A redox-based model for carbonate platform drowning and Ocean Anoxic Events

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Key Points:

- A model for carbonate platform drowning was developed based on changing patterns of carbonate production and dissolution.
- Ocean anoxia reduces both carbonate dissolution and the amount of carbonate overproduction in the surface oceans.
- Linking carbonate chemistry to ocean redox conditions allowed slower sedimentation over long (10^5-10^6 year) timescales.

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Abstract

The deposition of marine carbonate rocks is influenced by climate and seawater chemistry. Carbonate platforms usually keep pace with subsidence and sea level rise but 'platform drowning occurs when carbonate sedimentation slows or when siliciclastics replace carbonates. Identifying specific mechanism(s) behind platform drowning is critical for understanding global environmental changes such as Ocean Anoxic Events (OAES).

We developed a model for OAEs which couples ocean basin redox processes to rates of carbonate sedimentation. Well-oxygenated oceans have steep gradients in saturation state such that deep-ocean dissolution is balanced by carbonate 'overproduction in shallow water. Through anaerobic metabolisms, deep-ocean anoxia reduces both dissolution and overproduction, leading to slower accumulation rates in shallow-water environments. This quasi-steady state response links carbonate sedimentation with longer timescales associated with redox changes. Redox-based drowning may have acted alongside other mechanisms to create spatially diverse patterns of platform drowning during Mesozoic OAEs and other Phanerozoic hyperthermal events.

Plain Language Summary

Carbonate minerals precipitate from ions dissolved in water. Thick packages of carbonate rocks often form in shallow, tropical waters, and their accumulation rate depends on the availability of ions as well as biological agents that catalyze carbonate deposition such as animals and microbes. Geologic patterns in carbonate rocks are sensitive to these controls on accumulation rates, tying them to Earths surface chemistry and ecosystems.

Sometimes chemical changes in the oceans cause far-reaching effects that influence patterns observed in carbonate rocks. During the Mesozoic Era, episodes of lowered dissolved oxygen in the world's oceans often coincided with a phenomenon known as platform drowning. Platform drowning occurs when carbonate platformssites of carbonate deposition like the modern Bahamian Islandsexperienced slower sedimentation rates and sank into deeper water. Interestingly, there are several chemical pathways that could cause platform drowning, and unraveling the underlying drivers is key for understanding the nature of past environmental changes. Here we present a concept for platform drowning that emphasizes the role of microbes and their effects on global ocean chemistry. This idea helps explain the long timescales of platform drowning and may explain similar patterns during other low-oxygen episodes in Earth's past.

1 Introduction

Carbonate sediments are the largest (by mass) physical products of Earths biogeochemical cycles. Consequently, changes in the rates, modes, and mechanisms of carbonate precipitation often accompany major carbon cycle perturbations such as Snowball Earth episodes (Hoffman et al., 1998, 2017), the end-Permian extinction (Baud et al., 2007; Kelley et al., 2020; Lehrmann et al., 2015), and the Paleocene-Eocene Thermal Maximum (PETM) (Penman et al., 2016; Zachos et al., 2005). Several well-known examples occur in strata spanning Ocean Anoxic Events (OAEs)—a series of carbon cycle changes that perturbed Mesozoic climate and the redox structure of marine basins (Arthur et al., 1987; Jenkyns, 2010; Schlanger & Jenkyns, 1976; Scholle & Arthur, 1980). In shallow-water carbonates, OAEs are marked by carbonate platform 'drowning' in which deeper, organic-rich deposits displaced shallow-water facies (Arthur & Schlanger, 1979; Schlager, 1981; Phelps et al., 2015)(Fig. 1a). Schlager (1981) christened this pattern as the 'paradox of drowned platforms' because growth rates in modern carbonates exceed all but the fastest rates of sea level rise. Hallock and Schlager (1986) provided an initial solution that invoked reduced sedimentation rates, and subsequent research has focused on chemical and biological mechanisms that hinder carbonate growth. Such mechanisms are valu-

able for understanding the nature of environmental changes at OAEs because they might provide a common factor linking geochemical records, platform drowning, and biotic turnover among calcifying organisms (Föllmi et al., 1994; Kiessling & Simpson, 2011; Krencker et al., 2020; Phelps et al., 2015; Trecalli et al., 2012).

OAEs are complex events in which a single cause—commonly thought to be a rapid injection of volcanic CO_2—triggers a cascade of related events that could lead to platform drowning (Jenkyns, 2010). However, anoxic conditions rarely impinge upon shallow-water environments because waves efficiently mix atmospheric oxygen into the water column (Beatty et al., 2008), and so many models of platform drowning focus on indirect linkages to deep-basin anoxia. Early work by Hallock and Schlager (1986) pointed to dissolved nutrients as possible causal drowning agents because many photosymbiotic reef-builders are adapted to low nutrient conditions and thrive in clear, non-turbid seawater. Under this hypothesis, elevated nutrient fluxes drown platforms by stimulating primary production, decreasing light penetration and allowing fleshy non-calcifiers to outcompete the prolific carbonate producers. Such a drowning mechanism is attractive because increased nutrients and primary productivity are also used to explain geochemical proxies for redox and weathering (Blättler et al., 2011; Jenkyns, 2010; Lechler et al., 2015). However, excess nutrients may simply shift carbonate sedimentation towards non-skeletal components (e.g., ooids and microbialites) which can comprise a significant portion of platform sediments near OAEs (Ettinger et al., 2020; Huck et al., 2010; Krencker et al., 2020). Nutrient-related drowning also implies that non-skeletal carbonates accumulate more slowly than the facies they replace, which may not be universally true given high rates of microbial reef production elsewhere in the Phanerozoic record (e.g., Franceschi et al., 2016).

Another plausible and popular mechanism for reduced carbonate production near OAEs is ocean acidification (Kiessling & Simpson, 2011) (Fig. 1b). By analogy to anthropogenic climate change, volcanic CO_2 invades the surface oceans over short timescales, causing a drop in pH and the saturation states of calcite and aragonite (Zeebe & Wolf-Gladrow, 2001); this drop in pH is ultimately mitigated over 10 ky timescales due to seafloor carbonate dissolution and associated carbonate compensation processes (Archer et al., 1997). While acidification has been invoked for many carbon cycle perturbations, there are several issues with implicating it as the sole driver of platform drowning. First, Earths carbon cycle has a negative feedback which negates ocean acidification over timescales longer than 10 ky (Hönisch et al., 2012; Knoll et al., 2011). In contrast, many platform drowning events and intervals of biotic turnover occur over intervals exceeding 100 ky. Second, carbon is well-mixed on millennial timescales such that the onset of ocean acidification should be synchronous, yet stratigraphic records for OAEs vary through both time and space (Heldt et al., 2010)(Fig. 1a). Together these factors suggest that additional processes were also important in developing the patterns observed in platform drowning associated with OAEs.

A third mechanism for platform drowning can been drawn from microbial metabolisms in the carbon cycle, which link Earth's large-scale redox and acid-base cycles (Reinhard & Fischer, 2019). We termed this the 'redox-drowning hypothesis'. While some of these metabolic pathways have long been incorporated into models of ocean-atmosphere chemistry (e.g., Lasaga et al., 1985), a growing number of studies have begun to explicitly consider their effects on sedimentary carbonates (Bergmann et al., 2013; Higgins et al., 2009; Tziperman et al., 2011; Reinhard & Fischer, 2019). In general, anaerobic respiration pathways produce alkalinity that locally increases the carbonate saturation state of seawater and shallow pore fluids. As such, many studies focus on anoxia as a possible driver of enhanced carbonate precipitation (Grotzinger & Knoll, 1995). However, a small subset of studies has instead considered the role of anaerobic metabolisms in setting alkalinity gradients in the ocean. In this framework, anaerobic metabolisms buffer the deep ocean against dissolution at the expense of oversaturation in surface waters (Higgins et

al., 2009; Knoll et al., 2011) (Fig. 1c). Although these studies mostly dealt with the long-term evolution of ocean redox budgets, Higgins et al. (2009) suggested that similar concepts could be used to interpret patterns in carbonate sedimentation during Phanerozoic carbon cycle perturbations such as OAEs. Here we built a simple biogeochemical carbonate sedimentation flux model to understand how carbonate platform drowning can be instigated by gradients in inorganic carbon and alkalinity driven by the biological pump under different redox conditions. We used this model to simulate the onset and dissipation of ocean anoxia by varying the ratio of alkalinity to dissolved inorganic carbon (DIC) produced during microbial respiration. Our results indicated that widespread onset of sulfate reduction within the shallow pore fluids and water column of marine basins would slow carbonate overproduction in shallow water environments and thereby shift the locus of carbonate deposition away from the surface oceans, resulting in platform drowning over geological timescales.

2 Background

2.1 Carbonate production and dissolution in the marine basins

The formation of carbonate rocks is the primary sink by which the products of weathering, especially inorganic carbon and alkalinity, are removed from natural waters and seawater. Over geologic timescales, seawater achieves a sort of quasi-steady state in which the outgassing and weathering fluxes of inorganic carbon and alkalinity is balanced by the formation of carbonate rocks in net (Walker et al., 1981; Archer et al., 1997):

$$F_{weathering} = F_{burial} \tag{1}$$

A naive interpretation of Eqn. 1 is that the surface oceans produce exactly as much carbonate as it needs to balance the alkalinity budget imposed by weathering. In fact, modern oceans produce carbonate minerals at a rate that is four times higher than weathering inputs (Broecker & Peng, 1982; Sarmiento & Gruber, 2006; Sigman & Boyle, 2000). This 'overproduction' of carbonate is compensated by carbonate dissolution within deep ocean basins and shallow oxic porewaters more broadly (Walter & Burton, 1990; Broecker, 1998; Laya et al., 2021; Melim et al., 2002):

$$F_{weathering} = F_{prod} - F_{diss} = F_{burial} \tag{2}$$

While Eqns. 1 and 2 are equivalent, the latter hints shows that there exist a spectrum of possible combinations of precipitation/dissolution that satisfy the geological steady state condition. While a number of studies have investigated how carbonate chemistry and production responds to changes in weathering fluxes (e.g., Zeebe & Westbroek, 2003; Reinhard & Fischer, 2019), Higgins et al. (2009) considered the special case of a fixed weathering flux ($F_{weathering}$). Under this scenario, a steady state characterized by reduced rates of carbonate dissolution would be balanced by reduced carbonate (over)production in the surface ocean, with a potential corollary of lower carbonate saturation states in surface seawater.

A reasonable question, then, is what factors drove patterns of precipitation and dissolution in the past. Carbonate dissolution in the modern ocean is governed by several factors. Some carbonate dissolves at depth because carbonate minerals are more soluble at low temperatures and high pressures (Zeebe & Wolf-Gladrow, 2001), but this inorganic effect is comparatively small and a substantial amount of dissolution is driven by aerobic respiration of organic matter, both in the water column and within sedimentary pore fluids (Archer, 1996; Dunne et al., 2012; Hales, 2003; Laya et al., 2021). Biologically-driven dissolution is widespread in the modern oceans because oxygenated bottom waters overlie >95% of the seafloor (Helly & Levin, 2004). However, a myriad of geological observations have indicated that marine dioxygen was not as ubiquitous in the past,

and oceans characterized by high rates of anaerobic respiration experienced less dissolutionor even net precipitationin porewaters and deeper parts of marine basins (Bergmann et al., 2013; Higgins et al., 2009; Knoll et al., 2016). Following Eqn. 2, a switch to more anaerobic conditions (less dissolution) in the deep oceans during OAEs could reduce carbonate production in the surface ocean because shallow-water sedimentation rate tracks local surface chemistry, rather than the global burial rate. Thus re-organizing patterns of precipitation and dissolution in the ocean may lead to slower local accumulation rates in platforms even if anoxia does not directly impinge on those shallow water settings.

2.2 OAEs and the extent of ocean anoxia

Testing the redox-drowning hypothesis for OAEs requires quantitative data on the extent of ocean anoxia—and ideally the carbon fluxes through aerobic and anaerobic metabolisms. Mass-balance studies of redox-sensitive elements can, in principle, provide such constraints, typically rendered as a percentage of the seafloor overlain by anoxic conditions. However it is useful to note that hindcasting the degree of ancient anoxia still carries uncertainties, and such estimates vary substantially by proxy and material during the same event. For example, the maximum extent of seafloor anoxia during OAE 2 was calculated as 1-2% from δ^{238}U in shales (Montoya-Pino et al., 2010), 8-15% from δ^{238}U in carbonates (Clarkson et al., 2018), and 40% from ϵ^{205}Tl in shales (Ostrander et al., 2017). However, trace element proxies have different oxygen thresholds for drawdown and enrichment, so percentages calculated from different proxies may not be interchangeable (Clarkson et al., 2018).

Another estimate for the extent of anoxia comes from biomarkers derived from specific groups of sulfur-oxidizing anoxygenic photoautotrophs (*Chlorobiaceae*) (Forster et al., 2008; Kuypers et al., 2002; Pancost et al., 2004).These aromatic carotenoid biomarkers track water-column euxinia and they are important marine redox proxies because they indicate that free H_2S was both present and sufficiently abundant within the photic zone (Damsté & Köster, 1998). For OAE 2, biogeochemical paleoceanographic models calibrated to biomarker data estimated that at least 50% of the seafloor was anoxic during peak OAE conditions (Monteiro et al., 2012). Biomarker observations are particularly useful as they provide direct evidence that the H_2S/SO_4 redox pair played an expanded role in photosynthesis and respiration at the expense of O_2/H_2O—a biogeochemical change in the carbon cycle that greatly ameliorates gradient in alkalinity generated by the biological pump. Together, the percentages calculated from trace element abundances and isotope ratios and biomarker data provide a range of conditions over which to evaluate the platform drowning model.

3 Model setup

We treated carbonate production and dissolution in marine basins with a simple two-box scheme that tracks fluxes of alkalinity (A) and dissolved inorganic carbon (C) following the scheme of Bergmann et al. (2013) and Higgins et al. (2009). In this idealized calculation, the equations for alkalinity balance (A) in the surface (A_1) and deep (A_2) oceans are:

$$\frac{dA_1}{dt} = \frac{1}{V_1}[A_i - 2F_{prod} - F_o\Delta_{alk} + J\nabla A] \tag{3}$$

$$\frac{dA_2}{dt} = \frac{1}{V_2}[2F_{diss} + F_o\Delta_{alk} - J\nabla A] \tag{4}$$

The coupled carbon (C_1 and C_2) equations are:

$$\frac{dC_1}{dt} = \frac{1}{V_1}[C_i - F_{prod} - F_o + J\nabla C] \tag{5}$$

$$\frac{dC_2}{dt} = \frac{1}{V_2}[F_{diss} + F_o - J\nabla C] \tag{6}$$

where V is water volume, F_{prod} is carbonate production in the surface ocean, F_o is organic production in the surface ocean, Δ_{alk} is the alkalinity produced per unit DIC during respiration, ∇ denotes a gradient between the surface and deep oceans, J is the volumetric exchange of water between the surface and deep boxes, and F_{diss} is the dissolution flux of carbonates in the deep oceans. Alkalinity is supplied to seawater by weathering (A_i) and removed by carbonate precipitation (F_{prod}). Some carbonate is dissolved in the deep oceans and porewaters, returning alkalinity to the system (F_{diss}). Carbonate production and dissolution within each box was described by a typical rate law of saturation state, Ω:

$$F_{prod} \propto (\Omega_{surface} - 1)^2 \tag{7}$$

$$F_{diss} \propto (1 - \Omega_{deep})^2 \tag{8}$$

In turn, the average saturation states in each reservoir were taken as a function of alkalinity and dissolved inorganic carbon, which were solved at each step using the solver implemented in CO2sys (Lewis & Wallace, 1998). By charge and/or mass conservation, any process that changes the concentrations of alkalinity and dissolved inorganic carbon in either box will also affect the carbonate precipitation and dissolution fluxes by way of Ω—expressed here as the saturation state of calcite.

Beyond carbonate precipitation and dissolution, we considered two additional processes that transfer alkalinity and carbon between the surface and deep ocean boxes. Physical exchange by advection and/or diffusion (J) transfers alkalinity and DIC according to the gradient, ∇A, between the two boxes. The second transfer mechanism is associated with an advective organic matter flux, F_o (i.e. the sedimentation of biological particles associated with the biological pump as well as omnipresent co-deposition of organic matter associated with fine sediment). Inorganic carbon is consumed in surface waters by photosynthesis and returned at depth through respiration/remineralization. This process also re-distributes alkalinity because metabolic processes either generate or consume alkalinity to a degree based on the identity of the participating redox pair. Rather than track individual redox species, we use the net ratios of DIC:alkalinity change, Δ_{alk}, balanced for typical marine organic matter by Bergmann et al. (2013).

4 Results

Using modern ocean basins as a starting point, the model was used to investigate the effects of changing Δ_{alk} on patterns of carbonate precipitation and dissolution. The default steady state is characterized by $\Delta_{alk} = 0$ (well-oxygenated seawater) and by setting the carbonate flux out of the surface ocean, F_c, to its modern value of four times the weathering flux, A_i. We then approximated an OAE using a 200 ky period of reduced oxygen availability ($\Delta_{alk} = 0.6$) with 50 ky onset and recovery periods (Fig. 2a). Rather than capturing the entire complexity of OAEs, dimensionalizing the model in this way couples the carbonate system to known redox changes over timescales empirically derived from observations of the sedimentary record (>100ky). After the 50 ky transition interval, the carbonate system settled into a new steady state that persisted until Δ_{alk}

changes again. As expected, the new steady state during the nadir of the OAE was characterized by lower Ω and lower rates of carbonate production in the surface ocean (Fig. 2b,c).

At timescales of >10 ky, disturbances associated with the simulated OAE could be approximated as quasi-steady changes. Plotting steady state solutions as functions of Δ_{alk} related changes in carbonate production and dissolution to the extent of anoxia given reasonable simplifying assumptions. First, we considered a simplified case of two redox pairs–O_2/H_2O ($\Delta_{alk} = 0$) and H_2S/SO_4 ($\Delta_{alk} = 1.2$)–so that the horizontal axis represents a weighted mixture between the two Δ_{alk} vectors. If the percentage of aerobic respiration replaced by sulfate reduction is roughly analogous to the percentage of the seafloor covered by anoxic bottom waters, then the maximum Δ_{alk} value can be estimated from studies of redox-sensitive elements and biomarkers for photic zone euxinia (Section 2.2). Second, we assumed that the sedimentation rate for shallow-water platforms closely follows the overproduction of the surface ocean rather than globally-averaged carbonate burial, (F_{prod}), which seems reasonable based on modern estimates of global accumulation rates (e.g., Milliman & Droxler, 1996), which is the same among all valid steady state solutions. Under these assumptions, carbonate accumulation on platforms decreases with the spread of ocean anoxia, presenting a plausible mechanism for platform drowning.

5 Discussion

5.1 Redox changes as a drowning mechanism during OAE2

The simple model presented above suggests that large scale redox changes in marine basins can provide a reasonable drowning mechanism for carbonate platforms. Results revealed that carbonate production is a non-linear function of these redox changes; the shape of this function indicated that significant decreases in carbonate sedimentation can occur during even modest expansion of anoxia (Fig. 2d). For OAE2, the concave-up response is important because estimates of peak anoxic conditions vary widely among proxies. While the lowest estimates of seafloor anoxia during this interval (1-2,% Montoya-Pino et al., 2010) would produce a very small response, a maximum extent of only 15% (Clarkson et al., 2018) would reduce carbonate sedimentation to 82% of its initial value. For proxy records that suggest 40-50% seafloor anoxia during OAE2 (Monteiro et al., 2012; Ostrander et al., 2017), carbonate sedimentation rates would fall precipitously to approximately half of their original values.

Another important aspect of the model results is the timescales of the processes involved. When Δ_{alk} is perturbed, negative feedbacks push the systems towards a new steady state, allowing lower sedimentation rates to be sustained over arbitrarily long timescales (Fig. 3a-c). The estimated timescale for OAE2 is between 250 and 885 kyr (Kolonic et al., 2005; Sageman et al., 2006), and some evidence suggests that the proto-Atlantic was partially anoxic before the event (Monteiro et al., 2012). Taken together, these results suggest that redox changes associated with OAEs could reduce carbonate sedimentation rates on carbonate platforms for $>10^5$ years. As discussed by Schlager (1999), drowning requires not only short-term stresses but also longer-term 'environmental deterioration' because carbonate accumulation rates are closely matched with thermal subsidence (<1 order of magnitude) over timescales of 10^5-10^6 years. In this context, a redox-based drowning mechanism provides a background stress that connects shorter-term environmental collapse (e.g., ocean acidification) with drowning due to long-term tectonic subsidence.

The shallow-water record for OAE2 shows a variety of carbonate platform responses consistent with the mechanisms outlined here. Platform drowning during and immediately after OAE2 has been documented in the Pyrenees (Drzewiecki & Simo, 2000), the

Adriatic platform (Korbar et al., 2012), and the southern Gulf of Mexico (Elrick et al., 2009). In the aforementioned cases, comparisons between geochemical and stratigraphic records suggested that drowning was related to OAE2, but the onset and termination of drowning varied among sections. Results for the idealized cases shown in Figure 2 depicted an average case for a global change in redox chemistry in ocean basins, but we recognized that patterns of carbonate accumulation in sedimentary basins also reflects an interplay between sedimentation and locally and/or regionally varying degrees of accommodation; and the extent to which OAE2 was characterized by platform drowning depended also on the tectonic setting. For example, platforms in the central Tethys (e.g., the Apulia Platform) experienced uplift and karstification near the Cenomanian-Turonian boundary, and these changes in basin development were locally more important than OAE2 in shaping platform stratigraphy (Bosellini et al., 1999). In short, a redox-drowning mechanism does not necessarily imply perfect synchronicity between the onset of carbon cycle and redox changes (e.g. evidenced by isotope excursions) and transgression, because some inherent variability in drowning patterns is to be expected due to regional tectonics.

The model presented here is idealized, and there are additional considerations when comparing it to the complexity of OAEs in the stratigraphic record. While platform drowning at OAEs is particularly common, it is not ubiquitous as some platforms experienced incipient drowning followed by rapid recovery (Parente et al., 2007) and yet others displayed little evidence of drowning at all (Navarro-Ramirez et al., 2016). An obvious simplification is that we treat the surface oceans as a single, well-mixed reservoir and do not consider the sorts of spatial variability in carbonate production and dissolution that result from climate and oceanographic factors. Patterns of carbonate dissolution in the modern oceans vary based on regional variations in temperature and circulation patterns and the strength of the biological pump (Archer, 1996). It is highly likely that ancient marine basins displayed similar heterogeneities, but the geological observables involving the degree of anoxia and pathways of ocean circulation and primary production is not sufficiently well-resolved spatially to support breaking up the model domains to more realistically simulate local or regional patterns in carbonate sedimentation. As this type of data is generated by future studies the redox-drowning model provides a testable hypothesis regarding local variations in platform drowning (Fig. 1a) and anoxia in the adjacent ocean basin.

5.2 Comparison with other drowning mechanisms

The redox-drowning mechanism has several interesting features that contrast with nutrient drowning and acidification-overshoot mechanisms. Numerical models of acidification-overshoot scenarios show that low Ω conditions decay in <100 ky because carbonate compensation and silicate weathering feedbacks operate to mitigate the perturbation over relatively short timescales (Archer et al., 1997; Hönisch et al., 2012; Knoll et al., 2011; Payne & Kump, 2007). Short-term acidification is followed by an alkalinity 'overshoot' where high Ω conditions prevail, which can help the platform recover and presents an impediment to sustained drowning. Reduced carbonate production under a redox drowning scenario instead labors over longer characteristic timescales related to the drivers of sustained anoxia; geological observations indicate that these anoxic events can last up to 1 My (Y.-X. Li et al., 2008), akin to the timescales associated with Earth's atmospheric dioxygen budget in terms of organic carbon burial. In this redox-drowning model there need not be any alkalinity overshoot and drowning can proceed over long timescales with ongoing basin subsidence.

The redox-drowning model has indirect overlap with the nutrient-drowning hypothesis since many interpretations of OAEs favor increased nutrients and primary productivity as the driver of anoxia (Jenkyns, 2010). However, a key difference is that the rate laws used in the model (Eqns. 7-8) are not specific to the animal and algal taxa that might

important for a particular carbonate factory—and while there may be real differences related to biological turnover and changes in the abundance and ecology of marine calcifiers during these events, that the dynamics can be generalized within a common carbonate precipitation rate law suggests that the results hold for a variety of skeletal and non-skeletal facies. This generality complements the nutrient-drowning hypothesis, which was calibrated to modern calcifying taxa and thus assumes that the dominant sediment producers are phototrophic organisms (Hallock & Schlager, 1986). Reduced sedimentation rates should apply to heterotrophic sediment producers (e.g., crinoids) and microbial build-ups, both of which are common in drowning successions (Ettinger et al., 2020; Huck et al., 2010; Föllmi et al., 1994). One limitation of the our model is that we grouped carbonate produced in the surface oceans as a singular pool and did not distinguish among pelagic, photozoan, heterozoan, and microbial modes of carbonate production. While this simplification generalizes the model, it does not account for the possibility that reduced carbonate production may not have been evenly distributed among these factories. Several studies have advanced the notion that expansion of microbial (Huck et al., 2010) and heterozoan (Föllmi et al., 2006) carbonate factories could partially compensate for reduced photozoan sedimentation, and mechanistic treatment of these factors and potential carbonate sedimentation tradeoffs may be useful in the future.

The redox-drowning model does not exclude other drowning scenarios (Godet, 2013), and it may have acted in conjunction with nutrient drowning and acidification-overshoot mechanisms. It is likely that local stratigraphic records show a combined drowning signal that depends on the relative strength and timescales of individual mechanisms (Fig. 3). Composite drowning scenarios may explain the diversity of patterns seen in the geologic record including 'pulsed' drowning events (e.g., Krencker et al., 2020).

5.3 Redox drowning and other anoxic episodes

The most important assumption of the redox drowning model is that, like today, the surface oceans were characterized by an overproduction of carbonate. The applicability of redox drowning—both for OAEs and for other anoxic episodes—depends on why the surface ocean overproduces carbonate as well as how overproduction has changed through time. At least two factors might have changed carbonate overproduction in the past: animal evolution and dioxygen availability. The evolutionary factor involves a Jurassic radiation of pelagic calcifying organisms—the primary sources of carbonate sediment fluxes into the deep oceans—in an event known as the mid-Mesozoic Revolution (e.g., Ridgwell, 2005).

Prior to this time, marine carbonate production was largely restricted to the continental shelves (i.e., carbonate platforms), limiting carbonate flux across the lysocline. In several previous models of Phanerozoic carbonate chemistry (e.g., Zeebe & Westbroek, 2003; Ridgwell, 2005), the mid-Mesozoic Revolution represents the onset of significant carbonate dissolution in deep marine basins, and thus carbonate overproduction is necessary to balance the alkalinity budget (Eqn. 2). Since we observed in the redox drowning model that the amount of change in carbonate sedimentation patterns is largest when the initial overproduction is high, this mechanism should be particularly applicable to conditions attained in the latter part of Phanerozoic time, and may even post-date the Toarcian OAE (Jenkyns, 2010). A evolutionary trend toward carbonate overproduction would emphasize similarities between Cretaceous OAEs, the PETM, and early Cenozoic hyperthermal events—but might differentiate these from earlier anoxic episodes such as the Toarcian OAE and the end-Permian extinction.

Nevertheless, the role of the biological pump underpinned by oxygenic photosynthesis and aerobic respiration in carbonate dissolution suggests that the condition of carbonate overproduction in the surface oceans may be substantially more ancient (Higgins et al., 2009; Knoll et al., 2016). Carbonate dissolution is not limited to the deep ocean

as aerobic respiration can drive significant dissolution above the lysocline (Milliman et al., 1999) and near-surface porewaters dissolve carbonate even in platform-top settings (Walter & Burton, 1990). These observations point to at least some degree of carbonate overproduction prior to mid-Mesozoic time and suggest that redox drowning might have affected carbonate platforms during Paleozoic and early Mesozoic anoxic episodes. The potential sensitivity of carbonate production and stratigraphy to changes in the redox structure of marine basins should motivate further efforts in the comparative sedimentology of drowning events; similarities or differences in the stratigraphic records may reveal much about how the Earth system's response to cycle perturbations has changed through time due to evolutionary and biogeochemical trends.

Data and Acknowledgements

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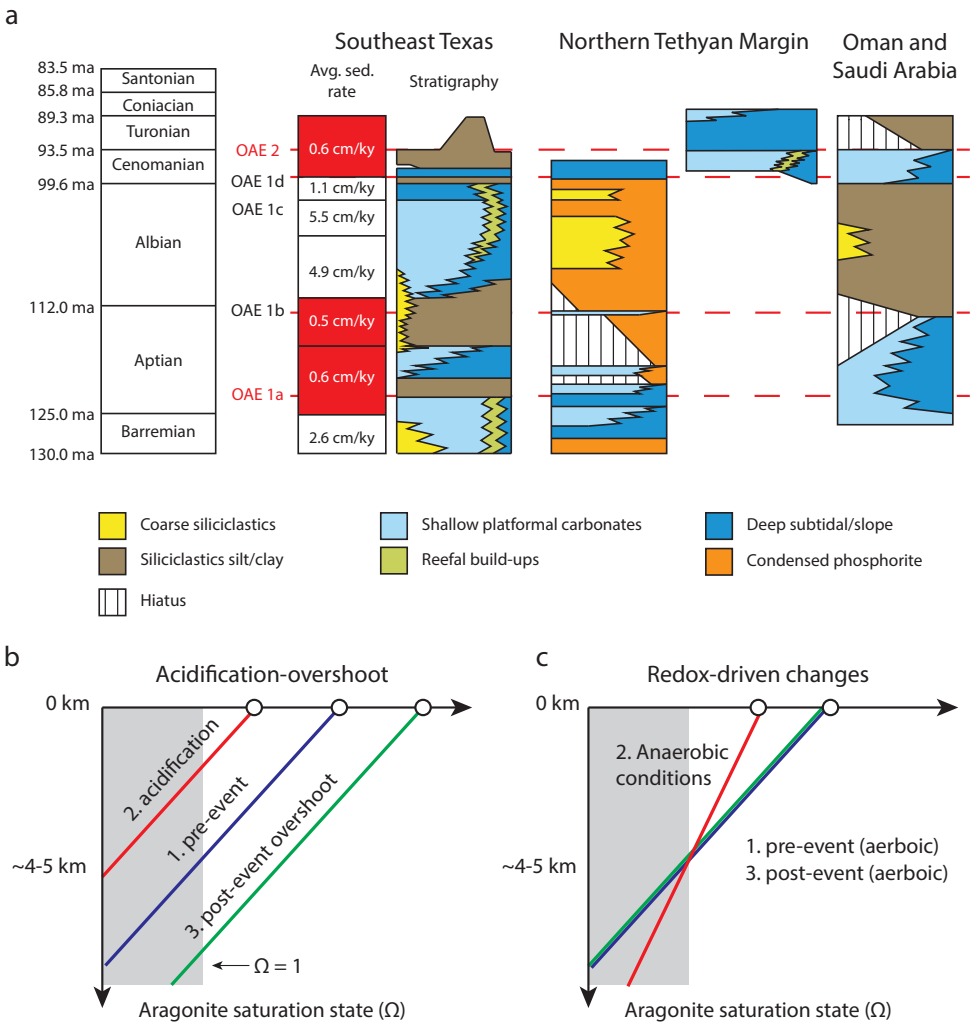

Figure 1. a. Simplified Wheeler diagrams showing stratigraphic patterns of Cretaceous platform drowning for the Texas Gulf Coast Phelps et al. (2014), Northern Tethyan Margin (Föllmi et al., 1994; Föllmi et al., 2006; Drzewiecki & Simo, 2000), and Oman (van Buchem et al., 2010). b,c. Possible effects of OAEs on depth-dependant trends in carbonate saturation state. b. Changes driven by ocean acidification and subsequent recovery of the carbonate system. Under this scenario, CO_2 sourced from volcanic systems or other carbon sources make their way into the atmosphere and oceans, reducing the saturation state and causing the carbonate compensation depth to shallow (red line). Over longer timescales, higher levels of atmospheric CO_2 bring more weathering-derived alkalinity into the oceans. In some cases, additional alkalinity causes the CCD to deepen and 'overshoot' its pre-event depth (green line, e.g., Penman et al., 2016). c. Respiration-driven changes in saturation state. Ω gradients (the slopes of the lines) reflect not only on depth-dependant trends in temperature and pressure, but also depend on primary productivity, the strength of the biological pump, and the availability of various electron donor/acceptor pairs. Changes in the availability of oxygen in ocean basins may trigger corresponding changes in the saturation state with depth as various anaerobic metabolisms replace aerobic ones (Higgins et al., 2009; Knoll et al., 2011)

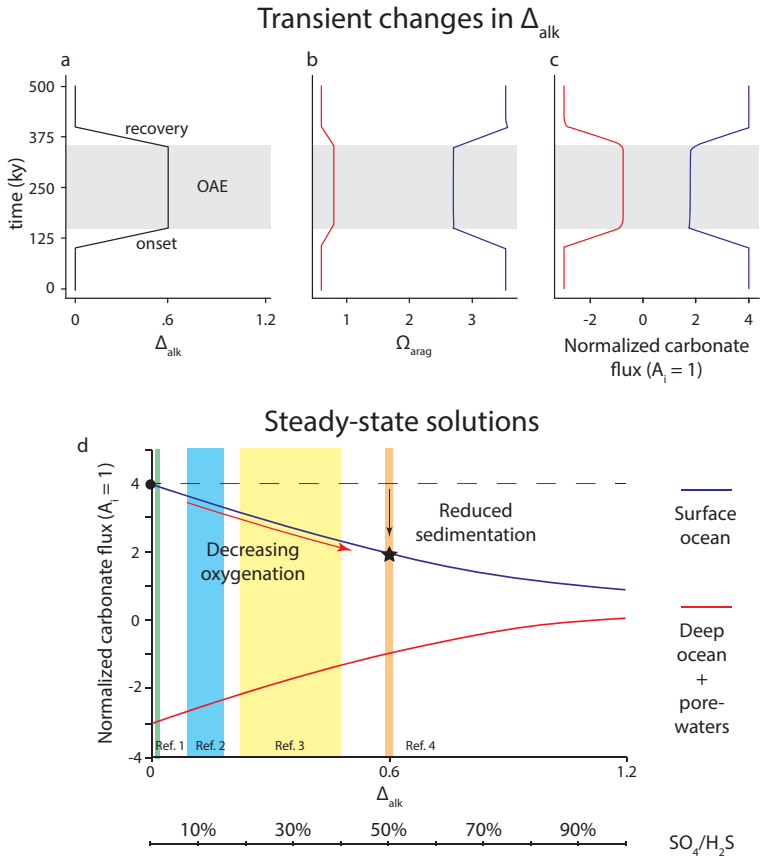

Figure 2. Model response to changes in Δ_{alk}. a. Modeling an OAE as a shift in Δ_{alk} away from aerobic respiration ($\Delta_{alk} = 0$) and towards sulfate reduction ($\Delta_{alk} = 1.2$). The maximum shift, $\Delta_{alk} = 0.6$, is equivalent to 50% of aerobic respiration being replaced by sulfate reduction. b. Changes in Ω caused by changes in Δ_{alk}. As Δ_{alk} increases, deep ocean and porewater Ω is buffered against dissolution at the expense of surface ocean Ω. c. Changes in carbonate fluxes associates with changes inΔ_{alk}. Fluxes are normalized to the alkalinity flux into the ocean, Ai, which is assumed to be constant. The surface ocean curve represents the degree of carbonate overproduction needed to balance out dissolution. As Δ_{alk} approaches increases, the degree of overproduction decreases, which can be interpreted as lower sedimentation rates in shallow water settings. Note that the lowered surface fluxes are a new steady state for the system which persists until Δ_{alk} changes again. References for 1c are 1) Montoya-Pino et al. (2010), 2) Clarkson et al. (2018), 3) Ostrander et al. (2017), and 4) Monteiro et al. (2012).

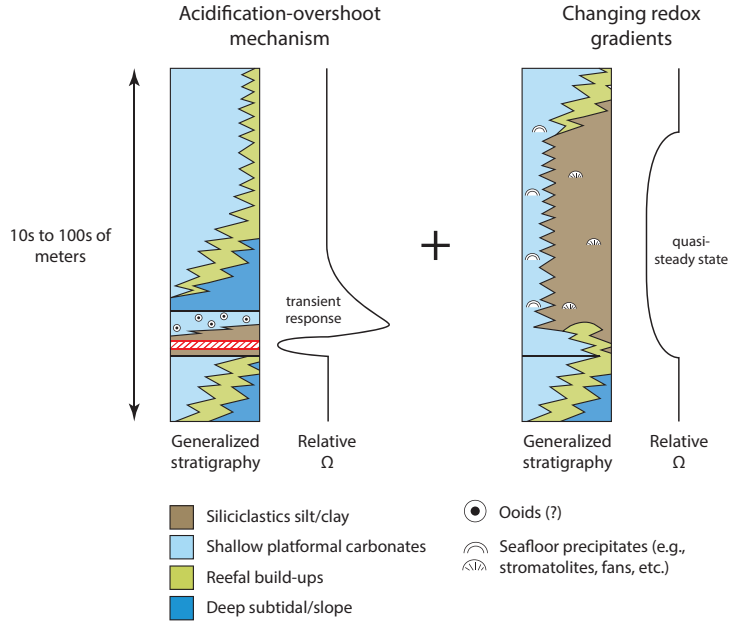

Figure 3. Comparisons between acidification-overshoot and redox-drowning models. The acidification-overshoot model operates over shorter (10-100 ky) timescales. In contrast, the redox-drowning model produces quasi-steady state changes that persist over arbitrarily long timescales. These mechanisms, along with nutrient-driven drowning, are not mutually exclusive; spatial variability and differences in drowning across separate events may be caused by variations in the relative strength of each driver.