pm 0.03$  Gt C/yr.

However, nearly-balanced atmosphere and land organic reservoir would leave the ocean in a negative balance, with nominal depletion times of only a few thousand years for the surface layer (Table 6). An inference that may be drawn from the magnitudes of the interreservoir fluxes, the short residence times, and imbalances that are rooted in the flux estimates is that the atmosphere and surface ocean are closely tied to the land and crustal reservoirs, yet the currently available observational evidence and analytical data-bases do not support a closer balanced cycle on millennial to dekamillennial time scales.

## 6. Conclusions

A general model analysis of  $\text{CO}_2$  evasion from a surface ocean layer was developed to demonstrate quantitatively that the process is strongly dependent on the amount of  $\text{CaCO}_3$  and biologically produced organic carbon that are removed from ocean water, temperature, atmospheric  $\text{CO}_2$  content, thickness of the surface layer, such chemical parameters of the system as the initial DIC concentration and total alkalinity ( $A_T$ ), and inputs of inorganic and organic carbon from land to the surface ocean layer. As anticipated, lower temperature promotes more dissolved  $\text{CO}_2$  formation and greater  $\text{CO}_2$  transfer to the atmosphere because of a higher concentration of uncharged  $\text{CO}_2$  at the expense of the bicarbonate and carbonate ions in seawater at lower temperatures. Other conditions being equal, the effect of a higher atmospheric  $\text{CO}_2$  is that there is more DIC and more dissolved  $\text{CO}_2$  produced for a given amount of precipitated carbonate. In addition, model calculations show that an increase in atmospheric  $\text{CO}_2$  depends on the surface ocean layer thickness: because of the back-pressure of the higher atmo-

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spheric CO<sub>2</sub>, its rise due to CaCO<sub>3</sub> precipitation is non-linear and  $\theta$  decreases slightly with increasing thickness of the emitting surface layer. Because net primary production and organic matter storage also remove DIC from the euphotic zone, these processes counterbalance at least to some extent the CO<sub>2</sub> production by CaCO<sub>3</sub> precipitation.

5 Model calculations also show that a mass of CO<sub>2</sub> equivalent to the atmospheric 85 ppmv rise that is comparable to the increase from 195 ppmv near the LGM to 280 ppmv at the end of pre-industrial time could be met by removal of 34 to 45% of initial DIC as CaCO<sub>3</sub> in a surface ocean layer of thickness ~100 m. Removal of such large fractions of DIC would lower the degree of calcite supersaturation of surface  
10 ocean water to a value of  $\Omega$  close to 1, making it essentially a limit for precipitation without replenishment. However, upwelling from the deep ocean and riverine input replenish alkalinity and calcium in the surface layer. Over a period of 18 ka, the atmospheric rise of 85 ppmv corresponds to a mean increase rate of  $0.84 \times 10^{12}$  mol/yr or 0.01 Gt C/yr. Such a flux is so much smaller than the other major fluxes in the  
15 carbon cycle that it is difficult, with the present data base, to construct a cycle on a millennial to dekamillennial time scale where 0.01 Gt C/yr would be a reliable measure of an imbalance of a reservoir mass.

Several authors (e.g. Berger, 1982; Opdyke and Walker, 1992; Walker and Opdyke, 1995) have proposed that the accumulation of carbonate sediments in coastal zone  
20 environments, reefs, and banks has led to the rise, or part of the rise, in atmospheric CO<sub>2</sub> since the LGM to pre-industrial time. Although the case for the precipitation and accumulation of carbonate in shallow-water sediments and consequent release of CO<sub>2</sub> to the atmosphere during the rise of sea level since the LGM has been largely dismissed because of the fact that the atmospheric CO<sub>2</sub> rise at the end of the penultimate  
25 glaciation, Termination II, about 130 ka b.p., was reported to precede the sea-level rise (Broecker and Henderson, 1998), our results demonstrate that the strength of this flux cannot be ignored. It appears that the oceans contained slightly more carbonate ion during the LGM than in pre-industrial times, leading to an average increase in the depth of the lysocline during the LGM (Broecker, 2002) and its shoaling as sea-level rose to-

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ward the present day. In such a scenario, it is likely that as sea level rose from the LGM to later Holocene time, carbonate accumulation was shifted in part from the deep sea to coastal environments, banks, and reefs drawing down the total alkalinity of the ocean, as proposed by Milliman (1993). This led to shoaling of the lysocline and evasion of CO<sub>2</sub> from seawater to the atmosphere during carbonate precipitation in these environments. Some of this CO<sub>2</sub> accumulated in the atmosphere, accounting for at least part of the rise in atmospheric CO<sub>2</sub> since the LGM. In addition, because the CO<sub>2</sub> flux is sensitive to several environmental parameters mentioned above, relatively small changes in any of these parameters are likely to affect the ocean-to-air CO<sub>2</sub> flux and the balance (or imbalance) of atmospheric CO<sub>2</sub>.

The current state of knowledge of the global carbon cycle in Last Glacial Maximum and pre-industrial times suggests that the atmosphere and surface ocean were losing CO<sub>2</sub> and the land organic reservoir (plants and soil humus) was gaining carbon. The imbalances of the individual reservoirs translate into relatively short times of 10<sup>3</sup> to 10<sup>4</sup> years for either their depletion or doubling of the mass. Some of these relatively large imbalances may be reduced if alternative CO<sub>2</sub> pathways are considered between the atmosphere and land reservoirs that involve CO<sub>2</sub> storage of organic carbon on land and its consumption in weathering.

## 7. Appendix

This Appendix describes the calculations of CO<sub>2</sub> release rates from a surface ocean layer, approximated by a 50-m-thick euphotic zone, under different conditions of temperature, atmospheric CO<sub>2</sub> concentration, total alkalinity (A<sub>T</sub>) and dissolved inorganic carbon (DIC) in ocean water, and different rates of CaCO<sub>3</sub> and organic carbon production and storage in sediments.

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## 7.1. Apparent dissociation constants for the carbonate system

In Table A1 and elsewhere, brackets [ ] denote concentrations of aqueous species in mol/kg,  $P_{\text{CO}_2}$  is partial pressure of CO<sub>2</sub> in the atmosphere (bar), and B<sub>T</sub> is total dissolved boron concentration (mol B/kg).

## 5 7.2. Basic equations

Dissolved inorganic carbon (DIC):

$$\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (\text{mol C/kg}) \quad (\text{A1})$$

$$= [\text{CO}_2] \left( 1 + \frac{K'_1}{[\text{H}^+]} + \frac{K'_1 K'_2}{[\text{H}^+]^2} \right) \quad (\text{A2})$$

$$= P_{\text{CO}_2} K'_0 \left( 1 + \frac{K'_1}{[\text{H}^+]} + \frac{K'_1 K'_2}{[\text{H}^+]^2} \right), \quad (\text{A3})$$

10 where  $K'_i$  are apparent dissociation constants given in Table A1 and other parameters as defined above.

Total alkalinity is the sum of three terms, carbonate alkalinity (A<sub>C</sub>), borate alkalinity (A<sub>B</sub>), and water alkalinity (A<sub>W</sub>):

$$A_T = A_C + A_B + A_W \quad (\text{mol-equivalent/kg}). \quad (\text{A4})$$

15 Total alkalinity, A<sub>T</sub>, as a function of DIC and H<sup>+</sup>-ion concentration is:

$$A_T = \frac{\text{DIC} \cdot (1 + 2K'_2/[\text{H}^+])}{(1 + [\text{H}^+]/K'_1 + K'_2/[\text{H}^+])} + \frac{B_T}{1 + [\text{H}^+]/K'_B} + \frac{K'_W}{[\text{H}^+]} - [\text{H}^+]. \quad (\text{A5})$$

In terms of dissolved  $[\text{CO}_2]$  or  $P_{\text{CO}_2}$  and  $[\text{H}^+]$ , total alkalinity is defined as:

$$A_T = \frac{[\text{CO}_2]K_1'}{[\text{H}^+]} \cdot (1 + 2K_2'/[\text{H}^+]) + \frac{B_T}{1 + [\text{H}^+]/K_B'} + \frac{K_W'}{[\text{H}^+]} - [\text{H}^+] \quad (\text{A6})$$

$$= \frac{P_{\text{CO}_2}K_0'K_1'}{[\text{H}^+]} \cdot (1 + 2K_2'/[\text{H}^+]) + \frac{B_T}{1 + [\text{H}^+]/K_B'} + \frac{K_W'}{[\text{H}^+]} - [\text{H}^+]. \quad (\text{A7})$$

Carbonate alkalinity of ocean water is not conserved in the process of  $\text{CaCO}_3$  precipitation and subsequent reequilibration with the atmosphere.  $A_C$  is defined as a function of atmospheric  $\text{CO}_2$  partial pressure or DIC as follows:

$$[A_C] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (\text{mol-equivalent/kg}) \quad (\text{A8})$$

$$= \frac{P_{\text{CO}_2}K_0'K_1'}{[\text{H}^+]} \left( 1 + \frac{2K_2'}{[\text{H}^+]} \right) \quad (\text{A9})$$

$$= \frac{(\text{DIC}_0 - y)}{(1 + 2K_2'/[\text{H}^+])} \left( 1 + \frac{[\text{H}^+]}{K_1'} + \frac{K_2'}{[\text{H}^+]} \right). \quad (\text{A10})$$

In Eq. (A10),  $y$  is the precipitated calcite, mol  $\text{CaCO}_3/\text{kg}$ , also as shown in Eqs. (A14)–(A19).

The degree of saturation of ocean water with respect to calcite:

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K'_{\text{cal}}}. \quad (\text{A11})$$

In  $\text{CO}_2$  production and release calculation,  $\Omega$  provides a check that the amount of  $\text{CaCO}_3$  precipitated in the model is not so large as to make ocean water undersaturated and  $\Omega$  smaller than 1.

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### 7.3. Calculation of $[H^+]$ from total alkalinity ( $A_T$ ) and DIC or $P_{CO_2}$

#### 7.3.1. $A_T$ and DIC

From known values of  $A_T$  and DIC, the  $H^+$ -ion concentration or the pH can be computed from (A5) as a root of the 5th-degree polynomial:

$$5 \quad a_5[H^+]^5 + a_4[H^+]^4 + a_3[H^+]^3 + a_2[H^+]^2 + a_1[H^+] + a_0 = 0. \quad (A12)$$

The coefficients  $a_i$  are algebraic expressions that include the individual apparent dissociation constants  $K'_i$ , DIC, and  $A_T$ . These are given below (Bacastow and Keeling, 1973; Zeebe and Wolf-Gladrow, 2001):

$$a_5 = 1.00$$

$$10 \quad a_4 = A_T + K'_1 + K'_B$$

$$a_3 = A_T(K'_1 + K'_B) + K'_1(K'_B + K'_2) - DIC - B_T K'_B - K_w$$

$$a_2 = A_T K'_1(K'_B + K'_2) - DIC \cdot K'_1(K'_B + 2K'_2) - B_T K'_B K'_1 - K'_w(K'_1 + K'_B) + K'_1 K'_2 K'_B$$

$$a_1 = K'_1 K'_2 K'_B (A_T - 2 \cdot DIC - B_T) - K'_w K'_1 (K'_B + K'_2)$$

$$a_0 = -K'_w K'_1 K'_2 K'_B.$$

15 The roots of the polynomial include a real positive root that is the value of  $[H^+]$  sought. Solutions of the equation can be obtained by a number of numerical techniques, such as FORTRAN 77 (Press et al., 1992) or software MAPLE, made by Waterloo Maple, Inc., of Waterloo, Ontario, Canada.

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### 7.3.2. $A_T$ and $[CO_2]$ or $P_{CO_2}$

When total alkalinity and either dissolved  $CO_2$  concentration or the partial pressure of atmospheric  $CO_2$  at equilibrium with ocean water are known ( $A_T$  and  $[CO_2]$  or  $P_{CO_2}$ ), then  $[H^+]$  is a root of the 4th-degree polynomial in Eqs. (A6) or (A7):

$$a_4[H^+]^4 + a_3[H^+]^3 + a_2[H^+]^2 + a_1[H^+] + a_0 = 0 \quad (A13)$$

the coefficients  $a_i$  of which are:

$$a_4 = 1.00$$

$$a_3 = A_T + K'_B$$

$$a_2 = K'_B(A_T - B_T) - [CO_2]K'_1 - K'_w$$

$$a_1 = -[CO_2]K'_1(K'_B + 2K'_2) + K'_w K'_B$$

$$a_0 = -2[CO_2]K'_1 K'_2 K'_B$$

### 7.4. Calculation of $\theta$

Starting with an initial DIC concentration and total alkalinity ( $A_T$ ), removal of  $y$  mol  $CaCO_3/kg$  results in the following new concentrations:

$$DIC = DIC_0 - y \quad (A14)$$

$$[Ca^{2+}] = [Ca^{2+}]_0 - y \quad (A15)$$

$$A_T = A_{T,0} - 2y. \quad (A16)$$

$\Delta[DIC]$  is the difference between the DIC concentration remaining after the carbonate deposition,  $[DIC_{0-y}]$ , and the DIC value after ocean water reequilibrated with atmospheric  $CO_2$ ,  $[DIC]_{eq}$ :

$$\Delta[DIC] = [DIC_{0-y}] - [DIC]_{eq} \quad (\text{mol/kg}). \quad (A17)$$

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The DIC concentration at equilibrium with atmospheric CO<sub>2</sub> (DIC<sub>eq</sub>) is smaller than DIC after carbonate precipitation (DIC<sub>0-y</sub>). This difference is the mass of inorganic carbon transferred to the atmosphere as CO<sub>2</sub>. Parameter  $\theta$  is the loss of DIC as CO<sub>2</sub> from surface ocean water per mol of CaCO<sub>3</sub> removed from ocean water by precipitation and storage in sediment:

$$\theta = \frac{\Delta[\text{DIC}]}{y} \quad (\text{mol/mol}) \quad (\text{A18})$$

$$= \frac{(1-f)[\text{DIC}_0] - [\text{DIC}]_{\text{eq}}}{f[\text{DIC}_0]}, \quad (\text{A19})$$

where  $y$  mol CaCO<sub>3</sub>/kg removed from ocean water is also fraction  $f$  of the initial DIC concentration.

From this point on, calculation of the DIC lost to the atmosphere, Eq. (A17), and parameter  $\theta$ , Eq. (A18), differs in a case of CO<sub>2</sub> emission to the atmosphere of constant  $P_{\text{CO}_2}$  and emission that increases  $P_{\text{CO}_2}$  of the atmosphere.

#### 7.4.1. CO<sub>2</sub> emission to an atmosphere of constant $P_{\text{CO}_2}$

At a constant atmospheric  $P_{\text{CO}_2}$ , dissolved CO<sub>2</sub> concentration is also constant and changes in DIC due to CO<sub>2</sub> transfer from ocean water to the atmosphere do not affect the total alkalinity value after the carbonate precipitation, A<sub>T</sub> in Eq. (A16). The value of [H<sup>+</sup>] is obtained from Eq. (A13) using the latter value of A<sub>T</sub> and [CO<sub>2</sub>] that corresponds to the constant  $P_{\text{CO}_2}$ . With the new value of [H<sup>+</sup>], [DIC]<sub>eq</sub> is computed from Eqs. (A2) or (A3), and the DIC mass transferred to the atmosphere is obtained from Eq. (A17), followed by  $\theta$  from Eq. (A18). In this model, the emitted CO<sub>2</sub> is not added to the atmospheric CO<sub>2</sub> mass that remains constant.



#### 7.4.2. CO<sub>2</sub> emission that increases atmospheric $P_{\text{CO}_2}$

An increase in atmospheric  $P_{\text{CO}_2}$  by CO<sub>2</sub> emission from surface ocean water depends not only on the environmental parameters and carbonate mass precipitated, as in the case of a constant atmospheric  $P_{\text{CO}_2}$ , but also on the volume or mass of the surface water layer from which the transfer occurs. As explained in Sect. 2.1, the mass of surface ocean layer is approximated by a euphotic zone, 50 m thick, of mass  $M_w = 1.854 \times 10^{19}$  kg, that can release CO<sub>2</sub> to the atmosphere. Initially, the surface water layer contains a DIC mass of  $4.06 \times 10^{16}$  mol C and the atmosphere, at 195 ppmv CO<sub>2</sub>, contains  $3.49 \times 10^{16}$  mol C. Precipitation of DIC fractions (0.1 to 45%) as calcite produces CO<sub>2</sub> that migrates to the atmosphere, increasing its CO<sub>2</sub> content. Because neither the CO<sub>2</sub> partial pressure nor the ocean water DIC is known after the carbonate precipitated and ocean water reequilibrated with the new CO<sub>2</sub> partial pressure in the atmosphere, the calculation of the DIC transfer and increase in atmospheric CO<sub>2</sub> is done by an iterative routine.

First, precipitation of CaCO<sub>3</sub> takes place in a closed system where DIC, [Ca<sup>2+</sup>] and total alkalinity decrease, as given in Eqs. (A17)–(A19). Dissolved CO<sub>2</sub> and [H<sup>+</sup>] concentrations in this closed system increase strongly: [H<sup>+</sup>] is obtained from the values of  $A_{\text{T},0} - 2y$  and  $\text{DIC}_0 - y$  that are used in Eqs. (A5) and (A12), and [CO<sub>2</sub>] is computed from Eq. (A2) using [H<sup>+</sup>] and  $\text{DIC}_0 - y$ . These are the [H<sup>+</sup>] and [CO<sub>2</sub>] concentrations in a closed system at the end of carbonate precipitation step.

In the next step, the ocean-water volume is opened to the atmosphere and the CO<sub>2</sub> mass transferred from water to the atmosphere ( $x$  moles) is approximated by the equilibrium partition between the dissolved CO<sub>2</sub> mass at the end of the precipitation stage and the atmospheric mass:

$$\frac{n_w - x}{n_a^0 + x} = \frac{K'_0 RT M_w}{V}, \quad (\text{A20})$$

where  $n_w$  is the mass of dissolved CO<sub>2</sub> in the closed system after the precipitation of

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CaCO<sub>3</sub> ( $n_w = [\text{CO}_2] \times M_w$ ) and  $n_a^0 = 3.487 \times 10^{16}$  mol is the atmospheric CO<sub>2</sub> mass at 195 ppmv CO<sub>2</sub>. Other parameters in Eq. (A20) are:  $K'_0$  is the CO<sub>2</sub> solubility coefficient (Table A1), the gas constant  $R = 8.315 \times 10^{-5}$  bar m<sup>3</sup> K<sup>-1</sup> mol<sup>-1</sup>, atmospheric temperature  $T = 288.15$  K, atmospheric volume  $V = 4.284 \times 10^{18}$  m<sup>3</sup> (thickness 8,400 m over the Earth surface area of  $5.1 \times 10^{14}$  m<sup>2</sup>), and  $M_w$  is the water mass of a 50-m-thick euphotic zone, as mentioned above. Eq. (A20) follows from the CO<sub>2</sub> solubility relationship (Table A1, 1)

$$K'_0 = \frac{[\text{CO}_2]}{P_{\text{CO}_2}} \quad (\text{mol C kg}^{-1} \text{ bar}^{-1}), \quad (\text{A21})$$

where the terms  $[\text{CO}_2]$  and  $P_{\text{CO}_2}$ , taking into account the transfer of  $x$  moles carbon from the ocean to the atmosphere, can be written as:

$$[\text{CO}_2] = \frac{n_w - x}{M_w} \quad (\text{mol C/kg}) \quad (\text{A22})$$

and

$$P_{\text{CO}_2} = \frac{(n_a^0 + x)RT}{V} \quad (\text{bar}). \quad (\text{A23})$$

In the next step, using  $x$  from Eq. (A20), new  $[\text{CO}_2]$  from Eq. (A22) is computed. From this  $[\text{CO}_2]$  and  $A_{T,0} - 2y$  are computed a new  $[\text{H}^+]$  from Eqs. (A6) and (A13), and DIC from Eq. (A2). The loss of DIC (mol) in the water layer, Eq. (A16), is added to the initial atmospheric CO<sub>2</sub> content ( $3.487 \times 10^{16}$  mol at 195 ppmv), and the new  $P_{\text{CO}_2}$  is used to obtain another  $[\text{CO}_2]$  from Eq. (A21). This step gives too much DIC transferred to the atmosphere and it is corrected through subsequent iterative solutions. The last  $[\text{CO}_2]$  value and  $A_{T,0} - 2y$  are used again to calculate  $[\text{H}^+]$  from Eqs. (A6) and (A13) and another incremental loss of DIC, which is added to the atmosphere. Three or four iterations produce stable values of DIC loss that converge within  $\leq 0.1\%$ . The initial data, intermediate results, and final values for a case of CO<sub>2</sub> rise from 195 ppmv at 25°C are shown in Table A2 and the values of  $\theta$  are plotted in Fig. 4a.

## 7.5. CO<sub>2</sub> emission in an open system

CO<sub>2</sub> emission from a surface ocean layer receiving input of inorganic ( $v$ ) and organic ( $w$ ) carbon from land is discussed in Sect. 2.3, Eqs. (4)–(6):

$$\text{DIC} = \text{DIC}_0 + v + w - y - z \quad (\text{A24})$$

$$A_T = A_{T,0} + v - 2y - z. \quad (\text{A25})$$

The solution of these equations for the amounts of DIC lost to the atmosphere due to carbonate ( $y$ ) and organic matter ( $z$ ) sequestration from ocean water follows the iterative method described in the preceding section: at first,  $[\text{H}^+]$  and  $[\text{CO}_2]$  concentrations are computed for a closed system; then the first-approximation mass of CO<sub>2</sub> transferred to the atmosphere,  $x$  in Eq. (A20), is computed, followed by the new values of  $[\text{H}^+]$  and DIC. The final DIC loss from the surface ocean layer of mass  $M_w$  is calculated by successive iterations. The main computational steps are shown in Table A3.

The calculation in Table A3 is done for the LGM conditions, at 5°C and initial atmospheric CO<sub>2</sub> concentration of 195 ppmv (Tables 3, 4), for a surface ocean layer 50,m thick, of mass  $M_w = 1.854 \times 10^{19}$  kg. The initial and input parameters are given below.

Input of inorganic carbon:

$$v = (23 \times 10^{12} \text{ mol HCO}_3^- / \text{yr}) / (1.854 \times 10^{19} \text{ kg}) = 1.241 \times 10^{-6} \text{ mol kg}^{-1} \text{ yr}^{-1}.$$

Input of organic carbon:

$$w = (10.4 \times 10^{12} \text{ mol C}_{\text{org}} / \text{yr}) / (1.854 \times 10^{19} \text{ kg}) = 5.502 \times 10^{-7} \text{ mol kg}^{-1} \text{ yr}^{-1}.$$

CaCO<sub>3</sub> net removal to sediments:

$$y = (18 \times 10^{12} \text{ mol CaCO}_3 / \text{yr}) / (1.854 \times 10^{19} \text{ kg}) = 9.710 \times 10^{-7} \text{ mol kg}^{-1} \text{ yr}^{-1}.$$

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Organic carbon net removal rate to sediments:

$$z = (18 \times 10^{12} \text{ mol C}_{\text{org}}/\text{yr}) / (1.854 \times 10^{19} \text{ kg}) = 9.710 \times 10^{-7} \text{ mol kg}^{-1} \text{ yr}^{-1}.$$

The final result shown in Table A3, CO<sub>2</sub> emission rate of  $20.2 \times 10^{12}$  mol/yr, is also given in Table 5.

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**Table 1.** Initial conditions of atmospheric  $P_{\text{CO}_2}$ , water temperature, total alkalinity ( $A_T$ ), pH, and dissolved inorganic carbon (DIC) used in CO<sub>2</sub> release calculations.

CO <sub>2</sub>	195 ppmv			280 ppmv			375 ppmv		
	5°C	15°C	25°C	5°C	15°C	25°C	5°C	15°C	25°C
Temperature	5°C	15°C	25°C	5°C	15°C	25°C	5°C	15°C	25°C
$A_T$ (10 <sup>-3</sup> mol/kg)	2.582	2.613	2.808	2.582	2.613	2.808	2.582	2.613	2.808
pH	8.35	8.35	8.35	8.22	8.23	8.23	8.11	8.12	8.14
DIC (10 <sup>-3</sup> mol/kg)	2.255	2.164	2.190	2.332	2.253	2.293	2.388	2.319	2.373

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**Table 2.** Factor  $\theta$  defining CO<sub>2</sub> release to the atmosphere as a function of CaCO<sub>3</sub> and C<sub>org</sub> formation in a surface ocean layer at different temperatures and atmospheric CO<sub>2</sub> concentrations, and surface layer thickness for rising CO<sub>2</sub> due to carbonate formation. Figures 2 and 4. The range of  $\theta$  within each cell is for increasing amounts of precipitated CaCO<sub>3</sub>, from  $\leq 0.1$  to up to 45% of initial DIC concentration.

CO <sub>2</sub> release process	Temperature		
	5°C	15°C	25°C
$\theta$ for CaCO <sub>3</sub> formation at constant atmospheric CO <sub>2</sub>			
$P_{\text{CO}_2} = 195$ ppmv	0.64-0.69	0.54-0.60	0.44-0.51
$P_{\text{CO}_2} = 280$ ppmv	0.70-0.74	0.61-0.66	0.51-0.57
$P_{\text{CO}_2} = 375$ ppmv	0.75-0.79	0.66-0.71	0.56-0.63
$\theta$ for CaCO <sub>3</sub> formation and rising atmospheric CO <sub>2</sub>			
50 m layer	0.57-0.65	0.48-0.56	0.38-0.49
Initial $P_{\text{CO}_2} = 195$ ppmv			
100 m layer	0.52-0.63		
300 m layer	0.50-0.58		
$\theta$ for CaCO <sub>3</sub> and C <sub>org</sub> formation (4:1) and rising atm. CO <sub>2</sub> (50 m layer)			
Initial $P_{\text{CO}_2} = 195$ ppmv	0.35-0.42	0.25-0.34	0.17-0.25

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**Table 3.** Conditions in pre-industrial time and at the Last Glacial Maximum used in estimation of CO<sub>2</sub> release from the surface ocean layer. Figures 1 and 6 and Eq. (4). LGM data in italics estimated as explained in the text.

Time	Temperature (°C)	River flow (10 <sup>16</sup> kg/yr)	Atmospheric CO <sub>2</sub> mass (10 <sup>16</sup> mol)	CO <sub>2</sub> uptake in weathering (10 <sup>12</sup> mol/yr)	CO <sub>2</sub> net land storage (10 <sup>12</sup> mol/yr)	River input to the ocean		CaCO <sub>3</sub> net sediment storage (10 <sup>12</sup> mol/yr)	Organic C net sediment storage (10 <sup>12</sup> mol/yr)
						<i>C</i> <sub>inorg</sub>	<i>C</i> <sub>org</sub>		
						(10 <sup>12</sup> mol/yr)			
LGM	9	<i>2.64</i>	3.48	<i>11</i>	<i>30</i>	23	<i>10.2</i>	18 to 32	<i>6.5 ± 1.8 to 18</i>
Pre-industrial	15	3.74	5.00	21	50	32	26	32.1	8.3

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**Table 4.** CO<sub>2</sub> flux from ocean to atmosphere due to CaCO<sub>3</sub> precipitation and imbalance between production and respiration of C<sub>org</sub>. Rates of CaCO<sub>3</sub> net storage (production less dissolution) are for a 50-m surface ocean layer, approximating the euphotic zone (water mass  $M_w = 1.854 \times 10^{19}$  kg). Starting conditions are given in Table 1. Input from land to the euphotic zone (Table 3): pre-industrial conditions, DIC  $1.726 \times 10^{-6}$  mol kg<sup>-1</sup> yr<sup>-1</sup> ( $32 \times 10^{12}$  mol/yr) and reactive organic carbon  $1.403 \times 10^6$  mol kg<sup>-1</sup> yr<sup>-1</sup> ( $26 \times 10^{12}$  mol/yr) (Ver et al., 1999; Mackenzie et al., 2004); LGM conditions, DIC  $1.241 \times 10^{-6}$  mol kg<sup>-1</sup> yr<sup>-1</sup> ( $23 \times 10^{12}$  mol/yr) and reactive organic carbon  $0.55 \times 10^{-6}$  mol kg<sup>-1</sup> yr<sup>-1</sup> ( $10.2 \times 10^{12}$  mol/yr).

Initial atmospheric CO <sub>2</sub> (ppmv)	Ocean surface layer temperature (°C)	Initial total alkalinity (A <sub>T</sub> ) (10 <sup>-3</sup> mol/kg)	Initial DIC (10 <sup>-3</sup> mol/kg)	C <sub>org</sub> net storage rate <sup>1)</sup> (10 <sup>12</sup> mol/yr)	CaCO <sub>3</sub> net storage rate <sup>2)</sup> (10 <sup>12</sup> mol/yr)	CO <sub>2</sub> flux from CaCO <sub>3</sub> and C <sub>org</sub> net storage	
						With NPP effect on A <sub>T</sub> <sup>3)</sup> (10 <sup>12</sup> mol/yr)	Without NPP effect on A <sub>T</sub> <sup>4)</sup> (10 <sup>12</sup> mol/yr)
195 (LGM rates)	25	2.808	2.190	6.5 to 18	18	<b>19.7</b> to <b>16.9</b>	<b>15.7</b>
	5	2.582	2.255	6.5 to 18	18	<b>22.1</b> to <b>20.2</b>	<b>17.3</b>
195 (Pre-industrial rates)	25	2.808	2.190	8.3	32.1	<b>40.6</b>	<b>35.4</b>
	5	2.582	2.255	8.3	32.1	<b>45.4</b>	<b>39.3</b>
280 Pre-industrial rates)	25	2.808	2.293	8.3	32.1	<b>43.6</b>	<b>38.0</b>
	5	2.582	2.332	8.3	32.1	<b>48.5</b>	<b>42.0</b>

<sup>1)</sup> Net primary production of organic matter (NPP = GPP – R<sub>auto</sub>) less heterotrophic respiration or remineralization (R<sub>hetero</sub>) in the water column and surface sediment.

<sup>2)</sup> Production rate less dissolution in the water column and surface sediment.

<sup>3)</sup> C<sub>org</sub> net storage from NPP is assumed to take up DIC, reducing A<sub>T</sub> by 1 unit per 1 unit DIC consumed (Sect. 2.4); lower flux corresponds to higher C<sub>org</sub> net storage rate.

<sup>4)</sup> C<sub>org</sub> net storage from NPP is assumed to take up only dissolved CO<sub>2</sub> (Sect. 2.3).

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**Table 5.** Comparison of CO<sub>2</sub> release rates from surface ocean from complete model computation and from the approximation in Eq. (10) and  $\theta$  values from Table 2 for a 50-m-thick surface layer. LGM conditions for  $P_{\text{CO}_2} = 195$  ppmv and pre-industrial for  $P_{\text{CO}_2} = 195$  and 280 ppmv given in Table 4.

	$P_{\text{CO}_2}$ (ppmv)	Temp. (°C)	$\theta$ (rising CO <sub>2</sub> ) $\theta$ (constant CO <sub>2</sub> ) (Table 2)	CO <sub>2</sub> release (10 <sup>12</sup> mol/yr)	
				Approximation, Eq. (10) $\Delta[\text{DIC}] \approx \theta y + w$	Computed (Table 4)
LGM conditions	195	5°C	0.57	$(0.57 \text{ to } 0.64) \times 18 + 10.2$ $= 21.1 \pm 0.6$	21.1 ± 1.0
			0.64		
	25°C	0.38	$(0.38 \text{ to } 0.44) \times 18 + 10.2$ $= 17.6 \pm 0.6$	18.3 ± 1.4	
		0.44			
Pre- industrial conditions	195	5°C	0.57	$(0.57 \text{ to } 0.64) \times 32 + 26$ $= 45.3 \pm 1.2$	45.4
			0.64		
	25°C	0.38	$(0.38 \text{ to } 0.44) \times 32 + 26$ $= 39.2 \pm 1.0$	40.6	
		0.44			
280	5°C	0.71	$0.70 \times 32 + 26 = 48.4$	48.5	
		25°C			0.51

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**Table 6.** Carbon residence times in pre-industrial and Last Glacial times in the atmosphere, surface ocean, and land organic reservoir (plants and soil humus) with respect to the input or output fluxes shown (fluxes and reservoir sizes in Table 3, Fig. 6, and the text). Roman numerals are for pre-industrial time reservoir sizes and fluxes, italics for the LGM.

Residence time in the reservoir with respect to the flux shown (yr)			
CO <sub>2</sub> flux from or to:	Atmosphere	Surface ocean	Land organic
	5.00×10 <sup>16</sup> mol <i>3.48×10<sup>16</sup> mol</i>	4.18×10 <sup>16</sup> mol <i>4.10×10<sup>16</sup> mol</i>	18 to 25.6×10 <sup>16</sup> mol <i>11.9×10<sup>16</sup> mol</i>
From volcanism	5000 <i>3500</i>	—	—
From surface ocean	1100 <sup>1)</sup> <i>1700</i>	—	—
To land organic	1000 <i>1200</i>	—	—
To rock weathering	2400 <i>3200</i>	—	—
From land	—	700 <sup>2)</sup> <i>1250</i>	—
To atmosphere	—	900 <sup>1)</sup> <i>2000</i>	—
To sediments	—	1000 <i>1700 to 800<sup>3)</sup></i>	—
From atmosphere	—	—	3600 to 5100 <sup>4)</sup> <i>4000</i>
To surface ocean	—	—	5300 to 7400 <sup>5)</sup> <i>7500</i>
Material imbalance <sup>6)</sup>	3600 <i>3500</i>	1400 <i>3400 to 1100</i>	11250 to 16000 <i>11800</i>

<sup>1)</sup> Based on mean value of ocean to atmosphere CO<sub>2</sub> flux of 47×10<sup>12</sup> mol/yr (Fig. 6).

<sup>2)</sup> Based on pre-industrial riverine input of 58×10<sup>12</sup> mol/yr of dissolved inorganic and reactive C<sub>org</sub> and LGM input of 23.2×10<sup>12</sup> mol/yr (Fig. 6).

<sup>3)</sup> Corresponds to the range of CaCO<sub>3</sub> and C<sub>org</sub> storage estimates at the LGM (Fig. 6).

<sup>4)</sup> Based on the range of soil humus and phytomass (pre-industrial 18 and 25.6×10<sup>16</sup> mol C, LGM 11.9×10<sup>16</sup> mol C) and net CO<sub>2</sub> storage of 50×10<sup>12</sup> mol/yr in pre-industrial time and 30×10<sup>12</sup> mol/yr at LGM.

<sup>5)</sup> Based on the two land C<sub>org</sub> masses as in footnote 4) and riverine pre-industrial transport of 34×10<sup>12</sup> mol/yr reactive and refractory C<sub>org</sub> and LGM transport of 15.9×10<sup>12</sup> mol/yr.

<sup>6)</sup> For imbalance of in and out fluxes in each reservoir (Fig. 6), the times in the table are either times to complete depletion of the reservoir (atmosphere and surface ocean) or to doubling of its content (land organic).

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**Table A1.** Apparent dissociation constants at ocean water salinity of 35, 1 bar total pressure, calculated from the equations of Mucci (1983), DOE (1994), and other sources, as summarized in Zeebe and Wolf-Gladrow (2001).

Parameter	At 25°C	At 15°C	At 5°C
1 $K'_0 = [\text{CO}_2]/P_{\text{CO}_2}$	$2.839 \times 10^{-2}$	$3.746 \times 10^{-2}$	$5.213 \times 10^{-2}$
2 $K'_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$	$1.392 \times 10^{-6}$	$1.119 \times 10^{-6}$	$8.838 \times 10^{-7}$
3 $K'_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$	$1.189 \times 10^{-9}$	$7.970 \times 10^{-10}$	$5.191 \times 10^{-10}$
3 $K'_w = [\text{H}^+][\text{OH}^-]$	$6.063 \times 10^{-14}$	$2.380 \times 10^{-14}$	$8.549 \times 10^{-15}$
5 $K'_B = [\text{H}^+][\text{B}(\text{OH})_4^-]/[\text{B}(\text{OH})_3]$	$2.526 \times 10^{-9}$	$1.921 \times 10^{-9}$	$1.431 \times 10^{-9}$
6 $B_T$ (mol/kg)	$4.160 \times 10^{-4}$	$4.160 \times 10^{-4}$	$4.160 \times 10^{-4}$
7 $K'_{\text{cal}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$	$4.273 \times 10^{-7}$	$4.315 \times 10^{-7}$	$4.309 \times 10^{-7}$

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**Table A2.** Release of CO<sub>2</sub> from CaCO<sub>3</sub> formation and atmospheric CO<sub>2</sub> increase from 50-m-thick euphotic zone (25°C, initial  $P_{\text{CO}_2} = 195$  ppmv, water mass in euphotic zone  $M_w = 1.854 \times 10^{19}$  kg) (Fig. 4a).

Precipitation of CaCO <sub>3</sub> and increase of [CO <sub>2</sub> ]									
Fraction of DIC <sub>0</sub> removed	Mass C or Ca removed <i>y</i>	Mass calcite precipitated globally <i>yM<sub>w</sub></i>	Change in DIC DIC - <i>y</i>	Change in total alk. <i>A<sub>T</sub></i> - 2 <i>y</i>	Eq. (A12) pH	Change in [Ca <sup>2+</sup> ] [Ca <sup>2+</sup> ] - <i>y</i>	Eqs. (A2), (A6) [CO <sub>2</sub> ]	Internal <i>P</i> <sub>CO<sub>2</sub></sub>	[CO <sub>2</sub> ] <i>M<sub>w</sub></i> <i>n<sub>w</sub></i>
<i>f</i>	10 <sup>-3</sup> mol/kg	10 <sup>12</sup> mol	10 <sup>-3</sup> mol C/kg	10 <sup>-3</sup> mol/kg		10 <sup>-2</sup> mol/kg	mol/kg	ppmv	10 <sup>12</sup> mol
0.000	0	0	2.190	2.809	8.350	1.028	5.537E-06	195	102.6
0.001	0.0022	244	2.188	2.805	8.348	1.028	5.555E-06	196	103.0
0.010	0.0219	2,436	2.168	2.765	8.334	1.026	5.729E-06	202	106.2
0.030	0.0657	7,308	2.125	2.678	8.300	1.021	6.159E-06	217	114.2
0.050	0.1095	12,180	2.081	2.590	8.264	1.017	6.658E-06	235	123.4
0.070	0.1533	17,052	2.037	2.502	8.225	1.013	7.246E-06	255	134.3
0.100	0.219	24,360	1.971	2.371	8.159	1.006	8.353E-06	294	154.8
0.130	0.285	31,669	1.905	2.239	8.083	1.000	9.856E-06	347	182.7
0.150	0.329	36,541	1.862	2.152	8.024	0.995	1.119E-05	394	207.5
0.160	0.350	38,977	1.840	2.108	7.992	0.993	1.201E-05	423	222.6
0.180	0.394	43,849	1.796	2.020	7.921	0.989	1.403E-05	494	260.0
0.200	0.438	48,721	1.752	1.933	7.838	0.984	1.682E-05	592	311.7
0.220	0.482	53,593	1.708	1.845	7.739	0.980	2.086E-05	735	386.6
0.250	0.548	60,901	1.643	1.714	7.552	0.973	3.138E-05	1105	581.6
0.270	0.591	65,773	1.599	1.626	7.396	0.969	4.399E-05	1550	815.5
0.300	0.657	73,081	1.533	1.495	7.132	0.962	7.678E-05	2704	1423.3
0.340	0.745	82,826	1.446	1.320	6.813	0.954	1.440E-04	5070	2668.7
0.350	0.767	85,262	1.424	1.276	6.745	0.951	1.631E-04	5746	3024.3
0.400	0.876	97,442	1.314	1.057	6.455	0.940	2.649E-04	9329	4910.2
0.450	0.986	109,622	1.205	0.838	6.209	0.929	3.708E-04	13061	6874.5

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Table A2. Continued.

Equilibrating open system				Final results							
1st approximation of CO <sub>2</sub> transfer											
Fraction of DIC <sub>0</sub> removed	[CO <sub>2</sub> ] mass transferred	In ocean water	In atmosphere	Eq. (A1)	Eq. (A6)		Eq. (A11)	Eqs. (A6), (A13)	Atmosphere	DIC released as CO <sub>2</sub> Eqs. (A16), (A14)	
<i>f</i>	<i>x</i> Eq. (A20)	<i>n<sub>w</sub> - x</i>	<i>n<sub>a</sub><sup>0</sup> + x</i>	DIC	pH	[CO <sub>3</sub> <sup>2-</sup> ]	Ω	[CO <sub>2</sub> ]	<i>P</i> <sub>CO<sub>2</sub></sub>	Δ[DIC]	<i>θ</i>
	mol	mol	mol	10 <sup>-3</sup> mol/kg		10 <sup>-3</sup> mol/kg		mol/kg	ppmv	10 <sup>-3</sup> mol/kg	mol/mol
0.000	0	1.026E+14	3.487E+16	2.190	8.350	0.459	11.05	5.537E-06	195.0	0	
0.001	3.454E+11	1.026E+14	3.487E+16	2.187	8.349	0.458	11.02	5.539E-06	195.1	0.0008	0.383
0.010	3.564E+12	1.026E+14	3.487E+16	2.160	8.343	0.447	10.74	5.561E-06	195.9	0.0084	0.385
0.030	1.150E+13	1.027E+14	3.488E+16	2.099	8.330	0.424	10.14	5.612E-06	197.6	0.0255	0.389
0.050	2.073E+13	1.027E+14	3.489E+16	2.038	8.316	0.401	9.56	5.663E-06	199.5	0.0430	0.392
0.070	3.160E+13	1.027E+14	3.490E+16	1.976	8.301	0.379	8.98	5.715E-06	201.3	0.0607	0.396
0.100	5.206E+13	1.028E+14	3.492E+16	1.883	8.279	0.346	8.15	5.795E-06	204.1	0.0880	0.402
0.130	7.984E+13	1.029E+14	3.495E+16	1.789	8.255	0.314	7.35	5.878E-06	207.0	0.1161	0.408
0.150	1.046E+14	1.029E+14	3.497E+16	1.726	8.238	0.294	6.84	5.934E-06	209.0	0.1353	0.412
0.160	1.196E+14	1.030E+14	3.499E+16	1.695	8.229	0.283	6.59	5.963E-06	210.0	0.1451	0.414
0.180	1.569E+14	1.031E+14	3.502E+16	1.631	8.211	0.264	6.10	6.021E-06	212.1	0.1649	0.418
0.200	2.085E+14	1.032E+14	3.507E+16	1.567	8.192	0.244	5.62	6.081E-06	214.2	0.1852	0.423
0.220	2.832E+14	1.035E+14	3.515E+16	1.503	8.173	0.225	5.17	6.142E-06	216.3	0.2058	0.427
0.250	4.776E+14	1.040E+14	3.534E+16	1.405	8.141	0.198	4.51	6.235E-06	219.6	0.2377	0.434
0.270	7.108E+14	1.047E+14	3.558E+16	1.339	8.119	0.180	4.09	6.299E-06	221.9	0.2595	0.439
0.300	1.317E+15	1.065E+14	3.618E+16	1.240	8.083	0.155	3.50	6.398E-06	225.4	0.2932	0.446
0.340	2.559E+15	1.102E+14	3.742E+16	1.106	8.030	0.124	2.78	6.536E-06	230.2	0.3399	0.456
0.350	2.913E+15	1.112E+14	3.778E+16	1.072	8.016	0.117	2.61	6.571E-06	231.5	0.3520	0.459
0.400	4.793E+15	1.167E+14	3.966E+16	0.900	7.935	0.083	1.83	6.755E-06	238.0	0.4143	0.473
0.450	6.752E+15	1.225E+14	4.162E+16	0.724	7.836	0.054	1.18	6.949E-06	244.8	0.4807	0.488

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**Table A3.** Computation of CO<sub>2</sub> flux from surface ocean layer to the atmosphere due to CaCO<sub>3</sub> and C<sub>org</sub> removal from water and storage in sediments at 5°C and initial atmospheric CO<sub>2</sub> concentration of 195 ppmv. Details in the text.

Computational step	Riverine input HCO <sub>3</sub> <sup>-</sup> , <i>v</i> mol kg <sup>-1</sup> yr <sup>-1</sup>	Riverine input C <sub>orgs</sub> , <i>w</i> mol kg <sup>-1</sup> yr <sup>-1</sup>	CaCO <sub>3</sub> net removal, <i>y</i> mol kg <sup>-1</sup> yr <sup>-1</sup>	C <sub>org</sub> net removal, <i>z</i> mol kg <sup>-1</sup> yr <sup>-1</sup>	pH	Dissolved inorganic carbon, DIC mol/kg	Total alkal- inity, A <sub>T</sub> mol- equivalent/kg	<i>P</i> <sub>CO<sub>2</sub></sub> initial in atm., and internal ppmv	[CO <sub>2</sub> ] in surface layer, <i>n<sub>w</sub></i> mol	DIC transfer to atmosphere in 1 yr mol/kg	CO <sub>2</sub> emission mol/yr
<b>Initial</b>					8.350	2.2553E-03	2.582E-03	195.00	188.4E+12	0	0
Input and removal in a closed system	1.241E-06	5.502E-07	-9.710E-07	-9.710E-07	8.348	2.2551E-03	2.580E-03	196.07	189.5E+12	0	0
<b>Equilibration in open system</b>	[CO <sub>2</sub> ] to atmosphere, <i>x</i> mol	[CO <sub>2</sub> ] in surface layer, <i>n<sub>w</sub> - x</i> mol	CO <sub>2</sub> in atmosphere, <i>n<sub>a</sub><sup>0</sup> + x</i> mol					<i>P</i> <sub>CO<sub>2</sub></sub> in atmosphere ppmv			
<b>First iteration</b>	1.026E+12	188.5E+12	3.487E+16		8.350	2.2539E-03	2.580E-03	195.01	188.6E+12	1.213E-06	22.5E+12
<b>Final values</b>					8.350	2.2540E-03	2.580E-03	195.11	188.6E+12	1.090E-06	<b>20.2E+12</b>

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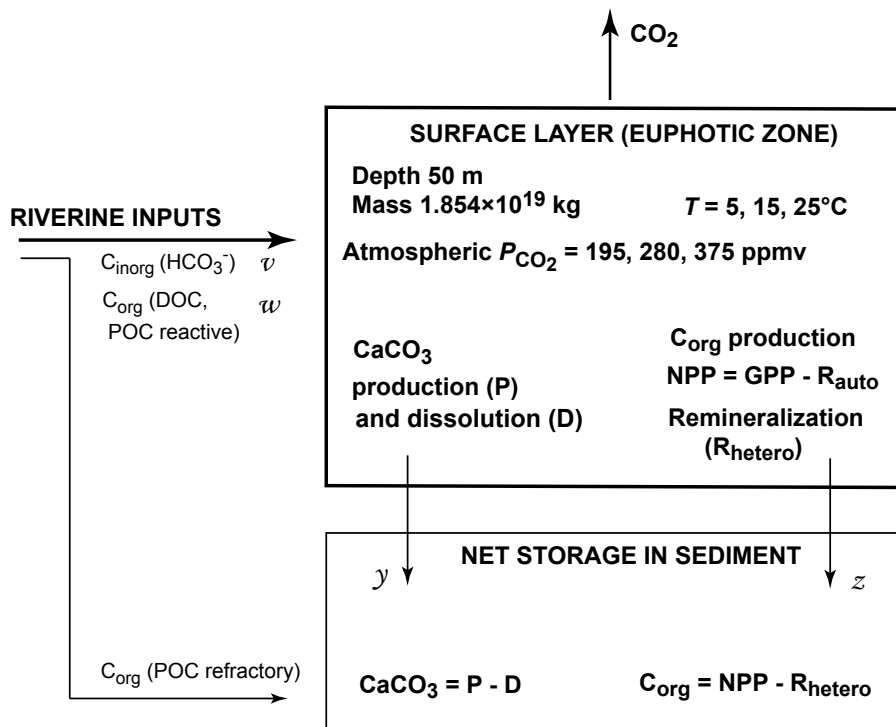
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**Fig. 1.** Schematic diagram of the surface ocean layer (50-m-thick euphotic zone) where calcium carbonate ( $\text{CaCO}_3$ ) and organic carbon ( $C_{\text{org}}$ ) are produced. Production, dissolution, NPP, and remineralization are discussed in the text.  $v$ ,  $w$ ,  $y$ , and  $z$  are fluxes (mol/yr, Eq. 4). Net storage in sediments are amounts produced less amounts dissolved or remineralized.

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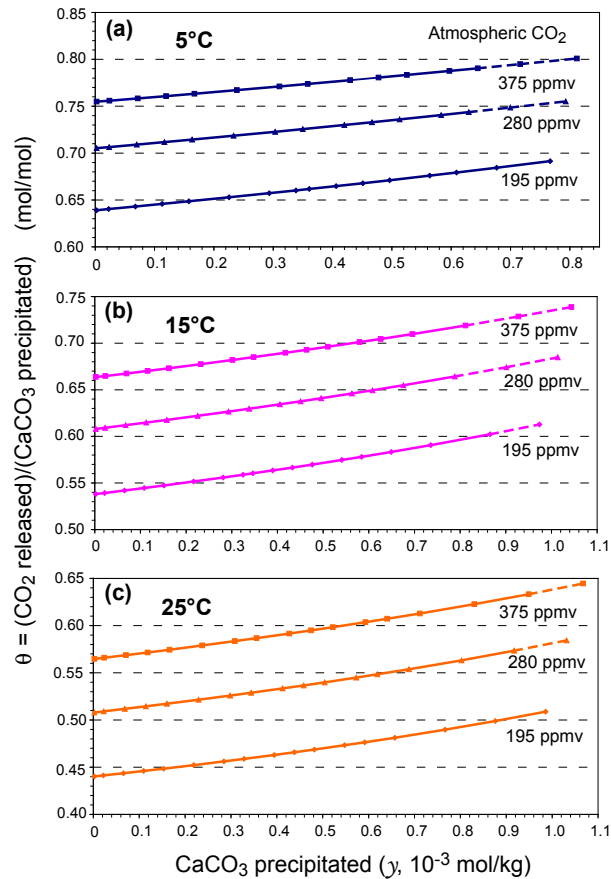
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**Fig. 2.** CO<sub>2</sub> release due to CaCO<sub>3</sub> precipitation from surface ocean layer into an atmosphere of a constant CO<sub>2</sub> of 195, 280, and 375 ppmv, at 5, 15, and 25°C. Initial ocean-water conditions given in Table 1. Note the differences in the horizontal and vertical scales. Dashed lines show regions of calcite undersaturation caused by precipitation of large fractions of dissolved inorganic carbon (DIC).

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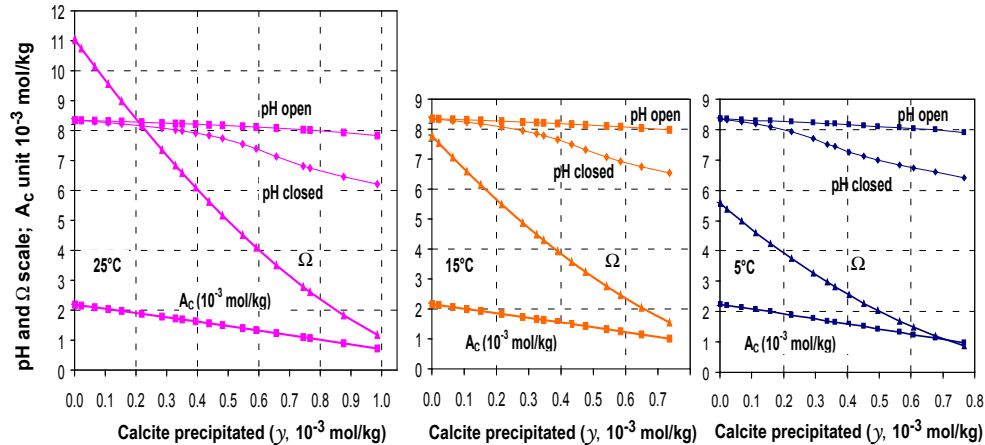
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**Fig. 3.** Changes in pH, calcite supersaturation ( $\Omega$ ), and carbonate alkalinity ( $A_C$ ) during  $\text{CaCO}_3$  precipitation in a 50-m-thick surface layer at three temperatures, starting atmospheric  $\text{CO}_2$  195 ppmv, and release of  $\text{CO}_2$  to the atmosphere. pH of the closed system is after calcite precipitation, and pH of the open system is after reequilibration with the atmosphere.  $\Omega$  is for an open system at each temperature. Note that the scale for pH and  $\Omega$  are the numbers on the vertical axis; for carbonate alkalinity ( $A_C$ ) the same scale is in units of  $10^{-3}$  mol/kg.

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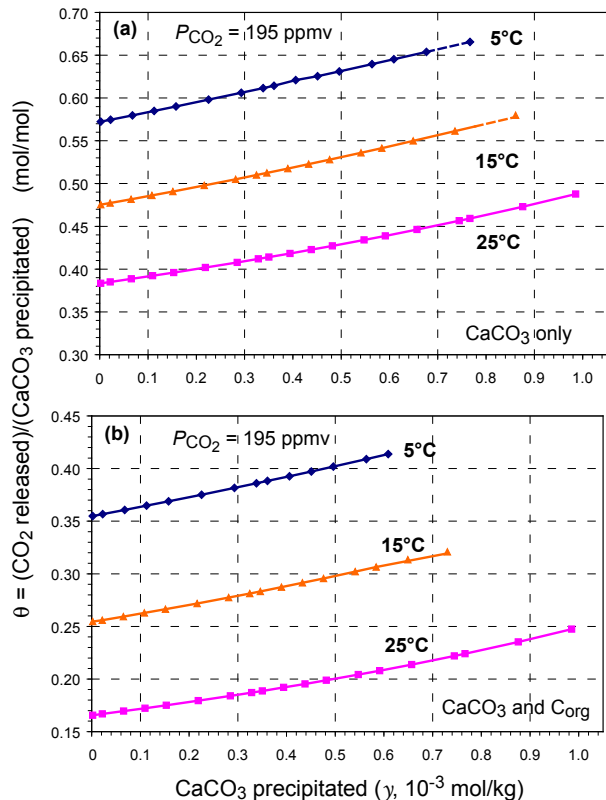
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**Fig. 4.** CO<sub>2</sub> release increasing atmospheric CO<sub>2</sub> concentration. **(a)** Release of CO<sub>2</sub> at 25, 15, and 5°C from surface ocean layer (a 50-m-thick euphotic zone) that increases the atmospheric CO<sub>2</sub> content, starting at 195 ppmv. Dashed lines indicate regions of calcite undersaturation. Compare with the curves in Fig. 2. **(b)** Release of CO<sub>2</sub> from ocean water where both CaCO<sub>3</sub> and organic carbon are stored (molar ratio of CaCO<sub>3</sub>/C<sub>org</sub> = 4/1) at 25, 15, and 5°C; initial atmospheric CO<sub>2</sub> 195 ppmv. Note that when additional DIC is removed by organic carbon storage  $\theta$  values are smaller than those for CaCO<sub>3</sub> precipitation only.

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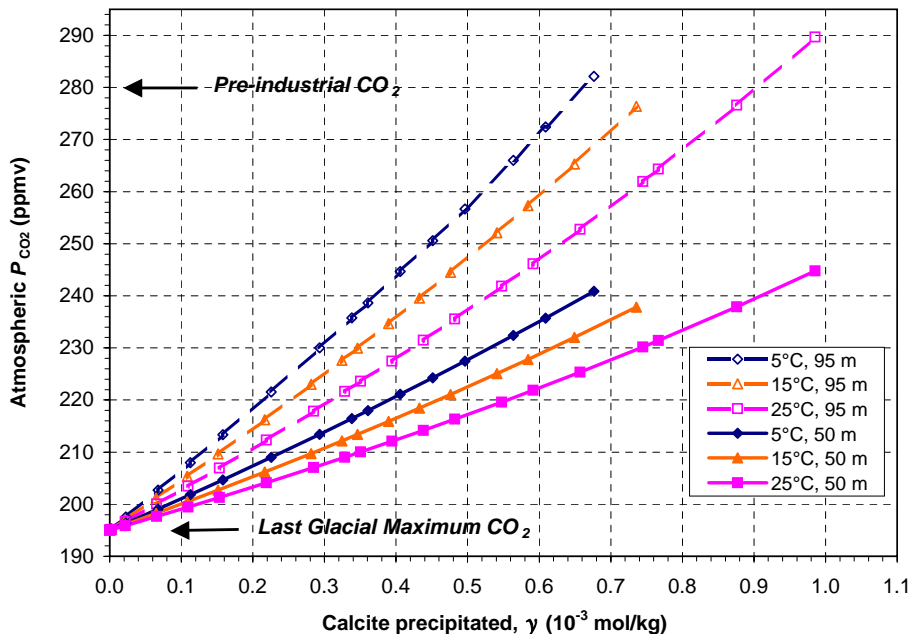
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**Fig. 5.** Increase in atmospheric CO<sub>2</sub> due to calcite precipitation in a 50- and 95-m-thick surface ocean layer. Amount of 85 ppmv increase since LGM to pre-industrial time is shown for comparison. Results for 5, 15, and 25°C, without replenishment of the dissolved carbon and calcium lost to precipitation. At the higher end of the abscissa, precipitated CaCO<sub>3</sub> amounts to 34 to 45% of the initial DIC concentration where the degree of calcite saturation has decreased to  $\Omega \approx 1.2$ .

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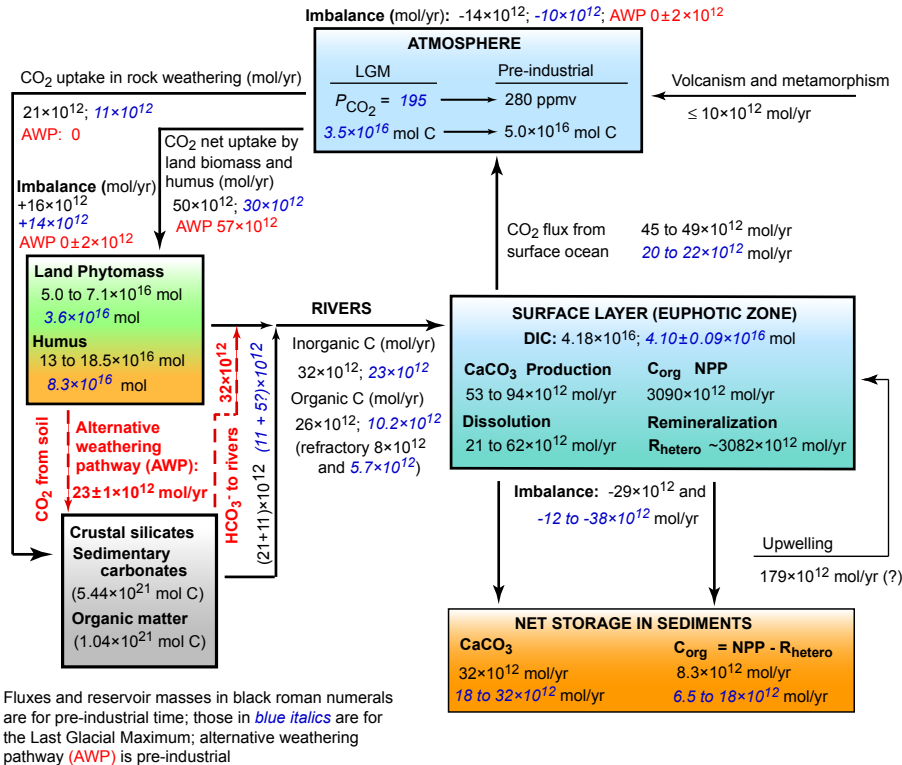


Fig. 6. Global carbon cycle showing the three main domains of the land, ocean, and atmosphere, interreservoir fluxes, and reservoir imbalances. Data in Sects. 4, 5, and Tables 3, 4, and 6. Discussion of the LGM, pre-industrial, and alternative weathering pathway (AWP) conditions in the text.

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