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Carbonate dissolution in copepod guts: a numerical model

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ABSTRACT: A numerical model is proposed for investigating the potential of calcium carbonate dissolution in copepod guts. A sensitivity analysis is performed to reveal critical parameters. Gut pH sets the dissolution rate and gut-clearance rate determines the time scale on which ingested calcite is subject to dissolution. Highest dissolution is obtained when the individual zooplankton is alternating between grazing and non-grazing and feeding is restricted to the night-time period. Model results show that up to 70% of the ingested carbonate may be dissolved in the guts, considering reingestion of faecal pellets in the absence of a phytoplankton bloom, while ~15% dissolution is to be expected in a bloom situation. An estimate is made for the contribution of calcite dissolution in copepod guts to the proposed global calcite loss in the water column.

KEY WORDS: Calcium carbonate dissolution · Copepod guts · Faecal pellets

INTRODUCTION

In a recent paper, Milliman et al. (1999) proposed that more than 60% of biogenically produced carbonate dissolves in the upper 1000 m of the water column. One process that may contribute to this is the dissolution of $CaCO_3$ in zooplankton guts. The guts of copepods, for example, can be sufficiently acidic to cause carbonate dissolution. Calcareous phytoplankton such as coccolithophorids are grazed by copepods, the predominant form of Crustacea (Pilskaln & Honjo 1987, Ishimaru et al. 1988). Calanoid copepods are present in all marine environments and usually make up ≥70% by mass of all net-collected zooplankton (Lalli & Parsons 1993, p. 88). Evidence for copepod grazing on *Emiliania huxleyi* was given by van der Wal et al. (1995), who observed large amounts of coccoliths in copepod faecal pellets. In a recent study of Arabian Sea copepods, thin sections of the guts of 17 specimens of the genus *Spinocalanus* contained 10 to 30% coccoliths (M. Gowing pers. comm.).

It has been proposed that copepods are able to regulate gut pH to enhance enzymatic activity (Mayzaud & Mayzaud 1981). The optimal pH for a variety of copepod digestive enzymes ranges from 4 to 9 (Mayzaud 1986). With decreasing pH, the carbonate system is increasingly undersaturated with respect to calcite; thus the coccoliths ingested are subject to dissolution. Pond et al. (1995) measured pH values in guts of starved individuals of *Calanus helgolandicus* between 6.9 and 7.2, whereas the gut pH of copepods of the same species feeding on coccolithophorids ranged from 8.0 to 8.2. We are not aware of measurements on other *Calanus* species or of measurements of their gut pH in the field.

To the authors' knowledge, modelling work on carbonate dissolution in zooplankton guts has hitherto not been pursued. Field work has provided contrary evidence for carbonate dissolution in zooplankton guts, as faecal pellets contain unbroken coccoliths which show no sign of dissolution (Honjo & Roman 1978, Bathmann et al. 1987). Van der Wal et al. (1995), however, in a study of an *Emiliania huxleyi* bloom between the Shetland Islands and Norway, found copepod faecal pellets that almost exclusively contained fragmented coccoliths. We believe that the evidence of unbroken coccoliths does not exclude dissolution in copepod guts.

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Table 1. Parameters describing zooplankton gut model

Parameter	Symbol	Range	Standard value	Source
Ingestion rate of C_{org}	–	0–50 µg C d^{-1}	5 µg C d^{-1}	Båmstedt et al. (1999)
Ingestion rate of $CaCO_3$	I	0–5 µg C d^{-1}	0.5 µg C d^{-1}	Nejstgaard et al. (1994) Huskin et al. (2000)
Gut-passage time	K^{-1}	12–85 min	30 min	Irigoien (1998), Dam & Peterson (1988)
Gut volume	V	$1–8 \times 10^{-9}$ l[a]	7×10^{-9} l	Harris (1994)
$CaCO_3$ dissolution-rate constant	κ	3–7 d^{-1}	5 d^{-1}	Keir (1980)
$CaCO_3$ dissolution-rate order	η	1–5	4.5	Keir (1980)
Critical carbonate concentration	$[CO_3^{2-}]_c$		42.7 µmol kg^{-1}	Millero (1995)
Bulk sea water DIC	$\sum CO_2$		2000 µmol kg^{-1}[b]	Takahashi et al. (1981)
Bulk sea water alkalinity	TA		2300 µmol kg^{-1}[b]	Takahashi et al. (1981)

[a]Calculated from faecal-pellet volume data; gut volume ~5 times faecal pellet volume (U. Bathman pers. comm.)
[b]North Atlantic value at 100 m depth

Indications exist that coccoliths are protected against dissolution by an organic membrane (Watabe & Kingsley 1990, Fagerbakke et al. 1994). As long as the coccoliths are complete, they thus escape dissolution, while a broken coccolith may be dissolved very effectively. Hence, the observation of complete, undissolved coccoliths is not necessarily contradictory to dissolution inside faecal pellets or copepod guts.

THE MODEL

The proposed model is formulated for copepods. It assumes the gut to be one box with influx and efflux. It features calcite C content (C, µmol) and alkalinity (A, µmol kg^{-1}) as independent variables. The model is consistent with the proposition of Penry & Jumars (1986) and Jumars & Penry (1989) that guts be viewed as chemical reactors. By their classification, our model uses a continuous-flow, stirred tank reactor (CSTR), which incorporates a constant flow of material through the gut and complete mixing within it. pH is a fixed value, and together with alkalinity determines the carbonate system (Millero 1995), i.e. dissolved inorganic carbon ($\sum CO_2$) and $[CO_3^{2-}]$, the latter being ultimately responsible for the saturation state with respect to calcite. For the calculation of $[CO_3^{2-}]$ from pH and alkalinity, the dissociation constants given by Zeebe (2001) have been used. The model's equations are as follows:

$$\frac{dC(t)}{dt} = I - (f(t) + K)\,C(t),$$
$$\frac{dA(t)}{dt} = KA_{bulk} - KA(t) + 2\frac{f(t)C(t)}{10^3 V(t)} \quad (1)$$

where I (µmol C min^{-1}) is the ingestion rate of calcite, K (min^{-1}) is the gut clearance rate and $f(t)$ (min^{-1}) is the fraction of carbonate dissolving per minute at time t, A_{bulk} is the alkalinity of bulk seawater, and $V(t)$ (m^3) is the effective gut volume, i.e. total gut volume minus particulate contents. Dissolution of $CaCO_3$ depends on possible undersaturation with respect to calcite in the gut via:

$$f(t) = \begin{cases} \kappa(1-\Omega(t))^{\eta} & \text{if } \Omega(t) < 1, \\ 0 & \text{if } \Omega(t) \geq 1 \end{cases} \quad (2)$$

where κ is the dissolution-rate constant (min^{-1}) and η is the dissolution-rate order. The saturation state $\Omega(t)$ is given by the quotient of $[CO_3^{2-}]$ in the gut and the critical carbonate concentration, $[CO_3^{2-}]_c$, the latter being depth-dependent due to pressure effects:

$$\Omega(t) = \frac{[CO_3^{2-}](t)}{[CO_3^{2-}]_c} \quad (3)$$

We assumed a surface ocean value for $[CO_3^{2-}]_c$ at 100 m depth of 42.7 µmol kg^{-1} (Millero 1995). Standard values for the parameters are given in Table 1. As observations of ingestion rates of organic carbon are much more abundant than for uptake rates for calcite particles, we assume a certain fraction of organic carbon uptake for calcite ingestion. In feeding experiments, Harris (1994) reported that $CaCO_3$ uptake amounted to 35–40% of organic carbon ingested. We use a lower value of 10%, reflecting the fact that in the field the food supply is very heterogeneous and copepods take up more organic carbon via noncalcareous phytoplankton than in culture experiments, where they are selectively fed with coccolithophorids. The calculated ingestion rates of calcite conform to those found by Huskin et al. (2000) for *Calanus helgolandi-*

cus, whereby significant ingestion was observed only when food supply was high. Huskin et al. (2000) reported an ingestion rate of 0.2 µg C ind.$^{-1}$ d^{-1} at an *Emiliania huxleyi* concentration of 161 µg C dm^{-3}. This food concentration is much higher than those found in the field. An *E. huxleyi* density of 10^6 cells dm^{-3}, which van der Wal et al. (1995) observed in coccolithophorid blooms, yields an organic carbon concentration of 10 µg C dm^{-3}. However, Huskin et al. (2000) mentioned that their results for *E. huxleyi* might be underestimations due to seasonal mismatch, a problem which is also discussed by Nejstgaard et al. (1995). In a mesocosm study, Nejstgaard et al. (1994) analyzed grazing of *C. finmarchicus* on an *E. huxleyi* bloom. In the pre-bloom situation with low prey concentrations, they calculated an uptake of 0.26 µg C ind.$^{-1}$ d^{-1}, which increased to 3 µg C ind.$^{-1}$ d^{-1} during the bloom. Significantly higher ingestion rates were found by Nejstgaard et al. (1997) in a further mesocosm study, in which they calculated uptake rates of 0.1 µg C ind.$^{-1}$ d^{-1}, which increased to 19 µg C ind.$^{-1}$ d^{-1} during the bloom.

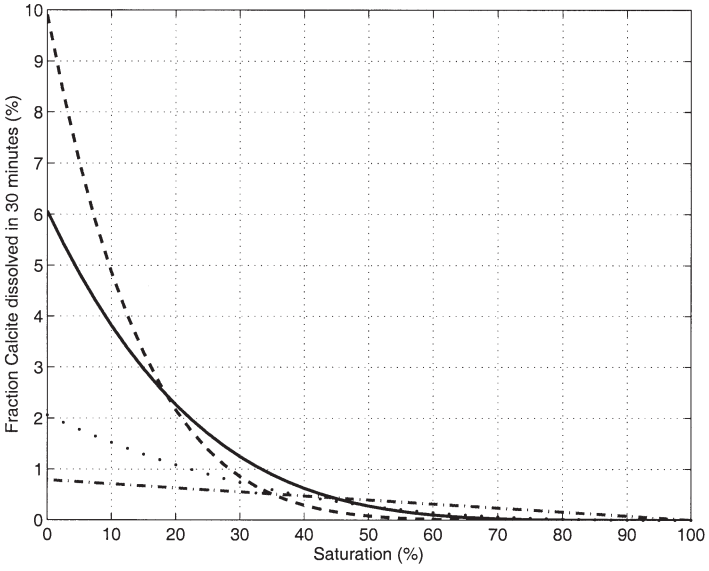

Fig. 1. $CaCO_3$ dissolution potential assuming gut-passage time of 30 min and the following dissolution kinetics: $dC/dt = -\kappa(1 - \Omega)^n$, continuous line, κ = 3 d^{-1}, n = 4.5 (Keir 1980; lower boundary for coccolithophorids); dashed line, κ = 7 d^{-1}, n = 4.5 (Keir 1980; upper boundary for coccolithophorids); dotted line, κ = 1 d^{-1}, n = 2.9 (Walter & Morse 1985); dash-dotted line, κ = 0.38 d^{-1}, n = 1.0 (Hales & Emerson 1997); where κ = dissolution-rate constant

RESULTS AND DISCUSSION

Constant grazing

Our first approach was to assume constant grazing with a gut-passage time of 30 min (Irigoien 1998). We applied the set of parameters in Table 1, and varied pH from 5 to 8. The fraction of calcite dissolved was calculated as the difference between uptake and egestion. Calculations yielded no dissolution for pH ≥7.5. The maximal amount of $CaCO_3$ dissolved was ~6% at pH 5. Thus, with constant grazing, no significant dissolution was evident. This may be due to the short gut-passage time compared to the rather slow dissolution kinetics (Fig. 1). Because of the very small volume of the gut, dissolution of $CaCO_3$ massively perturbs the carbonate system, removing any undersaturation very quickly, thus counteracting any significant dissolution. This effect has not been considered in Fig. 1, which thus illustrates an ideal upper limit of the amount of calcite that may be dissolved in 30 min.

Alternating grazing and non-grazing

We then tested the effect of alternating grazing and non-grazing. In this scenario, ingested calcite could also be dissolved during the longer non-grazing interval, during which the calcite stock was not replenished. We tried various combinations of grazing/non-grazing cycles, considering short gut-passage times during grazing (K_g^{-1} = 30 min) and long passage times during non-grazing intervals (K_n^{-1} = minimum {length of non-grazing time, 4 h}). Atkinson et al. (1996) observed gut-passage times of up to 4 h for diurnally migrating copepods. Fig. 2 shows a 24 h period of a model run alternating 140 min grazing with 30 min non-grazing. At the beginning of a grazing cycle, the calcite stock inside the gut increased strongly. Dissolution set in, raising the saturation state also. At the end of a grazing cycle, uptake of calcite and loss due to dissolution and egestion was almost in balance, so the standing stock was nearly constant. As grazing stopped, calcite was egested rapidly and, dissolution strength decreased, as did saturation.

The results of model runs varying pH and ingestion rate with a 30/120 min grazing/non-grazing cycle are given in Table 2. The uptake rates of $CaCO_3$ cover the range given by Harris (1994, his Table 3). The fraction of calcite dissolved was calculated as the difference between uptake and egestion during one grazing/non-grazing cycle. With a low ingestion rate, a moderate amount (up to ~19%) of the ingested calcite may be dissolved inside the gut. Obviously, dissolution efficiency increases with decreasing pH. Also, as the pH is lowered, the influence of the ingestion rate diminishes. Table 3 shows results at pH 6 and 5 when the non-grazing time was increased. The length of the non-

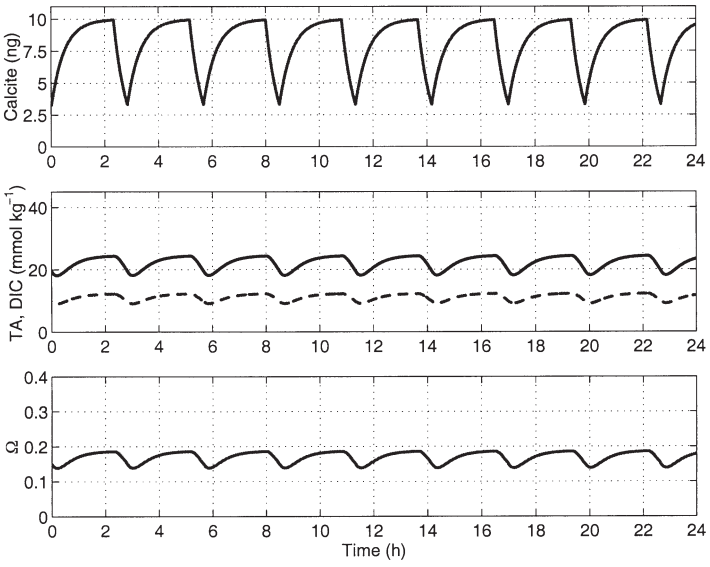

Fig. 2. Alternating grazing/non-grazing modes. pH set at 6, and length of grazing/non-grazing cycle = 140/30 min. Top graph: calcite standing stock in gut; middle graph: dissolved inorganic carbon (continuous line), and total alkalinity (dashed line); bottom graph: saturation state

grazing cycle mainly determines the fraction of calcite dissolved, as it determines the time the carbonate particles are subject to dissolution inside the gut. For very long non-grazing periods of 12 h, a maximal dissolution efficiency of 29% was reached. The impact of varying grazing and non-grazing interval lengths up to 4 h at pH 6 and 5 is shown in Fig. 3. At pH 5, dissolution of up to 23% of the ingested $CaCO_3$ was possible. This much higher value compared to the constant-grazing scenario can be explained by long gut-passage times during non-grazing, i.e. the coccoliths are subjected to dissolution for a prolonged period during which no additional calcite is taken up.

Long non-grazing times are not unusual, as food availability in the field is very heterogeneous. New *in situ* methods have shown that patch sizes of zooplankton and zooplankton food are spatially highly variable (Davis et al. 1996, Gallager et al. 1996, Norrbin et al. 1996, Greene et al. 1998). Furthermore, some zooplankton undergo diurnal migrations, which could result in zero food intake for several hours (Dagg et al. 1989, Atkinson et al. 1996). Even in the presence of a coccolithophorid bloom, it makes sense for a copepod not to graze constantly. Firstly, after a short time its digestive tract would be full; continuing to graze would reduce its effectivity in digesting the food. Secondly, a bloom site is rather a dangerous place for the copepod to be, as blooms also attract predators; thus, it would be more favourable to move somewhere else to digest. Microcinemato-graphic studies (Rosenberg 1980, Cowles & Strickler 1983) have shown that copepods alternate brief bouts of slow swimming and feeding with intervals during which swimming and feeding cease. There is also evidence that copepods reduce or interrupt their grazing for periods of up to a few hours in response to previous feeding success (Mackas & Burns 1986).

Table 2. Results of model runs using a 30/120 min grazing/non-grazing cycle. Dissolved fraction is heavily dependent on pH

$CaCO_3$ uptake (µg C d^{-1})	$CaCO_3$ loss (%) pH 4	pH 5	pH 6	pH 7
0.5	19.4	17.3	8.5	0.9
1.0	19.2	15.5	5.9	0.6
1.5	18.9	14.1	4.6	0.4
2.0	18.7	13.0	3.8	0.3
2.5	18.4	12.0	3.2	0.3

Table 3. Fraction (%) of calcite dissolved as a function of grazing (G) and non-grazing (N-G) interval length (min). Standard parameter values used, with pH 6 and 5. Gut-passage time = 30 min during grazing and maximal 4 h during non-grazing

N-G	G = 30	G = 60	G = 90
30 min			
pH 6	5.2	4.7	4.4
pH 5	8.7	8.5	8.4
60 min			
pH 6	6.6	5.4	4.9
pH 5	12.0	10.4	9.8
120 min			
pH 6	8.5	6.4	5.6
pH 5	17.3	13.6	12.0
240 min			
pH 6	10.8	7.6	6.4
pH 5	24.9	18.4	15.3
360 min			
pH 6	12.6	8.7	7.2
pH 5	26.9	19.9	16.4
480 min			
pH 6	13.9	9.4	7.7
pH 5	27.9	20.6	17.0
600 min			
pH 6	14.8	10.0	8.1
pH 5	28.4	21.0	17.3
720 min			
pH 6	15.4	10.4	8.3
pH 5	28.7	21.2	17.4

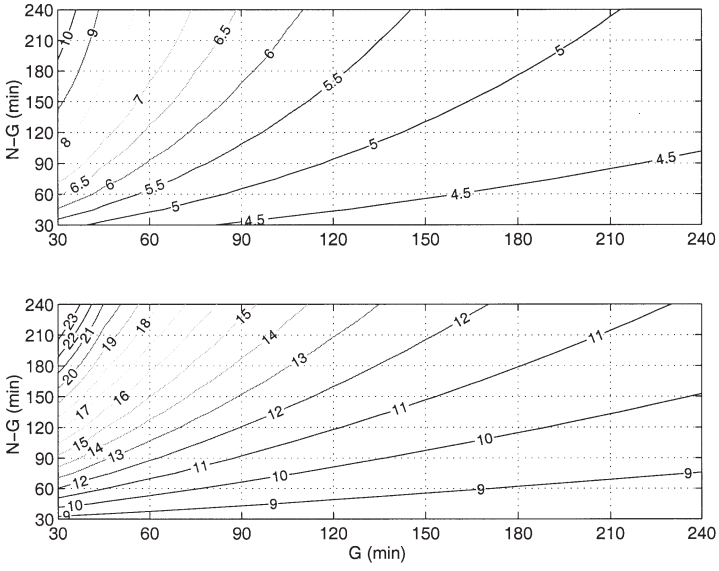

Fig. 3. Fraction (%) of ingested calcite dissolved as a function of grazing (G) and non-grazing (N-G) interval length (min). Constant pH: top graph pH 6, bottom graph pH 5

Adopting the measurements of Pond et al. (1995), who found high pH values during grazing and low pH values in starved individuals of *Calanus helgolandicus*, slightly lowered the amount of calcite dissolution. Model runs with pH 8 during grazing and pH 6 or 5 in non-grazing intervals both gave significant dissolution. However, a combination of pH 8 and 7 as measured by Pond et al. (1995) in *C. helgolandicus*, merely yielded 1.3% dissolution of the ingested calcite.

Night-time feeding

Copepods are commonly observed to undergo diurnal vertical migration from the top of the surface mixed layer at night to depth during daytime, with up to 100 m depth difference (Mauchline 1998). Atkinson et al. (1996) investigated a zooplankton community in the Polar Frontal Zone and found that all 9 copepod species examined restricted their grazing to the 8 h night-time period. Thus, we performed model runs with various grazing/non-grazing interval lengths for a period of 8 h, following a starvation interval of 16 h. An example is shown in Fig. 4. At the end of the nighttime period, a grazing cycle had just finished, so calcite standing stock was at its maximum. It then decreased to zero during the day, since daytime length (16 h) is significantly longer than gut-passage time (4 h). However, as gut-evacuation rate is lower during the day than at night, when gut-passage time is constantly 30 min, initially a large amount of calcite is dissolved rather than excreted, producing a spike in DIC and total alkalinity at daybreak. Note that this extra dissolution is the key difference compared to the model run in which grazing was not restricted to the nighttime period (Fig. 2). Results are given in Table 4 and Fig. 5. Because of the long daytime non-grazing interval, the dissolution efficiency is somewhat higher than in the model runs in which feeding was not restricted to the nighttime. The maximum dissolution at pH 5 was ~27%, compared to ~23% with 24 h grazing. Penry & Frost (1990) suggested that egestion might be modelled better as a discontinuous process. However, an appropriate formulation in the model did not significantly change the results: maximum dissolution at pH 5 was ~28% compared to ~27% with continuous egestion.

Critical parameters

The most critical parameter is gut pH, which determines the saturation state and thus dissolution strength. The next critical variable is gut-passage time, K^{-1}, as this determines the time available for carbonate dissolution; it is thought to depend on both temperature and food supply. Irigoien (1998) and Dam & Peter-

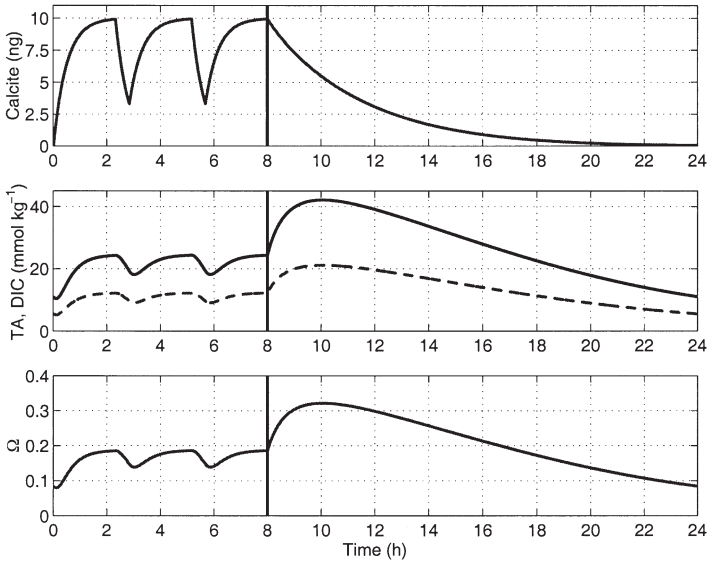

Fig. 4. Alternating grazing/non-grazing modes restricted to 8 h night-time feeding period, followed by 16 h starvation. pH set at 6, and length of grazing/non-grazing cycle = 140/30 min. Further details as in Fig. 2

Table 4. Fraction (%) of calcite dissolved as a function of grazing (G, min) and non-grazing (N-G) interval length. Feeding restricted to 8 h night-time period. Standard parameter values used, with pH 6 and 5. Gut-passage time = 30 min during grazing and maximal 4 h during non-grazing

N-G	G = 60	G = 120	G = 180	G = 240
30 min				
pH 6	5.8	5.3	5.1	5.0
pH 5	10.6	10.1	10.2	10.1
60 min				
pH 6	6.3	5.6	5.1	5.2
pH 5	11.6	11.3	9.8	10.6
90 min				
pH 6	7.5	6.1	5.4	5.4
pH 5	14.8	12.5	10.8	11.0
120 min				
pH 6	7.7	6.1	5.5	5.5
pH 5	15.4	12.1	11.5	11.5

son (1988) gave times of between 15 and 50 min for a temperature range of 5 to 25°C. The volume of the gut is critical in that it determines how strongly concentrations of dissolved substances are changed by dissolution of certain amounts of calcite. In a small gut, calcite dissolution drives the gut's chemical system into supersaturation more easily, counteracting continued dissolution. The dissolution-rate order of calcite is not well defined, as model and experimentally-derived values range between 1 (Hales & Emerson 1997) and 5 (Keir 1980). Fig. 1 shows the amount of biogenic carbonate that can dissolve in 30 min as the rate order is varied.

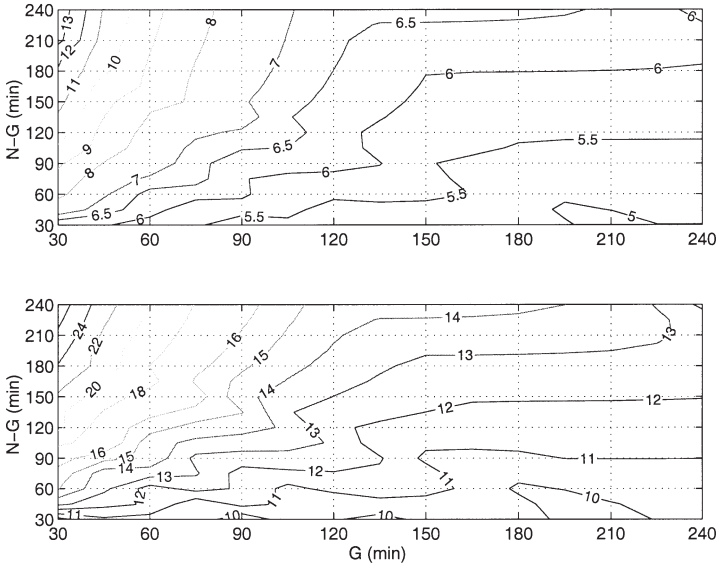

Fig. 5. Fraction (%) of ingested calcite dissolved as a function of grazing (G) and non-grazing (N-G) interval length. Feeding restricted to 8 h night time period. Constant pH: top graph = pH 6, bottom graph = pH 5

Even under the most favourable circumstances (low saturation and fast dissolution), not more than 10% of the ingested calcite can be expected to dissolve. This calculation represents an upper limit for carbonate dissolution, since effects of released CO_3^{2-} on saturation have not considered, but are taken into account in the model. On the other hand, prolonged gut-passage times are likely during non-grazing intervals (Atkinson et al. 1996, Irigoien 1998), enhancing the potential of $CaCO_3$ dissolution in zooplankton guts. Thus, during alternating grazing and non-grazing cycles, the length of the non-grazing cycle is the critical parameter.

Contribution to calcite water column dissolution

To estimate how much of the calcite dissolution observed in the water column is attributable to the mechanism proposed here, the community grazing pressure of copepods such as *Calanus* spp. on coccolithophorid blooms must be considered. Grazing pressure is defined as that fraction of either standing stock or daily primary production of a coccolithophorid bloom grazed by the copepod community. If not stated otherwise, grazing pressure refers to standing stock. Although numerous studies have been made on copepod grazing pressure on diatom- or flagellate-dominated blooms (Bautista & Harris 1992, Bautista et al. 1992, Thibault et al. 1999), to the authors' knowledge, no field work on copepod community grazing of coccolithophorids is available. Thus, we estimated *Calanus* spp. standing stock and calculated grazing pressure by measuring ingestion rates. Head et al. (1998) investigated a bloom of *Emiliania huxleyi* in the northern North Sea, and observed *C. finmarchicus* and *E. huxleyi* concentrations of 428 ind. m^{-3} and 2.24×10^9 cells m^{-3} respectively, with 1 coccolithophorid cell containing on average 12 pg C as calcium carbonate and 90 pg C as organic carbon. Assuming an ingestion rate of 10 µg C ind.$^{-1}$ d^{-1} of organic carbon leads to a community grazing pressure of 2.1% d^{-1}. This is comparable to observed grazing pressures on diatom blooms, which range up to 10% with a mean of 3 to 5% (Bautista et al. 1992, Bautista & Harris 1992, Thibault et al. 1999). However, as Nejstgaard et al. (1997) raised the question as to whether copepod grazing rates on small algae have been underestimated in field studies due to methodological problems, copepods may have a larger impact on coccolithophorids than previously thought, making this calculation a conservative one. Assuming 15% of the

ingested calcite to be dissolved during gut-passage, *Calanus* spp. grazing thus may remove less than 1% of the calcite standing stock per day. Hence, this mechanism appears unable to contribute significantly to water-column dissolution during a bloom. In a post-bloom situation, however, grazing pressure is likely to be considerably higher, since microzooplankton exert the largest grazing pressure on coccolithophorid blooms, with copepods arriving later, and feeding on the microzooplankton. During a summer bloom in the northeastern Atlantic Ocean, Burkill et al. (1993) reported a grazing pressure of microzooplankton accounting for between 39 and 115% of the production of the phytoplankton (which consisted of large size fractions dominated by diatoms and coccolithophorids: Joint et al. 1993) compared to a 1 to 2% grazing pressure of copepods. As there is evidence that microzooplankton are grazed by copepods (Sherr et al. 1986), coccoliths may eventually end up in copepod guts: presumably they cannot dissolve in microzooplankton guts, whose volume is so small that supersaturation is attained at very small amounts of dissolved calcite. Slagstad et al. (1999) reported annual mesozooplankton grazing pressures on primary production in the Bering Sea Shelf and the Northern Norwegian Shelf of between 16 and 41%, to be mediated by microzooplankton, and recently Hansen et al. (2000) observed a copepod grazing pressure of 100% on primary production in a mesocosm experiment. Furthermore, with decreasing food availability, the importance of re-ingestion of faecal pellets ('coprophagy': Frankenberg & Smith 1967, Bathmann et al. 1987, Lampitt et al. 1990) increases. A pellet may be recycled 5 to 10 times through a copepod gut (Noji & Estep 1991). In this way, even low dissolution fractions add up to significant amounts. If a faecal pellet loses 5% of its calcite content during gut-passage, it has lost 23 and 41% of its carbonate after 5 and 10 gut-passages respectively. Dissolution of 10% of the calcite in 1 gut-passage corresponds to 65% loss after 10 gut-passages. Thus, we can make the following calculation for a post-bloom situation: with 20% calcite dissolving during gut-passage, 70% of the ingested calcite would be lost after 5 passages; assuming a grazing pressure of 20%, this would mean that 14% of the calcite standing stock would be removed in this way. This corresponds to 23% of the calcite loss observed by Milliman et al. (1999).

Conclusions

The proposed model demonstrates that carbonate dissolution in zooplankton guts is possible. When grazing is continuous, model results yield no significant dissolution. Thus, we cannot reproduce the high amounts of dissolution (up to 73%) observed by Harris (1994) under the assumption of constant grazing. The most likely scenario, however, involves alternating grazing and non-grazing periods. This approach yields dissolution fractions of up to ~25% with or without feeding restricted to the nighttime period. The potential for calcite dissolution increases with increasing length of non-grazing cycles. The most critical parameter is gut pH, as only pH values less than 6.5 lead to significant dissolution. Since pH data to date are very limited, it may well be that gut pH is much lower than measured by Pond et al. (1995). The parameters of calcite dissolution kinetics were taken from experiments by Keir (1980) on complete coccoliths. As it is likely that the coccoliths are broken during ingestion or mechanical action inside the gut, dissolution should be somewhat more effective, and hence our data are probably conservative. In bloom situations, community grazing pressure of copepods seems to be too low to significantly contribute to water-column calcite dissolution. However, in pre- or post-bloom situations, grazing pressure is assumed to be higher, including grazing on microzooplankton and consumption of faecal pellets, giving rise to ~14% of standing stock calcite dissolved in copepod guts. Compared to $CaCO_3$ dissolution in the upper water column on the order of 60% as reported by Milliman et al. (1999), we conclude that dissolution of calcite in copepod guts does not account for the bulk of observed carbonate loss in the water column, but may constitute a significant portion. Other mechanisms may include localized acid production by bacteria (Troy et al. 1997) or dissolution fuelled by organic carbon remineralization in marine snow aggregates (Jansen et al. unpubl. data). However, further measurements on gut pH, ingestion rates and grazing pressure in the field are needed to better define the numerical results of the model presented here, as well as to extend the model to include other zooplankton known to feed on coccolithophorids, e.g., pelagic tunicates (Urban et al. 1992, 1993).

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