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## An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes

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**Abstract**—Stable oxygen isotope ratios of foraminiferal calcite are widely used in paleoceanography to provide a chronology of temperature changes during ocean history. It was recently demonstrated that the stable oxygen isotope ratios in planktonic foraminifera are affected by changes of the seawater chemistry carbonate system: the  $\delta^{18}\text{O}$  of the foraminiferal calcite decreases with increasing  $\text{CO}_3^{2-}$  concentration or pH. This paper provides a simple explanation for seawater chemistry dependent stable oxygen isotope variations in the planktonic foraminifera *Orbulina universa* which is derived from oxygen isotope partitioning during inorganic precipitation. The oxygen isotope fractionation between water and the dissolved carbonate species  $S = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  decreases with increasing pH. Provided that calcium carbonate is formed from a mixture of the carbonate species in proportion to their relative contribution to  $S$ , the oxygen isotopic composition of  $\text{CaCO}_3$  also decreases with increasing pH. The slope of shell  $\delta^{18}\text{O}$  vs.  $[\text{CO}_3^{2-}]$  of *Orbulina universa* observed in culture experiments is  $-0.0022\text{‰} (\mu\text{mol kg}^{-1})^{-1}$  (Spero et al., 1997), whereas the slope derived from inorganic precipitation is  $-0.0024\text{‰} (\mu\text{mol kg}^{-1})^{-1}$ . The theory also provides an explanation of the nonequilibrium fractionation effects in synthetic carbonates described by Kim and O'Neil (1997) which can be understood in terms of equilibrium fractionation at different pH. The results presented here emphasize that the oxygen isotope fractionation between calcium carbonate and water does not only depend on the temperature but also on the pH of the solution from which it is formed. Copyright © 1999 Elsevier Science Ltd

### 1. INTRODUCTION

Since the pioneering work of Urey (1947), McCrea (1950), and Epstein et al. (1953) the use of stable oxygen isotope ratios ( $^{18}\text{O}/^{16}\text{O}$ ) as a paleotemperature indicator has become a standard tool in paleoceanography. The isotopic composition of sedimentary marine carbonates, particularly that of foraminiferal calcite ( $\text{CaCO}_3$ ) (e.g., Erez and Luz, 1983; Bouvier-Soumagnac and Duplessy, 1986; Bemis et al., 1998) is widely used to reconstruct the temperature of ancient oceans (for review, see e.g., Emiliani, 1966; Wefer and Berger, 1991). The interpretation of stable oxygen isotope values as a temperature proxy is complicated by several factors which have been studied in the past: the unknown  $^{18}\text{O}$  content of the ancient oceans, metabolic effects on carbonate precipitation, and the isotopic preservation of primary oxygen in the carbonates [an overview has been given by Hoefs (1987)].

In recent culture experiments with living foraminifera a new key variable influencing stable oxygen isotope partitioning in foraminifera was discovered: the seawater carbonate chemistry. Spero et al. (1997) demonstrated that higher pH values or increasing  $\text{CO}_3^{2-}$  concentrations result in isotopically lighter shells in the planktonic foraminifera *Orbulina universa* (Fig. 1) and *Globigerina bulloides*. In another series of experiments this effect was also observed in *Globigerinoides sacculifer* and *Globigerinoides ruber* (Bijma et al., in press). Consequently, higher pH values during the last glacial maximum [as indicated by boron isotope analysis in foraminifera (Sanyal et al., 1995)], would result in  $^{18}\text{O}$  depleted shells. Lower  $\delta^{18}\text{O}$  values are

interpreted as higher temperatures and therefore result in sea surface temperature (SST) estimates that might be up to  $1^\circ\text{C}$  too high. Correcting for this effect would bring tropical SST closer to estimates based on other marine proxies, e.g., Sr/Ca ratios in corals and terrestrial indicators such as snowline and ice-core  $\delta^{18}\text{O}$ .

A comprehension of the effect of seawater carbonate chemistry changes on stable oxygen isotopes is necessary before experimental relationships are utilized for the reconstruction of ocean history. The aim of this paper is to provide a simple explanation for the described effect. The results of the inorganic precipitation experiments by McCrea (1950) and Ussdowski et al. (1991) are examined. It is shown that the oxygen isotope depletion in, for example, *Orbulina universa* can be explained by a change of the isotopic composition of the dominant chemical species in solution from which the calcite is formed.

The basic mechanism can be described as follows: the total dissolved inorganic carbon ( $\Sigma\text{CO}_2 = [\text{CO}_2] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ ) present in solution is mainly in the form of  $\text{HCO}_3^-$  at intermediate pH and mainly in the form of  $\text{CO}_3^{2-}$  at high pH. Since  $\text{HCO}_3^-$  is isotopically heavier than the  $\text{CO}_3^{2-}$  (see the next section and Fig. 3), the oxygen isotopic composition of the total dissolved carbonate species decreases with increasing pH. Provided that the calcite is formed from a mixture of the carbonate species in proportion to their relative contribution to  $S = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  the oxygen isotopic composition of the calcite also decreases with increasing pH. This hypothesis will be discussed in more detail in secs. 2 and 4.

The obtained results suggest that oxygen isotope effects associated with inorganic and biological calcification are quite

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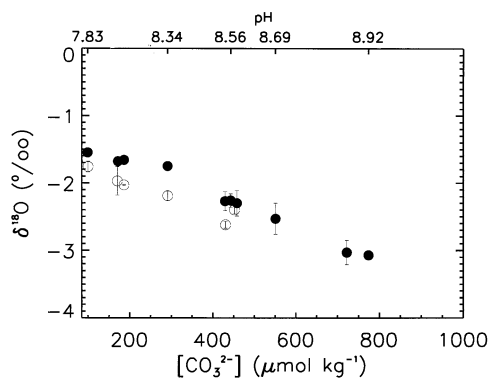


Fig. 1. Oxygen isotopic composition of foraminiferal calcite (*Orbulina universa*) as a function of  $[\text{CO}_3^{2-}]$  ( $\Sigma\text{CO}_2 = \text{const.} \sim 2032 \mu\text{mol kg}^{-1}$ ). The shells are depleted in  $^{18}\text{O}$  as  $[\text{CO}_3^{2-}]$  or  $p\text{H}$  increases. The mean slope given by Spero et al. (1997) of shell  $\delta^{18}\text{O}$  vs  $[\text{CO}_3^{2-}]$  is  $-0.0022 \pm 0.0004\text{‰} (\mu\text{mol kg}^{-1})^{-1}$  in the dark (filled circles) and  $-0.0015 \pm 0.0008\text{‰} (\mu\text{mol kg}^{-1})^{-1}$  in the light (open circles).

similar in the case of *Orbulina universa*. This does not hold true in general as will be discussed in the concluding section. Inorganic oxygen isotope effects observed in quantitative precipitation (i.e., none of the carbonate in solution escapes precipitation) (McCrea, 1950; Usdowski et al., 1991) are compared to effects observed in nonquantitative (slow) precipitation of synthetic carbonates (Kim and O'Neil, 1997) which can be explained on the basis of the theory described in this paper.

## 2. INORGANIC OXYGEN ISOTOPE PARTITIONING

Inorganic calcite precipitation in solution consumes calcium, carbon, and oxygen with a certain isotope ratio from the surrounding medium. Thus, the isotopic composition of the precipitated calcite depends on the isotopic composition of the source material. Concerning the source of oxygen-bearing compounds for calcification it is therefore necessary to understand the chemistry and isotopic composition of the dissolved car-

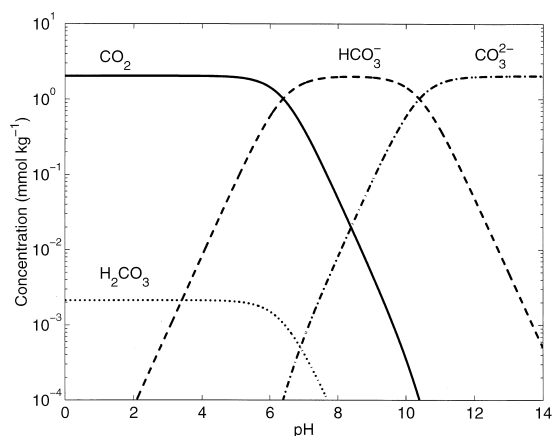


Fig. 2. The concentration of the dissolved carbonate species as a function of  $p\text{H}$ :  $\text{CO}_2$  (solid line),  $\text{H}_2\text{CO}_3$  (dotted line),  $\text{HCO}_3^-$  (dashed line), and  $\text{CO}_3^{2-}$  (dotted-dashed line). The values shown correspond to fresh water conditions ( $T = 19^\circ\text{C}$ ,  $\Sigma\text{CO}_2 \sim 2 \text{ mmol kg}^{-1}$ ).

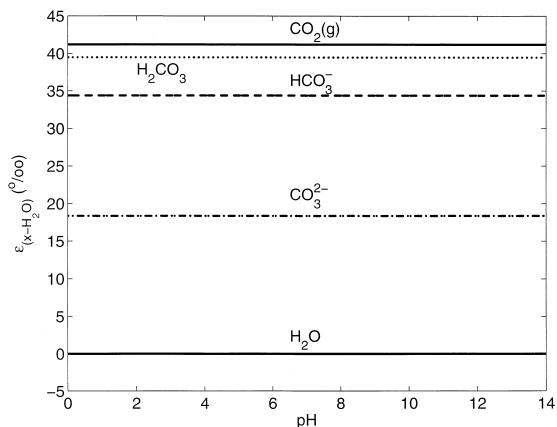
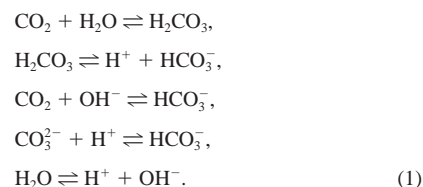


Fig. 3. The oxygen isotope partitioning between the dissolved carbonate species relative to  $\text{H}_2\text{O}$ :  $\text{CO}_2$  (solid line),  $\text{H}_2\text{CO}_3$  (dotted line),  $\text{HCO}_3^-$  (dashed line), and  $\text{CO}_3^{2-}$  (dotted-dashed line). The fractionation is expressed as  $\epsilon_{(x-\text{H}_2\text{O})} = [\alpha_{(x-\text{H}_2\text{O})} - 1] \times 1000$ , where  $x$  denotes the respective carbonate species. Since the oxygen reservoir in the water is more than four orders of magnitude larger than the reservoir of oxygen contained in the carbonate species, the isotopic composition of the water and of each carbonate species does not change with  $p\text{H}$  (see the text).

bonate species  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  (in this paper  $\text{CO}_2$  refers to aqueous  $\text{CO}_2$ ). Figure 2 displays the concentration of the carbonate species as a function of  $p\text{H}$  typical for fresh water ( $T = 19^\circ\text{C}$ ). At low  $p\text{H}$  aqueous  $\text{CO}_2$  is the dominant species, whereas  $\text{HCO}_3^-$  is most abundant at intermediate  $p\text{H}$ , and  $\text{CO}_3^{2-}$  is the dominant carbonate species in solution at high  $p\text{H}$ . The concentration of carbonic acid ( $\text{H}_2\text{CO}_3$ ) is small compared to  $[\text{CO}_2]$  ( $\sim 0.1\%$ ). However,  $\text{H}_2\text{CO}_3$  is important for the oxygen isotope equilibrium because the exchange between water and the carbonate species occurs via carbonic acid. The chemical reactions considered are



From the work of McCrea (1950) and Usdowski et al. (1991) the isotope partitioning between the carbonate species and water in equilibrium can be calculated (Usdowski and Hoefs,

Table 1. Oxygen isotope fractionation factors for the carbonate species with respect to water ( $19^\circ\text{C}$ ).

Species	$\epsilon_{(x-\text{H}_2\text{O})}(\text{‰})$
$\text{CO}_2(\text{aq})$	57.9 <sup>a</sup>
$\text{CO}_2(\text{g})$	41.2 <sup>b</sup> ( $25^\circ\text{C}$ )
$\text{H}_2\text{CO}_3$	39.5 <sup>a</sup>
$\text{HCO}_3^-$	34.3 <sup>c</sup>
$\text{CO}_3^{2-}$	18.4 <sup>a</sup>

<sup>a</sup> Usdowski et al. (1991);

<sup>b</sup> Kim and O'Neil (1997);

<sup>c</sup> recalculated after Usdowski et al. (1991).

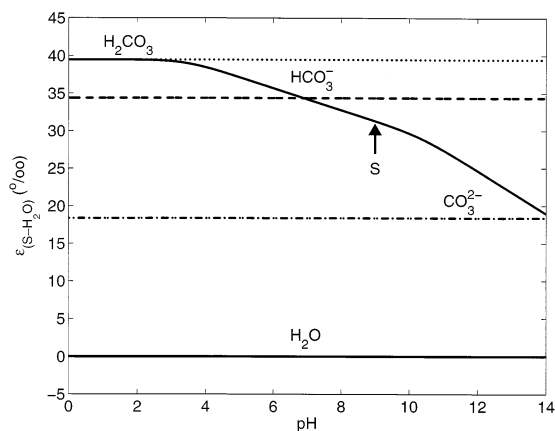


Fig. 4. The oxygen isotope partitioning between water and  $S = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  as a function of  $p\text{H}$ . As  $p\text{H}$  increases the concentration of the carbonate species in solution changes from mainly  $\text{H}_2\text{CO}_3$  to  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  resulting in a decrease of  $\varepsilon_{(S-\text{H}_2\text{O})}$  with increasing  $p\text{H}$ .

1993). The results are summarized in Fig. 3 and Table 1. [The value for the fractionation between  $\text{HCO}_3^-$  and water was recalculated; it differs by 0.8‰ from the one given by Usdowski et al. (1991) and is the correct value (Usdowski, private communication).] The fractionation between water and a carbonate species is expressed as

$$\varepsilon_{(x-\text{H}_2\text{O})} = [\alpha_{(x-\text{H}_2\text{O})} - 1] \times 1000$$

with  $x$  denoting the respective carbonate species. For example, the fractionation factor  $\alpha_{(\text{CO}_2-\text{H}_2\text{O})}$  is given by

$$\alpha_{(\text{CO}_2-\text{H}_2\text{O})} = \frac{2[\text{C}^{18}\text{O}^{18}\text{O}] + [\text{C}^{18}\text{O}^{16}\text{O}]}{2[\text{C}^{16}\text{O}^{16}\text{O}] + [\text{C}^{18}\text{O}^{16}\text{O}]} \times \frac{[\text{H}_2^{16}\text{O}]}{[\text{H}_2^{18}\text{O}]},$$

which describes the oxygen isotope partitioning in equilibrium. The time to establish oxygen isotope equilibrium in the system is about 680 minutes at  $p\text{H}$  8.3, whereas only ca. 30 s are required to achieve carbon isotope equilibrium [cf. e.g., Usdowski et al. (1991) and Zeebe et al. (1999a)]. It should be emphasized that by far the most oxygen atoms of the system are contained in  $\text{H}_2\text{O}$  (the molar ratio of  $\Sigma\text{CO}_2$  and  $[\text{H}_2\text{O}]$  in seawater is approximately 1:28000). The isotopic composition of the water can therefore be assumed constant which in turn means that independent of  $p\text{H}$  the carbonate species equilibrate with the water without changing its isotopic composition. For instance, as the dominant species in solution changes from  $\text{CO}_2$  to  $\text{HCO}_3^-$  as  $p\text{H}$  increases, the water is marginally enriched in  $^{18}\text{O}$  because  $\text{CO}_2$  is isotopically heavier than  $\text{HCO}_3^-$ . The enrichment is, however, virtually equal to zero (ca. 0.0004‰). Since the isotope partitioning in thermodynamic equilibrium between two chemical species at specified temperature and pressure is constant (i.e.,  $\alpha_{(\text{CO}_2-\text{H}_2\text{O})} = \text{const.}$ ) the isotopic composition of  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  is constant over the entire  $p\text{H}$  range (see Fig. 3). Carbon dioxide is the isotopically heaviest species followed by  $\text{H}_2\text{CO}_3$  (enriched in  $^{18}\text{O}$  compared to  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ), whereas  $\text{CO}_3^{2-}$  is the isotopically lightest species. Combining the results shown in Figs. 2 and 3 the isotopic fractionation factor  $\alpha_{(S-\text{H}_2\text{O})}$  between water and the sum of the species which contain the carbonate group

$S = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  at a given  $p\text{H}$  can be calculated (Fig. 4). It is noticed that  $S$  differs from  $\Sigma\text{CO}_2 = [\text{CO}_2] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ . Thermodynamic calculations yield a linear relationship between  $\ln \alpha_{(S-\text{H}_2\text{O})}$  and  $\ln S/[\text{CO}_2]$  (Usdowski and Hoefs, 1993):

$$\ln \alpha_{(S-\text{H}_2\text{O})} = -6.10 \times 10^{-4} \ln(S/[\text{CO}_2]) + 0.03452. \quad (2)$$

At a limiting  $p\text{H} = 0$  the fractionation factor  $\alpha_{(S-\text{H}_2\text{O})}$  is equal to the fractionation between  $\text{H}_2\text{CO}_3$  and  $\text{H}_2\text{O}$  (all dissolved carbonate is essentially carbonic acid), whereas at a limiting  $p\text{H} = 14$ ,  $\alpha_{(S-\text{H}_2\text{O})}$  equals  $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}$  (all dissolved carbonate is essentially carbonate ion). At intermediate  $p\text{H}$ ,  $\alpha_{(S-\text{H}_2\text{O})}$  largely reflects the fractionation between  $\text{HCO}_3^-$  and  $\text{H}_2\text{O}$  (Fig. 4).

In summary, the isotopic composition of the sum of the species containing the carbonate group ( $S$ ) is decreasing with  $p\text{H}$ . If calcium carbonate is quantitatively precipitated from a bicarbonate-carbonate solution (i.e., none of the carbonate in solution escapes precipitation) the oxygen isotopic composition of the precipitate is the average of the oxygen present in the bicarbonate and carbonate at the time of precipitation (McCrea, 1950). Thus, the calcium carbonate simply reflects the isotopic composition of  $S$  and is also decreasing with  $p\text{H}$ . The key hypothesis of this paper is that also in a nonquantitative precipitation of biogenic carbonate (foraminiferal calcite) and synthetic carbonate (calcite, whiterite) the calcium carbonate is built from a mixture of bicarbonate and carbonate proportional to their respective contributions to  $S$ . The validity of this hypothesis is confirmed by the coincidence of the observed and calculated slope of  $\delta^{18}\text{O}$  vs  $[\text{CO}_3^{2-}]$  in foraminiferal calcite and  $S$ , respectively (next section) and the agreement between oxygen isotope effects observed in synthetic carbonates (Kim and O'Neil, 1997) and theoretical predictions (Sec. 4).

### 3. COMPARISON WITH CULTURE DATA OF *ORBULINA UNIVERSA*

The results of the oxygen isotope partitioning of inorganic precipitation discussed in the previous section are compared to shell  $\delta^{18}\text{O}$  vs  $[\text{CO}_3^{2-}]$  observed in culture experiments with living foraminifera (Spero et al., 1997). In order to (a) avoid complications associated with metabolic effects (such as photosynthesis of the symbiotic algae in light) and (b) ensure that  $\Sigma\text{CO}_2$  of the culture medium remained constant, the dark experiments of Spero et al. (1997) ( $\Sigma\text{CO}_2 = \text{const.} \sim 2032 \mu\text{mol kg}^{-1}$ ) are chosen for comparison. The fractionation factors reported by Usdowski et al. (1991) refer to a fresh water system at  $19^\circ\text{C}$  (the dependence on temperature was not examined in their experiments). On the other hand, foraminifera were cultured in seawater at  $22^\circ\text{C}$ . Since both systems exhibit different temperatures and salinities, absolute values ( $\delta^{18}\text{O}$ ) of the carbonate species in solution and of the calcite are not compared. However, the calculated slope of the fractionation between the major carbonate component in solution ( $S$ ) and the water can be compared to the slope of foraminiferal  $\delta^{18}\text{O}$  as a function of  $[\text{CO}_3^{2-}]$  (Fig. 5). The intercept of the calculated curve of  $S$  (solid line) with the vertical axis is chosen arbitrarily whereas the slope is predicted by theory.

The observed slope of shell  $\delta^{18}\text{O}$  vs  $[\text{CO}_3^{2-}]$  in *Orbulina universa* is  $-0.0022 \pm 0.0004\%$  ( $\mu\text{mol kg}^{-1}$ ) $^{-1}$  in dark ex-

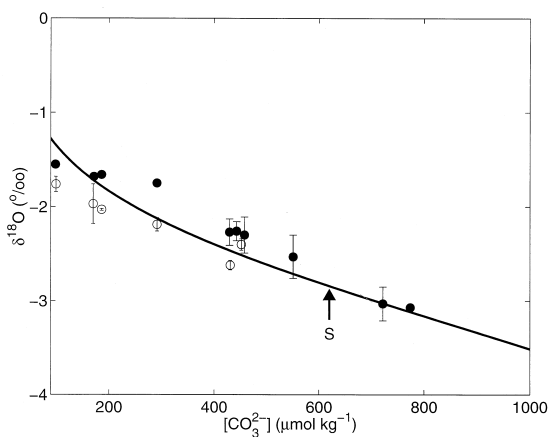


Fig. 5. Oxygen isotopic composition of foraminiferal calcite (closed/open circles: dark/high light) and of  $S = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  vs  $[\text{CO}_3^{2-}]$  as predicted from theory (solid line). The mean slope given by Spero et al. (1997) of shell  $\delta^{18}\text{O}$  vs  $[\text{CO}_3^{2-}]$  for their constant  $\Sigma\text{CO}_2$  experiments is  $-0.0022 \pm (\mu\text{mol kg}^{-1})^{-1}$  in the dark. The mean slope predicted from theory is  $-0.0024 \pm (\mu\text{mol kg}^{-1})^{-1}$ .

periments, whereas the mean slope of  $S$  vs  $[\text{CO}_3^{2-}]$  within the interval from 100–1000  $\mu\text{mol kg}^{-1}$  calculated from theory is  $-0.0024\%$  ( $\mu\text{mol kg}^{-1}$ ) $^{-1}$ . From this coincidence the following conclusion is drawn: the depletion of  $^{18}\text{O}$  in *Orbulina universa* with increasing carbonate ion concentration can be explained by the uptake of bicarbonate and carbonate for calcification proportional to their respective contribution to  $S$ . [Note that this description is simplified—the calculation of the isotope partitioning is not a simple mass balance calculation, for details see Usdowski and Hoefs (1993)]. As the species in solution change from mainly  $\text{HCO}_3^-$  (isotopically heavy) at intermediate  $\text{pH}$  to mainly  $\text{CO}_3^{2-}$  (isotopically light) at high  $\text{pH}$  the isotopic composition of  $S$  decreases and so does the isotopic composition of the calcite.

It is reasonable to assume that the calcite carries an isotopic fingerprint of  $\text{HCO}_3^-$  at  $\text{pH}$  6.9 and of  $\text{CO}_3^{2-}$  at  $\text{pH}$  14. The ratio of  $[\text{HCO}_3^-]/S$  and  $[\text{CO}_3^{2-}]/S$  is 0.9994 and 0.9998 at these  $\text{pH}$  values, respectively, implying that calcification consumes exclusively  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  (all other carbonate species exhibit negligible contributions to  $S$  here). Thus, it is not surprising that the isotopic composition of the precipitate is decreasing with increasing  $\text{pH}$ . However, the presented results suggest more: the calcite is obviously formed from a mixture of bicarbonate and carbonate such that the oxygen isotope composition of the calcite (solid) and of  $S$  (dissolved) are equally decreasing with increasing  $[\text{CO}_3^{2-}]$ .

#### 4. COMPARISON WITH SYNTHETIC CARBONATES (SLOW PRECIPITATION)

Similar to the comparison described in the preceding section, the results of the inorganic oxygen isotope partitioning (quantitative precipitation) are compared to oxygen isotope effects in synthetic carbonates that have been precipitated slowly from solution (nonquantitative precipitation) as reported by Kim and O'Neil (1997). In this case, however, the analysis of the experimental data is not as straightforward as the analysis of the culture data of *Orbulina universa*.

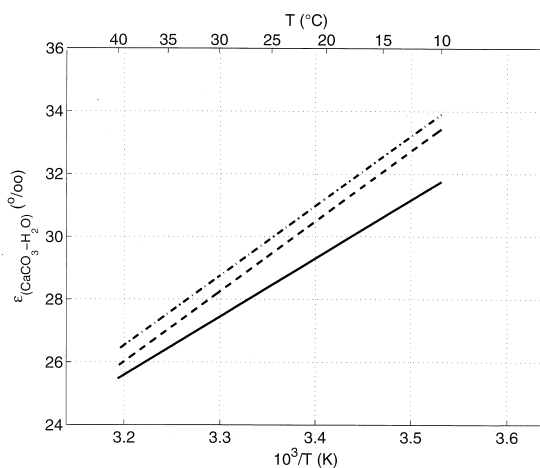


Fig. 6. The oxygen isotope fractionation between calcite and water as determined by Kim and O'Neil (1997) as a function of temperature and different initial concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ : 5  $\text{mmol kg}^{-1}$  (solid line), 15  $\text{mmol kg}^{-1}$  (dashed line), and 25  $\text{mmol kg}^{-1}$  (dotted-dashed line). Note that  $\epsilon_{(\text{CaCO}_3-\text{H}_2\text{O})} = [\alpha_{(\text{CaCO}_3-\text{H}_2\text{O})} - 1] \times 1000$  is shown [this value slightly differs from  $10^3 \ln(\alpha)$ ].

Kim and O'Neil (1997) thoroughly examined equilibrium oxygen isotope effects in synthetic carbonates and determined new values for the oxygen isotope fractionation between water and several carbonates at low temperatures. Surprisingly, they also found that the isotopic fractionation between water and well soluble carbonates such as calcite ( $\text{CaCO}_3$ ) and whiterite ( $\text{BaCO}_3$ ) increased with increasing initial concentrations of  $\text{Ca}^{2+}/\text{Ba}^{2+}$  and  $\text{HCO}_3^-$  at a given temperature (Fig. 6). They judged these effects to be nonequilibrium fractionations since there should be only one equilibrium fractionation at any temperature. However, I suggest that the observed effects are equilibrium fractionations expressed at different  $\text{pH}$  of the solution.

In the following discussion calcite is considered, however, the results presented should hold for carbonates in general as will be demonstrated for whiterite. Kim and O'Neil (1997) prepared their solutions by dissolving equimolar concentrations of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  in deionized water, with concentrations ranging from 5 to 25  $\text{mmol kg}^{-1}$ . Slow precipitation was promoted by bubbling nitrogen gas through the solution to remove  $\text{CO}_2$ , therefore increasing the supersaturation of the solution. Removal of  $\text{CO}_2$  is accompanied by increase of  $\text{pH}$  and  $[\text{CO}_3^{2-}]$  until a critical state of supersaturation ( $[\text{CO}_3^{2-}]_c$ ) is reached and calcium carbonate starts to precipitate (no seeds were used). Since the corresponding critical  $\text{pH}$  is a function of the total dissolved inorganic carbon, the critical state of supersaturation depends on the initial concentration of  $\text{HCO}_3^-$ . This effect can be illustrated utilizing the concentrations of the dissolved carbonate species as a function of  $\text{pH}$  shown in Fig. 2. As  $\text{pH}$  increases,  $\text{HCO}_3^-$  is converted to  $\text{CO}_3^{2-}$  and the carbonate ion concentration increases until all dissolved carbonate is essentially carbonate ion. For the composition of the solution displayed in Fig. 2 ( $\Sigma\text{CO}_2 = 2 \text{ mmol kg}^{-1}$ )  $\text{pH}$  must increase to about 8 to reach a critical state of supersaturation of, e.g.,  $[\text{CO}_3^{2-}]_c = 10^{-2} \text{ mmol kg}^{-1}$ . However, if  $\Sigma\text{CO}_2$  is smaller (corresponding to a lower initial concentration of

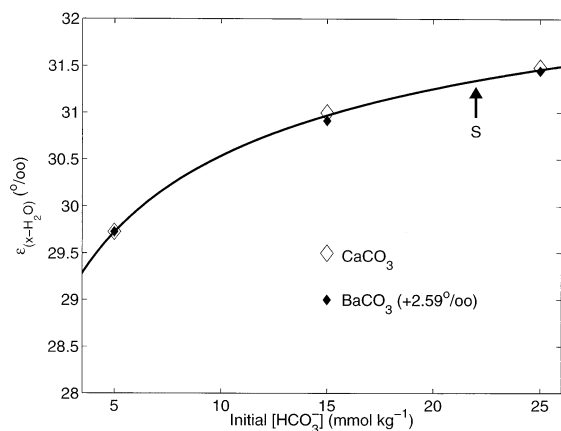


Fig. 7. The oxygen isotope fractionation between water and calcite (open diamonds), and water and whiterite (filled diamonds) as determined by Kim and O'Neil (1997) and of S (solid line) as a function of the initial concentration of  $\text{HCO}_3^-$  at  $19^\circ\text{C}$ . The intercept of the calculated curve was chosen arbitrarily; the supersaturation was set at  $s_c = 2$  (see text). A value of  $2.59\text{‰}$  was added to the values for whiterite. In this representation, the values for calcite and whiterite for an initial concentration of  $5 \text{ mmol kg}^{-1}$  are identical.

$\text{HCO}_3^-$ )  $p\text{H}$  must increase further to reach the same critical state of supersaturation.

As described in detail in the Appendix the critical  $p\text{H}$  values of the solutions studied by Kim and O'Neil (1997) can be estimated as 7.8, 6.9, and 6.6 for initial concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  of 5, 15, and  $25 \text{ mmol kg}^{-1}$ , respectively. (The values were calculated for calcite precipitation, assuming a critical supersaturation of  $s_c = 2$ .) The essential result of the consideration presented so far is as follows. Provided that the critical  $p\text{H}$  represents a mean  $p\text{H}$  at which calcite was precipitated and that at every  $p\text{H}$  oxygen isotope equilibrium was established between the carbonate species and water, it follows from the theory presented in Sec. 2 (cf. Fig. 4), that the isotopic composition of S and thus of the calcite decreases with critical  $p\text{H}$  (or lower initial concentration).

The values of the oxygen isotope fractionation between calcite/whiterite and water as given by Kim and O'Neil (1997) for different initial concentrations at  $19^\circ\text{C}$  (diamonds) and the fractionation between S and water as calculated from the critical  $p\text{H}$  values at  $19^\circ\text{C}$  and a critical supersaturation of  $s_c = 2$  (solid line) are shown in Fig. 7. In order to plot the values for calcite and whiterite in the same graph, the difference of the equilibrium fractionation between calcite and water, and whiterite and water ( $\sim 2.59\text{‰}$ ) at  $19^\circ\text{C}$  and an initial concentration of  $5 \text{ mmol kg}^{-1}$  was added to the values for whiterite. It is emphasized that the intercept of the calculated curve of S with the vertical axis is chosen arbitrarily. Since the actual critical  $p\text{H}$  values of the experiments are not known, absolute values cannot be compared. The influence of different critical  $p\text{H}$  values was examined by varying the supersaturation  $s_c$  between 1 and 8 which had only a marginal effect on the shape of the curve. Keeping in mind the assumptions necessary to obtain the theoretically derived fractionation the calculated curve and the experimental data show excellent agreement.

Even though the absolute fractionation between water and  $\text{CaCO}_3$ , and water and  $\text{BaCO}_3$  are quite different, the increase

of the fractionation with increasing initial concentration of  $\text{HCO}_3^-$  in solution is almost identical for these minerals. This result and the fact that experimental results were well reproducible suggest that the described effect is caused by the solution chemistry rather than by different nonequilibrium (kinetic) fractionation effects associated with crystal growth. In summary, the nonequilibrium fractionation as described by Kim and O'Neil (1997) can be explained by multiple equilibrium fractionations at a single temperature but at different  $p\text{H}$ .

The results also suggest that the oxygen isotope partitioning observed in quantitative precipitation experiments (i.e., none of the carbonate in solution escapes precipitation) as observed by McCrea (1950) and Usdowski et al. (1991) also holds for nonquantitative precipitation of synthetic carbonates. This is in complete analogy to the oxygen isotope effects observed in *Orbulina universa*. Figure 7 also shows that for lower initial concentrations (more dilute solutions) the theory predicts further decreasing fractionation between water and the carbonates. However, this effect can only be observed if isotopic equilibrium is achieved between the water and the carbonate species at any  $p\text{H}$  for which the equilibration time is crucial. The time required to establish oxygen isotope equilibrium in the system strongly increases with  $p\text{H}$ . For example, the time required for 99% equilibration is ca. 4 and 100 h at  $p\text{H}$  7.67 and 10.3, respectively. It would be very interesting to compare the theoretical predictions with the results of experimental work that takes into account the time required for oxygen isotope equilibration. Experiments as proposed by Kim and O'Neil (1997) (experiments will be made with extremely dilute solutions in the future to test that we have indeed reached a limiting value) are desirable.

## 5. DISCUSSION AND CONCLUSIONS

On the basis of the theoretical background presented in this paper the observed  $\delta^{18}\text{O}$  variations in foraminifera appear no longer to be an isolated phenomenon. Stable oxygen isotope depletions with increasing  $[\text{CO}_3^{2-}]$  or  $p\text{H}$  are an inevitable result of changes in the seawater carbonate chemistry. The described mechanism responsible for oxygen isotope depletion in carbonates with increasing  $p\text{H}$  should be applicable to marine (and also fresh water) carbonates built from a mixture of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . This may have important consequences for the interpretation of stable oxygen isotope values as a paleotemperature indicator. An increase of seawater  $p\text{H}$  of 0.2–0.3 units causes a decrease of ca. 0.22–0.33‰ in  $\delta^{18}\text{O}$  of foraminiferal calcite which is usually interpreted as a temperature increase of the seawater. Applying this relationship to the last glacial maximum [see Sanyal et al. (1995)] estimates of tropical sea surface temperatures based on foraminiferal oxygen isotopes would yield lower SST which is more compatible with other proxy data (Spero et al., 1997). In fresh water environments where  $p\text{H}$  may have been much more variable in the past, the effect on stable oxygen isotopes might be even more pronounced.

It was shown that the effect of carbonate seawater concentration on the stable oxygen isotopes of inorganic calcite is virtually indistinguishable from the effect observed in the planktonic foraminifer *Orbulina universa*. This does not hold for biogenic carbonates in general. For instance, the slope of

$\delta^{18}\text{O}$  vs  $[\text{CO}_3^{2-}]$  in *Globigerina bulloides* is about twice the slope in *Orbulina universa*, implying that additional mechanisms such as an internal pool or kinetic isotope effects are active. The described mechanism might also not be applicable to isotope effects in carbonates which are built mainly from  $\text{CO}_2$  as is likely to be the case in corals. McConnaughey (1989) showed that isotope depletions in corals can be explained by a kinetic effect during the hydroxylation of carbon dioxide ( $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$ ). The precipitated calcium carbonate is therefore not built from  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  in equilibrium with the surrounding medium which is a prerequisite for the application of the mechanism described in this paper.

The theory also provides an elegant explanation of the fractionation effects interpreted to be nonequilibrium effects by Kim and O'Neil (1997). As demonstrated, the oxygen isotopic fractionation between water and carbonates is not only a function of temperature but of the pH of the solution as well. Kim and O'Neil (1997) speculated on an equilibrium system responsible for the observed isotope effects. This equilibrium system certainly is the chemistry of the solution.

In conclusion, the observed decrease of  $\delta^{18}\text{O}$  vs  $[\text{CO}_3^{2-}]$  in *Orbulina universa* can be explained by a simple mechanism which involves the oxygen isotope partitioning between the dissolved carbonate species in water. The presented results suggest that the average oxygen present in the dissolved bicarbonate and carbonate at the time of precipitation equals the average oxygen in the precipitate. It is pointed out that there is no analogous mechanism that could account for stable carbon isotope depletions in foraminifera with increasing pH. Wolf-Gladrow et al. (1999) and Zeebe et al. (1999b) explained the decrease of  $\delta^{13}\text{C}$  vs  $[\text{CO}_3^{2-}]$  by an interaction of the seawater chemistry and the vital effects of the living organism within the microenvironment (diffusive boundary layer) of the foraminifer. Even though their model correctly predicts carbon isotope variations in the calcite to a large degree, some discrepancies between model results and observations remained. They concluded that an additional kinetic effect might be responsible for the remaining inconsistency. Is a kinetic effect the key variable responsible also for the larger oxygen isotope effects in *Globigerina bulloides* in comparison to *Orbulina universa*, and could it be the reason for the observed covariance of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in these organisms?

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## APPENDIX

### Calculation of critical pH

The critical state of supersaturation ( $s_c$ ) of the solutions used by Kim and O'Neil (1997) that is required to initiate nucleation can be written as (Stumm and Morgan, 1996)

$$s_c = \left( \frac{\gamma_{\text{Ca}^{2+}}[\text{Ca}^{2+}]\gamma_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}]_c}{K_{sp}} \right)^{\frac{1}{2}}, \quad (\text{A1})$$

where  $\gamma$ 's are activities,  $[\text{CO}_3^{2-}]_c$  is the critical carbonate ion concentration, and  $\log k_{sp} = -8.45$  is the solubility product of calcite in fresh water at 19°C (Plummer and Busenberg, 1982). Thus, the critical carbonate ion concentration is (the calcium concentration is constant over pH and equal to the initial concentration of  $[\text{HCO}_3^-]$ ):

$$[\text{CO}_3^{2-}]_c = \frac{s_c^2 K_{sp}}{[\text{Ca}^{2+}]\gamma_{\text{Ca}^{2+}}\gamma_{\text{CO}_3^{2-}}}. \quad (\text{A2})$$

On the other hand, carbonate ion concentration is always given by

$$[\text{CO}_3^{2-}] = \frac{\Sigma\text{CO}_2}{1 + [\text{H}^+]/K_2 + [\text{H}^+]^2/(K_1K_2)}, \quad (\text{A3})$$

where  $\log K_1 = -6.39$  and  $\log K_2 = -10.39$  correspond to the first and second dissociation constants of carbonic acid at 19°C (Plummer and Busenberg, 1982). The critical hydrogen ion concentration can therefore be calculated from (A2) and (A3):

$$[\text{H}^+]_c = -\frac{K_1}{2} + \sqrt{\left(\frac{K_1}{2}\right)^2 - K_1K_2\left(1 - \frac{\Sigma\text{CO}_2[\text{Ca}^{2+}]\gamma_{\text{Ca}^{2+}}\gamma_{\text{CO}_3^{2-}}}{s_c^2K_{sp}}\right)}, \quad (\text{A4})$$

where  $\Sigma\text{CO}_2$  is the total dissolved inorganic carbon which is approximately equal to the initial concentration of  $\text{HCO}_3^-$ . Assuming  $\gamma_{\text{Ca}^{2+}} = \gamma_{\text{CO}_3^{2-}} = 0.5$  [ionic strengths of the solutions used by Kim and O'Neil (1997) were about 0.05], and  $s_c = 2$ , the critical pH values of solutions are 7.8, 6.9, and 6.6 for initial concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  of 5, 15, and 25  $\text{mmol kg}^{-1}$ , respectively. That the actual value of  $s_c$  is unknown is of minor importance for the key result of the discussion presented in Sec. 4: higher initial concentrations lead to smaller critical pH values (varying the supersaturation  $s_c$  merely results in a shift of all critical pH values). The influence of different critical pH values was examined by varying  $s_c$  between 1 and 8 which had only a marginal effect on the shape of the curve shown in Fig. 7.