

ON A REACTIVE CONTINUUM REPRESENTATION OF ORGANIC MATTER DIAGENESIS

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ABSTRACT. We present a theory for the decay of sedimentary organic matter made of a spectrum (a continuous distribution of an infinite number) of reactive types which can be characterized by a variable function of the decay constant, k . A fundamental property of the continuum theory is that it can generate an apparent order of reaction for the decay of the total mixture greater than one. The apparent order is related to the predominance of the more refractory components of the continuum relative to the more reactive.

A Gamma distribution of reactivities is a particularly valuable model for the initial distribution, $g(k, 0)$. The Gamma distribution, $g(k, 0) = g_0 k^{\nu-1} e^{-ak}/\Gamma(\nu)$, is characterized by two free parameters, "a" and ν where "a" measures the average life-time of the more reactive components of the mixture and ν is a nondimensional parameter solely related to the shape of the distribution near $k = 0$ (and $\Gamma(\)$ is the Gamma function).

Analysis of the experimental data reported in Westrich and Berner (1984) illustrates that the continuum model, based on the Gamma distribution, requires half as many parameters as the traditional multi-exponential model. This analysis indicates that the decay reaction is characterized by $\nu = 0.125$ (equivalent to an apparent 9th order reaction). A similar treatment of nine organic C profiles from the historical zone of various shallow and deep-water sediments shows that these cores can be divided into two groups. The larger group of five profiles displays ν values that range primarily from 0.1 to 0.2 (6th-11th order). A second group of three cores is characterized by $\nu \approx 1.0$ (apparent 2nd order reactions), but two of these cores may contain data from the mixed zone or may not be at steady state. The apparent order of the experimental data agrees with that of the first group of profiles and suggests that there may be an important similarity to such data over broad spatial/time scales. In addition, we also examined the decay of Westrich's (1983) hypothetical 8-component organic matter and found that it can be represented with $\nu = 0.1$ (11th order). If this similarity in ν values is substantiated by further studies, it would be a valuable tool in theoretical studies. Though the data set is small, the analysis also suggests that the parameter "a" varies systematically with the sedimentation rate.

In the mixed zone of marine sediments, the continuum model generates rather complicated integrals for the organic matter concentration profiles. In general, these integrals are amenable to numerical methods only. They will, however, reduce to analytically manageable forms, if the mixed zone can be assumed to extend to infinity and advective transport ignored.

The theory of reactive continuums suggests, in general, that a standard Arrhenius plot of $\log_e(\text{rate})$ versus T^{-1} ($T \equiv$ absolute temperature) will curve upward with falling T^{-1} . However, we have found that

because of the restricted temperature range normal to sedimentary environments, this plot will exhibit little deviation from linearity. Therefore, a single apparent activation energy, E_{eff} for the decay of the total mass can be calculated from the slope of such a plot.

INTRODUCTION

It is widely recognized and acknowledged that the decay (oxidation) of natural organic matter is a primary, if not the dominant, process leading to diagenetic changes in marine sediments (Berner, 1974, 1980; Froelich and others, 1979; Emerson and others, 1980). This process determines not only the amount and "quality" of organic matter preserved in sediments, but also the extent of nutrient remineralization and fluxes from sediments and the formation of authigenic mineral phases such as metal sulfides. It is, therefore, not surprising that considerable effort has been expended to arrive at quantitative models that can account for laboratory measured kinetics of this process or to infer its rate from geochemical data.

The first mathematical model for organic matter diagenesis in marine sediments originated with Berner (1964). His formulation stated simply that the rate of disappearance by decay was proportional to the concentration of organic matter, G ,

$$\frac{dG}{dt} = -kG \quad (1)$$

where t is time and k is an empirical rate constant for net decay. A similar first-order model for organic matter decay was developed (or implied) quite independently by soil scientists and marine biologists working in different environments (Jenny and others, 1949; Olson, 1963; Minderman, 1968; Flanagan and Bunnell, 1976; Hunt, 1977). This formulation ignores the influence of the oxidant concentration, which is the normal procedure for diagenesis (Berner, 1980).

While eq (1) has enjoyed success in describing some data (Berner, 1964), most analyses of decay experiments (Westrich and Berner, 1984; Grant and Hargrave, 1987; Pett, 1989) and determinations of *in situ* decomposition rates (Jørgensen, 1978; Berner, 1980, 1981; Müller and Mangini, 1980; Wapples and Sloan, 1980; Pelet, 1984) have concluded that a simple first-order dependence on the concentration of total organic matter, G , was not consistent with the observations. Specifically, the overall rate of decay was seen to diminish slower than predicted by eq (1), and G appeared to reach a positive non-zero asymptote as time (or depth) increased. Equivalent behavior was apparent during organic matter decomposition in soils and freshwater sediments (Jewell, 1971; Godshalk and Wetzel, 1978).

To explain this discrepancy, it was suggested that the organic matter was composed of a variety of discrete organic matter types that differed in amount and reactivity, but that each component followed a first-order decay as given by eq (1) (Jørgensen, 1978; Berner, 1980; Westrich, *ms*;

Westrich and Berner, 1984; but also Minderman, 1986; Parnas, 1975; Bunnell, Tait and Flanagan, 1977; Smith, 1979)

$$\frac{dG_i}{dt} = -k_i G_i \quad (2)$$

where G_i is the concentration of the i -th reactive component, and k_i is the corresponding decay constant, which varies from some maximum value to zero for the refractory component. Thus, the total organic matter concentration changes as

$$\frac{dG}{dt} = - \sum_{i=0}^n k_i G_i \quad (3)$$

where n is the total number of reactive types.

This approach is not without its own flaws. The number of reactive types and their associated k -values must be determined empirically as curve fitting parameters. This procedure is open to at least two avenues of criticism. Middelburg (1989), reviving the analysis of van Liew (1962), points out correctly that the graphical analysis performed to extract the number of reactive types and their reactivities will result in the identification of two or three types from a given data set regardless of the actual number involved. The fact that the eight reactive types identified ultimately by Westrich (1983) differ in reactivity by almost exactly an order of magnitude strongly suggests that this difference is in part a function of the selectivity of the method of analysis (or the experimental system) than an inherent property of the distribution of organic matter types. In addition, it is essentially impossible to identify a specific organic substance (or even coherent groups of substances) with the empirically defined reactive types. The strongest argument in favor of the multiple- G model is its conceptual and mathematical simplicity.

Westrich (ms) and Middelburg (1989) both recognized that as an alternative to the discrete multiple- G model, one could assume instead that k was a continuously varying parameter and that there existed a spectrum of reactive types, that is, an infinite number. Westrich (1983) did not pursue this proposal because of the mathematical difficulty presented by the continuum model. Middelburg (1989) interpreted the continuum alternative to imply a continuous and direct dependence of the rate constant, k , on time, t . Although Middelburg's treatment leads to informative and pleasing correlations, we cannot sanction this approach. The apparent reactivity of a continuum mixture of organic matter types is a function of the changing composition of the mass with time, not time itself. Creating a functionality directly based on time severs the mechanistic link between the properties of the organic matter and the rate of decay. The ambiguous meaning of time, or more specifically age, for organic matter at a given depth in a sediment that has been subject to bioturbation is also extremely bothersome.

A more suitable implementation of the continuum hypothesis is available in the form of the theory of reaction in continuous mixtures as

advanced by Aris and Gavalas (1966), Aris (1968, 1989), Hutchinson and Luss (1970), Ho and Aris (1987), and Krambeck (1988). According to this theory, the organic matter is described by a distribution function, $g(k, t)$, which gives the amount or concentration of organic matter having reactivities between k and $k + dk$ at time t . Each of the infinite reactive types characterized by a given value of k undergoes a decay reaction, which we assume to be first-order. The total amount of organic matter as a function of time is then the integral of the distribution, $g(k, t)$, over all possible values of k . Apparently unaware of the work of Aris (1968), this approach was developed independently by Carpenter (1981, 1982) and Bosatta and Ågren (1985) in their studies of soil organic matter decay.

It is the aim of this paper to develop the theory of reactive continuums as it applies to organic matter diagenesis in marine sediments. In so doing we will explore the properties and implications of this model. We will also apply the model to experimental and natural data sets to evaluate not only its practical utility, but also to determine if it can identify fundamental properties of the organic matter decomposition process that are not obvious from the multi-G model.

KINETICS OF A REACTIVE CONTINUUM

General properties.—As stated above, the basic premise of the continuum theory is the existence of a spectrum of reactive types characterized by a distribution function, $g(k, t)$, which determines the concentration of organic matter having reactivities between k and $k + dk$ (where dk is in infinitesimal increment in k). If each reactive types undergoes a first-order decay reaction¹, then $g(k, t)$ will change with time according to the decay equation

$$\frac{dg(k, t)}{dt} = -kg(k, t) \quad (4)$$

which has as its familiar solution

$$g(k, t) = g(k, 0)e^{-kt} \quad (5)$$

The true observable quantity in both experimental and natural situations is the total amount or concentration of organic matter, $G(t)$, and this is calculated as the integral of the distribution function over the range of all possible values of k , which can be taken to be zero to infinity (Aris, 1968),

$$G(t) = \int_0^\infty g(k, t) dk \quad (6)$$

or with eq (5)

$$G(t) = \int_0^\infty g(k, 0)e^{-kt} dk \quad (7)$$

¹ Nonlinear individual reactions are considered by Astarita and Ocone (1988), Chou^{*} and Ho (1988, 1989), Astarita (1989), Aris (1989), and Ho (in press).

Eq (7) is, in fact, the definition of a Laplace transform (Abramowitz and Stegun, 1972, p. 1020; Hildebrand, 1976, p. 55; Spanier and Oldham, 1987, p. 241), and this property will be employed later. Although we will deal later exclusively with an initial distribution, $g(k, 0)$, that provides for a closed-form solution of eq (7), numerical integration is a viable option for other choices (see Press and others, 1986, chap 4; also Davis and Rabinowitz, 1984).

The rate of change of total organic matter with time can be related to the change in the distribution by differentiating eq (7),

$$\frac{dG(t)}{dt} = - \int_0^{\infty} kg(k, 0) e^{-kt} dk \quad (8)$$

The problem in applying this continuum model lies in specifying $g(k, 0)$, that is to say, the initial distribution of reactive types. For example, past studies (Jørgensen, 1978; Berner, 1980, 1981) have *assumed* that there are m discrete types of organic matter each with initial concentration $G_i(0)$ and reactivity k_i . This is equivalent to a distribution composed of m delta functions, $\delta(k - k_i)$. The delta function has the property that its integral is equal to one, so that

$$\int_0^{\infty} \delta(k - k_i) f(k) dk = f(k_i) \quad (9)$$

Therefore, the $G(t)$ calculated from a distribution composed of the sum of m delta functions is

$$G(t) = \int_0^{\infty} \sum_{i=1}^m \delta(k - k_i) G_i(0) e^{-kt} dk \quad (10)$$

or with eq (9)

$$G(t) = \sum_{i=1}^m G_i(0) e^{-k_i t} \quad (11)$$

and we recover the organic matter decay model of Jørgensen (1978), Berner (1980, 1981), Westrich (ms), Westrich and Berner (1984).

Yet, a finite set of discrete organic matter types is simply one of an infinite number of possible distributions and one that is an unlikely description of natural distributions. We know, for example, that marine organic matter is composed of a wide variety of organic substances including protein, lignin, cellulose, chitin, plus all the other products of biosynthesis and the geopolymerization process. It would be truly astounding that the decay of all these compounds would fall neatly into a small finite number of reactive types. More likely, the sensitivity of the measurement methods forcibly divides the true distribution into the distinct categories. The adoption of a continuous distribution presents, in all probability, a more realistic assumption than its discrete counterpart.

Before trying to discover possible representations for natural distributions, it is worthwhile discussing some of the properties associated with

continuous distributions because they are quite startling. We start with the example of a very simple finite distribution, that is, a constant, g_0 , from $k = 0$ to some finite value, k_0 ,

$$g(k, 0) = \begin{cases} g_0 & 0 \leq k \leq k_0 \\ 0 & k > k_0 \end{cases} \quad (12)$$

Substitution into eq (7) and integration gives

$$G(t) = \frac{g_0}{t} (1 - e^{-k_0 t}) \quad (13)$$

and into eq (8)

$$\frac{dG}{dt} = \frac{g_0}{t^2} (e^{-k_0 t} (1 + k_0 t) - 1) \quad (14)$$

It might first appear that $G(t)$ and the rate given by eqs (13) and (14) are infinite or undefined as $t \rightarrow 0$. This is not the case. At small times, the exponential is well represented by the first few terms of a Maclaurin series,

$$e^{-k_0 t} \approx 1 - k_0 t + \frac{(k_0 t)^2}{2} - \dots \quad (15)$$

so that from eq (13), we obtain in the limit as $t \rightarrow 0$

$$G(t) \approx k_0 g_0 \quad (16)$$

Thus, the total amount of organic matter remains well-defined in this limit.

Using the same procedure, we find that the rate is also well defined as $t \rightarrow 0$,

$$\frac{dG}{dt} \approx -\frac{k_0^2 g_0}{2} \quad (17)$$

or with eq (16)

$$\frac{dG}{dt} \approx -\frac{k_0}{2} G(t) \quad (18)$$

This means that this particular organic mixture would appear initially to decay as a first-order process with a decay constant of $k_0/2$.

After enough time had passed, a different picture would emerge to an observer. As $t \rightarrow \infty$, and $e^{-k_0 t} \rightarrow 0$, then

$$G(t) \approx \frac{g_0}{t} \quad (19)$$

and given infinite time, all $G(t)$ would disappear, because all is reactive in a continuum model. At this point, we stress that the model applies to the decay of organic matter fully available to the microbial population. For example, organic matter trapped within shell lattices is specifically excluded if it cannot be reached by microorganisms.

The rate of decay has the asymptotic form

$$\frac{dG}{dt} \approx -\frac{g_0}{t^2} \quad (20)$$

or with eq (19)

$$\frac{dG}{dt} \approx -\frac{G^2}{g_0} \quad (21)$$

So that after a sufficiently long period of time, the reaction would seem to be second order with rate constant $1/g_0$ (Ho and Aris, 1987).

Why does this perceived change in the order arise? In the beginning ($t \rightarrow 0$), decay is dominated by the most reactive component(s) so that the bulk organic matter vanishes according to a first-order reaction. However, for longer times ($t \rightarrow \infty$), the highly reactive fraction of this material will have been completely consumed, and the overall reaction must slowdown to reflect the behavior of the less reactive components. This deceleration in the rate looks to an observer like a shift toward a higher order of reaction. On a plot of concentration versus time, the curve defining the evolution of the system adopts a shallower slope with time, and this is exactly what is seen in the data of Westrich and Berner (1984, fig. 1).

This change in the apparent order will occur not only for the special distribution given by eq (12), but for a wide class of initial distributions, $g(k, 0)$. To illustrate the generality of this assertion, consider the case where $g(k, 0)$ can be represented as a power series in k (no singularity at $k = 0$) to at least the arbitrarily large value k_0 ,

$$g(k, 0) = g_0 + g_1 k + g_2 k^2 + \dots \quad (22)$$

where g_0, g_1, g_2 , et cetera, are constants. Substituting into eq (7) produces

$$G(t) = g_0 \int_0^{k_0} e^{-kt} dk + g_1 \int_0^{k_0} k e^{-kt} dk + g_2 \int_0^{k_0} k^2 e^{-kt} dk + \dots \quad (23)$$

Upon integration,

$$G(t) = \frac{g_0(1 - e^{-k_0 t})}{t} + \frac{g_1(1 - e^{-k_0 t}(1 + k_0 t))}{t^2} + \dots \quad (24)$$

or, for $t \rightarrow \infty$,

$$G(t) = \frac{g_0}{t} + \frac{g_1}{t^2} + \frac{g_2}{t^3} + \dots \quad (25)$$

which is true even if we let $k_0 \rightarrow \infty$. Differentiating eq (25) suggests that in this limit

$$\frac{dG}{dt} \approx -\frac{g_0}{t^2} - \frac{2g_1}{t^3} - \frac{3g_3}{t^4} - \dots \quad (26)$$

Now if $g_0 \neq 0$, that is to say that there is a finite non-zero amount of highly refractory material, then as the elapsed time becomes very long, $G(t)$ becomes well approximated by the first term in eq (25). If this is substituted into eq (26) with only the first term retained, then

$$\frac{dG}{dt} \approx -\frac{G^2}{g_0} \quad (27)$$

which is eq (21). The effect of a finite non-zero contribution near $k = 0$ on the reactive spectrum is to create an apparent shift to second order kinetics in the observed decay of the mixture.

Apparent lower order reactions are also possible. If, for example, $g_0 = 0$ while all other coefficients are non-zero, then the long time behavior of $G(t)$ is given by second term in eq (25) and, consequently,

$$\frac{dG}{dt} \approx -\frac{2G^{3/2}}{g_1^{1/2}} \quad (28)$$

which indicates a 1.5 order reaction with time. The absence of the first term in eq (25) implies that there is less refractory material near $k = 0$ than in the case where $g_0 \neq 0$, so that its behavior has a lesser influence on the kinetics as time passes. In general, if the first $n - 1$ terms of the expansion given by eq (25) are zero, then

$$\frac{dG}{dt} \approx -\frac{nG^{1+1/n}}{(g_{n-1})^{1/n}} \quad (29)$$

which tends to a first-order reaction as $n \rightarrow \infty$. The successive loss of low order terms in eq (25) reflects progressively less refractory material and so less of a need for higher order kinetics to accommodate the decay of this material.

It is also possible and quite reasonable to obtain apparent kinetics greater than order 2. It was assumed in eq (25) that $g(k, 0)$ was expressible as a simple power series; however, we should also consider initial distributions that are weakly singular, that is, those that have a behavior like $k^{-\alpha}$ as $k \rightarrow 0$, where $\alpha < 1$ if the total amount of organic matter is to remain finite. The weak singularity for $g(k, 0) \sim k^{-\alpha}$ if $0 < \alpha < 1$ poses no problem in terms of physical significance. It simply indicates a massive preponderance of refractory material. Natural organic matter mixtures may be commonly characterized by such distributions.

As Krambeck (1988) has aptly established, if $g(k, 0) \sim k^{-\alpha}$, then the limit theorem of Laplace transforms (Spanier and Oldham, 1987, p. 250)

immediately allows us to conclude that eq (7) will behave like

$$G(t \rightarrow \infty) \sim t^{\alpha-1} \quad (30)$$

Differentiating eq (30)

$$\left. \frac{dG}{dt} \right|_{t \rightarrow \infty} \sim -t^{-(2-\alpha)} \quad (31)$$

or substituting eq (30) into (31)

$$\left. \frac{dG}{dt} \right|_{t \rightarrow \infty} \sim -G^{(2-\alpha)/(1-\alpha)} \quad (32)$$

A physically realizable solution is limited to α values less than 1. For $\alpha = 0$, we recover an apparent second order reaction. As α rises toward 1, the order also increases. For example, at $\alpha = 0.5$, there results a third order reaction, and $\alpha = 0.75$ generates a fifth order reaction. By choosing α arbitrarily close to 1, one can obtain arbitrarily large apparent orders for the decay of the mixture reaction.

It must be emphasized at this point that the occurrence of higher apparent orders of reaction does not imply nonlinearity in the true kinetics of decay reaction. The infinite collection of decay reactions that make up the distribution at any time all continue to be strictly first order. This means that if the system is perturbed by adding organic matter, the change in the real rate will be linear in this increment. This can be proven by considering eq (8). If the initial $g(k, 0)$ is doubled, then we can substitute $2 \cdot g(k, 0)$ for $g(k, 0)$, and the rate is simply twice that calculated previously. Thus, there is a fundamental difference between the perceived order of a mixture and the real order of the constituent reactions. Higher apparent orders of reaction and the linear response to perturbations found by Westrich and Berner (1984) are not, therefore, in conflict.

Finite range distributions.—To illustrate the type of changes in the perceived order of reaction that can occur during the course of decomposition, we consider the behavior of six $g(0, k)$ -distributions with finite k -ranges:

1. Step:

$$g(k, 0) = g_0 \quad 0 \leq k \leq k_0 \quad (12, \text{repeated})$$

2. Linear increasing:

$$g(k, 0) = \frac{g_0 k}{k_0} \quad 0 \leq k \leq k_0 \quad (33)$$

3. Linear decreasing:

$$g(k, 0) = g_0 \left(1 - \frac{k}{k_0} \right) \quad 0 \leq k \leq k_0 \quad (34)$$

4. Concave quadratic:

$$g(k, 0) = 4g_0 \left(\frac{k}{k_0} - \frac{1}{2} \right)^2 \quad 0 \leq k \leq k_0 \quad (35)$$

5. Convex quadratic:

$$g(k, 0) = g_0 \frac{k}{k_0} \left(1 - \frac{k}{k_0} \right) \quad 0 \leq k \leq k_0 \quad (36)$$

6. Inverse power law:

$$g(k, 0) = \left(\frac{k_0}{k} \right)^n \quad n < 1 \quad \& \quad 0 \leq k \leq k_0 \quad (37)$$

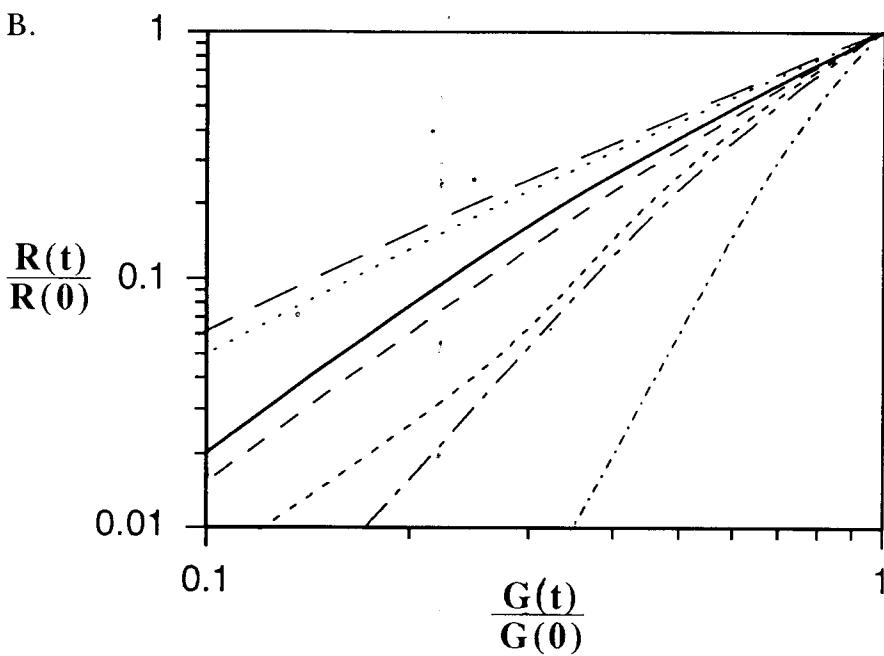
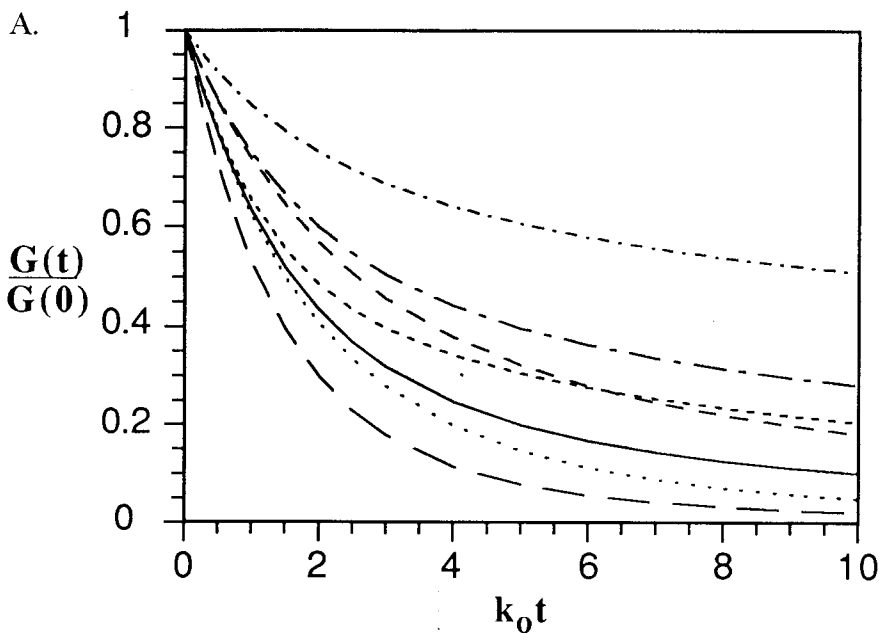
and $k = 0$ for $k > k_0$ in all cases. Figure 1A shows the change in the organic matter relative to its initial concentration, $G(t)/G(0)$, as a function of the dimensionless time, $k_0 t$, for these six $g(0, k)$ -distributions.

The Linear Increasing and Convex Quadratic distributions have zero intercepts at $k = 0$ while the Step, Linear Decreasing and Concave Quadratic have finite intercepts, that is, $g(0, 0) = g_0$. According to the reaction continuum theory, the first two distributions should both generate long-time apparent orders of 3/2. The latter three will asymptote to an apparent second order reaction. The Inverse Power Law is a weakly singular distribution of the type described by eq (30), and it will produce apparent orders of 3 and 5 for $n = 0.5$ and 0.75, respectively. All these distributions have an initial order of 1.

Figure 1B plots the rate of reaction normalized to the initial rate, $R(t)/R(0)$, against the normalized concentration of organic matter for each of these initial distributions, that is, eqs (12) and (33) to (37). The slope of the various lines in this diagram is the apparent order of reaction at a stage of decomposition where a fraction $G(t)/G(0)$ of the original material remains. The smaller the ratio $G(t)/G(0)$, the further the decomposition has progressed. Except for the case of the Inverse Power Law

Fig. 1. Kinetic behavior associated with the finite-range $g(0, k)$ -distributions given by eqs (12) and (33) to (37). Diagram A displays the change in the normalized organic matter concentration, $G(t)/G(0)$, as a function of time as normalized by the mean life-time of the most reactive component, k_0^{-1} . Diagram B illustrates the normalized rate of reaction, $R(t)/R(0)$, plotted against the normalized total organic matter concentration generated by the same initial reactive distributions. The slope at each point on these curves in diagram B represents the apparent order of reaction at a given stage of decomposition. Key for both diagrams:

_____	Step Function, eq (12)
.....	Linear Increasing, eq (33)
-----	Linear Decreasing, eq (34)
-----	Concave Quadratic, eq (35)
-----	Convex Quadratic, eq (36)
-----	Inverse Power Law ($n = 0.5$), eq (37)
.....	Inverse Power Law ($n = 0.75$), eq (37)



distribution, the curves do not reach their predicted asymptotic slopes, that is, reaction orders, until the $G(t)/G(0) < 0.2$, which is quite late in the degradation process. The Inverse Power Law distributions reach their asymptotic slopes much earlier in the process, as early as 20 percent decay for $n = 0.75$. This means that there is, in that case, a relatively rapid deceleration in the observed rate shortly after initiation of the process, which can be seen in figure 1A.

The Gamma distribution.—Even though an analysis of the finite range distributions given above has proven to be informative, they are probably not the best choice for data diagnoses. Their integrations are reasonably complicated, and many forms should presumably be examined to determine the optimum fit. Aris (1968, 1989) and Ho and Aris (1987) have advanced the use of the infinite k-range Gamma distribution:

$$g(k, 0) = \frac{g_0 k^{\nu-1} e^{-ak}}{\Gamma(\nu)} \quad (38)$$

where $\Gamma(\)$ is the Gamma function (Abramowitz and Stegun, 1972, p. 255; Hildebrand, 1976, p. 76; Spanier and Oldham, 1987, p. 411), and "a" and ν are, in principle, free-parameters. In the context of organic matter decay, the a-parameter is a measure of the average life-time of the more reactive components of the mixture described by eq (38). The exponent ν is a nondimensional parameter solely related to the shape of the distribution near $k = 0$. If ν is greater than one, then $g(0,0) = 0$, and a mid-distribution maximum results. If $\nu = 1$, then the Exponential distribution is obtained. Finally, if $0 < \nu < 1$ then the distribution is weakly singular near $k = 0$, like eq (30), but exponential-like in the limit of large k . This behavior is displayed in figure 2A (see also Tsokos, 1972; Ramanarayanan and Howard, 1986). Eq (38) is consequently quite remarkable in its flexibility. The time evolution curves for these distributions are shown in figure 2B. Additionally, Aris (1989) has demonstrated that the Gamma distribution has the interesting and useful property that the apparent order of decay for the mixture remains constant independent of the fraction decomposed (fig. 2C), unlike the finite-range distributions of figure 1 that change order with time.

What is arguably the most important consideration is that eq (38) corresponds to an exceedingly simple $G(t)$ function with highly desirable properties (Abramowitz and Stegun, 1972, p. 1022; Spanier and Oldham, 1987, p. 246)

$$G(t) = \frac{g_0}{(a + t)^\nu} \quad (39A)$$

or, if $G(0)$ is the initial total organic matter,

$$G(t) = G(0) \left(\frac{a}{a + t} \right)^\nu \quad (39B)$$

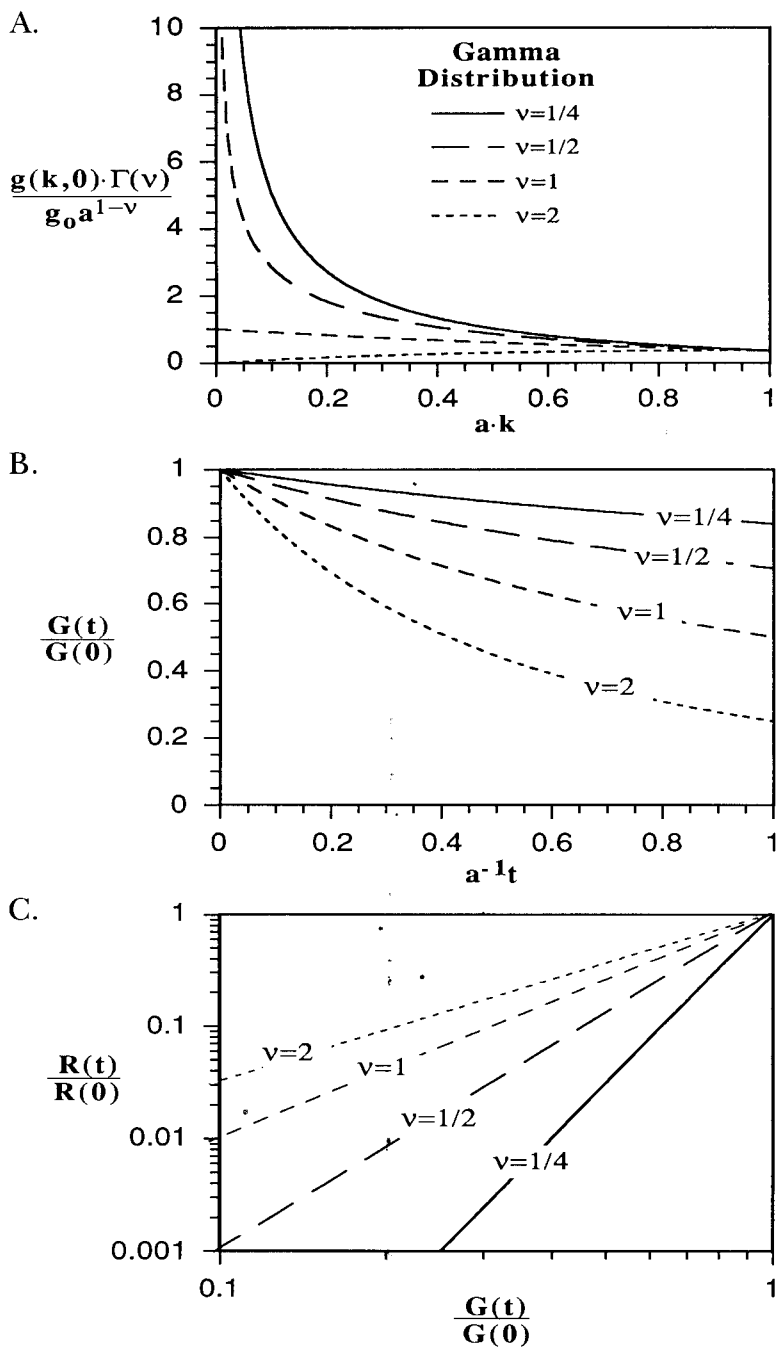


Fig. 2. Kinetic behavior associated with the Gamma distribution, eq (38). Diagram A displays the shape of this distribution as a function of the normalized rate constant, $a \cdot k$, for four values of the parameter ν . The parameter "a" is a measure of the mean life-times of the fast decaying components of the distribution, and ν determines the behavior near $k = 0$ (see text). Diagram B shows the time evolution of the (normalized) total organic matter corresponding to the distributions in diagram A. Diagram C illustrates the normalized rate of reaction, $R(t)/R(0)$, plotted against the normalized total organic matter concentration, $G(t)/G(0)$, generated by the Gamma distribution. The slopes are constant and correspond to apparent reaction orders of 5, 3, 2, and 1.5 for $\nu = 0.25, 0.5, 1$, and 2, respectively.

The rate of disappearance of the total organic matter is the derivative of eq (39) with respect to time,

$$\frac{dG}{dt} = -\frac{\nu g_0}{(a + t)^{\nu+1}} \quad (40)$$

Eqs (39) and (40) together lead to

$$\frac{dG}{dt} = -k_m G^{1+1/\nu} \quad (41)$$

which confirms the apparent higher orders attainable from small values of ν . The parameter k_m is the apparent rate constant for the decay of the mixture and is equal to $\nu/(g_0)^{1/\nu}$. Using eq (39A), we can establish that $g_0 = a^\nu G(0)$, which leads to the equality,

$$k_m = \frac{\nu}{a[G(0)]^{1/\nu}} \quad (42)$$

The simple form offered by eq (39) is easy to use for curve fitting purposes, and we will utilize it extensively in the course of data analysis in the next sections. We are fully cognizant that natural distributions of reactivity are likely to be highly complex and that our choice of the Gamma distribution is guided by a degree of mathematical expediency. Nevertheless, eqs (38) and (39) contain most of the essential behavior-determining characteristics that could be found in nature. Following Occam's directive, we adopt the simplest approach that still contains the essential features.

APPLICATION OF THE MODEL

Experimental studies.—Decomposition experiments where the (marine) organic matter concentration was monitored accurately during the procedure are not abundant, and of that limited set, Westrich and Berner (1984) quite likely have gathered the best data available. The traditional treatment of this data employs exponentials and constants for fitting purposes, that is, delta function distributions. Westrich and Berner (1984) required at least two exponential terms plus a constant to obtain an acceptable fit to the data, and a similar fitting is displayed in figure 3A ($r = 0.999$). This approach involves five arbitrary constants (that is, a_1, b_1, a_2, b_2, a_3), of which only four are truly independent.

If instead, eq (39) is utilized, then the fit shown in figure 3B is obtained ($r = 0.998$). Notice that only two parameters are needed to arrive at this fit. All else being equal, the reactive continuum model has the distinct advantage of demanding half the number of free parameters as the traditional model. The parameter ν takes a value of 0.125 which is equivalent to an apparent 9th order reaction. This is indicative of the strong preponderance of the relatively inert material in the mixture. The

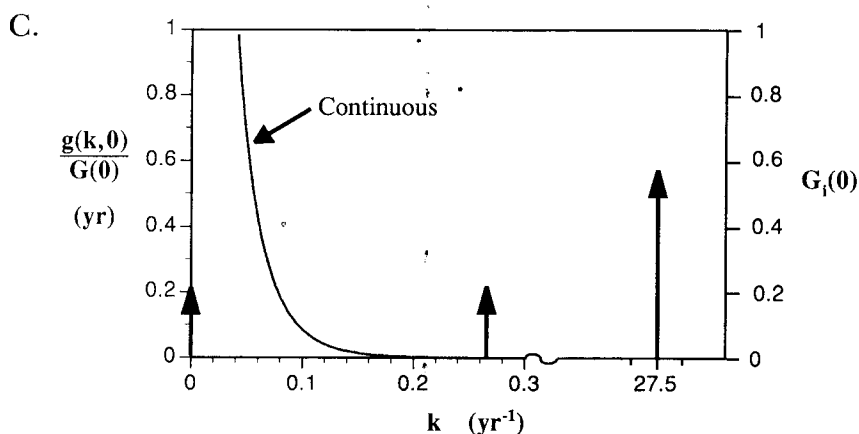
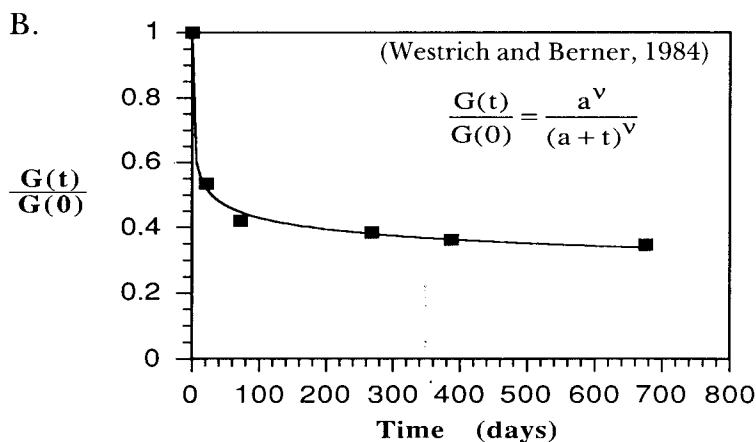
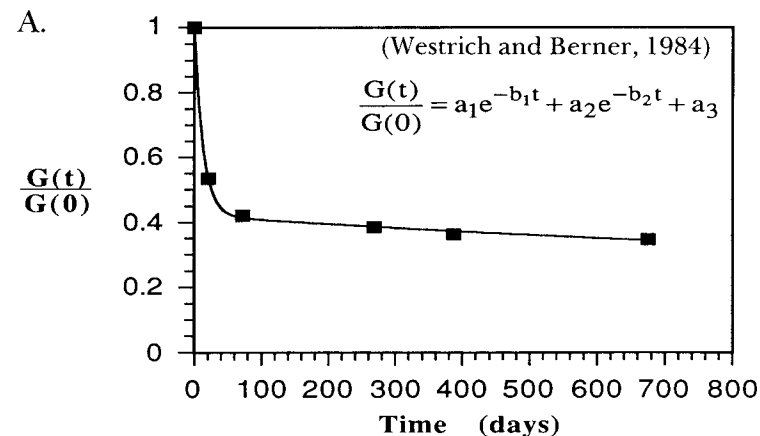


Fig. 3. Experimental data presented by Westrich and Berner (1984) as interpreted with the traditional multi-G (exponential) model in diagram A and with the reactive continuum model, eq (39B), in diagram B. The fit in diagram A gives $a_1 = 0.205$, $b_1 = 0.261 \text{ yr}^{-1}$, $a_2 = 0.578$, $b_2 = 27.5 \text{ yr}^{-1}$, and $a_3 = 0.217$ for $r = 0.999$, where a_3 is not independent of a_1 and a_2 . The fit to eq (39) given in diagram B generates $a = 0.113 \text{ day}$ and $v = 0.125$ for $r = 0.998$ and corresponds to an apparent 9th order reaction. There are also only two curve-fitting parameters in the continuum representation. Diagram C illustrates the distributions that correspond to the fits in (A) and (B). The curve labelled "continuous" is the distribution that coincides with the fit of eq (39) in (B), and the vertical arrowed lines (that extend to infinity) represent the three delta-functions that generate the exponential fit in (A). (Note the break in the x-axis of (C).)

other parameter, a , has a calculated value of 0.113 days which indicates that the initial material to decay is reactive indeed.

The reactive distributions that correspond to the fits in figure 3A and B are illustrated in figure 3C. The smooth curve labelled "continuous" is the Gamma distribution (divided by the initial organic matter concentration) that coincides to the fit of eq (39) to the data in figure 3B divided by $G(0)$. (The ratio $g(k, 0)/G(0)$ can be thought of as the analogue to the probability density function.) The continuous distribution approaches infinity as $k \rightarrow 0$.

The discrete distribution of delta-functions that corresponds to the exponential fit in figure 3A is given by the vertical arrowed lines in figure 3C, one at $k = 27.5 \text{ yr}^{-1}$, a second at $k = 0.261 \text{ yr}^{-1}$, and a third at $k = 0$. The height of these lines extends to infinity on the $g(k, 0)/G(0)$ -axis. However, the integral of each delta function is the finite amount of organic matter for each of the three reactivities. These amounts are given by reading-off the actual plotted heights against the right-hand axis. This graphical comparison illustrates the vast differences between the continuous and discrete distributions. That both distributions can be made to fit the data equally well tells us that the inverse problem will never yield a unique solution without additional (outside) constraints.

Sediments without mixing or below the mixed-layer.—There is a unique relationship in these sediments between the depth (below the mixed zone) and elapsed time at constant porosity,

$$x = \omega t \quad (43)$$

where x is the depth below the sediment-water interface for non-mixed sediments or below the mixed layer for mixed sediments, and ω is the burial velocity. This permits substitution of x/ω for t in eq (39) or any other $G(t)$ -function that results from a chosen distribution function.

Nine organic matter profiles from various sedimentary environments were modelled using eq (39). They span burial velocities from 0.2 cm yr^{-1} at the FOAM site (Westrich, 1983) to 0.2 cm kyr^{-1} for a siliceous ooze at 13.5°N in the Pacific (table 1). The data for each core along with the non-linear least squared fits of eq (39) are presented in figures 4 and 5. The best fits for parameters ν and a can also be found in table 1.

The cores are divided into two groups on the basis of the calculated value of the exponent ν . The majority of cores in figure 4 possess ν 's between 0.1 and 0.2 (apparent 6th–11th order reactions). The ν -values of this group are similar to that derived from the experimental data of Westrich and Berner (1984). The small values of the parameter ν for this group argue that the total organic matter is dominated by refractory components clustered near $k = 0$. (We believe that core PC2 & TW2 is anomalous, and this is discussed below.) The other three cores in figure 5 are described by exponents between roughly 0.8 and 1.0 (apparent

TABLE I

Continuum model fits (eq 39) to selected organic matter profiles in histotical layer of marine sediments

Core	Location	ω (cm kyr ⁻¹)	Source	ν	Apparent Order	a (yr)	r*
FOAM	Long Island Sound	200	Goldhaber and others (1977) and Westrich (1983)	0.152	7.57	4.2	0.930
SCR-44	Santa Cruz Basin	60	Shaw (ms)	0.202	5.95	70.4	0.929
BX-6	Peru Margin	230	Froelich and others (1988)	0.278	4.60	22.5	0.929
PC2 & TW2	Peru Margin	230	Froelich and others (1988)	0.052	20.2	0.16	0.937
10127	Central Equatorial Pacific	0.2	Müller and Mangini (1980)	0.139	8.19	14,000	0.926
10141&2	same	1.2	Müller and Mangini (1980)	0.193	6.18	10,184	0.935
7706-41K	Peru Margin	150	Reimers (1982)	0.910	2.10	141.3	0.974
7706-36	Peru Margin	40	Reimers and Suess (1983)	0.804	2.25	231.7	0.978
DSDP 58	North Philippine Sea	2.0	Wapples and Sloan (1980)	1.080	1.93	20,224	0.917

*Correlation coefficient

orders between 2–2.25) and, consequently, a much more even distribution of reactive types along the continuum (see fig. 2A).

The reason for this apparent dichotomy is not clear. If the difference is real, it speaks of intrinsically different initial k-distributions between these two groups. There are no obvious geographic or oceanographic differences or similarities to explain these groupings. The Peru margin profiles (cores 7706-36 and 7706-41K) probably include some data from a surficial zone which is appreciably bioturbated. Kim and Burnett (1988) have demonstrated the existence of measurable particle mixing even in laminated sediments of this region. Mixing may result in higher apparent value for the exponent, but we simply don't have any strong evidence to back this statement. (The higher ν of core BX-6 of the group in figure 4 is also from the Peru Margin and does appear to contain some data from a weakly bioturbated surficial layer, that is, $\omega L/D_B < 1$, where D_B is the biodiffusion coefficient.) In addition, there may be non-steady state effects in core 7706-41K (Boudreau, 1990).

The ν value for the DSDP 58 site cannot be explained by these mechanisms and constitutes a greater enigma. We cannot rely on geopolymerization as an explanation, because this would shift organic matter to the less reactive end of the spectrum and, therefore, decrease the value of the exponent, ν . Wapples and Sloan (1980) discount any thermal (catagenic) effects, and the organic matter content is not terribly different from that in the Müller and Mangini (1980) core of figure 4. This core

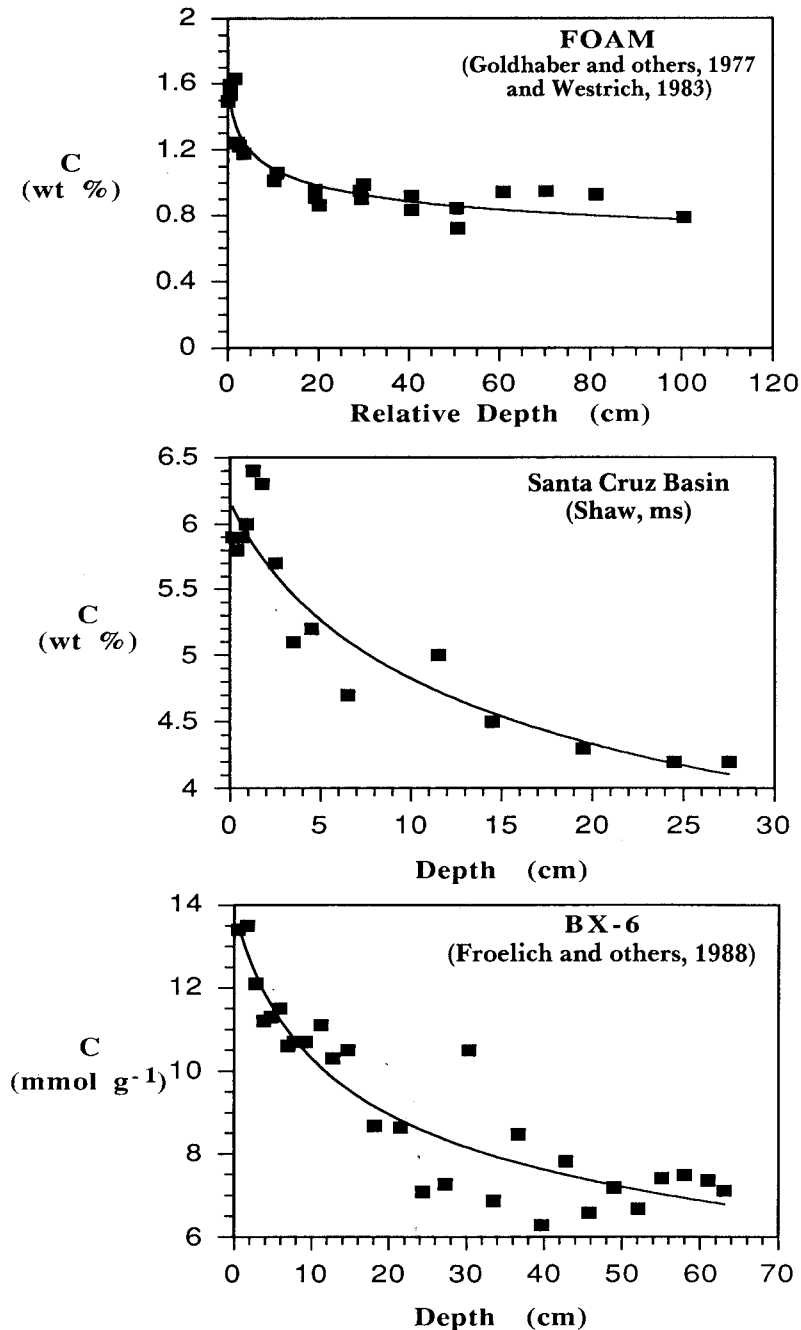


Fig. 4. Six marine organic matter (carbon) profiles and the best fits to this data using eq (39), which corresponds to a Gamma distribution of reactivity, eq (38). The literature source for each core is quoted in each figure, while the location and sedimentation velocities can be found in table 1. Correlation coefficients for these fits are found in table 1. The cores in this figure are characterized by calculated ν -values that center on the range of 0.1 to 0.2 (see table 1), that is to say, apparent 6th to 11th order reactions. (Depth relative to the sediment-water interface is designated simply as Depth, while depth below the base of the surficial mixed zone is labelled as Relative Depth.)

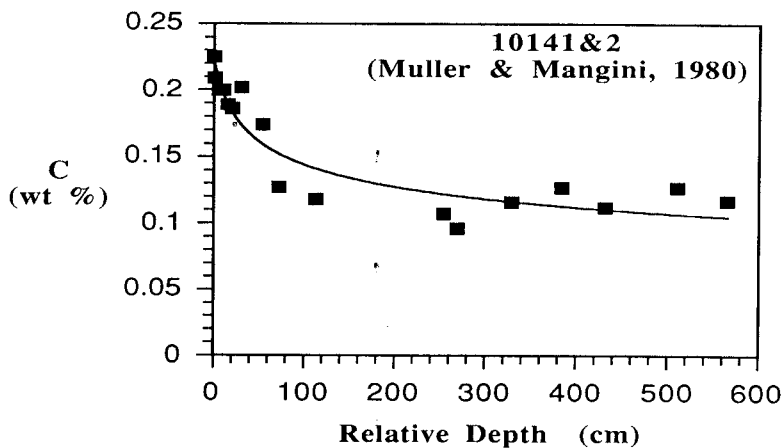
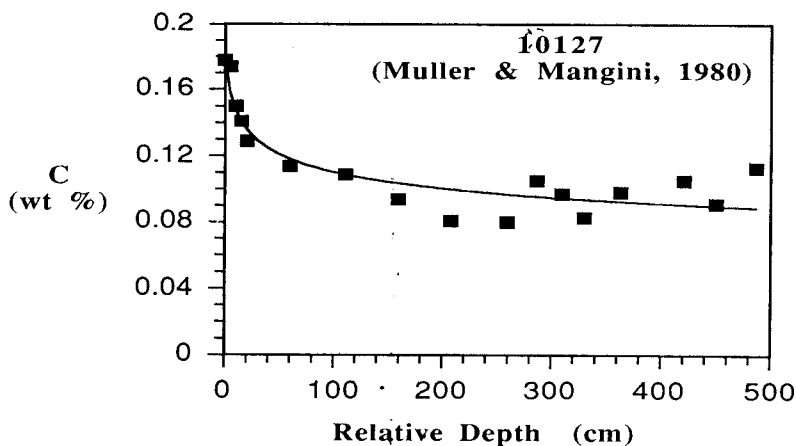
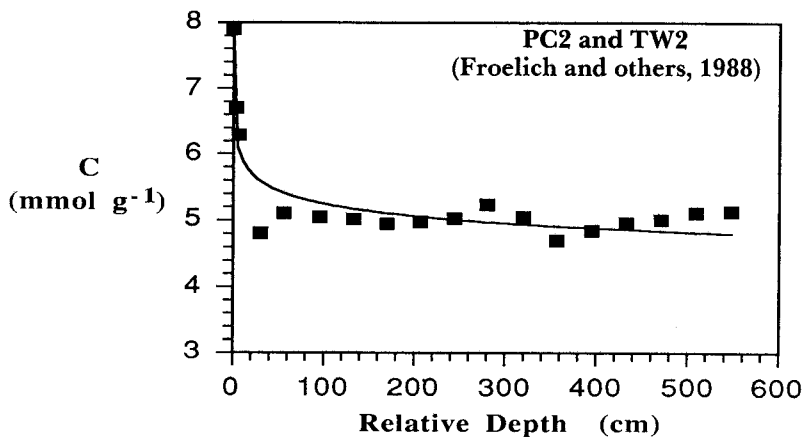


Fig. 4 (continued)

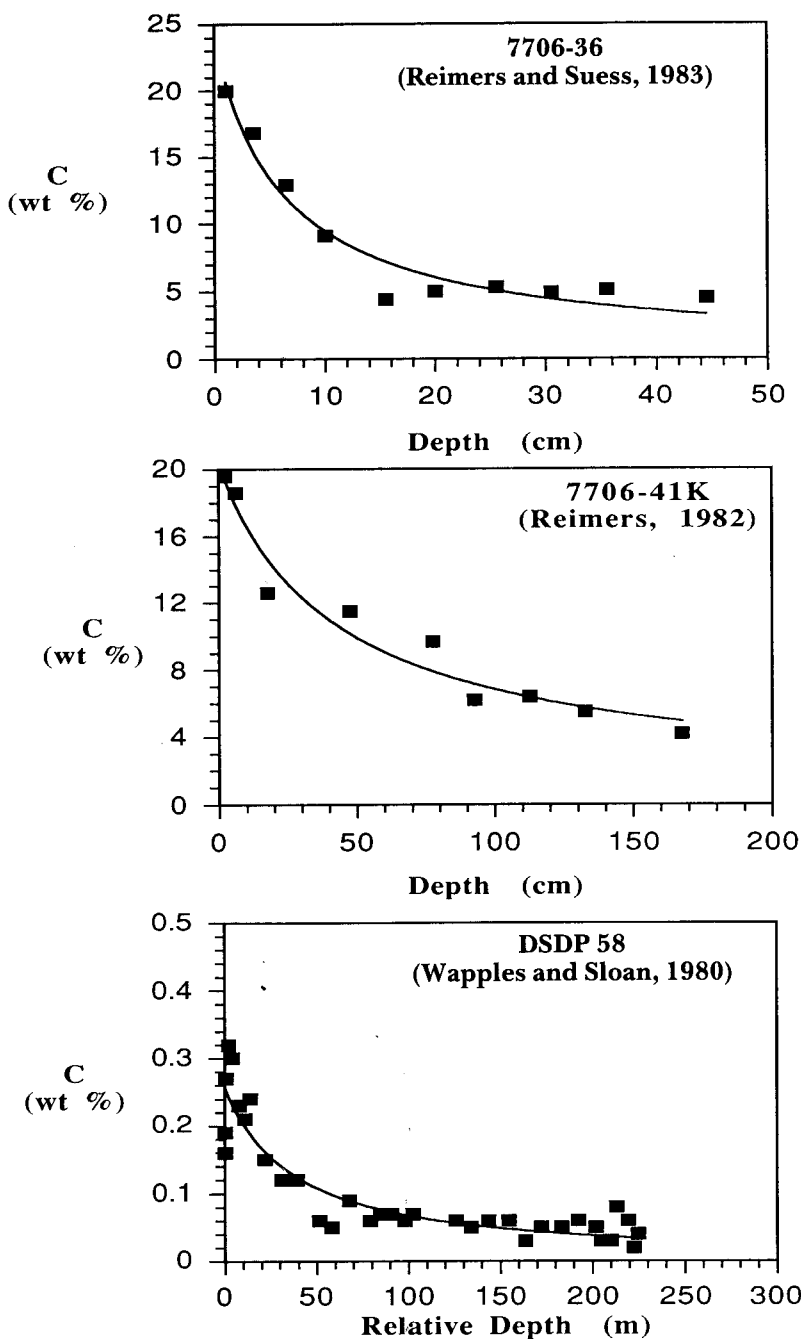


Fig. 5. Three marine organic matter (carbon) profiles and, as in figure 4, the best fits to these data using eq (39). The cores in this figure are, however, characterized by larger ν -values that center on the range of 0.8 to 1.0 (see table 1), which is equivalent to apparent orders of 2 to 2.25. Again, the literature sources for each data set are given in each diagram, and the location and sedimentation velocities can be found in table 1.

remains a quandary. Similar analyses on more data sets are needed to establish firmly the trends, if any, in ν values and determine the underlying causes.

If we accept that the first grouping is real (if only for the sake of argument), then the calculated exponents are comparable to that derived from the laboratory experiments of Westrich and Berner (1984). This may be indicative of a fundamental similarity in the shape of decay profiles, over vastly different time and space scales. (This last statement can be understood by remembering that eq (43) links time and space; consequently, sampling over different time scales in an experiment is equivalent to sampling over different space scales in a core.)

We have not yet discussed the parameter "a" that results from these distributions. Calculated values are shown in table 1. As stated earlier, this parameter is a measure of the average life-span of the fast decaying portion of the distribution. One would guess intuitively that a should increase in value as the sedimentation velocity decreases, because the fast decaying material is removed before it is incorporated into the historic zone, either at the sediment-water interface or in the mixed zone. This general trend is indeed confirmed in the data as seen in both table 1 and figure 6. While this correlation must be considered tentative in light of the small data set, it is analogous in the continuum model to the k versus ω relationship derived by Toth and Lerman (1977) for the discrete model.

In creating figure 6 we have omitted the a -value corresponding to core PC2&TW2, as this value is anomalously low. Common sense argues that a life-time of only 0.16 yrs is far too short for reactive organic matter in a sediment with such a modest accumulation rate (that is, compare with FOAM). The ν for this core also stands out for its small value (0.052). All in all, the organic carbon gradient in this core is far sharper than expected and is perhaps related to non-steady state conditions.

The profiles examined above have been in many cases treated by the traditional method of fitting with an exponential plus a constant (Westrich, 1983; Müller and Mangini, 1980; Wapples and Sloan, 1980), and the resulting fits were found to be equally pleasing and statistically significant. A curve generated by eq (39) and that by an exponential plus a constant are not mathematically equivalent, and in perfect data, the discrepancy would be apparent. Real sedimentary data are, however, riddled with random variations, and within such noise the two functions are often statistically undifferentiable. As a result, it is easy to argue that one choice is as good as another in dealing with sedimentary data. The only guiding light is one's conviction in the validity of either one of these conceptual-mechanistic models, that is, some continuous distribution versus discrete types.

Westrich's "Gedanken" experiment.—In his seminal work on the G-model, Westrich (1983) conducted a thought-experiment wherein he created a hypothetical sediment containing all eight of the discrete reactive types that he had identified as components of natural organic

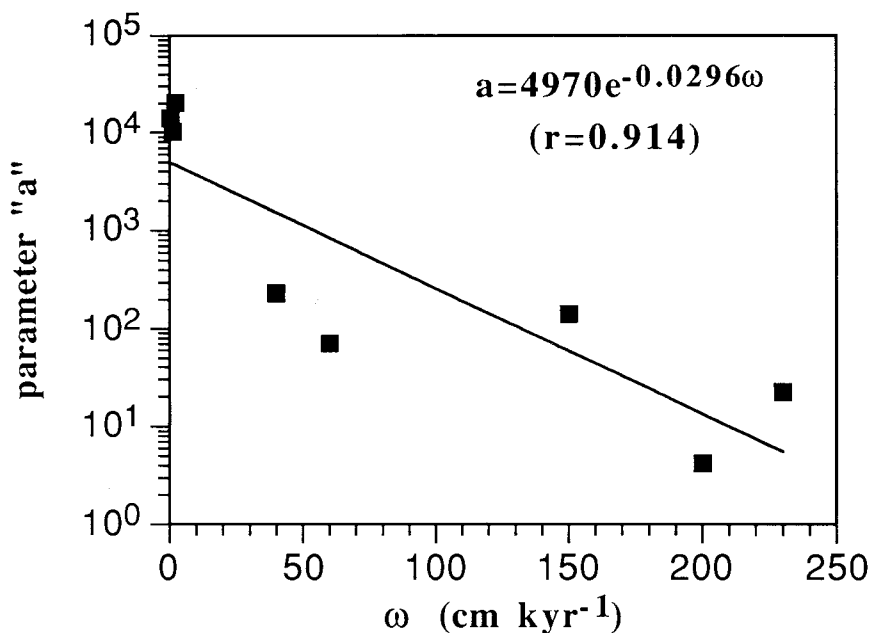


Fig. 6. A plot showing the correlation between the parameter "a" in eq (39) with the sedimentation velocity of the cores listed in table 1. (Note core PC2&TW2 is not included.) The best fit to an exponential is shown in this diagram with "a" in units of yrs and ω in units of cm kyr⁻¹.

matter. (We call this the Westrich distribution, although the sum of the corresponding delta functions is in fact the actual distribution.) Specifically he proposed a sediment mixture in which each organic matter type constituted 0.4 percent by weight, except for the inert fraction ($k = 0$) which made up only 0.05 percent. He then examined the decay of this mixture under different sedimentary conditions.

The Westrich distribution does not represent a true known organic matter but rather a hypothetical composite. Nevertheless, it is legitimate to ask—what type of continuous Gamma distribution is implied by Westrich's discrete distribution? To answer this question, we plot the Westrich distribution (solid line in fig. 7) and then carry out a nonlinear fit of eq (39) (dotted line in fig. 7). The equivalent continuous representation of the Westrich distribution is then,

$$\frac{G(t)}{G(0)} = \frac{0.879}{(0.342 + t)^{0.1}} \quad (44)$$

with a correlation, r , of 0.986. This fit required only two parameters, compared to the original eight separate k 's and $G_i(0)$'s, which is a considerable reduction.

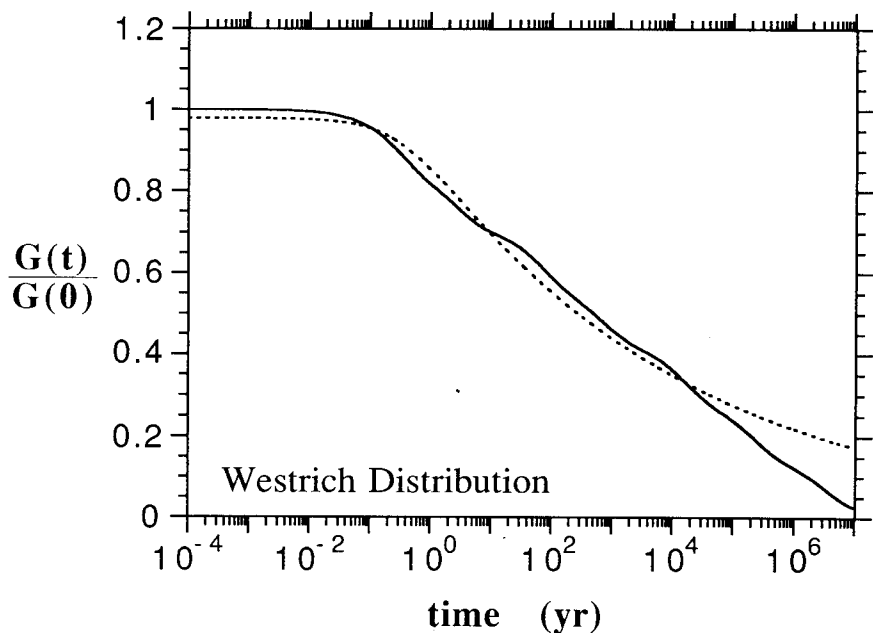


Fig. 7. Nonlinear fit of eq (39)—dotted line—to the Westrich distribution of eight organic matter types—solid line. The parameters ν and “a” have values of 0.1 and 0.342 yrs, respectively, for a correlation coefficient, r , of 0.986.

At least two significant observations can be made in comparing the fit in figure 7. First, the ν for the continuous distribution is indicative of an 11th order reaction, which is consistent with the major grouping discussed above. Secondly, the two distributions diverge after long periods of time ($> 10^5$ yrs). This is attributable to the faster decay inherent to exponentials compared to forms like eq (39). Note that the discrepancy is small.

Mixed sediments.—We now take a cursory look at a version of the continuum model that includes mixing of the organic matter. In the presence of diffusive mixing, the constant porosity diagenetic equation for a component of the continuum is

$$\frac{\partial g}{\partial t} = D_B \frac{\partial^2 g}{\partial x^2} - \omega \frac{\partial g}{\partial x} - kg \quad (45)$$

Restricting ourselves to the steady state and imposing the boundary conditions

$$g = g(k, 0) \quad x = 0 \quad (46A)$$

$$\left. \frac{dg}{dx} \right|_{x=L} = 0 \quad (46B)$$

where L is the depth of the mixed layer, the standard solution to eq (45) is

$$g(x, k) = \frac{g(k, 0)}{\left(1 - \frac{\mu}{\sigma} e^{(\mu-\sigma)L}\right)} \left(e^{\mu x} - \frac{\mu}{\sigma} e^{(\mu-\sigma)L} e^{\sigma x} \right) \quad (47)$$

where

$$\mu = \frac{\omega - (\omega^2 + 4D_B k)^{1/2}}{2D_B} \quad (48A)$$

and

$$\sigma = \frac{\omega + (\omega^2 + 4D_B k)^{1/2}}{2D_B} \quad (48B)$$

The equation that governs the total amount of organic matter at any depth is obtained by substituting eq (47) into eq (6)

$$G(x) = \int_0^\infty \frac{g(k, 0)}{\left(1 - \frac{\mu}{\sigma} e^{(\mu-\sigma)L}\right)} \left(e^{\mu x} - \frac{\mu}{\sigma} e^{(\mu-\sigma)L} e^{\sigma x} \right) dk \quad (49)$$

Generally, eq (49) can be integrated numerically (if not analytically) for any reasonable $g(k, 0)$. Many readers may find it sufficiently unwieldy that the discrete G -model looks like a superior alternative.

The problems associated with implementing the continuum model with a finite mixed zone do not end with the complexity presented by eq (49). To match the concentrations at $x = L$, the formal procedure would require that the shape of the distribution be calculated and fed into the equations governing the non-mixed zone. This could be quite an involved calculation. From a practical point of view, there is little to recommend the continuum model under these circumstances.

If the mixed layer can be assumed to extend to infinity (for example, if we are interested only in obtaining the correct behavior of the fastest decaying components), then some of the simplicity of the non-mixed situation is regained. The solution for $g(k, x)$ reduces to

$$g(x, k) = g(k, 0) e^{-\kappa x} \quad (50)$$

where

$$\kappa = \left(\frac{k}{D_B} \right)^{1/2} \quad (51)$$

The total organic matter is

$$G(x) = \int_0^\infty g(k, 0) e^{-\kappa x} dk \quad (52)$$

which is reminiscent of eq (7). There is a Gamma-like distribution for $g(k, 0)$ that leads to the simple form of eq (39), that is, $g(k, 0) \approx g_0 k^{\nu-1} e^{-a\sqrt{k}}$; however, we shall not pursue this topic further.

ENERGETICS OF DECOMPOSITION

The past discussion has implicitly assumed an isothermal environment. The decay of organic matter is, however, a rate process and, therefore, a function of the ambient temperature. To be complete, the theory must recognize the effects of variable temperature. This is particularly important in shallow-water sediments subject to seasonal fluctuations in temperature (for example, Aller, 1980).

The standard approach in dealing with temperature effects on rates is to assume the validity of an Arrhenius-type dependence (for example, Vosjan, 1974; Abdollahi and Nedwell, 1979; Aller and Yingst, 1980; Aller, 1980; Crill and Martens, 1987; Westrich and Berner, 1988; and Mackin and Swider, 1989). Does this Arrhenius approach apply to the decay of total organic matter as represented by the integration over a reacting continuum, that is eq (41)?

To answer this question, we introduce the work of Crickmore (1989) who has developed a complete theory for temperature effects on a reactive continuum. This theory assumes that the Arrhenius formula is a valid description of the temperature dependence of each individual reaction of the continuum; thus,

$$k = A(k)e^{-E(k)/RT^2} \quad (53)$$

where $A(k) \equiv$ pre-exponential factor for a rate constant of value k

$E(k) \equiv$ activation energy for a rate constant of value k , kJ mole^{-1}

$R \equiv$ gas constant, $8.3 \text{ kJ } ^\circ\text{K}^{-1} \text{ mole}^{-1}$

$T \equiv$ absolute temperature, $^\circ\text{K}$

Both $A(k)$ and $E(k)$ are now functions of k rather than constants, but they are usually considered independent of T . (The units of $A(k)$ depend on the value of ν .)

In particular, for a Gamma distribution, Crickmore (1989) has shown that the effective or apparent activation energy of the continuum, E_{eff} , is given by

$$E_{\text{eff}} = \frac{a}{\nu G(0)} \int_0^\infty kg(k, 0)E(k)dk \quad (54)$$

and k is given by eq (53). The derivation of eq (54) is a bit obscure and is repeated in the appendix of this paper for the convenience of the reader.

As Crickmore (1989) aptly points out, eq (54) implies in general that the slope of an Arrhenius plot, that is to say $\log_e(\text{rate})$ versus T^{-1} , will not be a straight line, because E_{eff} is a function of temperature due to the $\exp(-E(k)/RT^2)$ term within the integral. Only if $E(k)$ is a constant, E , can

we unequivocally say that the line on this plot is straight; that is if $E(k) = E$,

$$E_{\text{eff}} = \frac{aE}{\nu G(0)} \int_0^\infty kg(k, 0)dk \quad (55)$$

but (see app.)

$$\int_0^\infty kg(k, 0)dk = \frac{G(0)\nu}{a} \quad (56)$$

so that

$$E_{\text{eff}} = E \quad (57)$$

If $E(k)$ is not a constant, then Crickmore (1989) further proves that the Arrhenius plot should be concave up, with the greater slope at higher temperature (lower T^{-1}). This results from the fact that reactions with higher activation energies will dominate this plot at higher temperatures.

The Arrhenius plots of experimental and field data found in Abdollahi and Nedwell (1979), Westrich and Berner (1988), and Mackin and Swider (1989) do not exhibit appreciable curvature within the errors of their data. At the same time, we know that as the rate of organic matter decay slows with the disappearance of the more reactive components, the activation energy increases somewhat (Westrich and Berner, 1988). Is a linear Arrhenius plot consistent with this observation of non-constant $E(k)$?

The answer is yes, and the reason lies in the restricted temperature range that prevails in sedimentary experiments. The normal temperature variation possible in sediments is 273 °K to 303 °K (0–30 °C). On a mean of 288°K, this represents a fluctuation of only 5.2 percent. It is demonstrated below that an Arrhenius plot will likely appear linear over the corresponding range of T^{-1} values.

To begin, write T as

$$T = T_0 + T' \quad (58)$$

where T_0 is the mean of the temperature range (288 °K), and T' is the possible variation (± 15 °K). Then, using the binomial theorem and the fact that $T'/T_0 \ll 1$, we obtain the approximation

$$\frac{1}{T^2} \approx \frac{1}{T_0^2} \left(1 - \frac{2T'}{T_0} \right) \quad (59)$$

Eq (59) implies that the exponential in the Arrhenius law, eq (53), can be written as

$$e^{-E(k)/RT^2} \approx e^{-E(k)/RT_0^2} e^{2E(k)T'/RT_0^3} \quad (60)$$

If we now expand the second exponential on the right-hand side of eq (60) in a Maclaurin series, then

$$e^{-E(k)/RT^2} \approx e^{-E(k)/RT_0^2} \left(1 + \frac{2E(k)T'}{RT_0^3} + \dots \right) \quad (61)$$

The question now centers on the relative importance of the second and higher order terms in the large bracket on the right-hand side of eq (61). If these terms are negligibly small, it then follows that the slope of an Arrhenius plot will appear linear within the noise of the data, as these are the only terms explicitly dependent on T' .

To make this determination, we estimate the size of the term $2E(k)T'/(RT_0^3)$. The tricky part is specifying a likely maximum value for $E(k)$ which, in turn, generates the largest value possible for $2E(k)T'/(RT_0^3)$. The measured E_{eff} values range from 23 to 132 kJ mole⁻¹ (Vosjan, 1974; Jørgensen, 1977; Goldhaber and others, 1977; Abdollahi and Nedwell, 1979; Aller and Yingst, 1980; Crill and Martens, 1987; Westrich and Berner, 1988; Mackin and Swider, 1989). While these may represent mean values for various continua, they may not be good surrogates for the maximum $E(k)$. Setting an arbitrary upper limit of 200 kJ mole⁻¹ for these values generates a maximum of 0.03 for $2E(k)T'/(RT_0^3)$ or a 3 percent deviation from linearity.

One might argue that the highly refractory nature of some organic matter components might imply even higher values of $E(k)$, but the small k 's associated with this material must be in part due to small values of $A(k)$. Nevertheless, as an extreme upper limit, we note that thermal cracking of kerogen is characterized by E_{eff} values of no greater than 400 kJ mole⁻¹ (Tissot and Welte, 1978). Therefore, if we adopt an extraordinarily large maximum $E(k)$ of 1000 kJ mole⁻¹ (which is probably physically impossible), the correction offered by the term $2E(k)T'/(RT_0^3)$ would still be only 15 percent. Because all the other subsequent terms in the Maclaurin series are much smaller than the second, we can conclude that an Arrhenius plot for E_{eff} for decomposition of sedimentary organic matter should be linear within the normal scatter in the data. We note for interest that the curvature expected from the Crickmore theory is observed in Arrhenius plots dealing with catagenesis where a much broader temperature change is involved (Tissot and Welte, 1978).

CONCLUDING REMARKS

This paper has presented the theory of a reactive continuum representation of marine organic matter decay, and it has explored the advantages and limitations of this approach. Using the Gamma distribution as a model function, it was found that the equations generated by the reactive continuum model fit the experimental data generated by Westrich and Berner (1984) with half the number of parameters of the

multiple-G model. Based on the exponent of the curve fit in eq (39), that is, $\nu = 0.125$, the apparent order of reaction for this data was ninth order.

The continuum model was applied to nine organic matter profiles taken in non-mixed sediments or below the mixed layer in bioturbated sediments. All fits were quite acceptable ($r > 0.9$), and it was found that this process divided the profiles into two groups. The first group consisted of five cores for which the exponent, ν , in the curve fit to eq (39) centered in the range 0.1 to 0.2, that is, 6th to 11th order. This result is consistent with the analysis of the Westrich and Berner (1984) experimental data and hints at a fundamental similarity of decay profiles at all time and space scales. The second group of three had exponents in the 0.8 to 1.0 range (apparent orders of 2–2.25). Westrich (ms) established with his multiple-G model a hypothetical initial distribution for typical organic matter consisting of eight discrete reactive types. If this is translated into a continuous distribution, then there results an apparent 11th order decay, which is again consistent with the main grouping of experimental and observational data. The explanation for this dichotomy is not immediately evident, and more data analyses are needed. Overall the continuum model presents a valid and equally accessible alternative to the G-model for modelling organic matter diagenesis (decay) in the historical zone of marine sediments.

The mathematics of applying the continuum model to a finite-thickness mixed zone sediment are dramatically more involved than those of the G-model. For those who insist on an analytical solution, it would appear that the continuum model would then be at a practical, but not conceptual, disadvantage in this case unless the mixed zone can be assumed to extend to infinity. Those willing to attempt numerical methods should find only moderate difficulty in the continued use of the continuum model.

While the continuum theory may initially suggest a complicated treatment for the energetics of the decay process, it is shown in this paper that for the temperature-range normal to sedimentary environments, the Arrhenius plot can still be used to derive an effective activation energy for the total organic matter mass.

The presentation of the continuum theory contained in this paper is not exhaustive, and more needs to be done if this technique is to become a standard tool of diagenetic modelling. To keep the size of the paper within reasonable bounds, we have conducted only a superficial examination of mixing effects. Additionally, we have not even attempted to show how the continuum model will fit into diagenetic equations for oxidant species or regenerated nutrients. If this initial introduction to the continuum theory finds favor with the scientific community, it will be necessary to address these issues.

ACKNOWLEDGMENTS

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APPENDIX

This appendix displays the derivation of eq (54) of the text. We start with the Arrhenius rate law, eq (53),

$$k = A(k)e^{-E(k)/RT^2} \quad (A1)$$

From this equation, we wish to derive the formula for the effective activation energy for the decay of the total organic matter, E_{eff} ; that is to say, the activation energy for k_m in eq (41). The standard definition of activation energy is (Laidler, 1965; Lasaga, 1981)

$$E = -R \frac{\partial \ln k}{\partial (1/T)} \quad (A2A)$$

or, upon expansion,

$$E = -\frac{RT^2}{k} \frac{\partial k}{\partial T} \quad (A2B)$$

We are interested in the case where E is replaced by E_{eff} and k by k_m .

To begin, we will need the derivative of eq (A1) with respect to T ,

$$\frac{\partial k}{\partial T} = \frac{A(k)E(k)}{RT^2} e^{-E(k)/RT^2} \quad (A3)$$

Now multiply each side of eq (A3) by $g(k, 0)/[G(0)]^{1+1/\nu}$ and then integrate with respect to k ,

$$\frac{1}{[G(0)]^{1+1/\nu}} \int_0^\infty g(k, 0) \frac{\partial k}{\partial T} dk = \frac{1}{[G(0)]^{1+1/\nu} RT^2} \int_0^\infty kg(k, 0)E(k)dk \quad (A4A)$$

where we have employed eq (A1). We must now make the crucial assumption that we can exchange the order of differentiation and integration on the left-hand side of eq (A4A). There is no obvious reason why this should not be possible, and the result is

$$\frac{1}{[G(0)]^{1+1/\nu}} \frac{\partial}{\partial T} \int_0^\infty kg(k, 0)dk = \frac{1}{[G(0)]^{1+1/\nu} RT^2} \int_0^\infty kg(k, 0)E(k)dk \quad (A4B)$$

However, we must stress the somewhat unproven aspect of this maneuver.

For a Gamma distribution, eq (38),

$$\int_0^\infty kg(k, 0)dk = \frac{g_0}{\Gamma(\nu)} \int_0^\infty k^\nu e^{-ak} dk \quad (A5A)$$

or, Spanier and Oldham (1987, p. 245),

$$\int_0^\infty kg(k, 0)dk = \frac{g_0 \nu}{a^{\nu+1}} \quad (A5B)$$

But, we have established with eq (39) that $g_0 = G(0) a^\nu$, so that eq (A5b) reduces to

$$\int_0^\infty kg(k, 0)dk = \frac{G(0)\nu}{a} \quad (A6)$$

Therefore, with eq (42) and eq (A6), we further establish that

$$\frac{1}{[G(0)]^{1+1/\nu}} \frac{\partial}{\partial T} \int_0^\infty kg(k, 0)dk = \frac{\partial k_m}{\partial T} \quad (A7)$$

which, substituted into eq (A4B), gives

$$\frac{\partial k_m}{\partial T} = \frac{1}{[G(0)]^{1+1/\nu} RT^2} \int_0^\infty kg(k, 0)E(k)dk \quad (A8)$$

Using the definition provided by eq (A2B) and substituting E_{eff} , k_m and eq (A8), we find that

$$E_{\text{eff}} = \frac{1}{k_m [G(0)]^{1+1/\nu}} \int_0^\infty kg(k, 0)E(k)dk \quad (A9)$$

or, with eq (42),

$$E_{\text{eff}} = \frac{a}{\nu G(0)} \int_0^\infty kg(k, 0)E(k)dk \quad (A10)$$

which is the desired eq (54). Before leaving, we note one other form of eq (A10). Substituting eq (A6) gives,

$$E_{\text{eff}} = \frac{\int_0^\infty (kg(k, 0)E(k)dk)}{\int_0^\infty kg(k, 0)dk} \quad (A11)$$

which clearly indicates that if k can be shown to be independent of T over some range in this variable, E_{eff} will be a constant as $g(k, 0)$, and $E(k)$ are by definition independent of T . This is what is done in the text.

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