

# Seawater pH and isotopic paleotemperatures of Cretaceous oceans

Richard E. Zeebe<sup>a,b,\*</sup>

<sup>a</sup>Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen, D-27570 Bremerhaven, Germany

<sup>b</sup>Lamont-Doherty Earth Observatory of Columbia University, Palisades, USA

Received 13 June 2000; accepted for publication 30 January 2001

## Abstract

Stable oxygen isotope ratios ( $\delta^{18}\text{O}$ ) of foraminifera are widely used to reconstruct the climatic history of Earth. It is well known that temperature reconstructions based on  $\delta^{18}\text{O}$  are complicated by factors such as the unknown isotopic composition of the ocean. In addition, recent experimental and theoretical work has shown that the seawater pH has a marked effect on the  $\delta^{18}\text{O}$  of foraminifera. Here I employ this effect to demonstrate that reconstructions based on  $\delta^{18}\text{O}$  of foraminifera may underestimate sea surface temperatures in the geological past. Ocean surface temperatures for the mid-Cretaceous are estimated to have been  $\sim 2\text{--}3.5^\circ\text{C}$  higher than previously thought. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Oxygen isotopes; Paleotemperatures; Cretaceous; pH effect; SSTs; Cool tropics

## 1. Introduction

The ratio of the stable oxygen isotopes  $^{18}\text{O}/^{16}\text{O}$  in foraminiferal calcite from sediment cores is commonly used to estimate ocean temperatures and surface ocean equator-to-pole temperature gradients during the Cretaceous (e.g. Sellwood et al., 1994; Huber et al., 1995; D'Hondt and Arthur, 1996; Norris and Wilson, 1998; for summary, see Frakes, 1999). Foraminiferal  $\delta^{18}\text{O}$  and the paleobotanical record provide convincing evidence that the Cretaceous period was substantially warmer than today (Crowley and North, 1991; Spicer and Corfield, 1992). Globally averaged temperatures were probably  $6\text{--}12^\circ\text{C}$  higher than today with pronounced warming at the poles (Barron, 1983; Barrera and Johnson, 1999). Coral

reefs extended  $5\text{--}15^\circ$  of latitude poleward of their present range and ancient organisms intolerant of cold conditions have been discovered at high-latitudes — a vertebrate assemblage including chamososaurs, a relative of the crocodile, has recently been discovered in the high Canadian Arctic ( $\sim 72^\circ\text{N}$  paleolatitude (Tarduno et al., 1998)). On the contrary, considering that today's tropical SSTs are  $27\text{--}29^\circ\text{C}$ , Cretaceous tropical SSTs as derived from foraminiferal  $\delta^{18}\text{O}$  are surprisingly low, varying between  $18\text{--}26^\circ\text{C}$  for the Early Cretaceous,  $\sim 130$  million years ago (Ma) (cf. Barrera, 1994),  $24.4\text{--}25.9^\circ\text{C}$  for the Cenomanian,  $97.5\text{--}91$  Ma (Sellwood et al., 1994),  $20\text{--}23^\circ\text{C}$  for the Late Campanian/Maastrichtian,  $74\text{--}68$  Ma (Barrera and Savin, 1999), and  $20\text{--}21^\circ\text{C}$  for the Late Cretaceous,  $\sim 66$  Ma (D'Hondt and Arthur, 1996).

Tropical climate is crucial to the global climate since it controls the global heat transport, which drives the atmospheric and oceanic circulation. It is therefore unsatisfactory that modeling efforts using

\* Present address: Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen, D-27570 Bremerhaven, Germany. Tel.: +49-471-4831-1848; fax: +49-471-4831-1425.

E-mail address: rzeebe@awi-bremerhaven.de (R.E. Zeebe).

general circulation models to simulate Cretaceous tropical SSTs and equator-to-pole temperature gradients as derived from foraminiferal  $\delta^{18}\text{O}$  proved to be difficult (Crowley and North, 1991; Crowley, 1991; Barron et al., 1995). In order to explain Cretaceous climates, modeling studies focused on paleogeography, increased levels of atmospheric  $\text{CO}_2$  and increased poleward oceanic heat transport (e.g. Barron et al., 1995). New insight into the problem was gained by investigating the role of water vapor and effects of terrestrial ecosystems on Cretaceous climates (Hay et al., 1997; Hay and DeConto, 1999; DeConto et al., 1999). However, the problem associated with the results of those climate models and the  $\delta^{18}\text{O}$  record is that simulations of warm Cretaceous climate conditions, assuming high atmospheric  $\text{CO}_2$ , result in high tropical SSTs (up to  $34^\circ\text{C}$  (Hay and DeConto, 1999)) which are incompatible with the interpretation of foraminiferal  $\delta^{18}\text{O}$  (D'Hondt and Arthur, 1996).

During the past decade, a number of papers and discussions have been published on Cretaceous temperatures in order to gain a better understanding of this subject. The topic is highly controversial (e.g. Crowley, 1991; Spicer and Corfield, 1992; Sellwood et al., 1994; Barron et al., 1995; Huber et al., 1995; Huber and Hodell, 1996; D'Hondt and Arthur, 1996; Price et al., 1996; Norris and Wilson, 1998; Price et al., 1998; Norris and Wilson, 1999; Price and Hart, 1999; Crowley and Zachos, 2000). Several factors, such as shortcomings of the oxygen isotope thermometry (see e.g. Poulsen et al. (1999) and Section 2), have been called upon in order to resolve the controversy. However, the pH effect on foraminiferal  $\delta^{18}\text{O}$  has hitherto not been taken into account. In this paper, I attempt to quantify the effect of a lower surface ocean pH on isotopic paleotemperatures of Cretaceous oceans.

## 2. Oxygen isotope composition of past oceans

Isotopic paleotemperature reconstructions rely on the isotopic composition of the past ocean ( $\delta_w$ ) and therefore depend on (i) estimates of the continental ice-volume of the Earth, (ii) long-term variations in  $\delta_w$  driven by weathering and hydrothermal processes, and (iii) the latitudinal gradient of  $\delta_w$  in the past which is related to the salinity gradient. Uncertainties

associated with the assumptions commonly used to estimate mean oceanic  $\delta_w$  and the salinity gradient may partially explain estimates of low tropical SSTs of Cretaceous oceans. For instance, it is believed that Earth was ice-free for the most part of the Cretaceous, and mean  $\delta_w$  is therefore usually assumed to have been  $-1.0\text{‰}$  relative to SMOW (equivalent to  $-1.2\text{‰}$  PDB (Shackleton and Kennett, 1975)). Tropical SST estimates for Late Cretaceous oceans based on foraminiferal  $\delta^{18}\text{O}$  approached modern values only if mean oceanic  $\delta_w$  was  $+1.0\text{‰}$  which is, however, extremely unlikely (D'Hondt and Arthur, 1996). Latitudinal changes in  $\delta^{18}\text{O}$  of the surface ocean may lead to an underestimation of tropical SSTs since tropical surface waters are relatively enriched in  $^{18}\text{O}$  due to high net evaporation rates (Norris and Wilson, 1998; Price et al., 1998). Based on the assumption that the salinity gradient of the past ocean was similar to the present (Zachos et al., 1994; Poulsen et al., 1999), a correction of tropical SSTs of  $3\text{--}4^\circ\text{C}$  may be applied — which is, however, subject to controversy (Price et al., 1996; Huber and Hodell, 1996; Price and Hart, 1999; Norris and Wilson, 1999). Even with the salinity adjustments, in a number of cases low-latitude SSTs are still lower than modern values (e.g. Huber et al., 1995; Barrera and Savin, 1999), and Maastrichtian summer SSTs approached modern values only if sea surface salinity was 39–41 (D'Hondt and Arthur, 1996).

In summary, discussions of Cretaceous SSTs have hitherto mainly concentrated on the unknown value of mean ocean  $\delta_w$  or on the salinity gradient. Here I employ a physicochemical mechanism to demonstrate that temperature reconstructions based on foraminiferal  $\delta^{18}\text{O}$  may underestimate Cretaceous SSTs by  $\sim 2\text{--}3.5^\circ\text{C}$ . Deep ocean temperatures and the equator-to-pole temperature gradient are discussed in Section 4.

## 3. Revised Isotopic Paleotemperatures

Spero et al. (1997) demonstrated that the  $\delta^{18}\text{O}$  of planktonic foraminifera decreases with increasing carbonate ion concentration ( $[\text{CO}_3^{2-}]$ ). This effect has been observed in four planktonic species tested — the magnitude of the effect appears to be species-dependent (experiments were conducted at  $17, 22, 27$  and  $29^\circ\text{C}$ ). The observed slope of  $\delta^{18}\text{O}$  vs  $[\text{CO}_3^{2-}]$  in the planktonic

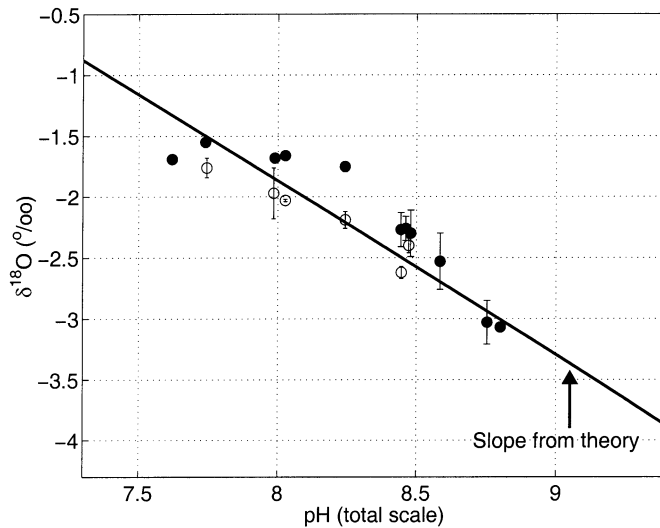


Fig. 1.  $\delta^{18}\text{O}$  of the planktonic foraminifer *Orbulina universa* from laboratory experiments in the light and in the dark (open and closed circles, respectively) as a function of pH ( $S = 33.5$ ,  $T = 22^\circ\text{C}$ ) (Spero et al., 1997). The pH values were calculated from total alkalinity and total dissolved inorganic carbon of each experiment (Bijma, personal communication) and refer to the total pH scale (cf. DOE, 1994). The slope of the solid line ( $-1.42\text{‰}$  per pH unit) (Zeebe, 1999) was derived from theory using results from inorganic precipitation experiments (McCrea, 1950; Usdowski and Hoefs, 1993). Theory predicts pH to be the key variable controlling  $\delta^{18}\text{O}$ .

foraminifer *Orbulina universa*, *Globigerina bulloides*, *Globigerinoides sacculifer*, and *Globigerinoides ruber* is  $-0.0020$ ,  $-0.0045$ ,  $-0.0014$ , and  $-0.0022\text{‰}$  ( $\mu\text{mol kg}^{-1}$ )<sup>-1</sup>, respectively (Spero et al., 1999), giving a mean slope of  $-0.0025\text{‰}$  ( $\mu\text{mol kg}^{-1}$ )<sup>-1</sup>.

A theoretical study by Zeebe (1999) revealed that this effect has a thermodynamical basis that can be derived from inorganic carbonate precipitation (McCrea, 1950; Usdowski and Hoefs, 1993). Briefly, as the major component of total dissolved inorganic carbon ( $\Sigma\text{CO}_2$ ) changes from  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$  in solution as pH increases, the isotopic composition of the oxygen-bearing substrate for calcification decreases (for a discussion of carbon isotopes cf. Zeebe et al. (1999)). This is because  $\text{CO}_3^{2-}$  is isotopically lighter than  $\text{HCO}_3^-$ . Over the pH range shown in Fig. 1, the theoretically derived curve is nearly linear and the average slope of  $\delta^{18}\text{O}$  vs pH is  $-1.42\text{‰}$  per pH unit. The pH values of the culture data were calculated from total alkalinity and total dissolved inorganic carbon of each experiment (Bijma, personal communication). For the calculations, the dissociation constants as summarized in DOE (1994) were used and pH values refer to the total pH scale.

Theory predicts that pH is the variable that controls

$\delta^{18}\text{O}$  and not  $\text{CO}_3^{2-}$  because pH determines the ratio of  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$  in solution. In a series of experiments with *O. universa* in which the pH was held constant and carbonate ion concentration varied over a wide range from ca. 100 to 800  $\mu\text{mol kg}^{-1}$ , virtually no effect was observed on  $\delta^{18}\text{O}$  (Bijma et al., 1999). This observation corroborates the theoretical prediction. If pH and  $\text{CO}_3^{2-}$  covary as in the experiments reported by Spero et al. (1997), one may express the effect on  $\delta^{18}\text{O}$  either in terms of pH or  $\text{CO}_3^{2-}$ . The theoretical slope then is  $-0.0024\text{‰}$  ( $\mu\text{mol CO}_3^{2-} \text{kg}^{-1}$ )<sup>-1</sup> (Zeebe, 1999) which is in excellent agreement with the mean slope observed in all planktonic foraminifera tested and with the slope in *O. universa*.

In the following, the pH effect on  $\delta^{18}\text{O}$  is examined using *O. universa* as a model species (for a discussion of the pH effect on other species cf. Section 4). For example, a decrease of modern seawater pH from 8.2 by 0.6 units to 7.6 would result in a 0.85‰ heavier shell of *O. universa* than at pH 8.2, equivalent to a 4.1°C increase (if corrected) of isotopic paleotemperature (Bemis et al., 1998) (Fig. 2). The magnitude of this correction is comparable to the effect of melting of the entire Antarctic Ice Sheet, which has been estimated (Shackleton and

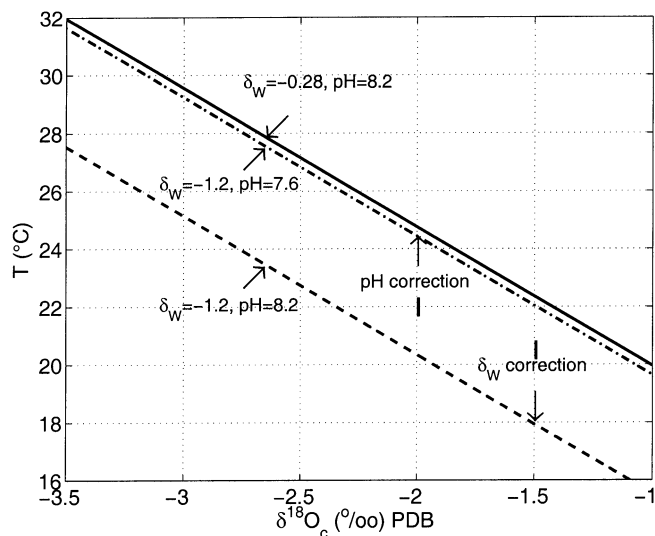


Fig. 2. Illustration of the effect of  $\delta_w$  and pH on the calculated seawater temperatures from foraminiferal calcite ( $\delta^{18}\text{O}_c$ ) using the paleotemperature equation of *O. universa*:  $T(^{\circ}\text{C}) = 16.5 - 4.80(\delta_c - \delta_w)$  (Bemis et al., 1998). The solid line represents average modern ocean conditions ( $\delta_w = -0.28\text{‰}$  with respect to the PDB standard (Shackleton and Kennett, 1975),  $\text{pH} = 8.2$ ). Assuming a largely ice-free world and no change in surface ocean pH ( $\delta_w = -1.2\text{‰}$ ,  $\text{pH} = 8.2$ ) the correction for  $\delta_w$  yields a temperature ca.  $4.3^{\circ}\text{C}$  lower than at present (dashed line). On the contrary, assuming the same change of  $\delta_w$  and a decrease of surface ocean pH ( $\delta_w = -1.2\text{‰}$ ,  $\text{pH} = 7.6$ ) the correction for pH yields a temperature very similar to that at present (dot-dashed line).

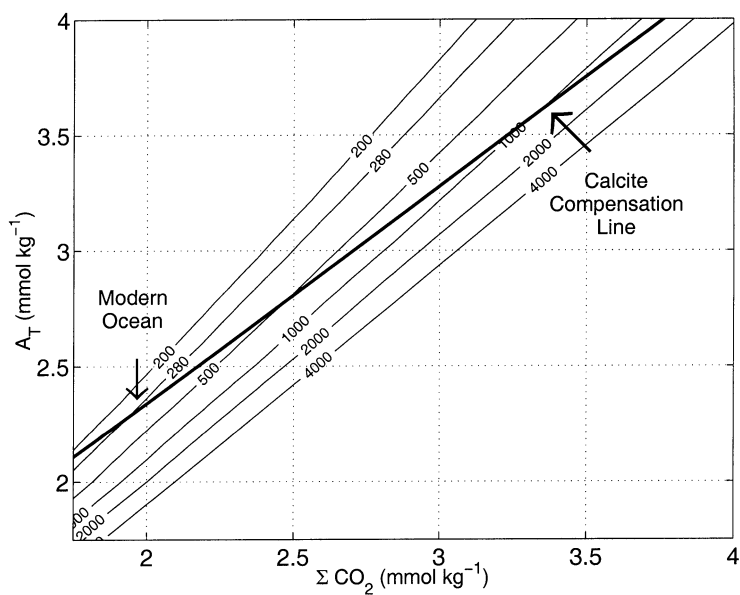


Fig. 3. Isocontours of surface ocean  $p\text{CO}_2$  in  $\mu\text{atm}$  as a function of total dissolved inorganic carbon ( $\Sigma\text{CO}_2$ ) and total alkalinity ( $A_T$ ) at  $T = 20^{\circ}\text{C}$  and  $S = 35$  (thin lines). Starting at modern ocean conditions, one moves along the calcite compensation line (thick line) when  $\Sigma\text{CO}_2$  or  $A_T$  are changed. For example, for  $p\text{CO}_2 = 1000 \mu\text{atm}$ , surface ocean carbonate chemistry is set by the intercept of the  $1000 \mu\text{atm}$  contour and the calcite compensation line.

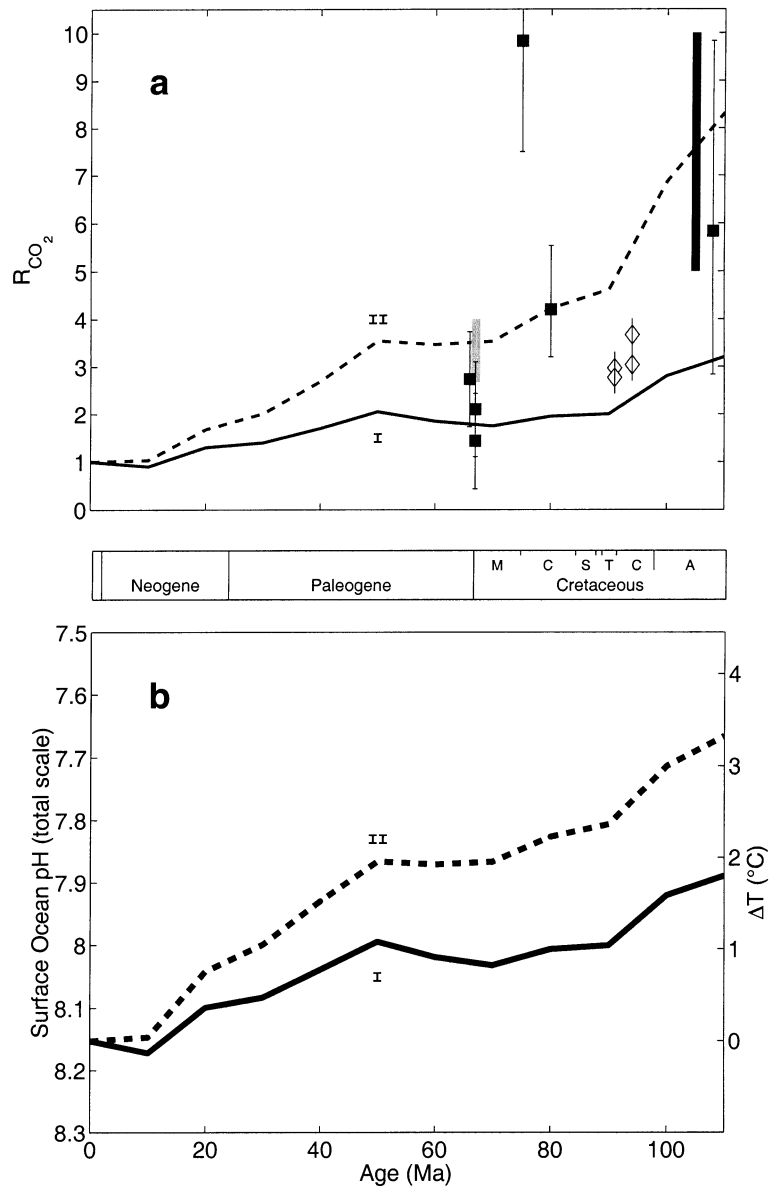


Fig. 4. (a) Estimates of atmospheric  $\text{CO}_2$  during the past 110 Ma, where  $R_{\text{CO}_2}$  is  $\text{CO}_2$  at time  $t$  divided by 300 ppmv. Scenario I: solid line, based on the long-term carbon cycle model (Berner, 1994). Scenario II: dashed line, assuming  $\text{CO}_2$  to have been  $\sim 8$  times today's value in the mid-Cretaceous. Also shown are independent estimates of  $\text{CO}_2$  for the Cretaceous based on (i) differences in  $\delta^{13}\text{C}$  of specific biomarker compounds and  $\text{CaCO}_3$  (diamonds, (Freeman and Hayes, 1992)) and (ii)  $\delta^{13}\text{C}$  of palaeosols (shaded vertical bar (Ghosh et al., 1995); dark vertical bar (Cerling, 1991); filled squares (Ekart et al., 1999)). (b) Surface ocean pH calculated (DOE, 1994) using the  $\text{CO}_2$  curves depicted in (a) and the calcite compensation line (Fig. 3). The correction of SSTs taking into account the pH effect on foraminiferal  $\delta^{18}\text{O}$  is indicated by the right vertical axis.

Kennett, 1975) to result in a decrease of  $\delta_w$  (and thus also of foraminiferal  $\delta^{18}\text{O}$ ) by about 0.9‰ (4.3°C).

If surface ocean pH was lower in the past, the stable

oxygen isotope fractionation between water and foraminiferal calcite would have been greater (Fig. 1), resulting in isotopically heavier shells, which are erroneously interpreted as lower temperatures. The

Table 1

Calculated seawater carbonate chemistry from  $p\text{CO}_2$  and calcite compensation (All values at  $T = 20^\circ\text{C}$  and  $S = 35$  using dissociation constants as given in DOE (1994).)

| $p\text{CO}_2$ ( $\mu\text{atm}$ ) | $\Sigma\text{CO}_2$ ( $\mu\text{mol kg}^{-1}$ ) | $A_T$ ( $\mu\text{mol kg}^{-1}$ ) | $\text{CO}_3^{2-}$ ( $\mu\text{mol kg}^{-1}$ ) | pH <sup>a</sup> |
|------------------------------------|---|-----------------------------------|--|-----------------|
| 300                                | 2000  | 2340                              | 244  | 8.16            |
| 500                                | 2482  | 2790                              | 239  | 8.04            |
| 1000                               | 3350  | 3610                              | 230  | 7.88            |
| 2000                               | 4539  | 4737                              | 218  | 7.72            |

<sup>a</sup> Total pH scale.

crucial question is, if there is evidence for Cretaceous surface ocean pH to have been different from modern values. The  $p\text{CO}_2$  of the Cretaceous atmosphere has been estimated to have been 2–10 times higher than today (Cerling, 1991; Berner, 1994; Ekart et al., 1999) (see Fig. 4a). Provided that the partial pressure of  $\text{CO}_2$  of the atmosphere and that of the surface ocean were approximately in equilibrium, also the concentration of dissolved carbon dioxide ( $\text{CO}_2(\text{aq})$ ) of the surface ocean must have been higher, suggesting that seawater carbonate chemistry in the Cretaceous was different from that of today. Given a value of  $[\text{CO}_2(\text{aq})]$ , one has to specify one more parameter of the carbonate system in order to determine the carbonate chemistry of the Cretaceous surface ocean, i.e. pH, alkalinity or  $\Sigma\text{CO}_2$ .

First of all, it is very unlikely that paleo-pH was similar to modern pH. Assuming  $p\text{CO}_2$  to have been four times higher, while keeping pH at its present value, the carbonate saturation state of the surface ocean would also have been four times higher than at present (assuming the concentration of  $\text{Ca}^{2+}$  to be similar to today's value). This appears to be unrealistic because the saturation state of the ocean is buffered by the dynamics of the lysocline, which maintains the saturation state at an approximately constant value by calcite compensation (e.g. Sundquist, 1986; Broecker and Sanyal, 1998). This constraint can be used to determine the carbonate chemistry of the Cretaceous surface ocean.

Starting at conditions typical for the modern ocean, a change in total dissolved inorganic carbon ( $\Sigma\text{CO}_2$ ) or total alkalinity ( $A_T$ ) results in a change in the carbonate chemistry that follows the calcite compensation line (Fig. 3). Given a value for  $p\text{CO}_2$  in the surface ocean, the intercept of the corresponding  $p\text{CO}_2$ -isocontour and the calcite compensation line yields

oceanic  $\Sigma\text{CO}_2$  and  $A_T$  (cf. Sundquist, 1986). From these values, the carbonate chemistry and, in particular, the surface ocean pH can be calculated (Table 1). For the calculations presented in this paper, dissociation constants as summarized in DOE (1994) at  $T = 20^\circ\text{C}$  and  $S = 35$  were used and all pH values refer to the total pH scale.

In the following, possible paleo-pH scenarios of the Cretaceous surface ocean are examined. Since our knowledge of Cretaceous seawater chemistry is incomplete, calculated pH values should be considered to be approximate values. Scenario I and II assume that  $R_{\text{CO}_2}$  (atmospheric  $\text{CO}_2$  at time  $t$  divided by 300 ppmv) (Berner, 1994) has decreased from  $\sim 3$  and  $\sim 8$  in the mid-Cretaceous, respectively, to  $R_{\text{CO}_2} \approx 1$  in the Quaternary (Fig. 4a). Using the calcite compensation constraint, corresponding changes of surface ocean pH during the past 110 Ma can be determined (Fig. 4b). From the pH change, a correction of isotopic paleotemperatures ( $\Delta T_i$  ( $^\circ\text{C}$ )) at any time for each scenario ( $i$ ) can be calculated according to:

$$\Delta T_i(^\circ\text{C}) = \Delta\text{pH}_i b s \quad (1)$$

where  $\Delta\text{pH}_i$  is the difference in pH between modern ocean and past ocean for scenario  $i$ ,  $b = -4.80^\circ\text{C} (\text{‰})^{-1}$  is the coefficient of the linear term of the paleotemperature equation (Bemis et al., 1998), and  $s = -1.42\text{‰}$  per pH unit is the slope of  $\delta^{18}\text{O}$  of calcite vs pH as derived from theory (Fig. 2). The fact that the effect of pH on  $\delta^{18}\text{O}$  has a thermodynamical basis, enabling us to derive the slope theoretically, corroborates the general applicability of the pH effect to planktonic foraminifera. Since hitherto published paleotemperature estimates are based on a variety of species, the calculated slope

was used for the correction of isotopic paleotemperatures (for discussion, see Section 4).

Depending on the scenario of pH change, SSTs of the mid-Cretaceous surface ocean are then estimated to have been between 2 and 3.5°C higher (corresponding to pH values of  $\sim 7.9$  and  $\sim 7.7$ ) than the temperatures calculated without taking into account the effect of pH on foraminiferal oxygen isotopes. These corrections do not depend on any assumptions concerning the unknown isotopic composition of the ocean; i.e. regardless of the value chosen for  $\delta_w$ , if surface ocean pH was lower in the past, then SSTs as calculated from foraminiferal  $\delta^{18}\text{O}$  without taking into account the pH effect are too low.

#### 4. Discussion

The revision of isotopic paleotemperatures for the Cretaceous surface ocean presented in this paper depends on the pH of the surface ocean at a given time. As stated earlier, uncertainties remain concerning the exact change of the surface ocean pH in the past because our knowledge of Cretaceous seawater chemistry is incomplete. However, there is a strong case for appreciably lower pH during the Cretaceous when the atmospheric  $p\text{CO}_2$  and the calcium carbonate saturation state of the ocean are taken into account. Different scenarios have been presented in order to cover a possible range of surface ocean pH changes during the Cretaceous.

One might ask whether the pH effect on foraminiferal oxygen isotopes as observed in recent species is applicable to Cretaceous planktonic foraminifera. This approach appears to be reasonable for mainly two reasons. Firstly, the effect has a well-understood thermodynamical basis from which the slope of  $\delta^{18}\text{O}$  vs pH can be predicted. Secondly, all planktonic foraminiferal species cultured so far clearly showed a decrease of  $\delta^{18}\text{O}$  with increasing pH (the mean slope observed in culture experiments being very close to the theoretically predicted slope). These results suggest that the pH effect is a universal phenomenon, although the magnitude of the effect may be species-dependent.

Spero et al. (1999) studied the effect of seawater carbonate chemistry on stable oxygen isotopes in three symbiotic and in one non-symbiotic foraminiferal

species (*Globigerina bulloides*). The slope of  $\delta^{18}\text{O}$  vs  $[\text{CO}_3^{2-}]$  observed in *G. bulloides* was about twice the slope observed in the symbiotic species. From the analysis of the  $\delta^{18}\text{O}$ - and  $\delta^{13}\text{C}$ -shell size relationship of 10 Cretaceous planktonic species, Norris and Wilson (1998) concluded that these taxa lacked algal symbionts. If so, and provided that non-symbiotic species show a correspondingly larger response to pH changes than symbiotic species do, the correction of isotopic paleotemperatures for the Cretaceous would be even larger.

As pointed out previously, the physicochemical mechanism described in Zeebe (1999) should be applicable to organisms that build their calcium carbonate shells from a mixture of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in equilibrium with the surrounding medium. This is obviously the case for the low-latitude species tested in the temperature regime 17–29°C (Spero et al., 1999). Based on the assumption that Cretaceous and modern low-latitude planktonic foraminifera behave similarly, revisions of isotopic paleotemperatures were presented in this paper. The question to be asked is: is the proposed mechanism also applicable to high-latitude or benthic foraminifera?

A priori there is no reason to assume that the  $\delta^{18}\text{O}$  of those species is immune to the described physicochemical mechanism. However, in order to gain more confidence in the applicability of the pH effect to the 'low-temperature' regime (i.e.  $\sim 0$ – $10^\circ\text{C}$ ), it is very desirable to establish whether the pH effect can be observed in modern high-latitude and benthic foraminifera as well. Then, based on the assumption that Cretaceous and modern species behave similarly, the following conclusions could be drawn. If low- and high-latitude planktonic foraminifera show a similar response, the flat equator-to-pole temperature gradient as derived from differences in  $\delta^{18}\text{O}$  of low- and high-latitude foraminifera would remain unchanged because temperature estimates increase for both the tropics and the high latitudes. On the other hand, if responses for the two temperature regimes are different, it is possible that the thermal gradient was stronger, i.e. more similar to the modern gradient, or even flatter than previously thought.

Statements regarding deep ocean temperature corrections are more complicated. Even if the pH effect is applicable to modern and Cretaceous benthic species, estimates of deep ocean pH changes during

the Cretaceous are hindered due to the unknown seawater carbonate chemistry of the deep ocean. Whereas atmospheric and surface ocean  $p\text{CO}_2$  can be assumed to be roughly in equilibrium, this is not the case for atmospheric and deep ocean  $p\text{CO}_2$ . As discussed in Section 3, this constraint, and the calcite saturation state, is crucial for estimating pH changes of the past ocean.

Errors in the estimates of the oxygen isotope composition of seawater and the surface ocean salinity during the Cretaceous introduce uncertainties, which are likely to result in low tropical SST reconstructions. However, even with salinity adjustments, estimated Cretaceous tropical SSTs are often lower than today's tropical SSTs, which is difficult to bring into line with climate modeling results. It is concluded that the pH effect has the potential to explain why sea surface temperature estimates based on foraminiferal  $\delta^{18}\text{O}$  yield low values during periods of high atmospheric  $p\text{CO}_2$  such as the Cretaceous. This mechanism may therefore help to resolve the 'cool tropic paradox' (D'Hondt and Arthur, 1996).

## 5. Conclusion

The results presented here demonstrate that seawater pH has a major effect on the stable oxygen isotope fractionation between water and calcium carbonate and thus on isotopic paleotemperature estimates (Fig. 2). The present study points out that paleoreconstructions based on foraminiferal  $\delta^{18}\text{O}$  may underestimate SSTs in the past. This approach should help to resolve, at least partially, the controversial debate on the operation of the climate system during the Cretaceous.

## Acknowledgements

I thank J. Bijma for providing the data of the culture experiments. Howie Spero, Dieter Wolf-Gladrow, Ulf Riebesell, Wally Broecker, Lee Kump and R. Stein are acknowledged for their comments on an earlier version of the manuscript. I thank B.W. Sellwood and W.W. Hay for their reviews. R.E.Z was supported by the Deutsche Forschungsgemeinschaft. Alfred Wegener Institute for Polar and Marine Research publication awi-n10092.

## References

- Barrera, E., 1994. Global environmental changes preceding the Cretaceous-Tertiary boundary: Early-late Maastrichtian transition. *Geology* 22, 877–880.
- Barrera, E., Johnson, C.C. (Eds.), 1999. Evolution of the Cretaceous Ocean-Climate System. *Geol. Soc. Am. SP 332* Boulder, Colorado 445 pp.
- Barrera, E., Savin, S.M., 1999. Evolution of late Campanian–Maastrichtian marine climates and oceans. In: Barrera, E., Johnson, C.C. (Eds.), Evolution of the Cretaceous Ocean-Climate System. *Geol. Soc. Am. SP 332* Boulder, Colorado, pp. 245–282.
- Barron, E.J., 1983. A warm, equable Cretaceous: the nature of the problem. *Earth Sci. Rev.* 19, 305–338.
- Barron, E.J., Fawcett, P.J., Peterson, W.H., Pollard, D., Thompson, S.L., 1995. A 'simulation' of mid-Cretaceous climate. *Paleoceanography* 10, 953–962.
- Bemis, B.E., Spero, H.J., Bijma, J., Lea, D.W., 1998. Reevaluation of the oxygen isotopic composition of planktonic foraminifera: experimental results and revised paleotemperature equations. *Paleoceanography* 13, 150–160.
- Berner, R.A., 1994. GEOCARB II: a revised model of atmospheric  $\text{CO}_2$  over Phanerozoic time. *Am. J. Sci.* 294, 56–91.
- Bijma, J., Spero, H.J., Lea, D.W., 1999. Reassessing foraminiferal stable isotope geochemistry: impact of the oceanic carbonate system (experimental results). In: Fischer, G., Wefer, G. (Eds.), Use of Proxies in Paleoclimatology: Examples from the South Atlantic. Springer, Berlin, pp. 489–512.
- Broecker, W.S., Sanyal, A., 1998. Does atmospheric  $\text{CO}_2$  police the rate of chemical weathering? *Glob. Biogeochem. Cycles* 12, 403–408.
- Cerling, T.E., 1991. Carbon dioxide in the atmosphere: evidence from Cenozoic and Mesozoic Paleosols. *Am. J. Sci.* 291, 377–400.
- Crowley, T.J., 1991. Past  $\text{CO}_2$  changes and tropical sea surface temperatures. *Paleoceanography* 6, 387–394.
- Crowley, T.J., North, G.R., 1991. *Paleoclimatology*. Oxford University Press, New York 339 pp.
- Crowley, T.J., Zacher, J.C., 2000. Comparison of zonal temperature profiles for past warm time periods. In: Huber, B.T., Macleod, K.G., Wing, S.L. (Eds.), Warm Climates in Earth History. Cambridge University Press, Cambridge, pp. 50–76.
- DeConto, R.M., Hay, W.W., Thompson, S.L., Bergengren, J., 1999. Late Cretaceous climate and vegetation interactions: cold continental interior paradox. In: Barrera, E., Johnson, C.C. (Eds.), Evolution of the Cretaceous Ocean-Climate System. *Geol. Soc. Am. SP 332* Boulder, Colorado, pp. 391–406.
- D'Hondt, S., Arthur, M.A., 1996. Late Cretaceous oceans and the cool tropic paradox. *Science* 271, 1838–1841.
- DOE, Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2, edited by Dickson, A.G., Goyet, C., ORNL/CDIAC-74, 1994.
- Ekart, D.D., Cerling, T.E., Montañez, I.P., Tabor, N.J., 1999. A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. *Am. J. Sci.* 209, 805–827.



- Frakes, L.A., 1999. Estimating the global thermal state from Cretaceous sea surface and continental temperature data. In: Barrera, E., Johnson, C.C. (Eds.), *Evolution of the Cretaceous Ocean-Climate System*. Geol. Soc. Am. SP 332Boulder, Colorado.
- Freeman, K.H., Hayes, J.M., 1992. Fractionation of carbon isotopes by phytoplankton and estimates of ancient CO<sub>2</sub> levels. *Glob. Biogeochem. Cycles* 6, 185–198.
- Ghosh, P., Bhattacharya, S.K., Jani, R.A., 1995. Palaeoclimate and palaeovegetation in central India during the Upper Cretaceous based on stable isotope composition of the palaeosol carbonates. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 114, 285–296.
- Hay, W.W., DeConto, R.M., 1999. Comparison of modern and Late Cretaceous meridional energy transport and oceanology. In: Barrera, E., Johnson, C.C. (Eds.), *Evolution of the Cretaceous Ocean-Climate System*. Geol. Soc. Am. SP 332Boulder, Colorado, pp. 283–300.
- Hay, W.W., DeConto, R.M., Wold, Ch.N., 1997. Climate: is the past the key to the future?. *Geol. Rundsch.* 86, 471–491.
- Huber, B.T., Hodell, D.A., 1996. Middle–Late Cretaceous climate of the southern high-latitudes: stable isotopic evidence for minimal equator-to-pole thermal gradients: reply. *Geol. Soc. Am. Bull.* 108, 1193–1196.
- Huber, B.T., Hodell, D.A., Hamilton, C.P., 1995. Middle–Late Cretaceous climate of the southern high-latitudes: stable isotopic evidence for minimal equator-to-pole thermal gradients. *Geol. Soc. Am. Bull.* 107, 1164–1191.
- McCrea, J.M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* 18, 849–857.
- Norris, R.D., Wilson, P.A., 1998. Low-latitude sea-surface temperatures for the mid-Cretaceous and the evolution of planktonic foraminifera. *Geology* 26, 823–826.
- Norris, R.D., Wilson, P.A., 1999. Low-latitude sea-surface temperatures for the mid-Cretaceous and the evolution of planktonic foraminifera: reply. *Geology* 27, 858.
- Poulsen, Ch.J., Barron, E.J., Peterson, W.H., Wilson, P.A., 1999. A reinterpretation of mid-Cretaceous shallow marine temperatures through model-data comparison. *Paleoceanography* 14, 679–697.
- Price, G.D., Hart, M.B., 1999. Low-latitude sea-surface temperatures for the mid-Cretaceous and the evolution of planktonic foraminifera: comment. *Geology* 27, 857.
- Price, G.D., Sellwood, B.W., Pirrie, D., 1996. Middle–Late Cretaceous climate of the southern high-latitudes: stable isotopic evidence for minimal equator-to-pole thermal gradients: discussion. *Geol. Soc. Am. Bull.* 108, 1192–1193.
- Price, G.D., Sellwood, B.W., Corfield, R.M., Clarke, L., Cartledge, J.E., 1998. Isotopic evidence for palaeotemperatures and depth stratification of Middle Cretaceous planktonic foraminifera from the Pacific Ocean. *Geol. Mag.* 135, 183–191.
- Sellwood, B.W., Price, G.D., Valdes, P.J., 1994. Cooler estimates of Cretaceous temperatures. *Nature* 370, 453–455.
- Shackleton, N.J., Kennett, N.J., 1975. Paleotemperature history of the Cenozoic and the initiation of Antarctic glaciation: oxygen and carbon isotope analyses in DSDP sites 277, 279, and 281. *Init. Rep. Deep Sea Drill. Proj.* 29, 743.
- Spero, H.J., Bijma, J., Lea, D.W., Bemis, B.E., 1997. Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. *Nature* 390, 497–500.
- Spero, H.J., Bijma, J., Lea, D.W., Russell, A.D., 1999. Deconvolving glacial ocean carbonate chemistry from the planktonic foraminifera carbon isotope record. In: Abrantes, F., Mix, A.C. (Eds.), *Reconstructing Ocean History: A Window into the Future*. Kluwer Academic/Plenum Publishers, New York, pp. 329–342.
- Spicer, R.A., Corfield, R.M., 1992. A review of terrestrial and marine climates in the Cretaceous with implications for modeling the Greenhouse Earth. *Geol. Mag.* 129, 169–180.
- Sundquist, E.T., 1986. Geologic Analogs: their value and limitations in carbon dioxide research. In: Trabalka, J.R., Reichle, D.E. (Eds.), *The Changing Carbon cycle: A Global Analysis*. Springer, New York, pp. 371–402.
- Tarduno, J.A., et al., 1998. Evidence for extreme climatic warmth from Late Cretaceous Arctic vertebrates. *Science* 282, 2241–2244.
- Uzdowski, E., Hoefs, J., 1993. Oxygen isotope exchange between carbonic acid, bicarbonate, carbonate, and water: a re-examination of the data of McCrea (1950) and an expression for the overall partitioning of oxygen isotopes between the carbonate species and water. *Geochim. Cosmochim. Acta* 57, 3815–3818.
- Zachos, J.C., Stott, L.D., Lohmann, K.C., 1994. Evolution of early Cenozoic marine temperatures. *Paleoceanography* 9, 353–387.
- Zeebe, R.E., 1999. An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes. *Geochim. Cosmochim. Acta* 63, 2001–2007.
- Zeebe, R.E., Bijma, J., Wolf-Gladrow, D.A., 1999. A diffusion-reaction model of carbon isotope fractionation in foraminifera. *Mar. Chem.* 64, 199–227.