

Table 1. EnKF calibrated biogeochemical parameters in the GENIE-1 model.

Name	Prior assumptions (mean and range ^a)	Posterior mean ^b	Description
$u_0^{\text{PO}_4}$	$1.65 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ (0.3–3.0)	$1.91 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$	maximum PO_4 uptake (removal) rate (Eq. 3)
K^{PO_4}	$0.2 \mu\text{mol kg}^{-1}$ (0.1–0.3)	$0.21 \mu\text{mol kg}^{-1}$	PO_4 Michaelis-Menton half-saturation concentration (Eq. 3)
r^{POC}	0.05 (0.02–0.08)	0.055	initial proportion of POC export as fraction #2 (Eq. 6)
l^{POC}	600 m (200–1000)	556 m	e -folding remineralization depth of POC fraction #1 (Eq. 6)
$r_0^{\text{CaCO}_3:\text{POC}}$	0.036 (0.015–0.088) ^c	0.022 ^d	$\text{CaCO}_3:\text{POC}$: export rain ratio scalar (Eq. 8)
η	1.5 (1.0–2.0)	1.28	thermodynamic calcification rate power (Eq. 9)
r^{CaCO_3}	0.4 (0.2–0.6)	0.489	initial proportion of CaCO_3 export as fraction #2 (Eq. 11)
l^{CaCO_3}	600 m (200–1000)	1055	e -folding remineralization depth of CaCO_3 fraction #1 (Eq. 11)

^a the range is quoted as 1 standard deviation either side of the mean

^b quoted as the mean of the entire EnKF ensemble

^c assimilation was carried out on a \log_{10} scale

^d Note that the rain ratio scalar parameter is not the same as the $\text{CaCO}_3:\text{POC}$ export rain ratio as measured at the base of the euphotic zone, because $r_0^{\text{CaCO}_3:\text{POC}}$ is further multiplied by $(\Omega - 1)^\eta$ to calculate the rain ratio, where Ω is the surface ocean saturation state with respect to calcite (see Sect. 2.1). Pre-industrial mean ocean surface Ω is ~ 5.2 in the GENIE-1 model, so that the global $\text{CaCO}_3:\text{POC}$ export rain ratio can be estimated using the 8-parameter assimilation as being equal to $(5.2 - 1)^{1.28} \times 0.022 = 0.14$.

(Table 1). Because we explicitly resolve the individual “components” (i.e., C, ^{13}C , P, ...) of organic matter, the GENIE-1 model can be used to quantify the effect of fractionation between the components of organic matter during remineralization (e.g., Shaffer et al., 1999) as well as between different carbon isotopes. However, we assume no fractionation during remineralization in this present study. The residual flux of particulate organic material escaping remineralization within the water column is remineralized at the ocean floor, making the ocean-atmosphere system closed with respect to these tracers (i.e., there is no loss or gain to the system).

The modern ocean is oxic everywhere at the resolution of our model (e.g., see Fig. 6). However, O_2 availability may be insufficient under different ocean circulation regimes and continental configurations. To broaden the applicability of the GENIE-1 model to past climates and biogeochemical cycling, we limit remineralization according to the total availability of electron acceptors – if dissolved O_2 is depleted and NO_3^- is selected as an active tracer in the model, denitrification occurs to provide the necessary oxidant: $2\text{NO}_3^- \rightarrow \text{N}_2 + 3\text{O}_2$. If NO_3^- becomes depleted and SO_4^{2-} has been selected as an active tracer, sulphate reduction occurs: $2\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{O}_2$. If the total concentration of selected electron-accepting tracer species (O_2 , NO_3^- , SO_4^{2-}) is still insufficient, remineralization of POC is restricted. Our strategy thus differs from other modeling approaches in which remineralization always strictly conforms to a predetermined profile and the consequences of excess oxidation over O_2 availability are resolved either by numerically preventing negative oxygen concentrations occurring

(e.g. Zhang et al., 2001, 2003) or by allowing the tracer transport of negative O_2 concentrations (e.g., Hotinski et al., 2001). We treat the remineralization of dissolved organic matter in an analogous manner if O_2 availability is insufficient.

H_2S created through sulphate reduction is oxidized in the presence of O_2 at a rate ($\text{mM H}_2\text{S h}^{-1}$):

$$\frac{d[\text{H}_2\text{S}]}{dt} = k \cdot [\text{H}_2\text{S}] \cdot [\text{O}_2]^2 \quad (7)$$

where $[\text{H}_2\text{S}]$ and $[\text{O}_2]$ are the dissolved concentrations of hydrogen sulphide and oxygen, respectively, and $k = 0.625 \text{ mM}^{-2} \text{ h}^{-1}$ (Zhang and Millero, 1993).

While we account for remineralisation of carbon and nutrients within the water column as well as the associated depletion of dissolved oxygen, and in more extreme circumstances, of nitrate and sulphate, we do not explicitly account for important long-term sedimentary controls on ocean chemistry, with the exception of carbon and alkalinity associated with CaCO_3 – see Ridgwell and Hargreaves (2007). Thus, we are currently unable to assess feedback between bottom-water dysoxia and anoxia on global nutrient cycling, particularly involving phosphate, nitrate, and/or iron. For instance, O_2 -depleted bottom waters are known to be associated with enhanced phosphorous regeneration from marine sediments (Ingall and Jahnke, 1994), leading to the possibility of positive feedback between productivity and anoxia which might be central to the understanding of past Oceanic Anoxic Events (Van Cappellen and Ingall, 1994; Handoh and Lenton, 2003). Future developments to the GENIE-1 model will address the sedimentary control of nutrient cycling, as