

Impact of Increased Terrigenous Sediment in Near-Shore Reef Systems

Tyler Logie

1. Introduction

Over geologic timescales, the global rate of surface silicate weathering is controlled by atmospheric CO₂ levels (Berner 1990). At time periods with greater CO₂ concentrations, the rate of silicate weathering is higher. The increase in chemical weathering is explained with the Urey reactions (Urey 1952), which show how silicate weathering creates a carbon sink. This carbon sink is vital for regulating atmospheric CO₂, and through this regulation prevents runaway warming due to greenhouse gases. The increase in weathering rate also creates an immediate increase in terrigenous silicate sediment delivery to shallow water environments globally (Algeo et al., 2010).

An increase in the concentration of terrestrial sediment in a specific shallow water depositional setting may be due to local tectonic drivers such as the presence of a terrestrial mountain near the coast (Krencker et al., 2020), but global trends in terrigenous sedimentation of marine rocks are strongly correlated with the global silicate weathering rate (Percival et al., 2016; Algeo et al., 2010). Noticeable increases in global silicate weathering are often associated with extinction events such as the Permian/Triassic (P/Tr) extinction (Algeo et al., 2010) or the Early Jurassic extinction events (especially the Toarcian Ocean Anoxic Event) (Bodin et al., 2010). In both of these cases, the increase in silicate weathering is due to an increase in atmospheric CO₂ from large scale volcanism (Sedlacek et al., 2014; Cohen et al., 2004). Marine carbonate rocks across the world that were deposited during these time periods show significant increases in the amount of terrigenous siliciclastic sediment deposited (Algeo et al., 2010, 2011; Bodin et al., 2010; Percival et al., 2016).

An increase in terrigenous material affects reef communities in two broad ways. The most direct effect is physical sedimentation. Physical sedimentation is especially impactful for reef builders with photosymbionts, as an increase in suspended sediments in the water column decreases light quality in the water (Cortés et al., 1985; Yentsch et al., 2002). This decreases the photosynthetic efficiency of zooxanthellae, which limits the growth of reef builders with photosymbionts (Fabricius 2005). Lower photosynthetic efficiency also decreases the depths at which reef builders that host photosymbionts are able to survive (Yentsch et al., 2002). Sufficiently high sedimentation rates can even smother benthic organisms (Golbuu et al., 2003). The physical effects of increased sedimentation have been tested primarily in modern oceans, but evidence from the geologic record suggests notable impacts on ecosystems during time periods such as the late Permian (Algeo et al., 2011) and the Toarcian (Brame et al., 2019).

In addition to physical effects, terrestrial sediment influx can affect ocean nutrient content. The most significant effect is the introduction of increased dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) (Fabricius, 2005). These nutrients are necessary for marine organisms, but a rapid and sustained increase can be detrimental to corals and other metazoan reef builders (Fabricius, 2005). Many studies have shown that an increase in nutrients is advantageous for algae growth (Smith et al., 2010; Schaffelke et al., 1998), which can harm reef builders by providing competition for space, affecting access to light, and potentially increase disease risk (D'Angelo et al., 2014). At high enough levels of nutrient overloading eutrophication can occur, which decreases the oxygen content of the water (Zhang et al., 2020). Increased nutrient levels have been connected to major reef crises in the geologic record (Algeo et al., 2010; Bodin et al., 2010).

Due to the combination of physical effects from increased sediment flux and the associated increase in nutrient levels, increased terrigenous sediment flux into benthic marine communities can severely alter the overall ecosystem. This connection has been shown experimentally in modern oceans (Fabricius, 2005; Rabalais et al., 2014), and there is plentiful evidence of ecological disruption in the geologic record as well (Brame et al., 2019; Algeo et al., 2011). One set of tools used to quantify the environmental changes caused by increased silicate weathering and transport to reefs is using geochemical proxies in marine sedimentary rocks. These proxy relationships are based on modern studies and allow for the reconstruction of changes in silicate weathering (Percival et al., 2016; Sedlacek et al., 2014) and transport to shallow water reefs, as well as changes in nutrient concentration (Eagle et al., 2003; Mort et al., 2007) which affects the trophic state of the area.

2. Increased sedimentation

High levels of siliciclastic terrigenous sediments have been shown to negatively affect reef builders in modern oceans (Golbuu et al., 2003; Dutra et al., 2006) and have also been associated with reef collapse in the geologic record (Brame et al., 2019; Algeo et al., 2010). While different reef building taxa have different levels of tolerance to terrigenous sediments, sufficient inputs can affect even highly tolerant taxa (Wilson et al., 2002). The physical effects of increased terrigenous sedimentation affect reef builders in multiple ways. Reefs near sources of significant terrestrial input such as rivers can be physically buried by sedimentation (Golbuu et al., 2003). An increase in sediment concentration also decreases light quality in the water (Yentsch et al., 2002). For reef builders that host photosymbionts, a decrease in available light causes a decrease in photosynthetic efficiency and therefore lower energy from their zooxanthellae (Fabricius, 2005). Modern experiments have found a clear negative relationship between increasing terrigenous input and overall coral health (Dutra et al., 2006; Riegl 1995). Above certain thresholds, sediment influx can cause reef collapse.

Direct smothering of benthic organisms is an issue near areas with significant riverine input (Golbuu et al., 2003). This poses a threat to modern and ancient near-shore reef builders that are unable to process the sediment input in time. Certain modern corals, such as *Fungia*, are highly sediment tolerant and can survive prolonged exposure to direct sedimentation (Stafford-Smith et al., 1992). Other sediment-tolerant reef builders in the geologic record, such as Lithiotid bivalves in the early Toarcian, may have been able to survive the direct impacts of increased sedimentation up to a point (Brame et al., 2019). However, these same Lithiotid bivalves in Morocco are absent in the intervals with greatest amounts of terrestrial sediment (Brame et al., 2019), so there is likely an upper limit to sediment tolerance for all reef building organisms.

Sediment content in shallow water also has a direct negative impact on the light quality for reef building benthic organisms (Yentsch et al., 2002). Since many modern shallow water reefs contain photosymbionts, a decrease in light quality causes a decrease in photosynthetic activity and therefore less energy for the reef builder (Anthony et al., 2004), which can lead to decreased growth (Philipp et al., 2003), or even coral death (Riegl, 1995). Evaluating photosynthesis in ancient Phanerozoic corals is difficult but has likely been present for many shallow water reef builders since at least the early Mesozoic (Tornabene et al., 2017). A decrease in photosynthetic production would have been as damaging to ancient reef builders as it is to modern reef builders.

2.1 Terrestrial Sediment and Weathering Proxies

Direct measurement of turbidity and water clarity is difficult in fossil reefs, so bulk input of terrigenous sediment is commonly used. In some cases, the amount of input may be quantified based on sedimentology and bulk accumulation (Algeo et al., 2010). However, it is also possible

to determine the terrestrial fraction of the marine sedimentary rock using element concentrations. Of particular interest are Al and Ti concentrations. Both of these elements are far more common in terrestrial minerals than marine minerals, so their concentrations in the rock have traditionally been used to quantify the amount of terrestrial input into a marine rock (Eagle et al., 2003; Paytan et al., 1996). Because of this, they are commonly used to normalize values that need to specifically account for detrital impact (Paytan et al., 1992; Cole et al., 2017). These elements can help identify the amount of terrestrial sediment in a specific area, which can often be directly linked to reef collapse and local extinctions. It can also be useful in many situations to identify global trends in silicate weathering. This is because global increases in atmospheric CO₂ could lead to sediment-based disturbances to near-shore reef communities worldwide and help to better predict global damage to reefs.

Isotope ratios and trace element concentrations that are distinct in marine and terrestrial rock can be used to identify the global rate of terrestrial weathering and the transport of terrestrial sediment to the ocean (Sedlacek et al., 2014; Percival et al., 2016; Lear et al., 2003). As with local sediment concentration proxies, global continental weathering proxies are based on easily recognizable differences in the chemistry of continental and marine sediments. Two of these proxies are ⁸⁷Sr/⁸⁶Sr and ¹⁸⁷Os/¹⁸⁸Os ratios. In the geologic record, global carbon cycle perturbations which created an increase of atmospheric CO₂ were typically correlated with an increase in ⁸⁷Sr/⁸⁶Sr and ¹⁸⁷Os/¹⁸⁸Os ratios, which reflect the increase in global terrestrial silicate weathering (Fig. 1).

The ⁸⁷Sr/⁸⁶Sr of terrestrial sediments are higher than the ratio in ocean water, which is close to the average marine sediment ratio (Sedlacek et al., 2014). The residence time of Sr is significantly longer than the ocean mixing time, so significant amounts of terrestrial input will change the Sr chemistry of the entire ocean (Veizer et al., 1999). There is a strong correlation between δ¹³C and ⁸⁷Sr/⁸⁶Sr throughout the Phanerozoic (Veizer et al., 1999). Therefore, global terrestrial silicate weathering rates, as recorded by ⁸⁷Sr/⁸⁶Sr, are strongly linked to carbon isotope perturbations reflecting global changes in atmospheric CO₂ (Cohen et al., 2004). Since Sr concentration is higher in terrestrial sediments than marine sediments, bulk Sr/Ca values can also be used to record silicate weathering (Lear et al., 2003).

Another proxy for global silicate weathering rate is ¹⁸⁷Os/¹⁸⁸Os. Since Re is concentrated in continental crust during partial melting, and over time ¹⁸⁷Re decays into ¹⁸⁷Os, continental crust will have a higher ratio of ¹⁸⁷Os/¹⁸⁸Os than the ocean (Percival et al., 2016). Therefore, an

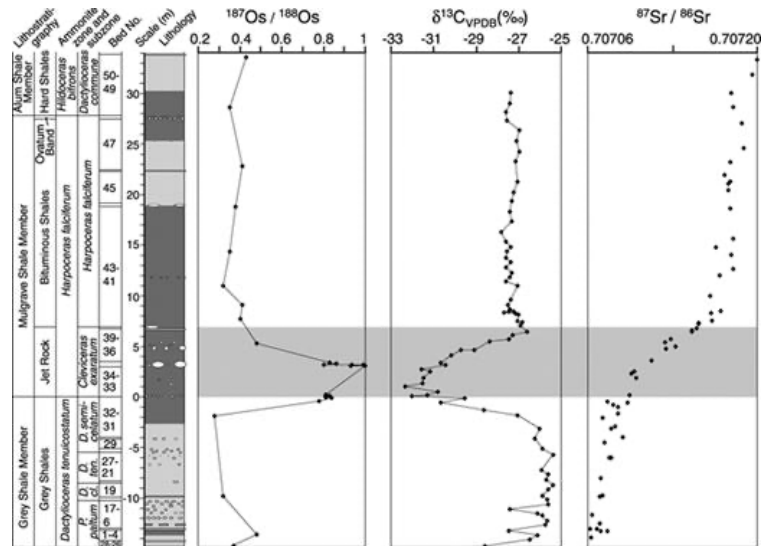


Fig 1. A comparison of Os, C, and Sr isotope ratio variations along a stratigraphic column (Cohen et al., 2004). A negative carbon isotope excursion associated with the Toarcian Ocean Anoxic Event, which significantly increased atmospheric CO₂, is shown by the grey shading. This increase in CO₂ caused an increase in global terrestrial silicate weathering rate. This is reflected by a spike in the ¹⁸⁷Os/¹⁸⁸Os and ⁸⁷Sr/⁸⁶Sr ratios. The shorter residence time of Os is shown by its faster return to baseline values than Sr.

increase in terrestrial weathering will increase ocean $^{187}\text{Os}/^{188}\text{Os}$. The residence time of Os is shorter than Sr (Oxburgh, 2001), so Os isotope excursions match closely to the timescale of the carbon isotope excursion. This is shown in Fig. 1, where Os and C return to their typical marine isotopic values at roughly the same time, but $^{87}\text{Sr}/^{86}\text{Sr}$ remains elevated long after the end of the event. Therefore, Os isotopes may be more useful than Sr isotopes for analyzing multi-pulse events such as the Pliensbachian/Toarcian boundary and the Toarcian Ocean Anoxic Event.

3. Nutrient influx

Increased terrestrial weathering rates are associated with an increase in nutrient delivery, especially to near shore communities (Fabricius, 2005). One effect of nutrient enrichment is the proliferation of algae that harm reef builders in multiple ways. Increased nutrient flux to the ocean favors fleshy algae over metazoan reef builders (Delgado et al., 1994), decreases light quality due to phytoplankton blooms (D'Angelo et al., 2014), and in extreme cases causes oxygen depletion through eutrophication (Zhang et al., 2020). Increased nutrient levels can also have direct negative effects on the net calcification of many reef-building organisms (Silbiger et al., 2018). The decrease in calcification is partially because of an increase in metabolic processes driven by increased nutrient concentrations, which can significantly decrease the local minimum pH and increase diel pH variation near the reef (Cyronak et al., 2014). The combined effects of increased nutrient levels have caused the collapse of many modern reefs (Fabricius, 2005). While the majority of modern nutrient overloading is due to direct anthropogenic causes such as agricultural runoff (Rabalais et al., 2014), there are many examples of significant increases in nutrient concentration due to natural causes throughout the geologic record. These increases often correlate with global events that caused an increase in terrestrial silicate weathering, such as the P-Tr (Algeo et al., 2010) and Toarcian extinction events (Bodin et al., 2010).

Coral reefs tend to thrive in oligotrophic environments where nutrients are a limiting factor for algae growth, but not for corals (Lapointe, 2003). Therefore, a large increase in the quantity of nutrients available in the water around a reef can lead to an ecological shift from coral-dominated to algae dominated (Smith et al., 2010; Adam et al., 2020). The most severe cases of modern macroalgae growth are due to anthropogenic nutrient input (Adam et al., 2020; Schaffelke et al., 1998). In most cases macroalgae does not fully kill off corals but can prevent recovery after other environmental forcing causes a decrease in coral cover (D'Angelo et al., 2014). In this way, macroalgae expansion due to nutrient increases can intensify the severity of extinctions, even if it is not typically a direct cause of reef extinctions.

Phytoplankton blooms are also associated with increases in marine nutrient concentration (Rabalais et al., 2014). These blooms have multiple effects; as more nutrients are available in the area, plankton populations expand until they are sufficiently concentrated in the water column to decrease light quality for corals (Hallock et al., 1986). Phytoplankton have been significant factors in near-shore communities throughout the entire Phanerozoic (Butterfield, 1997), so modern relationships between near-shore phytoplankton and terrestrial nutrient delivery are likely similar throughout the Phanerozoic. In extreme cases, phytoplankton expansion can lead to eutrophication and eventual anoxia (Rabalais et al., 2014). While proving causality of phytoplankton blooms to anoxia in the geologic record can be difficult, widespread anoxia has been shown during both the P/Tr extinction (Algeo et al., 2011) and the Toarcian Ocean Anoxic Event (Danise et al., 2015), and in both cases developed during or shortly after the beginning of anomalously high silicate weathering rates. Anoxia is devastating to benthic organisms and has been suggested as a probable cause of many past extinctions (Knoll et al., 2007; Jenkyns, 2010; Pietsch et al., 2016).

3.1 Nutrient Proxies

Measuring nutrient influx in the geologic record can be done using a variety of geochemical proxies. Nutrient levels are directly tied to marine primary productivity, and therefore proxies for productivity reflect the nutrient state of the ocean throughout time (Hallock et al., 1986). Paleoproductivity proxies measure the concentration of certain elements in either the bulk sedimentary rock or in specific fossils that are correlated with marine organic productivity. Common proxies for paleoproductivity include phosphorus (P) concentration (Bodin et al., 2010) and barium (Ba) concentration (Eagle et al., 2003). These paleoproductivity proxies must be applied to appropriate samples. For example, Ba_{excess} is most accurate in rocks with low terrigenous content (Dymond et al., 1992), so may not be a good measure of near-shore shallow water productivity. Since there are potential complications with the use of each individual proxy, it is often best to use a targeted multi-proxy approach.

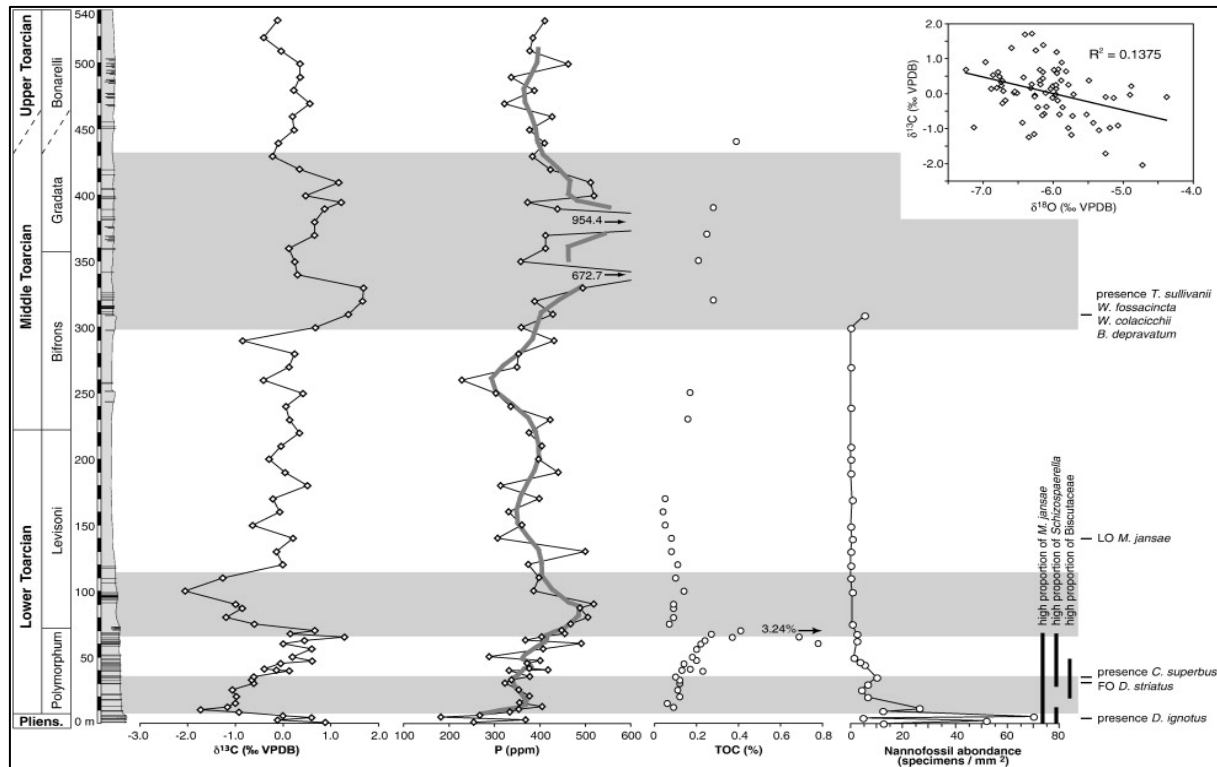


Fig. 2. A comparison of C isotope ratio, P concentration, total organic carbon (TOC), and nannofossil abundance across multiple extinction intervals in the Toarcian. (Bodin et al., 2010). Perturbations to the marine carbon isotope ratio due to large igneous province volcanism are accompanied by increases in local phosphorus content. These increases in phosphorus content are due to enhanced chemical weathering of the nearby continent, which causes an influx of nutrients

Phosphorus, typically in the form of phosphate (PO_4^{3-}), is a major nutrient in marine communities and is the main growth-limiting nutrient on geologic timescales (Tyrrell, 1999). An increase in P delivery to shallow water communities can significantly alter the trophic state, and lead to reef collapses (Fabricius, 2005). Bulk P content in carbonate mudstones has been used to reconstruct nutrient concentration of ocean water (Fig. 2) (Mort et al., 2007; Bodin et al., 2010). Since P is a vital nutrient for marine organisms, many other proxies for productivity are measured by their fidelity to P values in modern oceans (Katz et al., 2010); however, difficulties can arise when attempting to measure P in the fossil record. P signals from organics, detrital flux,

and other sources each have different factors affecting preservation (Mort et al., 2007), so environmental considerations have to be made when attempting to reconstruct total nutrient content from P concentration. Despite these potential limitations, P is a useful proxy to examine relative variations in non-restricted ancient marine areas, as is shown in Bodin et al. (2010).

While Barium (Ba) is not a primary nutrient like phosphate, it is still strongly correlated with primary marine productivity (Paytan et al., 1996). Terrestrial rock is the source of most Ba in the shallow ocean, and variations in concentration closely match major nutrient concentrations which increase during periods of heightened silicate weathering (Carter et al., 2020). There are multiple methods used to correlate Ba concentration to total organic carbon flux, and therefore marine primary productivity. Ba_{excess} is a measure of Ba phases that have been biologically processed and are not directly associated with terrigenous sediment (Dymond et al., 1992). This measurement, however, can only be performed in areas where terrigenous siliciclastic sediment is a minor fraction of the sediment, so it is more useful in deep water settings where most of the Ba was biologically processed by near-surface organisms (Dymond et al., 1992). It is therefore not a useful measure for determining nutrient changes in reef communities where the majority of fluctuations are due to changes in terrestrial input. Specifically measuring the Ba content in barite sediment (Ba_{barite}) is a more widely applicable way to reconstruct ocean productivity from bulk sedimentary rock (Paytan et al., 1996). Ba_{barite} is more accurate and useful in areas with significant terrestrial sediment, as long as they were deposited in oxic environments (Eagle et al., 2003). Therefore, Ba_{barite} is more useful than Ba_{excess} for reconstructing the changes in primary productivity of most shallow water settings. Ba is also advantageous over P for detecting small-scale changes in nutrient content, since Ba has a higher burial rate in marine sediment than P (Dymond et al., 1992).

4. In the Geologic Record

Global extinctions are frequently associated with global carbon cycle perturbations, such as the P/Tr (Algeo et al., 2010) and the Toarcian Ocean Anoxic Event (T-OAE) in the Early Jurassic (Krencker et al., 2015). These global events often result in several changes in shallow water environments, including increased sea surface temperatures (Gomez et al., 2008), lower pH (Müller et al., 2020; Trecalli et al., 2012), oxygen depletion (Knoll et al., 2007; Jenkyns, 2010), and increased storm activity (Krencker et al., 2015). However, carbon cycle perturbations are also strongly correlated with increases in global silicate weathering rate (Veizer et al., 1999; Percival et al., 2016) and marine nutrient concentration (Fabricius, 2005). There are many cases in the geologic record where increased sedimentation and nutrient concentration appear to be dominant factors causing widespread extinctions in near-shore shallow water communities (Algeo et al., 2011; Bodin et al., 2010; Sedlacek et al., 2014; Rodrigues et al., 2020).

4.1 Permian-Triassic (P/Tr) Mass Extinction

The P/Tr is the largest mass extinction of the Phanerozoic, resulting in the extinction of 90% of marine species and significant turnover of most marine fauna, and caused a gap in the metazoan reef record (Algeo et al., 2011). The probable cause of the extinction was the eruption of the Siberian Traps, a large igneous province whose eruption can be seen in the geologic record due to its impact on the global carbon cycle (Sedlacek et al., 2014). Many factors combined to cause this mass extinction including ocean acidification (Knoll et al., 2007), thermal stress (Joachimski et al., 2012), and regional anoxia (Frasier et al., 2007), along with a significant increase in global terrestrial weathering rate shown through a noticeable increase in $^{87}\text{Sr}/^{86}\text{Sr}$ (Sedlacek et al., 2014; Veizer et al., 1995). Based on bulk accumulation rate, transport of

terrestrial sediment to marine settings may have increased to seven times greater than before the event started (Algeo et al., 2010).

The amount of increase in sediment accumulation at specific sites were partially controlled by the tectonics and geography of the nearby continent, but sedimentation rates in sites around the world increased a significant amount (Algeo et al., 2011). Most of the increase in sedimentation was due to clay materials (Algeo et al., 2010), which indicates that the increase in weathering was primarily due to chemical processes (Sedlacek et al., 2014). This agrees with past studies, which determined that the leading cause for the increase in terrestrial sediment transport to marine communities was enhanced chemical weathering due to an increase in atmospheric CO₂ (Sun et al., 2018; Sedlacek et al., 2014). The increase in terrestrial sediment was a major factor in driving extinctions, as shown by the selective pressure causing increased extinction rates among organisms which required stable sediment influx (Algeo et al., 2011).

4.2 Toarcian Ocean Anoxic Event (T-OAE)

The T-OAE is one of multiple extinction events in the Early Jurassic linked to eruptions of the Karoo-Ferrar Large Igneous Province (Percival et al., 2016). While the global marine extinction rate was lower than at the P/Tr, widespread global extinctions and ecosystem turnovers occurred at the Pliensbachian/Toarcian boundary and T-OAE. The most well-known consequence of the event was a rapid expansion of ocean anoxic zones (Them et al., 2018). Other environmental factors also stressed reefs, including ocean acidification (Trecalli et al., 2012; Müller et al., 2020) and an increase in sea surface temperature (Gomez et al., 2008). In addition, some shallow near-shore sites show evidence suggesting that increased sedimentation was a primary direct factor driving reef collapse and local marine extinctions (Krencker et al., 2020). This is especially important in shallow water reefs from the NW Tethys ocean, because this area does not appear to have experienced anoxia during the T-OAE (Bodin et al., 2010; Krencker et al., 2015, 2020). The source for terrestrial sediment in this area is a nearby mountain range (Krencker et al., 2020), but the increase in terrestrial silicate weathering is seen globally (Percival et al., 2016; Cohen et al., 2004). At a shallow water site recording the Pliensbachian/Toarcian boundary and the T-OAE, a large increase in the amount of terrestrial sediment is associated with a temporary disappearance of reef-building bivalves and corals from the rock record (Brame et al., 2019). The increase in marine nutrient content associated with global increases in terrestrial weathering also was a primary cause in the development of anoxic zones through a large portion of the ocean (Erba, 2004).

5. Conclusion

It can often be difficult to determine the presence of specific mechanisms detrimental to reef growth in the geologic record. But while it may be difficult to prove that a decrease in water quality or increased competition from turf algae drove reef extinctions, it is possible to connect extinctions with broad increases in terrestrial sediment (Algeo et al., 2010) and nutrients (Bodin et al., 2010) as measured by geochemical proxies. These impacts can be analyzed on a local scale (Brame et al., 2019), but global silicate weathering trends can provide information on likely sediment impacts to near-shore reefs around the world (Sedlacek et al., 2014). It is also possible that increased terrestrial weathering could cause extinctions in less direct ways, such as by causing bottom water anoxia through eutrophication (Erba, 2004; Zhang et al., 2020). Modern experimental work determining the specific ways in which sedimentation (Philipp et al., 2003; Riegl, 1995; Yentsch 2002) and nutrient loading (Adam et al., 2020; D'Angelo et al., 2014; Zhang et al., 2020) affect reef communities can be used to decipher the intermediate mechanisms linking increased terrestrial silicate weathering to global reef collapses.

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