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Article

Ocean Acidification and the End-Permian Mass Extinction: To What Extent does Evidence Support Hypothesis?

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Abstract: Ocean acidification in modern oceans is linked to rapid increase in atmospheric CO₂, raising concern about marine diversity, food security and ecosystem services. Proxy evidence for acidification during past crises may help predict future change, but three issues limit confidence of comparisons between modern and ancient ocean acidification, illustrated from the end-Permian extinction, 252 million years ago: (1) problems with evidence for ocean acidification preserved in sedimentary rocks, where proposed marine dissolution surfaces may be subaerial. Sedimentary evidence that the extinction was partly due to ocean acidification is therefore inconclusive; (2) Fossils of marine animals potentially affected by ocean acidification are imperfect records of past conditions; selective extinction of hypercalcifying organisms is uncertain evidence for acidification; (3) The current high rates of acidification may not reflect past rates, which cannot be measured directly, and whose temporal resolution decreases in older rocks. Thus large increases in CO₂ in the past may have occurred over a long enough time to have allowed assimilation into the oceans, and acidification may not have stressed ocean biota to the present extent. Although we acknowledge the very likely occurrence of past ocean acidification, obtaining support presents a continuing challenge for the Earth science community.

Keywords: ocean acidification; end-Permian extinction; microbialite; ocean buffer; stylolite

1. Introduction and Background

Earth-surface change associated with the largest mass extinction in Earth history, the end-Permian extinction, which killed approximately 90% of all marine species 252 million years ago, is recognised to have a complex of components [1]. A debate is developing in the Earth sciences about possible effects of one of these components, ocean acidification, in the process of mass extinction, including the end-Permian event, e.g., [2]. Some authors favor ocean acidification as a process associated with mass extinctions, e.g., [3]. However, there has not yet been an assessment of the quality of the sedimentary evidence of ocean acidification through the end-Permian mass extinction interval, a gap that this paper aims to fill. Firstly, key features are examined, followed by discussion of the potential for ocean acidification in associated with the extinction. We conclude that the evidence is currently equivocal and investigation of past ocean acidification associated with mass extinctions is still in its early stages.

On a broad scale, the well-known GEOCARB III model [4] generated a rapid increase of atmospheric CO₂ through the latest Permian and earliest Triassic, which may be interpreted as being associated with ocean acidification. Certainly, modern oceans are observed to becoming more acid [5] and the cause of increased acidity is considered by most researchers to be rapid increase in CO₂ output to the atmosphere by human burning of fossil fuels [6]. CO₂ is increasing so rapidly that its transfer to the oceans causes ocean pH to fall, measurable over human timescales, with a recorded fall of *ca.* 0.1 pH units [7] over the past few decades. The effect on ocean wildlife includes living corals in particular, which show a reduction in ability to calcify [8].

2. Evidence of Ocean Acidification in the End-Permian Mass Extinction

2.1. Evidence in Sedimentary Rocks

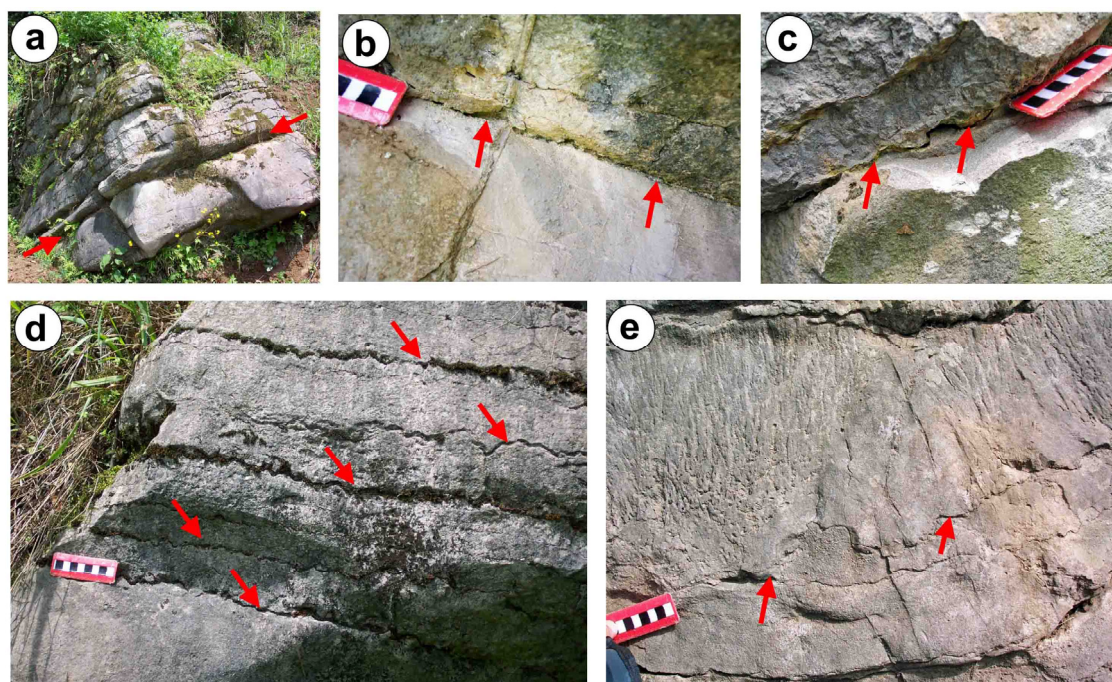
The following description of sedimentary rocks of the end-Permian extinction event is the main focus of this paper, and uses data principally from south China (which was located in eastern Tethys, see [9] for palaeogeographic map showing the locations described in this paper) to illustrate the issues surrounding physical evidence of ocean acidification. Additional information is provided from other regions. A significant aspect is data loss, considered first.

2.1.1. Data Loss Resulting from Erosion and Pressure Solution

Erosion surfaces are common in limestones from the Permian-Triassic transition [10–13] because shallow water limestones of the Permian-Triassic transition formed at a time when sea level was at its lowest position in Phanerozoic history [1]. Thus, exposure of the limestones above sea level was very likely and erosion may have removed evidence of submarine dissolution of carbonate rocks on the sea floor. However, pressure solution is a much greater problem, produced by weight of overlying rock, and/or compressive stresses in tectonically-active regions, leading to chemical instability in buried limestone, thus dissolution of calcium carbonate, with the dissolved matter being removed in

groundwaters through cavities and fractures in the limestone [14]. The resulting uneven to jagged lines (stylolites) in vertical cut sections of limestones may represent many centimeters of rock lost from the sedimentary record, easily noticed in outcrop (Figure 1). Furthermore, stylolites commonly form along bedding surfaces (Figures 1d and 2a), thereby obscuring palaeoenvironmental change, and are very problematic for study of facies in the end-Permian event.

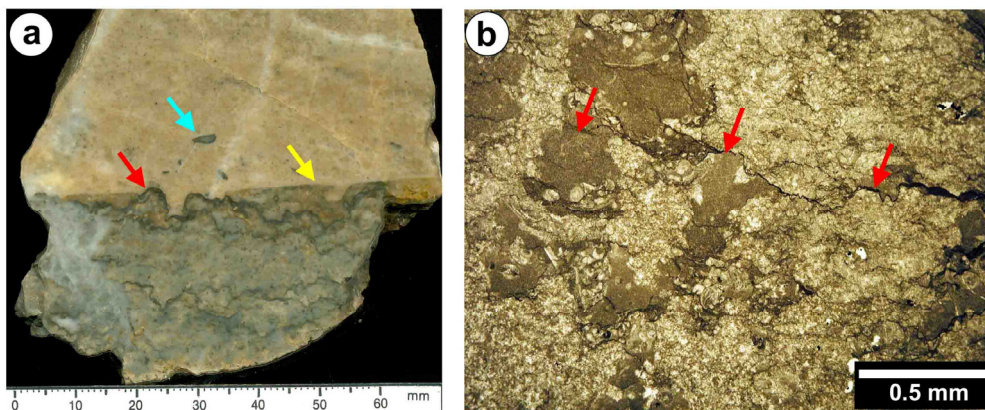
Figure 1. Field photographs of the Permian-Triassic boundary interval in Dongwan locality, Sichuan Province, South China. (a) Latest Permian Changhsingian limestones (below red arrows marking the boundary between Changhsingian limestones and the post-extinction microbialite) are conformably overlain by post-extinction microbialites; (b) and (c) Views of the contact between latest Permian limestones and microbialite; the contact represents the latest Permian pre-extinction beds, followed by post-extinction facies. The contact is bed-parallel but is marked by prominent irregular stylolites (red arrows) representing an unknown amount of dissolution of rocks in the critical extinction levels. No researchers have yet described an unstylolitized transition across the extinction boundary in the Sichuan and Chongqing sites; (d) Bed contacts in the microbialite are all marked by stylolites (red arrows); (e) Prominent stylolite (red arrows) near the top of the microbialite, representing substantial loss of limestone by dissolution.



Even small-scale pressure solution influences analysis of details (Figure 2b, and further images in Figures 3–5 described later). It is also important to be aware of the wide variety of occurrence of pressure solution. Stylolites may occur as seams lacking the familiar jagged appearance of stylolites [14] (Figure 4.18), so that the preserved pressure solution effects may be subtle. In Sichuan and Chongqing of South China, where post-extinction limestone sequences are widespread, *none* of the papers published on these rocks reported any places where the contact between pre- and post-extinction rocks was unaffected by stylolites; thus the original depositional nature of the contact has not been determined. Very good examples of pressure solution overprinting facies change are shown in

Figures 3 and 4, where interpreted erosion surfaces became the focus of stylolite formation because of change in the facies along the erosion surface. Such problems have so far prevented any possibility of determination of whether submarine dissolution of limestone on the sea floor, and therefore ocean acidification, affected extinction-interval deposits or not, in rocks of Sichuan and Chongqing (Figure 1).

Figure 2. Details of effects of pressure solution in microbialites after the end-Permian extinction. **(a)** Vertical section of polished slab from the microbialite formed after the end-Permian extinction at Yudongzi site, NW Sichuan [9] showing microbialite (dark grey in lower part) overlain by fine-grained grainstone that has a flat erosion surface (yellow arrow) shortly above the microbialite; the erosion surface is followed by more grainstone containing intraclasts (light blue arrow) of microbialite limestone. Note the interruption of the sequence by prominent thick stylolites (red arrow) in the microbialite, making the precise interpretation of the sequence of events unclear. Also the erosion surface demonstrates loss of rock, indicating a potential problem for identification of submarine dissolution if ocean acidification affected these facies; **(b)** Thin section of microbialite from the Huaying Mountains of Sichuan, showing material has been removed along stylolites (red arrows).

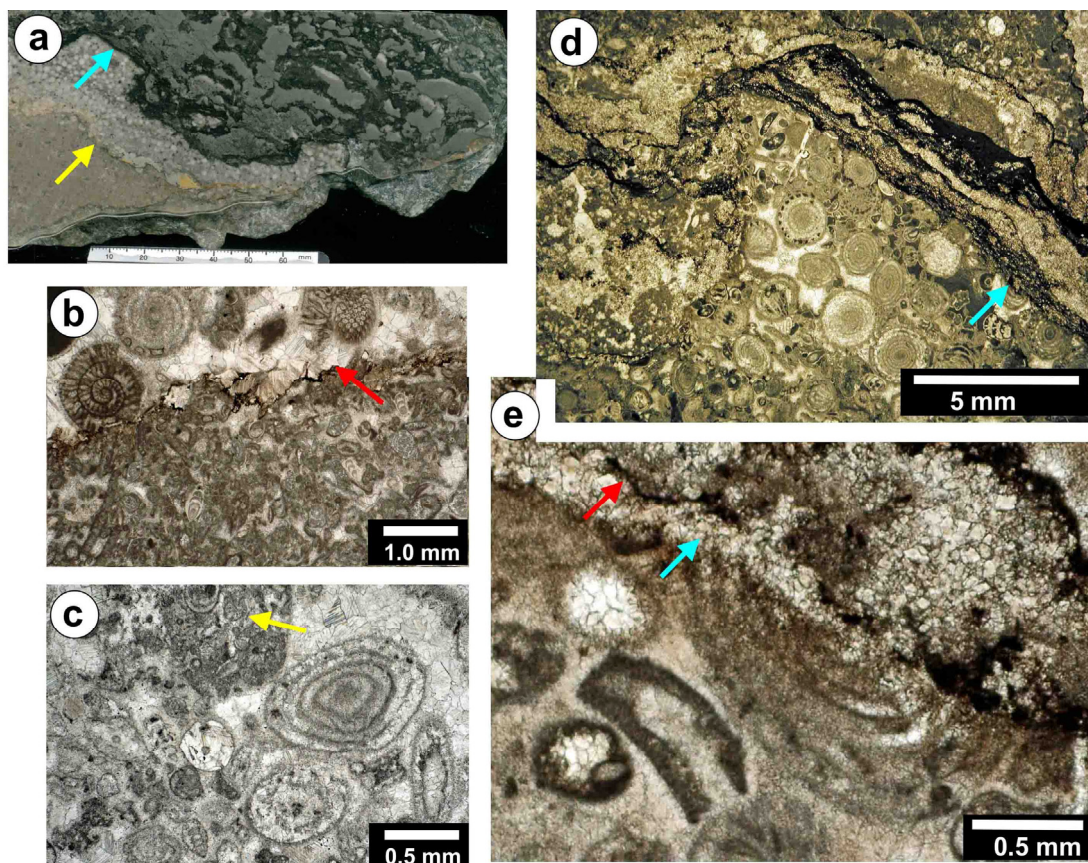


2.1.2. Possible Dissolution Surfaces in South China

The possibility of identifying ancient dissolution surfaces for the end-Permian extinction [12] was considered further in work [15,16] that drew attention to the problems of proving dissolution occurred below sea level, in contrast to dissolution in subaerial (vadose) conditions. The latter is simply the effect of acid rain on limestone. On one of those same surfaces (in Guizhou Province, China), evidence that the limestones were exposed above sea level is the presence of pendent and meniscus calcite cements [15] formed in spaces between grains occupied by air, not water; *i.e.*, the rock was above sea level when the cements formed. Nevertheless sea-floor dissolution may have occurred, but the evidence removed when the rocks were subject to freshwater processes; the difficulty is proving dissolution of the sea floor under marine conditions. An additional problem is that each geographic area with records of the shallow-water Permian-Triassic transition has its own tectonic and environmental history; the precise sequence of events in any one place throughout the extinction interval differs from others [9], with common interference by pressure solution.

Figures 3 and 4 show that stylolites formed a haphazard interruption, and careful searching of thin sections is necessary to find areas unaffected by them. Thus, even if it is possible to identify any one erosion surface that may have been affected by marine dissolution, a combination of effects of pressure solution and stratigraphic differences between sites are so great that the task of *correlating* a surface is likely to be impossible. Correlation of surfaces affected by ocean acidification would be a desirable goal if acidification is demonstrated in future work.

Figure 3. Vertical sections through the latest Permian limestones and overlying post-extinction microbialite at Langbai, Great Bank of Guizhou, South China [9,11,12]. (a) Polished block showing two erosion surfaces (yellow and blue arrows) in the latest Permian grainstones followed by dark-colored microbialite in micrite; (b) Enlargement of lower erosion surface in (a), showing the contact is a stylolite (red arrow); but (c) shows an intraclast (yellow arrow) of the lower limestone within the upper Permian limestone; therefore the lower limestone was eroded, but a stylolite along the erosion surface is the result of pressure solution that removed all evidence of the nature of that contact; (d) Enlargement of the upper Permian limestone (rich in foraminiferids), with a prominent erosion surface (light blue arrow) encrusted by altered microbialite, which also has abundant stylolites; (e) Enlargement of another area of the same thin section of the contact shown in (d), demonstrating the problems of stylolites in these rocks; the erosion surface (light blue arrow) is clear, but is close to stylolites (red arrow) cutting through the microbialite above it. On the lower right of the photo, the stylolite meets the erosion surface.



Dissolution surfaces are not limited to the contact between the latest Permian limestones and post-extinction facies; upper parts of the post-extinction microbialite in Sichuan contain evidence of solution (Figure 5, also [9]). Whether this surface represents dissolution below or above sea level is not currently determinable from present evidence. Thus whether this microbialite was affected by lowered ocean pH some time after extinction or not is open to interpretation. Instead it may simply be a subaerially-exposed surface that was dissolved and mineralized prior to submergence and burial by gastropod-rich grainstone.

Figure 4. Further views of the upper Permian limestones from Langbai site in Guizhou Province, China, shown in Figure 3d. **(a)** Montage showing that most of the erosion surface coincides with a stylolite (red arrows), and only in a small area in the lower right is the erosion surface clearly displayed (blue arrow), enlarged in **(d)**; **(b)** Enlargement of a foraminiferan in the centre of **(a)**, showing marginal dissolution of the test (yellow arrow); the intergranular space is filled with micrite after dissolution; **(c)** A portion of the same limestone a few cm below **a**, showing a foraminiferan grainstone, where foraminifera are substantially recrystallized; **(d)** Enlargement of the right hand portion of **(a)**, showing a complex pattern of erosion surface (blue arrows) and stylolites (red arrows), illustrating the detailed nature of the problem of pressure solution in determining the precise nature of grain boundaries and erosion surface contacts. Such problems have significant implications for identifying surfaces that may have been affected by sea-floor dissolution due to ocean acidification, discussed in the text. Small dolomite rhombs replaced some of the depositional fabric.

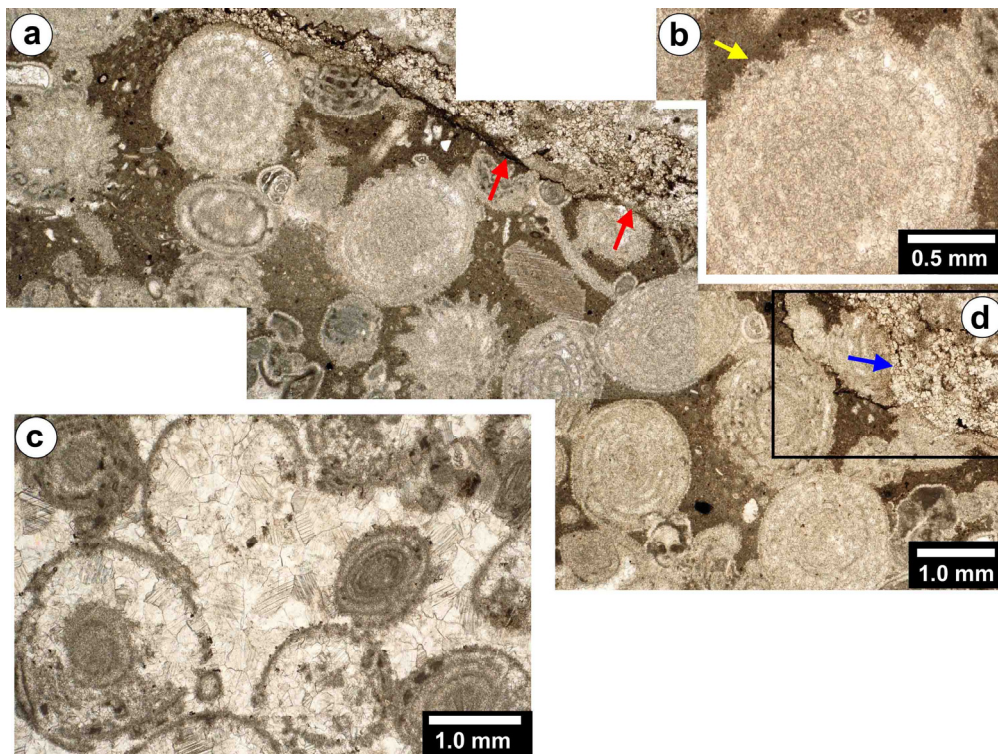


Figure 4. Cont.

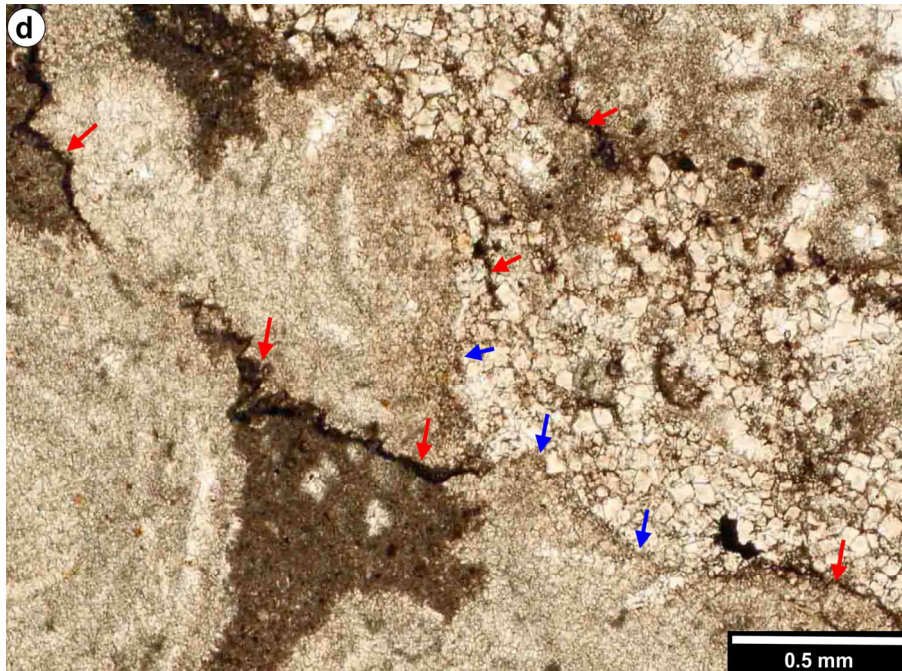
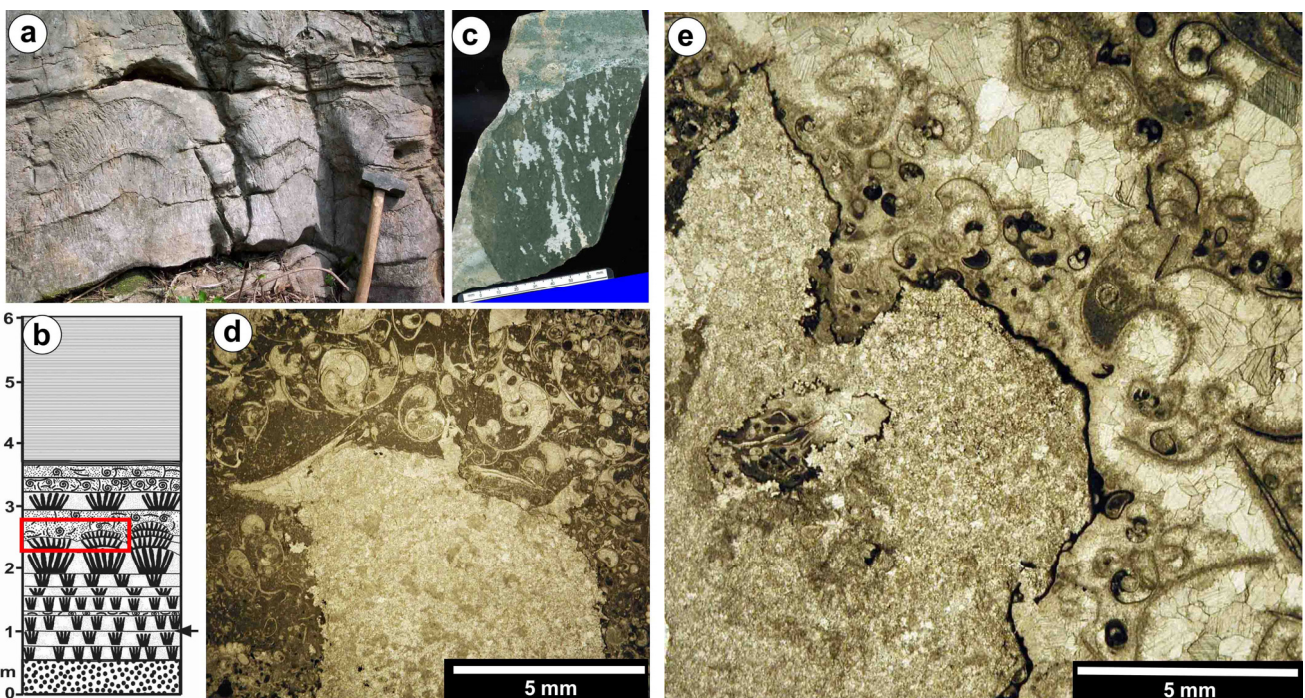


Figure 5. Erosion in the upper part of a post-extinction microbialite at Dongwan in Sichuan Province [9,15]. (a) Field view of microbialite domes; (b) Log of the microbialite, showing the location of the area of (a) in the red box. The arrow lower right shows the level of the lowest occurrence of *Hindeodus parvus*, the marker conodont for the Permian-Triassic boundary; (c) Vertical section of a polished block showing eroded upper surface of the dome, enlarged in (d); (e) Another view of the eroded surface showing apparent dissolution and mineralization of the surface with opaque minerals. The eroded mineralized surface is covered by gastropod grainstone prior to final growth of microbialite shown in (b).



2.1.3. Other Areas

Permian-Triassic transition facies in southern Turkey at the well-known Çürük Dag site [12] were located in a western Tethyan position on the Gondwana margin. The latest Permian rocks are wackestones with a smooth polished erosion surface; overlying this are beds of grainstones that have stylolitized contacts, followed by a complex sequence of microbialites and associated facies. None of these beds shows physical evidence that can be unequivocally attributed to submarine dissolution. Pressure solution forming stylolites at bed contacts is a significant problem for analysis of facies change in this locality [12].

In the Dolomites of Italy, at another western Tethyan site, grain dissolution is reported associated with an unconformity labeled U2 in the Permian-Triassic transition in the Dolomites of Italy [13]. The location is within the Bellerophon Gulf, which was largely surrounded by land. Grain dissolution in the shallow waters was interpreted [13] to be a result of enhanced atmospheric CO₂ which led to acid rainwater runoff from land into the shallow sea of the Bellerophon Gulf. In the foreshore-offshore transition zone, grain dissolution is not recorded [13] indicating that, if marine dissolution did indeed occur, it was localized to the shallowest waters and not applicable to the global ocean. The close proximity of the unconformity U2 also allows for the possibility that dissolution was in subaerial conditions or in the marine-freshwater mixing zone, instead of being marine. Finally, in the Permian-Triassic boundary transition in the western Tethyan site at Abadeh, Iran, interpretations of dissolution of sediment by oceans charged with CO₂ [17] are not supported by any physical evidence in the rocks [18].

2.2. Evidence from Fossil Groups

Interpretation of potential effects of ocean acidification has been recently well-described [19] and references therein, so an outline is provided here. Most fossils are made of calcium carbonate, and calcifying organisms may be divided into three groups [19]: heavy calcifiers (also called hypercalcifiers, including corals and sponges, common in ancient reefs), moderate calcifiers (including molluscs, abundant within microbialites after the extinction, Figure 5) and little-to-none calcifiers (including conodont animals, important for Permian-Triassic boundary stratigraphy). Recognition of these three groups provides a powerful argument for ocean acidification because the fossil groups most affected by the end-Permian extinction were heavy calcifiers [19]; such organisms are physiologically less capable of buffering against changes in ocean pH, and are subsequently adversely affected by small changes in pH. Hypercapnia is the term applied to organisms subject to adverse effects of CO₂. In contrast, moderate and little-to-none calcifiers are less affected and in the fossil record they are noticeably less subject to extinction, according to a recent compilation [19]. Because of their ecological importance as reef-builders, modern scleractinian corals (hypercalcifiers) are under intense scrutiny in relation to ocean acidification and an excellent summary of the current situation regarding coral growth in conditions of falling pH [8] shows that ocean acidification causes reduced coral growth. Ancient corals and other hypercalcifiers such as calcified sponges, which were also badly affected by the end-Permian event, as, therefore, were the organic reefs they built, leading to a significant time gap when reefs were absent in the Early Triassic [1].

3. Discussion

Three problems present a barrier to interpretation of ocean acidification during the end-Permian mass extinction, discussed briefly below.

3.1. Petrographic Observations and Proxy Data in Sedimentary Rocks

Lack of provable physical evidence of ocean acidification in the sedimentary rocks through the extinction interval, as illustrated in this paper, is a significant problem for the hypothesis of ocean acidification as a contributor to the end-Permian mass extinction. It is possible that ocean acidification was not sufficiently intense to dissolve limestone on the seafloor, but if that was the case, then no evidence would be expected, and no suggestions of observations of dissolution would be necessary. The rocks illustrated here are all from shallow marine carbonate facies, and it may be argued that deeper water settings could provide more information, because erosion of sediments is less important in the deep shelf, as discussed further below.

An important recent development in exploration of end-Permian ocean acidification uses Ca isotopes in shallow water [3] and deeper shelf [20] sections in China. The ratio between the important two stable Ca isotopes ($^{44/40}\text{Ca}$) shifts negative with increased ^{40}Ca input derived from terrestrial weathering since almost all Ca is ^{40}Ca ; such weathering implies an increase in atmospheric CO_2 , so a negative Ca isotope excursion should be compatible with increased ocean acidity. Nevertheless, the $^{44/40}\text{Ca}$ ratio in marine minerals is not a direct indicator of ocean pH; also, raised weathering of terrestrial rocks may be expected to also produce large amounts of bicarbonate, transported to the oceans in rivers along with the Ca, having the potential to limit the fall in pH.

To develop this discussion further, two features of the end-Permian event highlighted by [3] in relation to ocean acidification are considered briefly here. (1) Synchrony of post-extinction oolites and microbialites should reflect synchronous drastic changes in the oceans. Although we agree with this idea, the problem is that synchrony of Permian-Triassic boundary oolites and microbialites between widely-separated sites is not confirmed because of stratigraphic variation of the base of these facies in relation to both the first appearance of *Hindeodus parvus* (the zone fossil for the base of the Triassic) and the prominent negative carbon isotope excursion [9]. If it is assumed that both these features are (individually) globally synchronous, then variation in local and regional environmental processes may have created diachronism in the onset of post-extinction oolites and microbialites (see [9] for details), which awaits more precise stratigraphy before they can be fitted to interpretations of ocean acidification. (2) Rapid CO_2 release may be the reason for the prominent carbon isotope negative excursion associated with the end-Permian event; therefore a short-term large increase in CO_2 could have acidified the oceans, reflecting negative Ca isotope shift. Unfortunately this interpretation suffers from the fact that there are numerous interpretations of the carbon isotope curve [9], not all of which involve injection of CO_2 into the oceans and no certainty of any of them has been demonstrated; thus whether that excursion was due to a large CO_2 release capable of acidifying the oceans, or not, awaits more work. In addition, the use of one proxy (carbon isotopes) to provide support for another proxy (calcium isotopes) is problematic if neither are reliably tied to a known process.

The recent report of a negative Ca isotope excursion, in conodont phosphate, at the Global Stratotype Section and Point (GSSP) at Meishan, south China [20] is a valuable addition to calcium isotope work because it uses non-carbonate material and therefore shows the Ca isotope changes are not just in carbonate minerals. Also significant is that the setting of the Meishan GSSP is deeper shelf (too deep for microbialites [9]) and less likely to be eroded, although small erosion surfaces do exist and there is much bioturbation in the Meishan sediments across the Permian-Triassic Boundary [21]. Overall, therefore, Ca isotope work is an additional proxy in its early days of application and much more investigation is required before it can be considered a reliable indicator of ocean acidification at the end-Permian mass extinction.

3.2. Fossil Data

Fossil shells of marine animals that may have been affected by ocean acidification are an imperfect record of past environmental conditions. Key to understanding ocean acidification from fossil data is the extent to which particular groups of organisms are affected by lowered pH, so any classification of organisms that allows pH to be included as a mechanism leading to extinction or reduction of diversity and numbers of fossils will be of value. As noted earlier, a comprehensive compilation of data on hypercalcifiers in contrast to non-hypercalcifiers [19] shows an overall decline in hypercalcifiers in association with the end-Permian event. This trend is compelling evidence for lowered ocean pH at that time, but whether or not ocean acidification is the *only* reason for reduction in hypercalcifiers remains to be demonstrated. A big difference exists between a dataset that shows a tendency, on the one hand, and a proof of environmental process that drives that tendency, on the other hand. In the absence of another reason to explain selective extinction of hypercalcifiers, the effects of ocean acidification is currently the best interpretation, but it is yet to be verified.

3.3. Rate of CO₂ Increase, Dating Issues and Geography

Critical to interpretations of ocean acidification in the past is the rate of release of CO₂ into the ocean-atmosphere system. The current high rate of increase of CO₂, a measured change, may not reflect the rate of natural increase in the geological past, which in contrast cannot be assessed instrumentally and requires proxies to estimate the changes. The very recent past can be dated with precision on annual to sub-annual scales and resolution generally decreases in older rocks. Thus in the deep-time rock record, the resolution is on the order of thousands of years at best. Therefore a large past increase in CO₂ may have occurred over a long enough time period to allow the ocean systems to assimilate the excess, and acidification may not have excessively stressed ocean biota to the degree that is happening at present.

A glance at the Intergovernmental Panel on Climate Change compilations of changes in CO₂ during the Quaternary ice-age episode of Earth history [6] shows that the rate of rises and falls of CO₂ that accompany glacial and interglacial phases are rather small compared to the modern rapid unrelenting increase. Even so, the amount of CO₂ in the atmosphere in current and past Quaternary times is very small compared to the CO₂ levels of earlier millennia, tens to hundreds of million years ago [4]. Past catastrophic environmental events, such as the Siberian volcanics of the latest Permian, might be expected to have rapidly injected large amounts of CO₂ into the atmosphere. Therefore, if the rate of

CO₂ injection into Earth surface environments was more rapid in ancient past times, the resultant ocean acidification may be presumed to have been greater than present times [2,19,22]. On the basis of such information, it is feasible that ocean acidification played a part in past Earth surface crises, but the importance of the rate of change cannot be overemphasized. If the ancient natural rate of CO₂ rise was slower than is presently occurring, then the ocean may have been able to absorb the increase by shifting the balance between CO₂, HCO₃ and CO₃ dissolved in the oceans, a process called ocean buffering [14]. Thus, over 1000 years or more, the additional CO₂ dissolved in the oceans may be expected to equilibrate with the ocean carbonate system.

Because CO₂ is highly mobile in the ocean-atmosphere system, and therefore the flux of CO₂ is quickly responsive to change in amount of CO₂, ocean pH change is expected to accompany rapid CO₂ fluxes and probably occurred numerous times throughout the rock record [2]. The best known past event, that provides the best fitting data for ocean acidification, is the rapid environmental change of the Palaeocene-Eocene Thermal Maximum (PETM) 55 million years ago, for which it is hypothesized that the oceans showed an increase in acidity [8,22]. The evidence includes a gap in the preservation of coccolith oozes in deep-ocean cores at a level coincident with the PETM, interpreted as being due to dissolution on the sea floor [22]. For the end-Permian extinction, coccolith oozes were not available because they did not evolve until later; also there is a lack of preserved ocean crust of 250 million years ago, making it difficult to test the potential effects of ocean acidification in the late Permian oceanic realm. Several authors, e.g., [3,10,23] have proposed that ocean acidification was the result of large-scale environmental disruption caused by the giant Siberian volcanic eruption that occurred at approximately the same time as the extinction. Calculations of CO₂ output are provided in the literature, e.g., [24,25]; although there are large error bars on estimates of past CO₂ levels [4] these suggest sufficient output to enhance global temperatures, and it is a reasonable argument that ocean acidification took place. A recent comparison between the rate of CO₂ output by volcanoes and anthropogenic sources [26] shows that the latter is greater, emphasizing the importance of anthropogenic output. Thus, in the short term, the modern CO₂ rise may diminish, or perhaps even override, the ocean buffer to cause oceans to become acid. Conversely, although the output of CO₂ over the period of eruption of Siberian volcanics *ca.* 252 million years ago may have been huge, if this occurred over a long time period (estimated to be *ca.* 600,000 years, [1]), then the ocean pH buffer may have assimilated the increase and was not necessarily overridden. The extinction took *ca.* 150,000 years [1]; in contrast the modern oceans mix in around 1000 years, which is currently too slow to assimilate the anthropogenic CO₂ output. Gradual CO₂ output and absorption in the end-Permian event conflicts with the interpretation of negative Ca isotope shift as a fall in pH.

Another aspect of ocean buffering in relation to the debate about ocean acidification, that may have implications for the past, is the geographic distribution of the ocean buffer capacity. Modern oceanographic work [27–29] demonstrates variability in the ocean buffer, using the Revelle Factor (an indicator of the efficiency of the ocean buffer). Fundamentally, the ocean buffer is less efficient in low latitude warm subtropical-tropical waters and more efficient in cooler higher latitudes, but the detailed pattern is complicated, as shown by maps in [27], and is influenced by the geographic distribution of continents. This has relevance to the end-Permian event, because not only was the continental configuration hugely different from modern times (see palaeogeographic map in [9]), but also most of the Permian-Triassic boundary carbonate sequences are located within Tethys Ocean, in low latitude

settings distant from land. These include all the examples illustrated in this paper. Such concentration of carbonate sediments in shallow waters might have enhanced the buffering capacity within Tethys, but this is misleading because the modern ocean buffer is not related to the types of sediment on the sea floor at any point on the Earth's surface. Instead it is governed by the composition of dissolved matter in the oceans, and to a lesser extent the composition of unconsolidated sediments on the sea floor [27–29]. Revelle Factor distribution maps [27,29] show the carbonate buffer varies on oceanic scales, mostly a long way from land and in deep water; thus the formation of deposits in environments with abundant shallow-water carbonates versus environments lacking carbonates are not relevant, at least for the modern oceans. For the Permian-Triassic times, Tethys was substantially enclosed by land of northeastern Laurasia and southeastern Gondwana, and carbonates of the end-Permian event are most common in low latitude positions. It is even possible that the buffer was *less* efficient in such a low latitude setting, in keeping with modern Revelle Factor maps, where the buffer may be more likely to have been overridden, leading to carbonate rock dissolution on the shallow sea floor; but the illustrations in Figures 1–5 do not show this. Finally, Tethys had an open connection east to the Panthalassa ocean, which presumably led to global circulation of surface waters and opportunity for long-term equilibration of the carbonate buffer. Thus, although geographic variations in the carbonate ocean buffer would be expected for the end-Permian event, global ocean acidification during the end-Permian extinction is feasible, providing the CO₂ emission rates were high enough.

4. Conclusions

Despite the likely occurrence of ocean acidification in Earth's past history, and the valuable compilations of fossil and isotope data, to our knowledge no observations exist of cases where acidification can be unequivocally demonstrated, with the possible exception of the Palaeocene-Eocene Thermal Maximum. Regarding the end-Permian mass extinction, we are in full agreement with other researchers about the applicability of the concept of ocean acidification; the vast outpouring of volcanic products of the Siberian eruptions must have led to a large increase in atmospheric CO₂, and it is entirely reasonable that ocean acidification resulted, if the rates were great enough. However, until definite evidence is found in the rocks, nobody will be able to say with confidence that ocean acidification was a significant process in the end-Permian mass extinction.

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