

Interactive comment on “The fate of pelagic CaCO₃ production in a high CO₂ ocean: A model study” by M. Gehlen et al.

M. Gehlen et al.

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We wish to thank both reviewers for their constructive comments.

Referee 2

(1) Calcium carbonate dissolution kinetics

Referee 2 asks for clarification and additional information prior to the publication of our manuscript. Before answering his recommendations point by point, we wish to comment on the dissolution rate equation for calcium carbonate:

The dissolution of CaCO₃ has been extensively studied over the past decades (e.g. Morse and Berner, 1972; Ingle et al., 1973; Berner and Morse, 1974; Berner, 1976; Morse, 1978; Honjo and Erez, 1978; Plummer et al., 1978; Keir, 1980; Walter and Morse, 1985; Chou et al., 1989; Arakaki and Mucci, 1995; Morse and Arvidson, 2002;

Gehlen et al., 2005a, b). The dissolution reaction is in general described by a higher order dependence of the dissolution reaction on the degree of undersaturation of seawater: $R_{Diss} = k(1 - \Omega)^n$. Keir (1980) derived a reaction rate order of 4.5 from laboratory dissolution experiments with synthetic calcite. The higher order dependence was challenged by Hales and Emerson (1997b). The authors re-evaluated Keir's (1980) experimental data and concluded that the rate of dissolution is linearly dependent on undersaturation ($n = 1$). According to Hales and Emerson (1997), the high reaction order derived by Keir (1980) could be attributed to uncertainties in the saturation state of the experimental seawater. Moreover, first-order calcite dissolution kinetics proved to be more consistent with the interpretation of in-situ pore water pH measurements (Hales and Emerson, 1997a, b). As stressed by Gehlen et al. (1999), a satisfying reproduction of pore water profiles through diffusion-reaction models is, however, not a proof per se of the validity of a kinetic expression. Gehlen et al. (2005) carried out kinetic experiments with biogenic $CaCO_3$. They derived an average reaction rate order of $n = 2.3 \pm 0.4$ from 8 experiments with biogenic $CaCO_3$ in artificial seawater. The higher reaction order is explained in terms of a multiphase system. It results from the concomitant dissolution of carbonate fractions characterized by variable reaction rate constants.

While the in-depth discussion of $CaCO_3$ dissolution kinetics is out of the scope of our paper, the preceding section highlights the need for further experimental studies of the dissolution behavior of biogenic $CaCO_3$ phases. For the focus of this modeling study, we adopted a linear dependency of $CaCO_3$ dissolution on undersaturation. Since the extrapolation of experimental results from controlled laboratory experiments which express reaction rate constants normalized to the specific surface area of $CaCO_3$ (Keir, 1980; Gehlen et al., 2005) to the global scale is not straightforward, we used the evolution with depth of $CaCO_3$ fluxes recorded in sediment traps to derive the apparent reaction rate constant 'k'. We selected stations for which mean annual fluxes were reported from at least two different deployment depths from a comprehensive data set on particle fluxes (Dittert et al., 2005). This was the case at 11 stations. In order to

derive dissolution rates from CaCO_3 fluxes, the time it takes for settling particles to bridge the depth interval between trap deployments needs to be known. This calls for a priori knowledge of particle sinking speed. The particle sinking speed at depth of trap deployment was obtained from the model parameterization of sinking speed of large particles (see equation 2 of manuscript).

Knowing the sinking speed, allows to derive the concentration of CaCO_3 from flux observations. The fraction of CaCO_3 lost to dissolution was calculated as the difference in CaCO_3 concentrations between the respective upper and lower traps. The saturation state of seawater with respect to calcite was determined from GLODAP data (Key et al., 2004) at the location of the lower trap. At two of the stations even the lower traps were in waters oversaturated with respect to calcite. The slight decrease in CaCO_3 fluxes observed in the data suggests either the presence of a more soluble carbonate phase (e.g. aragonite) or shallow dissolution of calcite driven by the interaction between particles and biota (e.g. grazing and dissolution during gut passage or dissolution in acidic microenvironments, see Milliman et al. 1999 for references). Rearranging the model equation for calcite dissolution:

$$\text{RCALC} = [\text{CaCO}_3] k (1 - \Omega)$$

where: $[\text{CaCO}_3]$, concentration of calcite particles, mol/l

$$\text{yields } k = \text{RCALC} / ([\text{CaCO}_3](1 - \Omega))$$

where: RCALC corresponds to the fraction of CaCO_3 lost to dissolution as calculated from the difference in concentrations and the time necessary for settling particles to bridge the depth interval of trap deployment.

In a first step k was determined for each sediment trap array. This resulted in k estimates ranging from 0 to 479.2 mol day⁻¹ with an average value of 93.6 and a median of 12.1. This wide spread and also the large difference between average and median values suggested a further refinement of the determination of k . This fit was done

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by systematically varying k to predict for each sediment trap array the upper CaCO_3 concentration from the concentration at the respective lower trap. By systematically varying k , the rms-error for the predicted and measured CaCO_3 concentrations in the upper traps converged to a minimum value for $k=10.9 \text{ day}^{-1}$, which was then implemented into the PISCES model.

Possible drawbacks of this approach are that only data from a few stations (11) were available and for two of them calcite dissolution was theoretically impossible due to calcite oversaturation at the lower trap level. This might bias the k value towards low estimates, however, these traps contained among the lowest CaCO_3 concentrations and thus contributed relatively little error to the optimization of k by the rms. Furthermore, the gradient of CaCO_3 saturation between the two trap depths was not taken into account, only the degree of saturation at the lower trap level, as at all stations except for one the water surrounding the upper traps was still oversaturated with respect to calcite. This assumption may bias the obtained value for k towards lower values. Fitting k by minimization of the rms-error for predictions of the upper trap fluxes may lead to a high weight for traps with high CaCO_3 fluxes, as here the misfit between predicted and measured values may have a strong impact on the rms. However, this was obviously not the case as for example the two traps with highest CaCO_3 concentrations also had the highest individual k -value, but the resulting value for k is still relatively low and close to the median.

(2) Reply to specific recommendations:

Page 534; line 15. Provide reference for this statement. - Feely et al. (2004)

Page 534; line 22. Add Caldeira and Wickett, 2003. - will be done in the revised version

Page 535; line 12. Please provide a reference for this statement. - Gattuso et al., 1998; Bijma et al, 1999; Kleypas et al., 1999; Riebesell et al., 2000; Zondervan et al., 2001; Zondervan et al., 2002; Langdon et al., 2003.

Page 539; line 9. The authors need to be specific about which thermodynamic constants for the CO₂ system in seawater were used in their model. The Lewis and Wallace (1998) program provides a variety of different constants to choose from. - We used the constants by Mehrbach et al. (1973).

Page 541; line 20. Why was the model run with an atmospheric pCO₂ increasing at a rate of 1- Our intention was not to mimic the actual rate of pCO₂ increase, but rather to evaluate the potential impact of a standard scenario accepted in climate change research (Coupled Model Intercomparison Project, <http://www-pcmdi.llnl.gov/projects/cmip/index.php>) on pelagic calcification and CaCO₃ dissolution.

Page 542. The model should be depicting the calcite saturation state, not the lysocline as the authors suggest. Consequently, Figure 2 is not appropriate. What should be plotted is a map of the calcite saturation depth. This is an inappropriate use of the term lysocline, since the lysocline depth refers to the sediment depth where significant calcite dissolution is first observed. The calcite saturation depth is often shallower than the lysocline depth. - Yes of course the reviewer is right!

Page 542; line 25. The authors state that “model predicts a global dissolution flux of 0.5 PgC/yr and compares well to the Feely et al. (2004) estimate.” Since the Feely (2004) estimates includes dissolution of both aragonite and high-magnesium calcite forms in addition to calcite, why should the model agree with the Feely et al. (2004) estimate? - Feely et al. (2004) is not very explicit on the sources of excess alkalinity at shallow depths. He does not infer that its origin is aragonite or high-Mg calcite. Based on Fabry's (1990) estimate of the contribution of aragonite to the planktonic CaCO₃ production of 10 percent, Milliman et al. (1999) conclude that the shallow water dissolution flux is dominated by the dissolution of calcite.

Moreover, on Page 543; line 6 the authors say that “Model derived dissolution rates are low compared to in situ dissolution rates summarized by Feely et al. (2004). Please explain how both statements can be true at the same time? - Both statements are

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compatible. As pointed out in the manuscript, the model fails to reproduce the strong dissolution flux predicted for depths above 2000m. This does not imply that the global modeled dissolution flux is too low, but rather a discrepancy in the vertical distribution of dissolution predicted by the model and derived from the observations. The missing dissolution at shallow depth is compensated by dissolution below the saturation horizon.

Table 2. Should include the Lee (2001) CaCO_3 production rates. - Lee (2001) is quoted in Table 2 of our manuscript.

Figure 2a is not easy to read. - all figures will be edited for clarity.

Figure 2b. The authors should be plotting calcite saturation state, not lysocline depth.
- We plotted the calcite saturation horizon and not the lysocline. It is a wording error.

Figure 3. Why is the Pacific dissolution rate above the saturation index? - There are localized areas in the Pacific for which the model predicts a saturation index that is shallower than the basin-wide mean.

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