**2. Methods**

We have broadly partitioned the ocean floor into shelf, margin and abyss domains in order to specify values for some of the parameters required to carry out the modeling approach described below because they are not well-constrained on a global basis (see Table 2). The location of the continental margin boundaries was adopted from ([Vion and Menot, 2009](#_ENREF_61)): shelf environments roughly correspond to  water depths < 200 m, with the exception of the Antarctic region where shelf area corresponds to water depths < 500m; areas deeper than ~3500 m are taken to be abyssal plain. Accordingly, continental shelf underlies about 6.33% of ocean surface area, margins make up 10.78% and the abyssal domain constitutes the remaining 82.89%. The map depicted in Figure 1 shows the locations of these domains.

**2.1 *Reaction transport model***

A reaction-transport model is used to estimate the depth distribution of POC in global marine sediments, and to assess the amount of this POC that has been degraded throughout the Quaternary Period. The one-dimensional conservation equation for POC in porous media is given by (e.g., Berner, 1980; Boudreau, 1997):

(1)



where *POC* corresponds to the concentration of particulate organic matter; *t* stands for time; *Db* refers to the bioturbation coefficient; *ω* represents the sedimentation rate,and *RPOC* denotes the rate of heterotrophic organic matter degradation. The bioturbation coefficient is calculated as a function of water depth based on a compilation of empirical data collected by ([Middelburg et al., 1997](#_ENREF_37)). The porosity, **, of marine sediments in the shelf, margin and abyss domains was calculated as an exponential function of depth, *z* (m) (thus assuming steady state compaction), using a standard formulation commonly used in basin-to-global scale porosity studies ([Athy, 1930](#_ENREF_4)):

**(*z*) = **0 exp(-*c*0*z*) (2)

where **0 denotes the porosity at the SWI and *c*0 (m-1) stands for the compaction length scale, which characterizes how a given sediment type will compact under its own weight. For simplicity and clarity, values of **0 and *c*0 were chosen to describe the shelf, margin and abyss based on sediments that are representative of these domains ([Hantschel and Kauerauf, 2009](#_ENREF_18)) (see Table 2).

Quaternary sediments are divided into a bioturbated layer (top 10 cm) and non-bioturbated Holocene (< 11,700 yrs) and Pleistocene (< 2.59 Myrs or < maximum sediment thickness) layers. Equation (1) is then solved analytically assuming steady state conditions for each layer, thus resolving long-term changes in boundary conditions while neglecting short-term variations. A concentration condition is applied at the upper boundary while a zero gradient condition is appliedat the lower boundary. Organic matter degradation ,*RPOC*, is described by a reactive continuum model, RCM (Boudreau and Ruddick, 1991). The RCM assumes a continuous, yet dynamic distribution of organic matter compounds over a range of reactivities that encapsulates the decrease in apparent reactivity with depth/burial age as the most reactive compounds are successively degraded with two parameters. Within the RCM, the overall rate of organic matter degradation, *RPOC*, for a continuous distribution of organic compounds is given by the integral:

(5)



where *om*(*k*,*t*) denotes a probability density function that determines the concentration of organic matter having a degradability between *k* and *k* + *dk* at time *t*, with *k* being analogous to a rate constant. The initial distribution or organic compounds, *om*(*k,*0), may take different mathematical forms, but cannot be inferred by observations. Here, a gamma function is used, as proposed by Boudreau and Ruddick (1991), following ([Aris, 1968](#_ENREF_1)) and ([Ho and Aris, 1987](#_ENREF_21)). Assuming first order degradation kinetics, the initial (at t=0) distribution of om over k is the given by:



where POC(0) is the initial organic matter content, Γ is the Gamma function, *a* is the average live time of the more reactive components of the mixture and *υ* is a dimensionless parameter determining the shape of the distribution near *k* = 0. The free, positive parameters *a* and ** completely determine the shape of the initial distribution of organic matter compounds over the range of *k* values and thus the overall reactivity of POC. High ** and low *a* values indicate a mixture of organics dominated by compounds that are typically degraded rapidly. Low ** and high *a* values, on the other hand, indicate a larger fraction of less reactive compounds that degrade slowly. See Arndt et al. (2013) and the Appendix for a more in-depth description of these parameters.

Although the choice of the gamma function is partly guided by mathematical expedience, the gamma function has the advantage of capturing the organic matter degradation dynamics observed in nature. Under these assumptions, the evolution of the bulk particulate organic carbon concentration as a function of depth, *POC*(*z*), is given by (Boudreau and Ruddick, 1991):

(6)

where *a* and *ν* represent reactive continuum model parameters (Boudreau and Ruddick, 1991; Arndt et al., 2013) and *age*(*z*) refers to the age of the sediment layer at depth *z*. While the RCM has proven successful in predicting the down core evolution of organic matter reactivity in deep sediments, its application to the bioturbated layer of the sediment is compromised by the difficulty of constraining the age of organic matter in bioturbated sediments. Meile and Van Cappellen, 2005 showed that, within the bioturbated zone, the age distribution of reactive species are not only controlled by bioturbation and sedimentation but also by the reactivity of the reactive species. Similar to the approach proposed by Dale et al., 20XX, we here use a multi-G approximation of the RCM for the bioturbated sediment. Within the bioturbated zone, POC is represented by distinct fractions, *i=200*, each characterized by a first-order decay constant, *ki*. The fraction of total organic matter in fraction I, *Fi*, as well as their respective reactivity, ki, can be determined through the initial probability density function that determines the concentration of organic matter having a degradability between *k* and *k* + *dk* at time *0* (eq. highlighted in yellow ). The initial fraction of total POC characterized by a distinct reactivity k is given by:

f(k,0)=om(k,0)/POC(0)=

The initial fraction of POC within the reactivity range between 0 and k, i.e. having a reactivity <=k is then given by integrating eq. (above) assuming that a, nu, k>0:

F(k,0)=



=



where Γ(*ν*, ak) denotes the inverse Gamma function.

In the bioturbated sediment, the RCM is then approximated by dividing the reactivity range k=[10-15, -log(a)+2] into 200 equal reactivity bins kj thus ensuring that the Gamma function defined by the respective *a* and *ν* values is efficiently approximated. The initial fraction Fi of total POC within the reactivity bin kj-1 and kj (and thus with reactivity ki=kj-1 +( kj - kj-1)/2)in the 200G model can the be calculated as:

Fi=F(kj,0)-F(kj-1,0)

the most reactive fraction F200 with reactivity k200=10-log(a)+2 yr-1 is calculated on the basis of the upper incomplete Gamma function:

F200= 

Within the bioturbated zone, the depth evolution of POC is thus given by:

Below the bioturbated zone, values of *age*(*z*) can be calculated using burial rates, **(*z*), porosity depth profiles, **(*z*) and the apparent age of organic matter at the lower limit of the bioturbated zone, agezbio, which can be calculated by inserting POC at zbio into eq. 6 and solving for the age:

agezbio= -a\*(exp(ln(POCbio/POC0)/nu)-1)/exp(ln(POCbio/POC0)/nu)

Assuming an exponentially decreasing porosity, Eq. (1), and steady-state compaction, the burial velocity, ** at depth *z* is then (e.g., Berner, 1980):

(7)



where **0 corresponds to the burial velocity at the SWI. The age of a given sediment layer at depth *z* below the bioturbated zone, *age*(*z*), is given by (e.g., Berner, 1980):

. (8)



Substituting Eq. (7) into Eq. (8) results in

(9)



which, upon integration, leads to

(10)



The age of POC below the bioturbated zone is thus given by :

age(z)=agezbio+all the stuff from eq. 10 but with z=z-zbio

The depth distribution of organic matter in marine sediments deposited since the beginning of the Quaternary Period can thus be calculated if the burial rate, porosity, bulk organic matter concentration at the SWI and the distribution of organic compounds across the reactivity range at the sediment-water interface is known and/or specified.

**2.2*****Parameters and Forcings***

The concentration of Holocene and Pleistocene POC at the sediment water interface, *POC*0, and sedimentation rates, **, are constrained according to ([Wallmann et al., 2012](#_ENREF_63)) who used data from ([Seiter et al., 2004](#_ENREF_48)) and ([Romankevich et al., 2009](#_ENREF_43)) and an algorithm that correlates water depth and sedimentation rate ([Burwicz et al., 2011](#_ENREF_8)). The global depositional fluxes, *F*, of POC are thus given by

(11)



where ** refers to the density of sediment, taken to be 2.5 g cm-3. Values of *F* (Tg C yr-1) for the shelf, margin and abyss domains for Holocene and Pleistocene sediments are given in Table 1 and maps of the fluxes of POC to the SWI during the Holocene and Pleistocene are shown in Fig. 2.

The reactivity of organic matter deposited onto the seafloor and its evolution during burial is notoriously difficult to constrain. The heterotrophic degradation of organic matter involves a plethora of different organisms that degrade a wide range of organic compounds under varying environmental conditions, using a number of different terminal electron acceptors and producing a large range of different product compounds. Therefore, attempts to identify statistically significant relationships between organic matter degradation rate constants and individual factors such as water depth, deposition rate, or organic matter flux have not been very successful. None of these variables serves as a master proxy for all of the chemical, physical and biological factors that control organic matter degradation. As a result, a global scale analysis of sedimentary organic matter degradation cannot be reduced to a single factor. In general, the organic matter reactivity parameters of the 1G-model, *k*, and the RCM, *a* and **, are determined by finding a best fit to observed POC and pore-water profiles at specific sites (e.g., Arndt et al., 2013). There is currently no general framework that can be used to estimate these parameters on a global scale. Consequently, organic matter reactivities are associated with large uncertainties.

Here, we constrain a minimum and maximum reactivity parameter set for each environment based on the lower and upper bounds of published values (see Arndt et al., 2013 for review). A well-known effort to constrain values of **, based on an analysis of eight sediment cores from very different environments, concluded that the majority of the sediments are dominated by refractory components, as reflected by low ** parameters, between 0.1 and 0.2, while the rest are characterized by higher ** parameters, between 0.8 and 1.0 ([Boudreau and Ruddick, 1991](#_ENREF_7)). As these authors note, more data are needed to confirm such a trend and to determine its underlying causes. Because the *a* parameter is conceptually related to the average age of the organic matter at the SWI, its value should correlate with factors that control the transit time of organic matter from the euphotic layer to the seafloor. In general, this is the case:  *a* increases with increasing water depths and decreasing deposition rates, although it should be emphasized that the number of RCM parameter determinations is still limited and variability remains significant, especially at low deposition rates. For instance, published values of *a* vary over several orders of magnitude from 1e-4-100 yrs for shelf environments and up to 10,000 yrs for deep sediments (Arndt et al., 2013). In summary, values of the *a* and ** parameters are not known *a priori*, and must be estimated based on the type of material being deposited on the seafloor.

Following the porosity model described above, values of *a* and ** are specified for three types of oceanic sediment: shelf, margin and abyss. Although this is a rather simplistic assumption, it effectively resolves differences in the first-order characteristics that describe each of these environments, including the predominant type of organic matter, transit time through the water column and pre-aging effects. Using a recent review of marine sediment organic matter degradation models published in the literature (Arndt et al., 2013), a plausible set of high and low sets of *a* and ** values for each oceanic province has been adopted.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| ***Environment*** | ** | ***a (yr-1)*** | **Reference** | **Description** |
| ***High reactivity*** | | | | |
| Shelf | 0.125 | 3.10-4 | Boudreau et al. (2008) | degradation experiment of fresh phytoplankton over a 2 yr period Westrich and Berner, 1984. |
| Slope | 0.125 | 3.10-4 | Boudreau et al. (2008) | degradation experiment of fresh phytoplankton over a 2 yr period Westrich and Berner, 1984. |
| Abyss | 0.16 | 40 | Marquardt et al., 2010 | Peru sediments |
| ***Low reactivity*** | | | | |
| Shelf | 0.135 | 5 | Mogollon et al., 2011 | Arkona Bassin |
| Slope | 0.16 | 1000 | Wallmann et al., 2006 | Sea of Okhotsk |
| Abyss | 0.16 | 10000 | Middelburg, 1989; | Central Pacific |

Baseline values reflect typically observed values for such environments, while high and low values span nearly the entire range of observed values (e.g. Boudreau and Ruddick, 1991; Arndt et al., 2013). Values of these parameters for all three scenarios are listed in Table 2. See Appendix A for a discussion and illustration of the implications of using various combinations of RCM parameters on organic matter reactivity.