The Rate of Dissolution of Calcium Carbonate from the Surface of Deep-Ocean Turbidite Sediments

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The rate of dissolution of calcium carbonate from the surface of deep-ocean turbidite sediments

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It is known that past periods of high atmospheric carbon dioxide concentration are associated with poor carbonate preservation in the deep-ocean sedimentary record. Bottom water can become more aggressive towards carbonate sediments during such periods. To interpret the sedimentary record more exactly, and to predict future atmospheric carbon dioxide levels, it is necessary to know the rate of solution of carbonate for a given degree of bottom-water undersaturation.

In parts of the Atlantic Ocean, turbidite sedimentation mechanisms have emplaced carbonate-rich material in contact with undersaturated bottom water. The time of the emplacement event can be determined from natural radionuclide distributions, and the degree of carbonate dissolution in this time can be measured. This provides a direct measurement of dissolution rate from a natural sediment surface at a known degree of undersaturation. The range of applicability of the method is explored with a mathematical model, and field data from a 5430 m depth Atlantic site are presented.

INTRODUCTION

The solubility of calcium carbonate minerals increases with depth in the ocean. Surface waters are supersaturated, but at some geographically variable depth within the water column the seawater is just saturated with respect to solid calcium carbonate, and below this depth it is undersaturated. The two common calcium carbonate minerals, calcite and aragonite, differ in their solubility, aragonite being the more soluble. In any given region the preservation of these minerals in sediments is thus a function of the depth of the sea floor. Deep sediments contain neither, whereas both can exist in sediments at shallow water depths. Over a wide range of intermediate depths, calcite predominates.

The depth of saturation, and hence the global preservation of carbonate minerals in sediments, is determined by a dynamic equilibrium between the CO_2 content of the atmosphere and that of seawater. Thus, if the atmospheric CO_2 concentration rises, water sinking from the ocean surface will carry a higher total CO_2 content, and hence will be slightly more acidic. At depth, this water will cause the saturation depth within the ocean to rise (Sundquist 1986). Not only will this cause a larger fraction of the sinking particulate carbonate flux to dissolve, but sediments that formerly were in contact with saturated bottom water will now be in contact with undersaturated bottom water. The effect of the consequent solution is to tend to neutralize the added CO_2, so that it cannot return to the atmosphere. Over timescales of thousands of years, this process acts so as to resist changes in the atmospheric CO_2 concentration.

It follows that the history of atmospheric CO_2 change is linked to the preservation of carbonate minerals in the deep ocean. Periods of poor calcite preservation should correspond to periods of high atmospheric CO_2, and vice versa. This simple picture is complicated by changes in productivity and abyssal circulation (Mix & Fairbanks 1985), which locally may obscure or even reverse the more general relation.

Interpretation of the abyssal record and prediction of how quickly the system will respond to anthropogenic CO_2 are both hindered by a lack of detailed knowledge about the response of deep-ocean carbonate sediments to changes in bottom-water saturation. It is known that respiration within the pore waters induces some solution even above the bottom-water saturation depth, and also that bioturbation can expose to dissolution material that was buried within the upper layers of the sediments. Also, laboratory experiments show that the rate of solution of calcite, the most common deep-ocean carbonate mineral, increases only slowly until saturation level of around 60 % is reached; for greater degrees of undersaturation the solution rate increases much more rapidly. Experiments in which test materials were exposed to local sea-water at various depths within the water column have shown that this type of relation holds in the ocean as well as the laboratory. Attempts have been made to model the progress of carbonate solution theoretically, and *in situ* estimates of the viscous sublayer thickness have been made to provide data for such models (Santschi *et al.* 1983). It remains true, however, that no direct measurement of the behaviour of the real system has yet proved possible.

Although much of the sedimentation in the deep ocean occurs at a constant slow rate, under certain circumstances events may occur that supply large volumes of material to an area of the sea-floor in a short period. Unstable material can be dislodged from a shelf or sea-mount to flow rapidly downslope; the characteristic graded beds (fining upwards) produced by such an event are known as turbidites. It has recently become clear that the finest fractions of such material may travel considerable distances across the deep-ocean floor (Weaver & Kuijpers 1983; Weaver *et al.* 1986; Weaver & Rothwell 1987). The coarser material is lost rapidly as the flow spreads out and slows, so that the classic size grading is lost; distal turbidites are characteristically homogeneous and fine-grained. Because the source of the material is often much shallower than the final site of deposition, they are also often anomalously rich in calcium carbonate. In this way, carbonate sediments may be occasionally found even in very deep sites where such material is not normally preserved (Yamamoto *et al.* 1988). In principle, therefore, such deposits may permit a direct study of the behaviour of carbonate minerals in contact with undersaturated bottom water.

EXPERIMENTAL

To apply the approach outlined above, it is necessary to locate a carbonate-rich turbidite that has been exposed to undersaturated bottom waters for a period long enough to produce a measurable degree of solution at its upper surface. The high-level radioactive waste disposal study of an area of the Madeira Abyssal Plain, known from its position to the east of Great Meteor Seamount as GME, provides a suitable test site. The depositional régime at this site represented by Discovery station 11333 is unusually well characterized; the surficial sediment is a fine-grained coccolith-rich turbidite that probably derives originally from the African continental margin. The depth of deposition is 5430 corrected metres, which is well below the *ca.* 4000 m saturation level in this area (figure 1).

Because the sediments comprising this turbidite are derived from a common well-mixed source, they are remarkably uniform with depth and with geographical position. Major component data for the region (fig. 2 of Thomson *et al.* 1988) show that, except for the

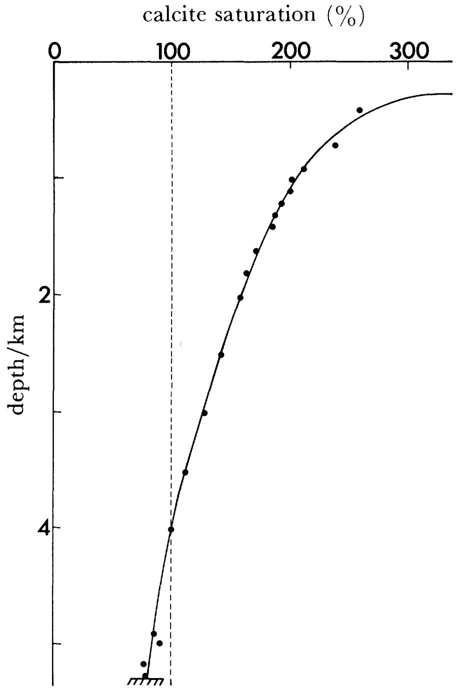

FIGURE 1. The degree of calcite saturation against depth at the GME site.

uppermost centimetre, all five of the cores obtained returned identical compositions, uniform with depth and over the 100 km distance studied. This uniformity of the material originally deposited provides an ideal background against which the effects of subsequent changes may be discerned and measured.

Radiometric dating provides the most reliable information on the age of the turbidite (time since deposition), and on bioturbative mixing. Thomson *et al.* (1988) discuss the distributions of both ^{210}Pb and ^{230}Th at this site; because of its longer half-life the latter provides the best estimate for both age and bioturbation coefficient. The major uncertainty derives from the fact that not all the ^{230}Th produced in the water column overlying a deep-ocean site reaches the sediments at that site (Anderson *et al.* 1983). An age of 500 years has been adopted for the purposes of this study; the discussion of Thomson *et al.* (1988) indicates that the uncertainty on this value is of the order of several decades.

To determine the calcium carbonate profile a boxcore subcore was sectioned into 1 mm slices using a fine-pitch extrusion device. The material from each slide was dried and ground using a TEMA swing mill to ensure uniformity before being analysed for carbonate using a LECO carbonate analyser. Soluble chloride ion was determined by potentiometric titration against silver nitrate, to calculate the porosity of each slice. The content of calcium carbonate as a fraction of the total sediment was derived from these values.

Information on the depositional régime at the GME site was derived from sediment trap measurements, supplemented by data on the composition of the pelagic sediment accumulated on nearby topographic highs that protrude 100–200 m above the turbidites of the abyssal plain. Trap data suggests that the current sedimentary flux consists of 60–70% calcium carbonate at this site (R. Lampitt, personal communication). The local pelagic accumulation rate is about 0.5 cm ka^{-1}, and the surficial sediments of the local hills are 50–80 % calcium carbonate. (J. Thomson & S. Colley, personal communication).

Model

To model the behaviour of the system studied here, it is necessary to include the effects of deposition, dissolution and bioturbation. As the composition of the current depositional rain at this site is close to that of the turbidite, it was assumed that deposition and dissolution could be combined in a net dissolution term. The advective term in the model then represents the net removal of material by dissolution, whereas the diffusive term describes the bioturbative mixing of the non-carbonate material remaining into the body of the sediment. If the origin is taken as the current sediment–water interface, the advective term is equivalent to an upward flux of sediment toward the origin, whereas non-carbonate material, continuously supplied at the origin, is mixed downward against this advective flux. The mathematical representation of this situation is

$$dC/dt = \alpha\, dC/dZ + D\, d^2C/dZ^2. \qquad (1)$$

This equation was solved numerically for the boundary conditions

(i) $C \rightarrow C_0$ as $z \rightarrow \infty$,

(ii) dC/dZ at the moving surface Z' is $K[1-(C_s/M)]/D$,

where C_s is the surface calcium carbonate concentration, D is the bioturbation diffusion coefficient, K is the dissolution rate, M is the density and $\alpha = K/M$. The derivation of boundary condition (ii) is given in the Appendix. The input data used for the model runs is summarized in table 1. As is demonstrated in figure 2, the quantitity of non-carbonate material represented by the area under the concentration–depth curve (A 1) should be equal to the quantity 'released' by carbonate solution, represented by area A 2. This equality was verified for each model run as a check on the numerical solution.

Table 1. Model parameters appropriate to GME turbidite best fit

initial calcite concentration	0.312 g cm^{-3}
total mass per unit sediment volume	0.500 g cm^{-3}
bioturbation diffusion coefficient	0.033 cm^{-2} a^{-1}
time of exposure of turbidite	500 years
vertical interval	0.25 cm
rate of dissolution of calcite	0.0003 g cm^{-2} a^{-1}

The bioturbation rate measured in these sediments (Thomson *et al.* 1988) depends on which tracer is chosen; the apparent coefficient is lower for the long-lived tracer $^{230}\text{Th}_{\text{xs}}$ (0.033 cm^2 a^{-1}) than for $^{210}\text{Pb}_{\text{xs}}$ (0.13 cm^2 a^{-1}), which has a much shorter half life. Both are higher than the value derived from foraminiferal distributions (0.019 cm^2 a^{-1}), which involves the movement of atypically large-sized particles of material. On theoretical consideration, the $^{230}\text{Th}_{\text{xs}}$ based method is probably most appropriate for present purposes. The value used in table 1 is the mean value reported by Thomson *et al.* (1988) for this turbidite. The actual value reported for station 11133 by Thomson *et al.* is 0.043 cm^2 a^{-1}. The difference between this value and the mean value used is not large enough to affect the conclusions of this paper significantly.

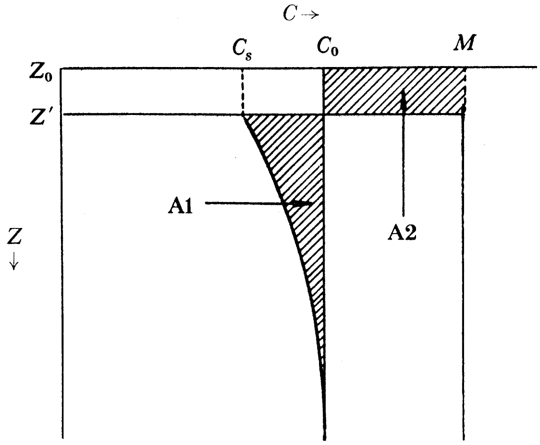

Figure 2. Schematic diagram of the dissolution model used. See text for details.

Results

The behaviour of the model with variation in bioturbation rate is shown in figure 3. For constant dissolution rate, the effect of an increase in this parameter is to deepen the penetration of non-carbonate material, and to reduce the size of the signal at the sediment–water interface. The higher value shown in figure 3 is derived from the $^{210}Pb_{xs}$ data. By using this value the calcite content approaches the bulk value well below 10 cm depth. The carbonate composition data obtained at station 11333 do not show significant bioturbative penetration beyond 4 cm depth, thus supporting the choice of the lower value for the bioturbation coefficient derived from $^{210}Th_{xs}$ data.

The method proposed here is valid for that range of dissolution rates which are great enough to produce a measurable depletion in calcite content, but no so great that all calcite is removed. The model was run with various values of dissolution rate to define this range. The results of

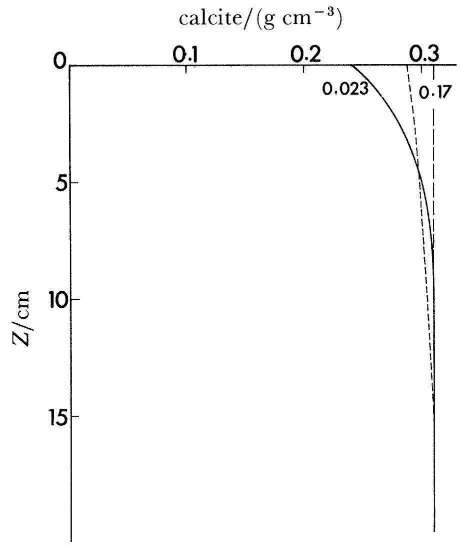

Figure 3. The output of the model for different bioturbation coefficients (solid 0.023, dotted 0.17 cm^2 a^{-1}) at a constant dissolution rate of 0.001 g cm^{-2} a^{-1}.

three of these runs are shown in figure 4, which shows that the model is valid for dissolution rates between *ca.* 0.005 and 0.0002 g $\mathrm{cm^{-1}\ a^{-1}}$. These limits are of course referred to a 500 year reaction time. For turbidites that have been exposed for a lesser period useful data could be obtained on faster dissolution rates. Conversely, for longer exposure periods, even smaller dissolution rates could be detected and measured. In this direction, the accuracy with which the depositional flux can be measured is likely to be the limiting factor.

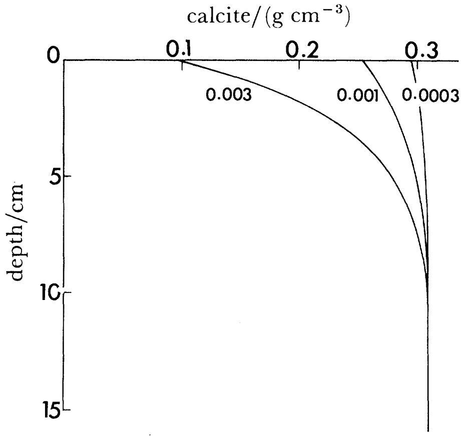

FIGURE 4. The output of the model for different dissolution rates (left to right 0.003, 0.001 and 0.0003 g $\mathrm{cm^{-2}\ a^{-1}}$) and a constant bioturbation coefficient of 0.033 $\mathrm{cm^{-2}\ a^{-1}}$.

Figure 4 shows the composition data points derived from the station 11333 boxcore; the superimposed line corresponds to the model output profile for the input parameters given in table 1. The depletion observed is consistent with a net dissolution rate of about 0.0003 g $\mathrm{cm^{-3}\ a^{-1}}$. A carbonate deposition rate close to 0.0002 g $\mathrm{cm^{-2}\ a^{-1}}$ can be estimated from the local abyssal hill accumulation rate and sediment trap data noted above. Thus, the total dissolution rate at the 11333 site, where the bottom water saturation value is about 80 % (figure 1), is probably about 0.0005 g $\mathrm{cm^{-2}\ a^{-1}}$.

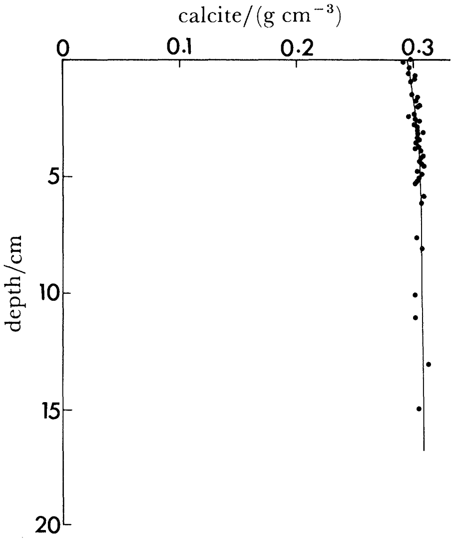

FIGURE 5. Composition data from the GME site. The line is the model solution for the conditions shown in table 1.

Discussion

Although there are no previous direct determinations of the dissolution rate of carbonate sediment exposed to undersaturated deep ocean bottom water, information from laboratory studies and model simulations may be used to calculate a dissolution rate for comparison with the present results.

A number of workers (see, for example, Morse 1978; Keir 1980; Walter & Morse 1985) have made studies of the relation between the degree of saturation and the consequent calcite dissolution rate. These experiments show that rates increase rapidly as the degree of saturation falls. Typically, the relation found by these workers is of the form

$$R = k(1-\Omega)^n, \qquad (2)$$

where R is the rate of dissolution and Ω is the degree of saturation, defined by

$$\Omega = [\mathrm{Ca}^{2+}]\,[\mathrm{CO}_3^{2-}]/K_{\mathrm{sp}}. \qquad (3)$$

The constant n of equation (2) varies with the carbonate mineral involved. For calcite the value of n reported by Keir was 4.5, whereas Walter & Morse reported a value of 3.4 for magnesium calcite. The constant k is strongly influenced by grain size and the source of the material. Keir (1980) and Walter & Morse (1985) report values for synthetic calcite (3.53 and 3.73 μmol g^{-1} h^{-1}), which agree surprisingly well in the circumstances.

However, there is some question as to the applicability of such values, obtained from stirred suspensions, to a situation in which a bed of sediment is exposed to undersaturated water. Keir (1983) investigated the behaviour of systems of the latter type in laboratory experiments using a stirred flow reactor, and obtained values for the calcite rate constant that were one to two orders lower than the values obtained for suspensions. These latter experiments, though similar in geometry to the natural system, were short-term and did not include the effect of bioturbation.

Several groups of workers have modelled the behaviour of the carbonate system at the sediment–water interface (Schink & Guinasso 1977; Berner 1980; Emerson & Bender 1981; Boudreau & Guinasso 1982; Keir 1982, 1984). An approximation for the solution flux used by the latter workers is

$$\text{flux} \approx [kf(1-(c/c_{\mathrm{e}}))^{n+1}]^{\frac{1}{2}}, \qquad (4)$$

where c is the carbonate ion concentration, c_{e} the ionic concentration at equilibrium, f is the carbonate fraction and n is empirically determined as 4.5. The constant k has units of mass squared, and is related to the rate constant k_c.

Applying the flux rate derived experimentally in the present work gives a value for k of 4.4×10^{-3} g^2 cm^{-4} a^{-2}. This corresponds to a calcite rate constant of 0.06 d^{-1}, about one third of the value obtained from the flow reactor experiments of Keir (1983). As already noted, Keir's value is in turn significantly less than the values suggested by laboratory experiments on stirred carbonate suspensions. This probably reflects the combination of the effect of the diffusional sublayer at the sediment–water interface (Schink & Guinasso 1977) and the higher resistance to dissolution exhibited by coccolith-derived calcite (Keir 1980). The results presented here provide a direct measure of the impact of these effects on deep-ocean calcite dissolution.

Conclusions

1. Dated turbidites from sub-lysocline depths can be used to determine the rate of solution of calcium carbonate for a known degree of undersaturation.

2. The useful range of the method varies with the age of the turbidite used. For an age of 500 years, model studies show that the method is useful for solution rates lying between about 0.0002 and 0.005 g cm^{-2} a^{-1}.

3. Previous methods involve extrapolation from laboratory studies using theoretical models. The approach utilized here includes the effect of all the processes that are active in the undisturbed deep-sea environment.

4. At the GME site, the degree of bottom-water saturation with respect to calcite is 80 %, and the resultant dissolution flux is 0.0005 g cm^{-2} a^{-1}. This result lies at the lower end of the range of dissolution rates which have been suggested on the basis of laboratory studies. In particular, studies of calcite dissolution based on stirred suspensions indicate rate constant values up to two orders of magnitude higher than the value derived from the present study. If this is confirmed by further work on turbidites at different bottom-water saturation levels, it follows that the efficiency of the deep ocean as a sink for anthropogenic carbon dioxide from the atmosphere may be rather lower than would be estimated from most of the existing literature data.

5. The application of the approach used in this paper is limited by our ability to locate suitable distal turbidites. It is likely, however, that many suitable sites exist. Only a very small proportion of the potentially suitable deep-ocean floor has been examined for this purpose. The method is unique in its conceptual simplicity. Because it provides data on undisturbed natural systems it is potentially of great value in the calibration of other approaches to the problem of calcite solubility.

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Appendix. Derivation of boundary condition (ii)

The ratio (α) between the density M (g cm^{-3} wet sediment) and calcite dissolution rate K (g cm^{-3} a^{-1}) is given by

$$\alpha = K/M.$$

The rate at which calcite is made available as a result of the advancing surface is αC_s. Therefore, the flux of calcite across the moving surface is

$$\begin{aligned} \text{flux} &= K - \alpha C_s \\ &= K[1-(C_s/M)], \end{aligned}$$

which implies that

$$D\,dC/dZ = K[1-(C_s/M)],$$

so that

$$dC/dZ = K[1-(C_s/M)]/D.$$

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