

# On the potential for ocean acidification to be a general cause of ancient reef crises

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## Abstract

Anthropogenic rise in the carbon dioxide concentration in the atmosphere leads to global warming and acidification of the oceans. Ocean acidification (OA) is harmful to many organisms but especially to those that build massive skeletons of calcium carbonate, such as reef corals. Here, we test the recent suggestion that OA leads not only to declining calcification of reef corals and reduced growth rates of reefs but may also have been a trigger of ancient reef crises and mass extinctions in the sea. We analyse the fossil record of biogenic reefs and marine organisms to (1) assess the timing and intensity of ancient reef crises, (2) check which reef crises were concurrent with inferred pulses of carbon dioxide concentrations and (3) evaluate the correlation between reef crises and mass extinctions and their selectivity in terms of inferred physiological buffering. We conclude that four of five global metazoan reef crises in the last 500 Myr were probably at least partially governed by OA and rapid global warming. However, only two of the big five mass extinctions show geological evidence of OA.

*Keywords:* climate change, mass extinctions, ocean acidification, Phanerozoic, reefs

Received 18 November 2009; revised version received 4 February 2010 and accepted 5 February 2010

## Introduction

In conjunction with climate change, ocean acidification (OA) is perhaps the most severe threat to marine ecosystems acting at global scales (Orr *et al.*, 2005; Hoegh-Guldberg *et al.*, 2007; Anthony *et al.*, 2008; De'ath *et al.*, 2009). OA, the reduction of the pH of the ocean by increasing  $p\text{CO}_2$ , appears to be most hazardous in ecosystems that hold a large proportion of calcifying organisms, although the response of calcification to ambient pH is quite variable and the exact mechanisms of how physiology is affected by pH are still poorly understood (Atkinson & Cuet, 2008; Fabry *et al.*, 2008; Jokiel *et al.*, 2008; Marubini *et al.*, 2008; Pörtner, 2008; Ries *et al.*, 2009). These obstacles aside, empirical evidence does suggest that coral reefs are especially affected by OA because the major reef builders, scleractinian corals and coralline red algae, respond readily by reduced growth rates, abundance and increased postmortem dissolution (Anthony *et al.*, 2008; Kuffner *et al.*, 2008; Silverman *et al.*, 2009).

The current anthropogenic rise in  $p\text{CO}_2$  is dramatic (IPCC, 2007) but perhaps not unprecedented in the geologic record. The best evidence for an ancient acidification event comes from the Paleocene–Eocene Thermal Maximum (ca. 55 Ma), when a massive injection of

isotopically light carbon to the atmosphere and oceans coincided with a reduced saturation state of seawater with respect to calcium carbonate (Zachos *et al.*, 2005) and with extinctions and evolutionary turnover in marine protists (Gibbs *et al.*, 2006; Thomas, 2007). More circumstantial evidence for substantial massive increases in  $p\text{CO}_2$  also exists for much older times, some of which were linked to mass extinctions in the sea (Knoll *et al.*, 1996, 2007; Hautmann, 2004). Several mechanisms for rapid and massive rises of  $p\text{CO}_2$  have been proposed for prehistoric times. These include (1) direct volcanic outgassing (Bernier & Beerling, 2007), (2) dissociation of methane hydrates from seafloor sediments (Dickens *et al.*, 1995), (3) methane buildup and release from intrusion of magma into organic-rich sediments (Svensen *et al.*, 2004), (4) oxidation of large amounts of sedimentary organic carbon (Higgins & Schrag, 2006) and (5) the buildup of  $\text{CO}_2$  in anoxic deep water and its rapid release by oceanic turnover (Knoll *et al.*, 1996).

Our study was motivated by Veron (2008), who suggested that ancient OA would not only have led to reduced growth rates of reef builders (leading to reef crises) but also to increased extinction rates, to a degree that all major mass extinctions (except for the Late Devonian) might be caused by OA, at least partially. We split this interesting idea into two testable hypotheses: (1) reef crises are generally caused by OA and (2) mass extinctions were associated with OA. We separate

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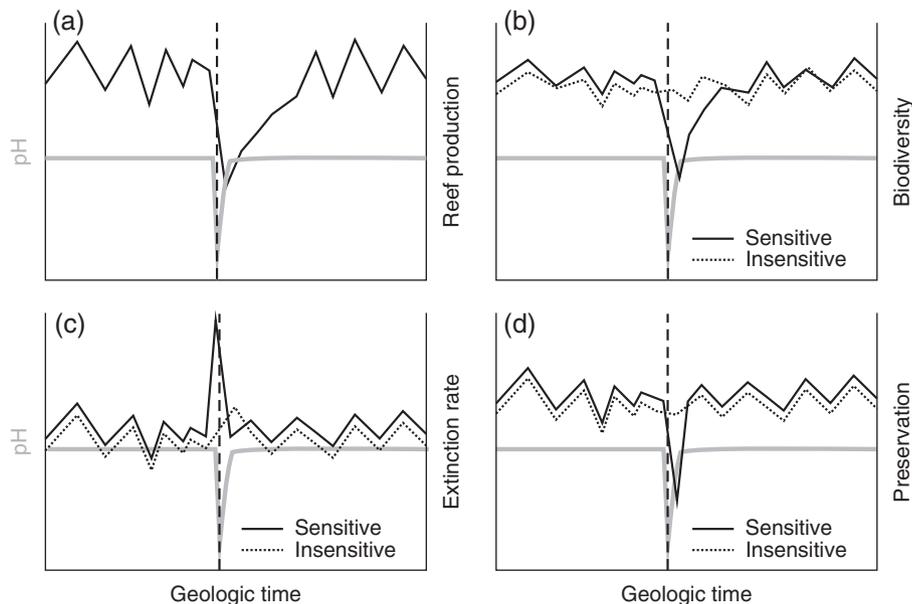
these hypotheses because it remains to be demonstrated that reef crises coincided generally with mass extinctions. The current coral reef crisis is defined by declines in reefal carbonate production rather than extinction (Pandolfi *et al.*, 2003; Bellwood *et al.*, 2004). This definition can be equally applied to ancient reefs (Flügel & Kiessling, 2002; Kiessling, 2009). Although an extreme reef crisis will likely be associated with extinctions at least of reef-building species, the rank-order distribution of extinction intensities and reef crises is different (Flügel & Kiessling, 2002) and low-diversity reefs can maintain high carbonate production values (Johnson *et al.*, 2008) suggesting that reef crises and the extinction of reef species are potentially decoupled.

If OA played a significant role in ancient reef crises, these crises – here defined by global declines in actively produced reefal carbonate volume per unit time – should occur when geological evidence suggests rapidly rising  $p\text{CO}_2$  levels and declining pH (Fig. 1a). If OA was involved in ancient mass extinction episodes we would also expect a temporal match of biodiversity loss and extinction intensity and in addition a preferential loss of sensitive taxa (Fig. 1b and c). Sensitive taxa would be those that invest strongly in the production of calcium carbonate skeletons and/or are physiologically unbuffered. Finally, if the response of organisms is by reduced

population sizes rather than extinction, fossil preservation should be degraded in the aftermath of OA.

These conditions set the stage for our analysis of the fossil record of reefs and marine organisms. We first assess the significance of ancient reef crises and look at their correspondence with inferred atmospheric chemistry. We then test if significant reef crises coincided with major mass extinction episodes and finally we assess the selectivity of extinctions. We emphasize acute events rather than long-term relationships between inferred saturation levels of seawater with respect to calcium carbonate and reef development. Although interesting correspondences have been identified on longer time scales (Riding & Liang, 2005), the impact of  $\text{CO}_2$  on oceanic pH and supersaturation with respect to calcium carbonate is much less constrained on time scales of more than  $10^5$  years (Sundquist, 1985; Caldeira & Wickett, 2003). Moreover, acute events seem to have a stronger impact on the trajectories of skeletal mineralogy than long-term changes in ocean chemistry (Kiessling *et al.*, 2008).

We focus on metazoan reefs, because those are best comparable with our modern coral reefs. In theory, we would expect microbial reefs to be especially sensitive to OA, because microbes precipitate calcium carbonate in direct contact with seawater without enzymatic control (Riding, 2000) and thus have no potential to buffer



**Fig. 1** Hypothetical scenarios of the biological response to acute ocean acidification (OA) events on geological time scales. Oceanic pH is constant and exhibits a geologically brief negative excursion in all panels. (a) Response of reef production (generated global reef volume per unit time). Reef production is generally volatile and declines rapidly after OA. Recovery is slow. (b) Biodiversity response is rapid (with some lag) for sensitive groups, whereas insensitive groups show no or negligible response. Recovery of sensitive groups is moderately slow. (c) Extinction rate of sensitive groups increases immediately during OA, while insensitive groups are not affected, or affected with some temporal lag due to cascade effects of important sensitive taxa on which they depend. (d) Preservation of sensitive groups declines rapidly after OA and also recovers rapidly.

against chemical insult. However, microbial precipitation should rapidly rebound as soon as seawater saturation levels are sufficient for calcium carbonate precipitation. Because our temporal resolution is limited, transient breaks in microbial carbonate precipitation are unlikely to be observed. It is therefore preferable to rely on more complex organisms to seek potential relationships between OA and reef crises.

## Materials and methods

The PaleoReefs Database (PARED) was used to assess global reef volume through time and to define reef crises. PARED compiles the geological and paleontological data of Phanerozoic reef sites (Kiessling *et al.*, 1999; Kiessling, 2001; Kiessling & Flügel, 2002), of which 4000 are currently recorded. We calculated the preserved volume of each reef site applying previous methods (Kiessling *et al.*, 2000). We also assessed the volumetric contribution of major taxonomic groups to reef construction by considering the two most prolific reef building groups within each reef complex. Reef-building groups in PARED are defined at the supra-ordinal level (Kiessling, 2005). We assigned a weight of 70% to the dominant group and 30% to the secondary group. These numbers are based on personal observations in Jurassic and Pleistocene reefs (W.K.) where the dominant reef-building group usually contributes 60–80% to reef construction. If secondary reef builders contribute <10% to reef construction, their contribution was ignored. We analysed total reef volume (irrespective of reef builders), reef volume constructed by nonmicrobial organisms, reef volume built by metazoans and reef volume constructed by corals and hypercalcifying sponges. The latter three categories yield much lower estimates than the total, not only because they are subcategories but also because they require information on which higher taxon built the reef. The sum of volumes per stratigraphic interval (geological stage) was then compiled to achieve an estimate of global reef volume ( $V$ ) per interval ( $i$ ). After normalizing for the duration of intervals the changes in volumes were calculated by

$$dV_i = \ln(V_i/V_{i-1}). \quad (1)$$

This equation is commonly applied in financial mathematics where it is known as log-return. Using logged ratios instead of proportional changes (= simple returns) as sometimes used to assess changes in biodiversity (Bambach *et al.*, 2004) has the advantage of making gains and losses potentially symmetrical around zero. Global reef crises are here defined by significant negative outliers in boxplots, that is, they are more than 1.5 times below the interquartile range of all  $dV$  values. For simplicity, we use the term change instead of log-return below.

Extinction intensity and extinction selectivity were assessed with the Paleobiology Database (PaleoDB; <http://paleodb.org>). In addition to providing a comprehensive compilation of fossil taxa, the PaleoDB allows for an assessment of abundance data and sampling completeness. The latter is important to assess the taphonomic signal of reef crises and to achieve unbiased rate estimates. Data were downloaded on October

20, 2009 using all 478 971 occurrences from the marine invertebrate working group except for vertebrates and doubtfully identified genera, that is, those genera listed in quotation marks, or qualified as '?', 'cf.' or 'aff.'. Data were filtered to include only marine invertebrate genera classified to a higher taxon (family, order and/or class), and genus occurrences assignable to one of 77 geological stages. This left 400 658 taxonomic occurrences. Extinction rates are calculated by

$$E = -\ln[N_{bt}/(N_{bL} + N_{bt})], \quad (2)$$

where  $N_{bt}$  denotes the number of taxa crossing both the bottom and top boundaries of an interval and  $N_{bL}$  is the number of taxa crossing the bottom interval but having its last appearance within it (Foote, 2000). To achieve a comparable metric for diversity crises as for reef crises we also used log-return of boundary-crossing taxa in the following way:

$$dD_i = \ln[(N_{bL} + N_{bt})_i / (N_{bL} + N_{bt})_{i-1}]. \quad (3)$$

The selectivity of extinctions was analysed based on Akaike's modified information criterion (AIC). AIC is a model selection metric derived from information theory that measures the relative support of a preselected set of models, with respect to data. Increasing the number of model parameters ( $K$ ) generally increases support [ $\log(L)$ ], so AIC compensates for this by penalizing models by their complexity. We compare two types of models here: in the first we measure the extinction rates of inferred sensitive and buffered genera separately. In the second model, we measure a single extinction rate for all genera. We select a model if its Akaike weight is 0.89 or above (Wagner *et al.*, 2006).

We tested two scenarios of extinction selectivity. First, we contrasted calcified sponges and stony corals with all other organisms. Corals and sponges are the dominant metazoan reef builders over Phanerozoic times (Kiessling, 2009) and they have an especially high skeleton/biomass ratio, that is, they invest strongly in the secretion of calcium carbonate.

Second, we tried to contrast groups that readily respond to lowered pH or hypercapnia from those that are less sensitive. This proved to be very difficult, because some sort of sensitivity exists in virtually all higher taxa (Pörtner *et al.*, 2005; Fabry *et al.*, 2008; Ries *et al.*, 2009) and is manifested not only in reduced calcification rates but also in declining rates of reproduction (Fabry *et al.*, 2008; Doney *et al.*, 2009) and changes in metabolism (Michaelidis *et al.*, 2007; Wood *et al.*, 2008). This makes it difficult to separate buffered from unbuffered organisms at supra-specific levels and thus to assess sensitivity for extinct organisms. Moreover, physiological sensitivity is not the same as elevated extinction risk (Widdicombe & Spicer, 2008). For example, some corals may respond to OA by losing their skeleton but are able to survive and recover from decalcification (Fine & Tchernov, 2007). On the other hand, an ophiurid species has been shown to increase calcification with lowered pH but at a metabolic cost (Wood *et al.*, 2008) that may increase extinction risk.

Without reliable data on the sensitivity of ancient species to OA, we tentatively use a modified categorization of previous authors to separate physiologically unbuffered from buffered organisms (Knoll *et al.*, 1996, 2007; Bambach *et al.*, 2002). These authors classified as unbuffered those higher animal taxa that secrete calcium carbonate skeletons or shells, lack gills, and

**Table 1** Delineation of higher taxa that should be especially sensitive to hypercapnia and ocean acidification in terms of growth rate and extinction risk (modified from Knoll *et al.*, 2007)

Higher taxon	Remarks
Calcareous algae	Demonstrated decline in calcification and competitive ability (Jokiel <i>et al.</i> , 2008; Kuffner <i>et al.</i> , 2008)
Calcareous foraminifers	Demonstrated decrease of shell mass, perhaps more important for nonsymbiotic species (Fabry <i>et al.</i> , 2008). Active maintenance of pH at calcification sites increase metabolic costs at low pH (de Nooijer <i>et al.</i> , 2009)
Hypercalcified sponges*	Probably no physiological buffering. Survival perhaps possible without calcareous skeletons. No experimental data
Corals	Demonstrated sensitivity of growth rates for tropical reef corals (Marubini <i>et al.</i> , 2008). Equivocal data for cool water (Rodolfo-Metalpa <i>et al.</i> , 2010) and cold water corals (Maier <i>et al.</i> , 2009)
Calcareous brachiopods	Limited buffering capacity and heavy carbonate load (Knoll <i>et al.</i> , 2007). No experimental data
Calcifying bryozoans	Claimed sensitive (Knoll <i>et al.</i> , 2007; Smith, 2009). No experimental data
Pelmatozoans	Crinoids and blastoids considered to be unbuffered (Knoll <i>et al.</i> , 2007). No experimental data

\*Calcarea, coralline demosponges and stromatoporoids.

have weak internal circulation and low metabolic rates. We follow this definition in a slightly modified and complemented version as presented in Table 1. We contrasted unbuffered organisms with all other organisms. Although other combinations are possible (e.g., a threefold partitioning or contrasting unbuffered and moderately buffered with well buffered organisms), these would strongly limit sample sizes and consequently statistical power.

Besides extinction, a realistic consequence of OA could be the degradation of the fossil record of those groups that respond ecologically by reducing their abundance or skeletons but manage to survive. A decline of fossil preservation in the aftermath of mass extinctions has long been observed. Many surviving taxa are not recorded in its immediate aftermath but reappear much later in the fossil record. This Lazarus effect (Jablonski, 1986) was originally ascribed to sampling bias, but is now regarded as a genuine decline of population sizes (Wignall & Benton, 1999). We have assessed preservation by measuring the completeness of the fossil record for each group and time interval. This is done by calculating the number of sampled genera divided by the number of sampling opportunities, that is, genera that occur before and after the focal interval. Range endpoints were excluded from this metric (Foote & Miller, 2007). Again, AIC was used to judge if preservation differed significantly between groups.

Because sampling gaps, edge-effects, and the Signor–Lipps effect (the backward smearing of last appearances) may strongly bias extinction rates, we applied the metrics developed by Alroy (2008) to adjust for these biases. In brief, extinction rates are measured by taking notion only of genera that are sampled in two or three of three consecutive time intervals. These are two-timers (*tt*), three-timers (*tht*) and part-timers (*ptm*). A two-timer is a genus sampled in two consecutive intervals, before and in the focal interval; *tht* denotes genera sampled in three consecutive intervals; and *ptm* are genera sampled in the first and third interval but not in the focal interval. Two-timer extinction rates (*Et*) are calculated by

$$Et = \log(tt/tht). \quad (4)$$

Preservation (*P*) for each time interval is estimated by

$$P = tht/(tht + ptm). \quad (5)$$

A corrected estimate of *Et* ( $= Et'$ ) in a time interval *i* can be achieved by

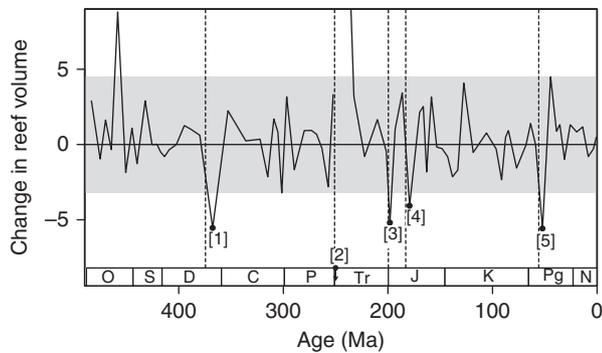
$$Et'_i = Et_i + \log(P_{i+1}). \quad (6)$$

The temporal resolution of our analyses is limited by the data. We have resolved the data as finely as possible, but stratigraphic correlations are still problematic at global scales, especially in the Palaeozoic era. Therefore, our resolution is coarser for the Palaeozoic than later when international stage names have been long established. We were able to parse the reef record into 83 stages with a mean of 6.5 Myr duration (see supporting information Table S1), whereas extinction rates had to be analysed on a somewhat coarser subset of 77 stages (7.0 Myr mean duration), mostly because the recent updates to the Ordovician time scale (Bergström *et al.*, 2009) are not yet implemented in the PaleoDB. The finer temporal resolution for reefs is critical because OA may only briefly interrupt reef building, whereas the consequences of extinctions are longer-lasting. The binning of data into temporal intervals and the way these data are analysed [Eqns (1)–(6)] are responsible for the fact that extinction rates are observed to rise in the interval before a deleterious event, whereas reef volume, biodiversity, and preservation decline in the interval after the event (Fig. 1). The interval after the event is called the crisis interval.

Owing to the great volatility of the Cambrian both in terms of reef growth and extinction rates, we excluded this period from all analyses. Owing to the absence of finely resolved trajectories of *p*CO<sub>2</sub> and pH through geologic time, we can only use anecdotal studies and semiquantitative proxies to infer changes at critical events. Appropriate references are cited in 'Discussion'.

## Results

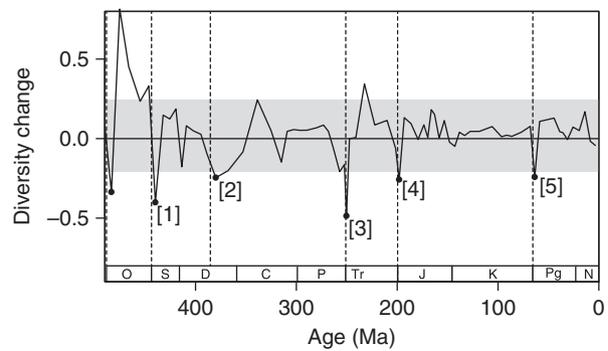
The geological record of reef volume that is generated per interval of time is generally very volatile (Fig. 2),



**Fig. 2** Changes (log-return) of global metazoan reef volume as recorded in The PaleoReefs Database (PARED). Significant reef crises are highlighted by black dots and the boundary of the precrisis is indicated by a dashed line. Note that all values below zero indicate loss relative to the former interval. The grey box delineates background fluctuations. Arrow indicates that the true value is below the plot margins after the Permian–Triassic boundary (log-return = minus infinity). The five numbers in brackets indicate the big five Phanerozoic reef crises that are emphasized in the discussion. [1] Late Devonian; [2] Permian–Triassic; [3] Triassic–Jurassic; [4] Early Jurassic; [5] Paleocene–Eocene. O, Ordovician; S, Silurian; D, Devonian; C, Carboniferous; P, Permian; Tr, Triassic; J, Jurassic; K, Cretaceous; Pg, Paleogene; N, Neogene.

which is in accordance with previous studies on the geologic record of reefs (Kiessling *et al.*, 2000; Kiessling, 2006, 2008). Therefore, only the most extreme depressions are identified as significant reef crises. The major post-Cambrian metazoan reef crises are identified as follows: (1) Late Devonian, Famennian stage, after the boundary of the Frasnian and Famennian stages (374.5 Ma), (2) Early Triassic, Induan and Olenekian stages, after the Permian–Triassic boundary (251 Ma), (3) earliest Jurassic, Hettangian stage, after the Triassic–Jurassic boundary (199.6 Ma), (4) Early Jurassic, Toarcian stage, at the boundary of the Pliensbachian and Toarcian stages (183 Ma) and (5) early Eocene, Ypresian stage, after the Paleocene–Eocene boundary (55.8 Ma). The importance of the early Eocene crisis has not been recognized before, because a previous analysis at the Phanerozoic scale considered total reef volume rather than only metazoan volume (Flügel & Kiessling, 2002). The loss of coral reef volume across the Paleocene–Eocene boundary was compensated by larger foraminifers building reefs in the early Eocene (Plaziat & Perrin, 1992). Crises are for all reefs, nonmicrobial reefs and coral–sponge reefs are indicated in the Supplementary Information (see Fig. S1).

Significant marine biodiversity crises (Fig. 3) follow the traditional big five mass extinctions (Raup & Sepkoski, 1982): the end-Ordovician, Late Devonian, end-Permian, end-Triassic and end-Cretaceous. An additional significant crisis is evident after the Cambro–

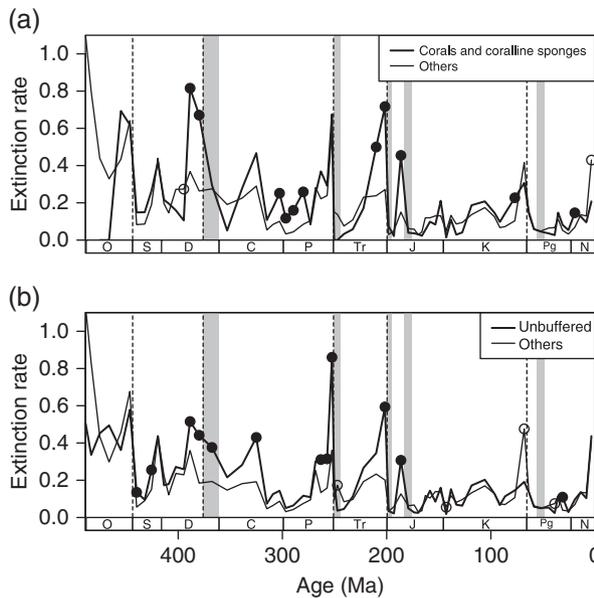


**Fig. 3** Changes (log-return) of marine animal genus diversity recorded in the PaleoDB. The traditional big five mass extinctions (Raup & Sepkoski, 1982) are clearly discernible. [1] Late Ordovician; [2] Late Devonian; [3] Permian–Triassic; [4] Triassic–Jurassic; [5] Cretaceous–Paleogene. An additional mass depletion of diversity occurred at the Cambrian–Ordovician boundary. See Fig. 2 for additional explanations.

Ordovician boundary, which represents a large extinction event even when standardized for sampling (Alroy, 2008). Although not all biodiversity crises are solely driven by elevated extinction rates (Bambach *et al.*, 2004; Alroy, 2008), we show here that our method of delineating significant crises is appropriate. This is important because we cannot separate growth and destruction rates in reefs the way we can separate origination and extinction rates of genera. We further show that the major post-Cambrian diversity crises that are seen in analyses of Sepkoski's (2002) compendium (Bambach *et al.*, 2004) can be replicated with the data in PaleoDB.

Extinction rates of inferred sensitive and insensitive groups are shown in Fig. 4. Four of the five significant metazoan reef crises were preceded by elevated extinction rates of corals and sponges (Fig. 4a) but only three mass extinctions are also characterized by a preferential extinction of corals and sponges relative to other groups: the Late Devonian, the end-Triassic and the Early Jurassic. Preferential extinctions of coral and sponges occur in two consecutive stages before the events in the Late Devonian and end-Triassic. During the major mass extinctions at the end of the Ordovician, Permian and Cretaceous periods corals and coralline sponges have indistinguishable extinction rates from other taxa. The Early Jurassic reef crisis is preceded by elevated extinction rates of corals and sponges (especially corals in this case), but no extinction pulse or extinction selectivity immediately predated the early Eocene reef crisis.

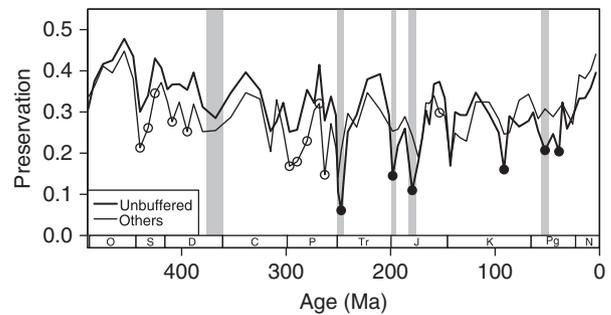
The extinction pattern is slightly different for unbuffered vs. buffered taxa (Fig. 4b). Extinction in the end-Permian mass extinction, while high in all groups, is much more severe for unbuffered groups (see also Knoll



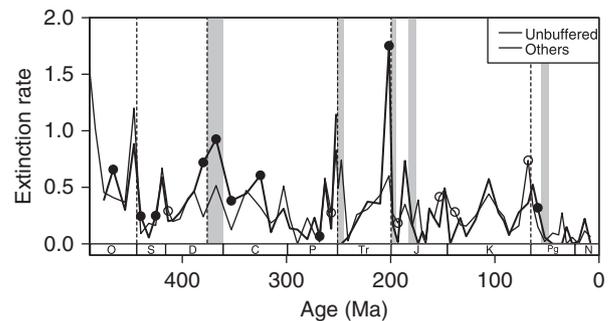
**Fig. 4** Raw extinction rates of marine animal genera in the Paleodb, grouped by taxonomy and inferred physiological buffering capacity. (a) Stony corals and coralline (hypercalcifying) sponges vs. all other organisms. (b) Physiologically unbuffered organisms vs. all others. Thick lines indicate extinction rates in the inferred sensitive groups (a, corals and sponges; b, physiologically unbuffered organisms). Solid black circles delineate times when extinction in sensitive groups is significantly higher than in the nonsensitive groups, and open circles designate times when insensitive groups were more affected. Grey vertical bars designate time intervals of metazoan reef crises (Fig. 2).

*et al.*, 2007). Significant differences in extinction rates are maintained in the Devonian, end-Triassic and Early Jurassic extinctions, whereas the end-Ordovician mass extinction remains unselective. An interesting dichotomy is observed in the end-Cretaceous mass extinction: unbuffered organisms were significantly less affected than others. This pattern holds even if moderately buffered taxa such as epifaunal bivalves and echinoids are removed from the analyses.

Fossil preservation (Fig. 5) closely follows the prediction that OA-driven reef crises should coincide with a degradation of the fossil record of surviving lineages. All reef crises are accompanied by the reduced preservation of all genera that are inferred to be present, but the degradation of the fossil record is especially strong for unbuffered taxa. The only exception is in the Late Devonian. The pattern is less pronounced for corals and coralline sponges, where only the Early Triassic depression in sampling strictly meets the expectations (Fig. S2). However, the reversed pattern of greater sampling probability of corals and sponges is never associated with reef crises, but is often found when reefs were common such as in the Late Triassic and Late Jurassic.



**Fig. 5** Preservation (sampling completeness) of physiologically unbuffered organisms vs. others. Circles indicate times when preservation was significantly different between groups: solid circles, preservation in unbuffered group is significantly lower than in buffered group; open circles, preservation in buffered group is lower. Grey vertical bars designate time intervals of metazoan reef crises (Fig. 2).



**Fig. 6** Three-timer estimates of extinction rates in inferred unbuffered and other organisms corrected for preservation bias. See Fig. 4 for additional explanations.

The decline of fossil preservation in the aftermath of mass extinctions might indicate that estimated extinction rates are exaggerated in the raw data, because many survivors that survived a mass extinction but became extinct in the aftermath may not be recorded. Using Eqns (4)–(6), we therefore constructed corrected curves for extinction rates (Fig. 6). As the three-timer rates are based on only those genera that are unsampled in intervals following the focus interval, rates are often much higher than in the raw data (Fig. 4b), but the correction for sampling allows for an estimate of extinction rates that are unaffected by edge effects and sampling gaps [Eqn (6)]. The most important difference to the raw data is (1) the shift of the Devonian extinction peak of unbuffered taxa from the Middle Devonian to the end of the Devonian, (2) the decline of intensity and lack of significant selectivity in the end-Permian mass extinction and Early Jurassic reef crisis, (3) the large increase in unbuffered extinction rates at the end-Triassic mass extinction and (4) the novel selectivity in the modest end-Paleocene extinctions.

## Discussion

### *Reef crises and OA*

The Late Devonian reef crisis has long been known and is usually attributed to the Kellwasser events (Buggisch, 1991), which are characterized by marine anoxia reaching shelf settings and strong positive carbon isotope excursions indicating enhanced burial or organic carbon and perhaps a drawdown of atmospheric CO<sub>2</sub> (Joachimski & Buggisch, 1993). An appealing model has been forwarded by Algeo & Scheckler (1998) who linked the reef crisis to the evolution of land plants, because the first forests developed in the Late Devonian. Tree roots might have mobilized nutrients on land that were transported into the sea where they led to massive algal blooms, carbon burial and mass kill of reefs. Although models of increased volcanism and sudden methane release have been evoked for the Late Devonian crisis (Gharaie *et al.*, 2007), evidence for OA is meagre (Veron, 2008).

Many models have been proposed for the Permian extinctions and in particular the end-Permian mass extinction. There is ample evidence for a sharp rise in *p*CO<sub>2</sub> near the Permian–Triassic boundary, which comes from two sources: geological evidence indicates massive volcanism (Reichow *et al.*, 2009) and sharp and pronounced negative excursions in δ<sup>13</sup>C suggest repeated pulses of CO<sub>2</sub> release (Payne & Kump, 2007). Palaeontological evidence supports hypercapnia at least as a partial kill mechanism (Knoll *et al.*, 1996, 2007). Our analyses support these contentions inasmuch as the most profound post-Cambrian reef crisis occurred after the Permian–Triassic boundary, extinctions were highly selective against unbuffered organisms, and there was a pronounced depression in the preservation of unbuffered organisms in the Early Triassic. A problem with an OA scenario is the relatively modest extinction of coralline sponges (Weidlich *et al.*, 2003), which is responsible for the absence of a significant difference in the coral–sponge vs. other extinction rates (Fig. 4a). However, skeletal characters in coralline sponges are considered homoplastic (Alvarez *et al.*, 2000; Wörheide, 2008) and some of the Triassic sponge genera may result from convergent evolution rather than representing true survivors.

The reef crisis following the Triassic–Jurassic boundary is well known to be associated with massive volcanism (Marzoli *et al.*, 1999, 2004; Cohen & Coe, 2007). A pronounced increase of *p*CO<sub>2</sub> has been inferred from decreasing densities of leaf stomata (McElwain *et al.*, 1999) and the carbon isotope composition of soils (Beerling, 2002). As this rise occurred over a geologically brief interval of time, OA is a feasible mechanism for this reef crisis, although claims that OA led to an undersaturation of the oceans with respect to calcium

carbonate (Hautmann, 2004) are probably exaggerated (Berner & Beerling, 2007). The earliest Jurassic reef crisis fits most of the hypothetical scenarios shown in Fig. 1. The reef crisis was massive, the end-Triassic mass extinction was highly selective against hypercalcifying sponges and corals and physiologically unbuffered taxa, and the preservation of unbuffered genera dropped markedly in the earliest Jurassic.

The Early Jurassic reef crisis hit reefs in the midst of recovery from the end-Triassic mass extinction. Massive volcanism, global warming, a rise in *p*CO<sub>2</sub>, and anoxia were reported from this interval (Beerling & Brentnall, 2007; Svensen *et al.*, 2007). Although not very pronounced for all organisms, extinctions were highly selective against unbuffered organisms in general and corals in particular. OA was likely involved in this event (Hermoso *et al.*, 2009).

The Paleocene–Eocene boundary is probably the time for which OA is best documented (Zachos *et al.*, 2005). OA is manifested directly by a shallowing of the calcium carbonate compensation depth in the deep ocean, but substantial effects on shallow water biota have also been suggested (Gibbs *et al.*, 2006; Stoll *et al.*, 2007). Not all effects were negative. For example, the productivity of oceanic plankton seems to have increased (Stoll *et al.*, 2007). In any case, the observation that the Paleocene–Eocene OA coincides with one of the five most substantial metazoan reef crises in the last 500 Myr does suggest a cause–effect relationship of some kind. Extinctions of corals and other unbuffered organisms were modest according to the raw data (Fig. 4), but the corrected rates are significantly elevated for unbuffered organisms, reaching almost the values of the end-Cretaceous mass extinction.

In summary, except for the Late Devonian crisis, all post-Ordovician reef crises were likely associated with OA. We cannot determine whether the magnitude of the crises is correlated with the mass of CO<sub>2</sub> released to the atmosphere and ocean and its timing. This is related to the difficulty of constraining the source of CO<sub>2</sub>. Carbon isotope excursions are usually so negative, that methane dissociation (yielding isotopically light carbon) rather than direct volcanic outgassing is evoked to explain the pattern (e.g., Dickens *et al.*, 1995; Hesselbo *et al.*, 2000). A methane source of the CO<sub>2</sub> would require much less gas to explain the isotope excursion than isotopically heavier sources, to a degree that the climatic and OA effects are not explainable (Zachos *et al.*, 2005; Panchuk *et al.*, 2008). Similarly, the OA effect critically depends on the timing of CO<sub>2</sub> release, which is often poorly constrained.

### *Mass extinctions and OA*

Two mass extinctions do not represent metazoan reef crises but substantial biodiversity crises: The late Ordovician

and the end-Cretaceous mass extinctions. The late Ordovician mass extinction is the one for which climate cooling is best documented as a potential trigger (Sheehan, 2001). Although it usually shows up as a single event in Phanerozoic-scale analyses (including ours), there were indeed two extinction pulses (Brenchley *et al.*, 1995) separated by about 1 Myr. The first extinction pulse occurred at the onset of glaciation near the base of the Hirnantian stage and the second hit during rapid global warming in the middle of this stage, near the end of the Ordovician. The warming event might have been associated with OA and the lack of selectivity in our analyses might be due to the different response of groups during each event. However, the modest decline in carbon isotope ratios (Brenchley *et al.*, 2003) and relatively well-developed reefs in the latest Ordovician (Copper, 2001) suggest that OA was not involved in the extinctions.

The end-Cretaceous was the one event where extinctions on land were as disastrous as in the seas. The extinction of dinosaurs, ammonites and rudists (bivalves with coral-like growth forms) has long been attributed to a bolide impact (Alvarez *et al.*, 1980). Evidence for an impact and its temporal link to the mass extinction is now extraordinarily strong (Schulte *et al.*, 2010). Although volcanism in India is roughly contemporaneous with the mass extinction (Chenet *et al.*, 2009), our results render it unlikely that volcanism contributed to the mass extinction at least with the OA effects that are usually associated with massive eruptions. There was no notable reef crisis (Fig. 2), extinction of corals was modest (Baron-Szabo, 2008), and there was a preferential extinction of physiologically buffered, but metabolically more active organisms (Figs 4b and 6) suggesting that starvation rather than OA was a proximate trigger of the extinctions (Aberhan *et al.*, 2007). Moreover, deep water corals, which should be affected by OA as strongly as shallow tropical corals (Veron, 2008), preferentially survived the end-Cretaceous mass extinction (Kiessling & Baron-Szabo, 2004). The profound extinctions of calcareous plankton such as coccolithophores and planktonic foraminifers (Smit & Hertogen, 1980; Pospichal, 1994) might at first glance suggest OA, perhaps due to acid rain caused by the impact (Macdougall, 1988). However, this selectivity is rather an epiphenomenon of life history traits such as the lack of ability to form cysts under acute stress (Bown, 2005; D'Hondt, 2005) than a result of OA.

#### *OA without pronounced effects?*

How about possible OA events that neither caused reef crises nor mass extinctions? The best candidates are in the Cretaceous period, in which several ocean anoxic

events (OAEs) are known. OAEs were short-lived episodes of organic carbon burial and pronounced carbon isotope excursions. The two most prominent OAEs occurred in the early Aptian (120.5 Ma) and at the Cenomanian–Turonian boundary (93.5 Ma) (Leckie *et al.*, 2002). The early Aptian OAE was probably associated with submarine volcanism (Tarduno *et al.*, 1991) and massive methane release from oceanic sediments (Jahren *et al.*, 2001), which, just like the Early Jurassic OAE, may have surpassed the release at the Paleocene–Eocene boundary (Beerling *et al.*, 2002). That not even a minor reef crisis can be observed in the Aptian stage (Fig. 2) might be due to our limited temporal resolution. However, it is also possible that the methane release was rapidly sequestered into organic carbon (Beerling *et al.*, 2002) thus leaving no effect on the shallow marine benthos. The Cenomanian–Turonian OAE was associated with a minor metazoan reef crisis but it is unlikely to be associated with methane release and OA because there was no negative carbon isotope excursion. It rather represents a high-productivity event driven by warming that led to an accelerated hydrological cycling (Scopelliti *et al.*, 2004). Another important OAE occurred in the Valanginian stage (ca. 132 Ma) and was associated with volcanism, positive carbon isotope excursions and a biocalcification crisis in marine plankton (Erba *et al.*, 2004) but neither were reefs affected nor was there a notable extinction.

#### *Global warming vs. OA*

Several authors have emphasized that global warming and OA act in concert to cause severe damage to coral reefs and other ecosystems (Hoegh-Guldberg *et al.*, 2007; Pörtner, 2008). One possibility to separate the effects could lie in geographic and environmental patterns. OA might preferentially affect those regions where the ocean is already less saturated with respect to calcium carbonate. These are high latitude and deeper water areas where corals are considered especially vulnerable to OA (Roberts *et al.*, 2006; Turley *et al.*, 2007). On the other hand, deep water corals might be adapted to low saturation levels and thus less sensitive to drops in pH or hypercapnia. The few experimental data at hand suggest that the azooxanthellate coral *Lophelia pertusa* is sensitive (Maier *et al.*, 2009), whereas the Mediterranean coral *Cladocora caespitosa* is not (Rodolfo-Metalpa *et al.*, 2010).

In any case, the geographic patterns of at least two reef crises suggest that global warming was probably the dominant trigger: the Triassic–Jurassic and the Paleocene–Eocene. In the end-Triassic mass extinction, tropical taxa were significantly more affected than non-tropical taxa (Kiessling & Aberhan, 2007) and earliest Jurassic reefs and reef corals were concentrated in

**Table 2** Summary of results and assessment of OA as a proximate cause

Time	Reef crisis	Biotic change	Evidence for OA
Late Ordovician (445.6–443.7 Ma)	Not evident	Mass depletion of biodiversity during double mass extinction. Unselective with respect to buffering	None
Late Devonian (374.5 Ma)	Mostly metazoan (especially corals and sponges)	Mass depletion of biodiversity. Selective extinction of corals and sponges over prolonged period of time	Weak
Middle–Late Permian (260.4 Ma)	Coral–sponge reef crisis only	Substantial extinction, weakly selective with respect to buffering	None
Permian–Triassic (251 Ma)	Massive for all reef types	Mass depletion of biodiversity and mass extinction, especially for unbuffered organisms	Strong
Triassic–Jurassic (199.6 Ma)	Massive for all reef types	Mass depletion of biodiversity and mass extinction, selective against corals and sponges and unbuffered organisms	Strong
Early Jurassic (183 Ma)	Coral reef crisis	Modest but selective extinction of corals and other unbuffered organisms	Strong
Cretaceous–Paleogene (65.5 Ma)	Not evident	Mass depletion of biodiversity and mass extinction, selective against buffered organisms	Weak
Paleocene–Eocene (55.8 Ma)	Coral reef crisis	Background extinction, except for benthic foraminifers	Strong

OA, ocean acidification.

mid-latitudes (Flügel & Kiessling, 2002; Lathuilière & Marchal, 2009) and in somewhat deeper water (Kiessling *et al.*, 2009) suggesting a heat escape rather than a pH escape. Similarly, in the Paleocene–Eocene crisis the disappearance of coral reefs propagated from tropical to subtropical latitudes (Scheibner & Speijer, 2008) such that global warming is the most plausible proximate cause of the crisis. The observation that extant tropical corals are at a higher risk of extinction in shallow water than in deeper fore-reef slopes (Carpenter *et al.*, 2008) may also suggest that the impact of global warming is currently more severe than that of OA.

An alternative test could be to look for reef crises for which there is evidence for global warming but not for OA. Only the Late Devonian reef crisis may qualify. This reef crisis has no evidence for major volcanism or otherwise caused increases in  $p\text{CO}_2$  but isotopic evidence for warming (Joachimski *et al.*, 2009). Admittedly, these tests are quite conjectural but they simultaneously suggest that global warming was the major trigger in ancient reef crises, augmented but not caused by OA.

## Conclusions

Neither all mass extinction events nor all metazoan reef crises were caused by OA (Table 2). First, reef crises and mass extinction are not always coincident. Five significant metazoan reef crises and five significant depletions in biodiversity are recognized in our data but only three are both reef crises and mass extinctions. Second, only

two mass extinctions concurred with geological evidence of OA. The four out of five matches between inferred OA events and metazoan reef crises is indeed impressive, although global warming associated with these events is at least as probable as a trigger as is OA. The double strike of OA and rapid warming thus seems to be really deleterious for reefs, to a degree that this can almost be seen as a general cause of reef crises.

Although an impressive number of experimental data has accumulated over last years on the sensitivity of marine organisms to OA (compiled in Fabry *et al.*, 2008; Doney *et al.*, 2009), there is a lack of data on many groups that have a rich fossil record. Data on groups such as coralline sponges, brachiopods, bryozoans and pelmatozoans are urgently needed to assess in more detail the potential of OA to play a role in ancient reef crises and mass extinctions.

## Acknowledgements

We thank U. Merkel, A. Hendy, A. Miller, M. Clapham, J. Sessa for recent contributions to the dataset used in this study. This work was supported by the VolkswagenStiftung. Three anonymous reviewers provided valuable comments. This is Paleobiology Database publication #110.

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### Supporting Information

Additional Supporting Information may be found in the online version of this article:

**Figure S1.** Changes (log-return) of globally preserved reef volume in three categories (supplementing Fig. 2). Significant crises are highlighted by black dots and the boundary of the pre-crisis is indicated by a dashed line. The grey box delineates background fluctuations. Arrows indicate that the true value is below the plot margins, which is the case for most reef types after the Permian-Triassic boundary, because no non-microbial reefs are known in the first stage of the Triassic period (log return = minus infinity). O = Ordovician; S = Silurian; D = Devonian; C = Carboniferous; P = Permian; Tr = Triassic; J = Jurassic; K = Cretaceous; Pg = Paleogene; N = Neogene.

**Figure S2.** Preservation (sampling completeness) of stony corals and hypercalcifying sponges versus all other organisms through time. See Fig. 5 for additional information.

**Table S1.** Definition of time intervals for reef crises.

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