

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: http://www.journals.elsevier.com/journal-of-palaeogeography/



Lithofacies palaeogeography and sedimentology

Beef and cone-in-cone calcite fibrous cements associated with the end-Permian and end-Triassic mass extinctions: Reassessment of processes of formation



Stephen Kershaw a,*, Li Guo b

- ^a Department of Life Sciences, Brunel University, Kingston Lane, Uxbridge, Middlesex, UB8 3PH, UK
- ^b CASP, University of Cambridge, 181a Huntingdon Road, CB3 0DH, Cambridge, UK

ARTICLE INFO

Article history: Received 5 August 2015 Received in revised form 17 November 2015 Accepted 17 November 2015 Available online 25 December 2015

Keywords:

End-Permian mass extinction End-Triassic mass extinction Beef Cone-in-cone calcite Ocean acidification

ABSTRACT

This paper reassesses published interpretation that beef and cone-in-cone (B-CIC) fibrous calcite cements were precipitated contemporaneously just below the sea floor in unconsolidated sediment, in limestones associated with the end-Permian (P/T) and end-Triassic (T/J) mass extinctions. That interpretation introduced the concept of a sub-seafloor carbonate factory associated with ocean acidification by raised carbon dioxide driven by volcanic eruption, coinciding with mass extinction. However, our new fieldwork and petrographic analysis, with literature comparison, reveals several problems with this concept. Two key points based on evidence in the T/J transition of the UK are: (1) that B-CIC calcite deposits form thin scattered layers and lenses at several horizons, not a distinct deposit associated with volcanic activity; and (2) B-CIC calcite is more common in Early Jurassic sediments after the extinction and after the end of the Central Atlantic Magmatic Province volcanism proposed to have supplied the carbon dioxide required.

Our samples from Late Triassic, Early Jurassic and Early Cretaceous limestones in southern UK show that B-CIC calcite occurs in both marine and non-marine sediments, therefore ocean processes are not mandatory for its formation. There is no proof that fibrous calcite was formed before lithification, but our Early Jurassic samples do prove fibrous calcite formed after compaction, thus interpretation of crystal growth in unconsolidated sediment is problematic. Furthermore, B-CIC crystals mostly grew both upwards and downwards equally, contradicting the interpretation of the novel carbonate factory that they grew preferentially upwards in soft sediment. Finally, Early Jurassic and Early Cretaceous examples are not associated with mass extinction.

Three further key points derived from the literature include: (1) B-CIC calcite is widespread geographically and stratigraphically, not clustered around mass extinctions or the Paleocene-Eocene Thermal Maximum (PETM) event; (2) isotope signatures suggest B-CIC calcite formed under high pressure in burial at 70-120 °C, incompatible with interpretation of formation of B-CIC calcite at the redox boundary below the ocean floor; and (3) B-CIC calcite reported in P/T boundary microbialites in one site in Iran is the only occurrence

E-mail address: Stephen.kershaw@brunel.ac.uk (S. Kershaw).

Peer review under responsibility of China University of Petroleum (Beijing).

^{*} Corresponding author.

known despite extensive published studies of similar shallow marine settings, demonstrating its formation is localized to the Iran site.

Based on the above evidence, our opinion is that B-CIC calcite is best explained as a later diagenetic feature unrelated to rapid Earth-surface environmental change associated with mass extinctions; thus a novel carbonate factory is highly unlikely.

Copyright © 2015 China University of Petroleum (Beijing). Production and hosting by Elsevier B.V. on behalf of China University of Petroleum (Beijing). This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction and aim

The occurrence of two types of fibrous diagenetic calcite called "beef" and "cone-in-cone" calcite in limestone has been known in the literature for a long time (e.g. Lang et al., 1923; Richardson, 1923). A commonly accepted explanation of these fibrous calcite types (see Cobbold et al., 2013 for a review) is that they formed under high hydraulic pressure and raised temperatures in deep burial (Cobbold and Rodrigues, 2007) and this has been used as part of the evidence of stresses in tectonic belts (e.g. Le Breton et al., 2013). Evidence that these fibrous calcite growths are additional precipitates on existing limestones (e.g. Marshall, 1982) includes growth on nodules such as the birchii nodules in the Lower Jurassic of southern England reported by Hesselbo and Jenkyns (1995) and well illustrated in photographs of the celebrated website of Ian West (http://www.southampton.ac. uk/~imw/Lyme-Regis-to-Charmouth.htm). Interpretations focus on formation in burial as a late diagenetic development. It is therefore of great interest that a completely different interpretation has been proposed by Greene et al. (2012) in relation to extreme environmental change in the oceans, associated with the Triassic-Jurassic boundary extinction event, employed also by Heindel et al. (2015, published online in 2013, but formally published in 2015) for the Permian-Triassic boundary extinction. These two studies presented arguments that such fibrous calcite fabrics were instead formed in the shallow sea floor, contemporaneous with deposition, as a response to enhanced carbon dioxide input into the atmosphere resulting from large-scale volcanic eruptions in the Late Permian and Late Triassic; the carbon dioxide was transferred to the oceans and interpreted to have acidified the seawater. Raised total dissolved inorganic carbon resulting from these changes is proposed by Greene et al. (2012) to have led to intense precipitation of fibrous calcite below the sea floor, at the redox boundary, for the end-Triassic event.

Although much published work exists on "beef" and "cone-in-cone" calcite (hereafter called B-CIC calcite), studies by Greene et al. (2012) and Heindel et al. (2015) are the only two that explore a relationship between mass extinctions and B-CIC calcite. The aim of our study is to further investigate this potential relationship; our focus is on B-CIC and mass extinctions and necessarily addresses data and interpretations presented by Greene et al. (2012) and Heindel et al. (2015). We wish to stress that readers should be aware this paper is not

intended as a critical comment of their work, but a reassessment of the concept of the subsea carbonate factory.

2. Brief literature review of beef and cone-incone (B-CIC) calcite

Recent comprehensive reviews of the literature on B-CIC calcite are provided by Cobbold et al. (2013) and Heindel et al. (2015), so only a brief outline is presented here; readers are directed to those two papers for detailed reviews. Three minerals may form these fibrous cements (calcite, gypsum and quartz), but only calcite is present in samples examined here, relevant to the work by Greene et al. (2012) and Heindel et al. (2015). Calcite beef comprises fibrous calcite with fibers orientated approximately normal to bedding. Cone-in-cone calcite (CIC calcite) consists of masses of nested crystals of calcite forming the appearance of stacked cones, similar to stacks of cone-shaped paper cups in public water dispensers. The crystals converge in three dimensions, the axes of cones being orientated approximately normal to bedding. Both beef and CIC calcite occur together in the Lower Jurassic at Lyme Regis in Dorset, southern England, with CIC calcite the most abundant. All the samples illustrated in this paper are CIC calcite; samples collected as beef are actually CIC form when examined in detail. Heindel et al. (2015) regarded B-CIC structures as consisting of several superficially similar types of fabric but which have differences in detail; they used the term "calyx-like" for the cone-in-cone structure they described.

Early detailed descriptions and discussion by Lang et al. (1923) and Richardson (1923) remain relevant today. The youngest portions of CIC calcite masses are the wider ends of the cones, which thus taper towards their origins (see detailed diagrams in Richardson, 1923). Published interpretations suggest that B-CIC calcite formed in open fractures (e.g. Cobbold et al., 2013) or formed additional growth in the sediment during diagenesis (see review in Heindel et al., 2015). The interpretation that B-CIC calcite represents formation in deeper burial at higher temperatures than surface conditions is based on calculations from oxygen isotopes (70-120 °C for calcite, Cobbold et al., 2013). Thus publications on B-CIC calcite largely interpret its formation in later diagenesis in deeper burial. However, earlier work by Franks (1969, p. 1446) viewed B-CIC in brackish conditions in the Cretaceous of Kansas as formed earlier, in shallow burial, because (1) sandstone layers and shale laminations are distorted by the B-CIC growths; and (2) quartz grains occur within the B-CIC layers. It is a matter of

debate as to whether the samples studied by Franks (1969) do actually represent early formation, because growth of fibrous calcite in buried shale is likely to induce distortion. Marshall (1982) showed how sandstone layers can be parted by the displacive force exerted during B-CIC calcite growth. The literature demonstrates varying opinions about the conditions of formation of B-CIC calcite. However, for the particular B-CIC deposits in the Triassic–Jurassic extinction horizons studied by Greene et al. (2012), the established interpretation is formation in later burial (see Cobbold et al., 2013). Thus the interpretation by Greene et al. (2012) (and Heindel et al., 2015 for the Permian–Triassic extinction) that these fibrous calcite layers represent early cementation in very shallow burial in marine environments associated with mass extinctions is a novel interpretation for those deposits.

3. Materials and methods

Materials and methods used in this paper include observations and interpretation from fieldwork, polished hand specimens and thin sections of new samples from key sites in the Upper Triassic, Lower Jurassic and Lower Cretaceous rocks of southern UK (Fig. 1). Material was collected from: (1) the Upper Triassic of Lavernock Point near Cardiff, South Wales (N 51°24′24.88″; W 3°10′10.73″), in a sequence that approximately

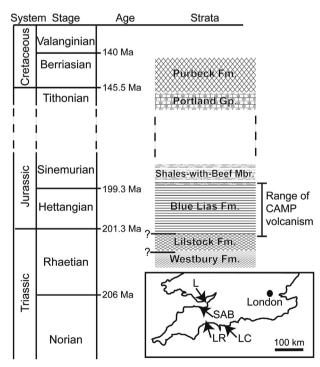


Fig. 1 — Outline stratigraphy of the deposits studied in this paper, not drawn to scale. Details are given in the text, including discussion of absolute ages. Inset shows locations of sites in southern England and South Wales discussed in the text. L = Lavernock Point, near Cardiff, South Wales; LR = Lyme Regis, Dorset, England; LC = Lulworth Cove, Dorset; SAB = St Audrie's Bay, Somerset, England. Gp. = Group; Fm. = Formation; Mbr. = Member; CAMP = Central Atlantic Magmatic Province.

coincides with the end-Triassic extinction event, as noted above; (2) the Lower Jurassic Shales-with-Beef Member at Lyme Regis, West Dorset (N 50°37′03.20"; W 2°14′39.09"), and nearby Charmouth; and (3) the Lower Cretaceous uppermost Purbeck limestones on the eastern side of Lulworth Cove, East Dorset (N 50°43′03.27"; W 2°56′55.00"). (2) and (3) are located on the Jurassic coastline of South Dorset, on the southern shore of central England. Observations are compared with the literature, for discussion of controls of the fabrics. Samples from Lavernock Point were collected in place, but all the material from Lyme Regis and Lulworth was from loose rock from cliff falls, partly to respect the World Heritage status of the Jurassic coast, but also because cliff falls covered the foot of cliffs at Lyme Regis at the time of our fieldwork and also created sample collection hazards. Field observations of inplace B-CIC layers at Charmouth (1 km east of Lyme Regis) supplemented the Lyme Regis work. Although precise stratigraphic horizons are not known in loose material, sample provenance is closely related to the outcrops. Determining way up of loose material of beef and cone-in-cone calcite can be problematic because these fibrous calcite cements grew antitaxially (away from their substrate), exemplified by their growth on concretions, as detailed by Marshall (1982) where fibrous calcite grew upwards, downwards and sideways away from the concretion substrate of his study. Nevertheless, geopetal fabrics are present in key samples illustrated here, so this study of the processes of formation of the fibrous calcite is unaffected by using loose material.

4. Observations of beef and cone-in-cone (B-CIC) calcite

4.1. Westbury Formation, Upper Triassic, Lavernock Point, South Wales

Lavernock Point (Fig. 1) has cliff exposures of Upper Triassic and Lower Jurassic rocks of the Rhaetian Rhaetipollis germanicus Zone (Mander et al., 2008; Fig. 2). Fig. 2A demonstrates the bed-parallel and interbedded nature of two prominent limestone beds in shales of the Westbury Formation (upper Penarth Group) at Lavernock Point (see also log in Mander et al., 2008, their Fig. 2).

CIC calcite forms at the upper and lower contacts between shales and limestones in both beds exposed at Lavernock Point and also occurs within shales. In the limestone beds, CIC calcite crystals are orientated upwards in the upper contact and downwards in the lower contact of each bed (Fig. 2B), thus displaying antitaxial growth (the crystals grew away from their substrate). Downward-growth of CIC calcite is shown in Fig. 3, with cone-in-cone crystal heads (informally called "nailheads") protruding downwards into underlying shales; nailheads also project upwards on the top surfaces of upwardorientated CIC calcite. Fig. 4 displays cross-sections through the upper and lower portions respectively of the upper limestone bed shown by the red arrow in Fig. 2; Fig. 4A has a prominent upper margin of upward-orientated CIC calcite, and a thin band in the middle of the limestone bed, located at the bottom of the sample illustrated in Fig. 4A. Fig. 4B shows

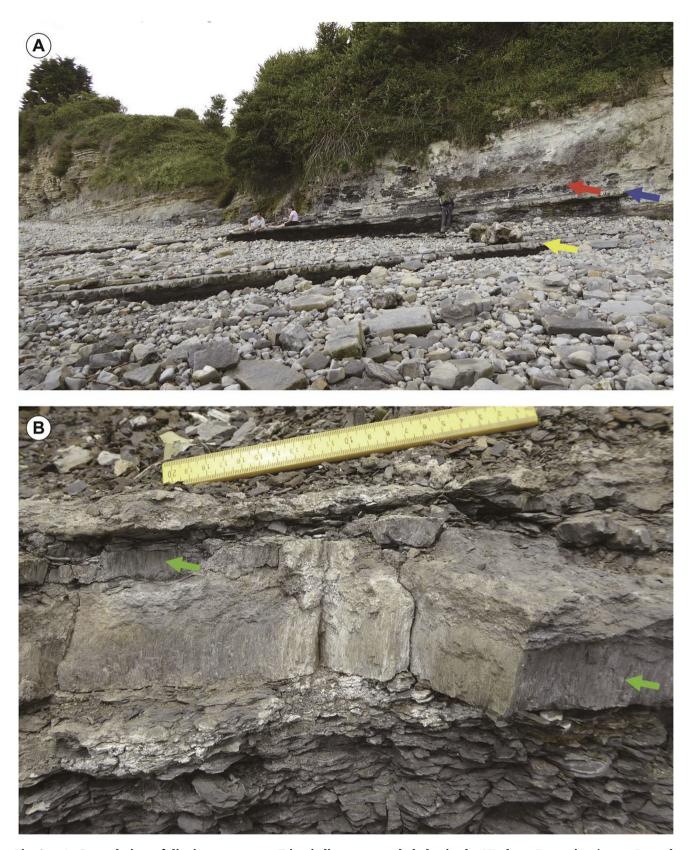


Fig. 2 – A—General view of dipping uppermost Triassic limestone and shales in the Wesbury Formation (upper Penarth Group) at Lavernock Point, 10 km south of Cardiff, South Wales. The red and blue arrows point to two limestone beds bearing cone-in-cone (CIC) calcite. The yellow arrow highlights a nodular limestone bed that contains no beef/CIC calcite and does not form part of this study; B—View of the upper limestone bed showing layers of CIC calcite (green arrows) in its upper and lower margins, with shales above and below.

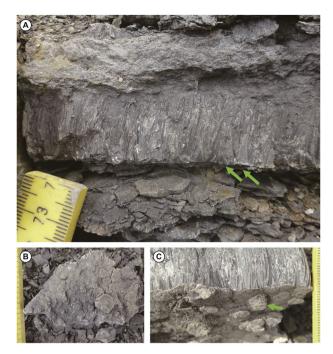


Fig. 3 — Views of lower CIC calcite layer in the lower of the two CIC-bearing limestone beds at Lavernock Point (see Fig. 1). A and C show the expanding tops of CIC calcite crystals, forming prominent protrusions (nailheads, green arrows). B shows basal view of bed with nailheads in plan view. This example is important because it shows the downward-orientated growth of the CIC calcite crystals.

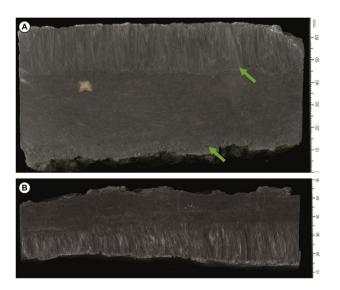


Fig. 4 – Polished vertical sections of hand specimens of CIC calcite layers in Lavernock Point. A–Uppermost CIC calcite layer at top of upper limestone bed (upper green arrow), crystals orientated upwards. Shale, lost when sample was collected, overlaid the top surface. At the bottom of the photo, a thin layer of CIC calcite lies in the middle of the bed (lower green arrow); B–Basal part of the upper limestone bed, showing downward-orientated CIC calcite.

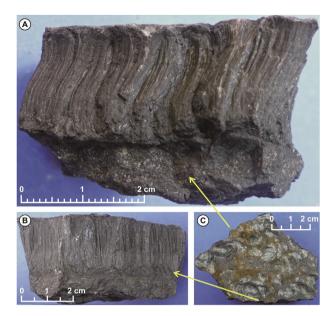


Fig. 5 — Sigmoidal (A) shape of CIC calcite crystals in one view of this field sample from the upper surface of the upper limestone bed at Lavernock Point, but another view almost at right angles (B) shows no sigmoidal structure. C shows the top view of the bed, indicating locations of A and B. This sample is from the only bed where sigmoidal growth is present, and is interpreted here to be due to bedding-plane slip as the CIC crystals developed, and is part of the evidence that the CIC crystals formed later in the history of the sequence.

the lowermost part of the same bed, with a prominent layer of downward-orientated crystals of CIC calcite.

Two additional aspects of CIC calcite observed at Lavernock Point are: (1) small compressional faulting leading to overlapping displacement of CIC calcite layers that seem to have undergone bedding-plane slip in relation to both the underlying limestone and overlying shale; and (2) sigmoidal growth of CIC calcite in the upper contact between limestone and shale in the lower limestone at Lavernock Point (Fig. 5). Sigmoidal growth is visible in only one plane of section. In detail the CIC calcite structure is quite complex (Fig. 6). In this case the CIC calcite structure grew upwards on the upper side of this shelly limestone bed, with sharp contact between the CIC calcite and limestone, consistent with additive growth described by Marshall (1982). Fig. 7A is an enlargement of the top right part of Fig. 6, where the B-CIC layer shows a mixture of larger and smaller CIC calcite crystals and entraps patches of clay. Fig. 7B shows another sample with CIC calcite growth amongst the shells as well as the prominent upper layer of crystals.

4.2. Shales-with-beef beds, Lower Jurassic, Lyme Regis, southern England

The Shales-with-Beef Member of the Lower Jurassic is ca. 35 m thick and occurs in the Semicostatum Zone of the Sinemurian Stage (Hesselbo and Jenkyns, 1995), the second stage of the Jurassic, dated at 199.3—190.9 Ma (Gradstein et al., 2005). Those

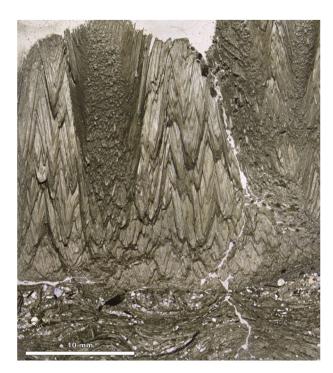
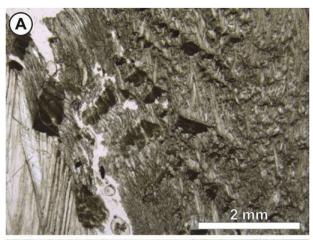


Fig. 6 — Vertical thin section view of upper limestone bed at Lavernock Point showing upward growth of GIC calcite crystals from the shelly limestone bed. The sharp contact between the shelly layer and the GIC calcite may be evidence of growth of the GIC calcite layer as additive, in a fracture. On the upper right side of the photo, the upward-protruding crystal mass is part of a "nailhead" in vertical section (see also Fig. 3C).

beds overlie ca. 25 m of Blue Lias Formation, Hettangian, the lowest stage of the Jurassic, the base of which is dated at 201.3 Ma (Hillebrandt et al., 2013). Thus the Shales-with-Beef formed about 2 million years after the end-Triassic extinction event.

At Lyme Regis and nearby Charmouth there is considerable complexity and diversity of CIC calcite structure, but has one key similarity with the Lavernock Point material: in both cases the CIC calcite commonly forms at the boundary between limestone beds and overlying and underlying shales, with antitaxial growth. In the Lyme Regis material, ammonites deposited parallel to bedding are common within the (argillaceous) limestones and are mostly crushed (Fig. 8) demonstrating compaction of the sediments before lithification. CIC calcite is visible in hand specimen at only the margins of this bed and shows complexity of intergrowth of crystals with cone-in-cone structure. Fig. 8B is an enlargement of the upper central part of Fig. 8A and shows a patch of shale (dark color) trapped in the CIC calcite, and also a crushed ammonite in cross-section. Note that this ammonite must have been crushed (and therefore compaction occurred) before the CIC calcite grew, because several other ammonites in the central part of the argillaceous limestone in the same photo are also crushed (Fig. 8A). Our observations of ammonites from other argillaceous limestones and shales in the Jurassic (e.g. Oxford Clay, Kimmeridge Clay) where B-CIC is lacking, also



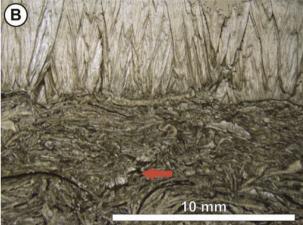


Fig. 7 – A-Enlargement of the upper right part of Fig. 6, from Lavernock Point, showing details of complex cone-in-cone structure, which may be due to a gradient of intensity of growth of CIC calcite to form larger crystals in the upper portion in these upward-orientated crystals. Clay trapped in the CIC calcite crystals was compressed into small pockets and appears to have been split by the CIC calcite crystal growth; B-Vertical section of another sample from Lavernock Point, showing small CIC crystals (red arrow) grew amongst the shells, which may represent partial recrystallization of the shelly limestone, providing an alternative interpretation to the common view that CIC calcite was formed by displacement.

demonstrate that ammonites are commonly crushed by compaction. In Fig. 8B, and several other samples from Lyme Regis, CIC calcite forms a solid crystalline mass around the already crushed ammonite. The central portion of the bed apparently lacks CIC calcite but Fig. 9A shows a thin section view of this portion, where very thin layers of CIC calcite, here called micro-B-CIC calcite, demonstrate partial modification of the fabric. In some places, CIC calcite forms clusters of layers, with the insoluble clay fraction concentrated in thin layers between layers of CIC calcite, presumed to have been collected into layers by displacive growth of CIC calcite (e.g. Fig. 9B).

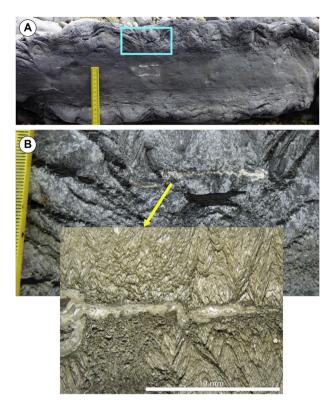


Fig. 8 - A-Vertical section of loose block of limestone from the Shales-with-Beef Member (Lower Jurassic) at Lyme Regis, Dorset, southern England. Although the way up of this bed cannot be determined, it is of great importance that the CIC calcite layers at the upper and lower margins of this block are orientated outwards, and therefore opposite each other (antitaxial of Marshall, 1982). Note numerous compacted ammonites in cross-section scattered through this bed, crushed by compaction of sediment; B-Enlargement of area of blue box in A showing a small angular patch of clay, interpreted here as the insoluble fraction remaining after reorganization (by displacement and/or replacement) of the original sedimentary carbonate that the rock comprised. Also visible is a crushed ammonite in cross-section. Inset shows the ammonite in thin section, demonstrating it was encased in CIC calcite after compaction, thus the CIC calcite formed later in diagenesis.

In polished vertical section, the complexity of CIC calcite at Lyme Regis can be seen in greater detail, in association with bioclastic limestones (Fig. 10). Thin sections (Figs. 11 and 12) show that small CIC calcite crystals grew in the sediment, both upwards and downwards. CIC calcite shows a large range of sizes of cones, from the mm-size early formed cones in Figs. 11 and 12, to cones several cm long (Fig. 13), where hand specimens clearly show small angular pieces of clay entrained in the margins of the cones.

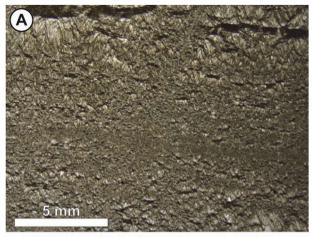




Fig. 9 - A-Vertical thin section from the central portion of the limestone bed illustrated in Fig. 8A, demonstrating increasing size of CIC crystals from the center, upwards and downwards. The fine lamination in the limestone is not disrupted by invasion of calcite cement; no fracturing is visible that might be attributed to increased volume of extra calcite. Thus we suggest the possibility that some of the CIC crystals were formed by recrystallization of existing limestone and not necessarily additive; B-Loose block of Shales-with-Beef Member (Lower Jurassic) at Lyme Regis, Dorset, southern England, showing prominent layers of CIC calcite and interlayered clays. The insoluble clay fraction is interpreted as being concentrated into layers as a result of CIC calcite growth. Thus this example is more evolved than that shown in Fig. 8. See also Figs. 11 and 12 for more details of fabrics, taken from other samples.

4.3. Upper Purbeck beds, Lower Cretaceous, Lulworth Cove, southern England

CIC calcite layers are interbedded with limestones in non-marine carbonates of the uppermost Purbeck beds at Lulworth Cove, in the Berriasian Stage of the earliest Cretaceous System (Barton et al., 2011) (Figs. 1 and 14). Polished blocks in Fig. 14 demonstrate the interruption of sediment by the CIC calcite structure, leaving cone-shaped areas of sediment entrapped in the CIC calcite layers (Fig. 14D and E in vertical and horizontal section respectively). These samples provide

evidence that the CIC calcite in this case replaced the carbonate fraction of pre-existing sedimentary material, discussed later. The presence of CIC calcite in upper Purbeck sedimentary rocks at Lulworth Cove are not indicative of any large scale Earth-surface environmental perturbation, discussed below.

5. Discussion

5.1. Stratigraphic and geographic distribution of CIC calcite

Greene et al. (2012) noted that fibrous calcite deposits occur in three places globally during the T/J transition, supporting their interpretation of global oceanic effects of acidification and the development of the novel subsea carbonate factory they envisaged. Three aspects are significant in relation to such global processes discussed below.

Firstly: Cobbold et al. (2013, their Table 1), published later than Greene et al. (2012), presented a compilation of global occurrence of CIC calcite structures showing that beef and CIC calcite was widespread both geographically and stratigraphically, with no clustering around mass extinctions; only one site was dated as Late Cretaceous, with no indication it relates to the Cretaceous/Cenozoic extinction. Similarly, no records in Cobbold et al.'s (2013, their Table 1) compilation coincide with the end-Permian extinction event, for which ocean acidification has been extensively discussed (see Kershaw et al., 2012a, for appraisal). Cobbold et al. (2013, see their Fig. 2A) proposed a temporal relationship between occurrence of CIC calcite and climate change, with maxima in the Paleozoic and Mesozoic and a minimum in the Permian-Triassic time, but this is a general relationship involving longer term Earth-surface and crustal interactions; also there is no evidence in their dataset of short-term coincidence between mass extinction episodes and maxima in CIC calcite. Observations presented in Fig. 14 of this paper (and by Franks, 1969) also demonstrate that CIC calcite includes examples in non-marine sediments and thus there is not an intrinsic link between CIC calcite and ocean processes involving dissolved inorganic carbon. Finally, Penman et al. (2014) provided evidence from boron isotopes of the wellknown interpreted event of ocean acidification at the Paleocene-Eocene Thermal Maximum (PETM), but there are no reports of fibrous calcite precipitation in beds of that time; the compilation by Cobbold et al. (2013, their Table 1) does not include the PETM horizon.

Secondly: Greene et al. (2012) reported fibrous calcite at St Audrie's Bay, Somerset, England (Fig. 1), using this in support of the hypothesis of a novel carbonate factory. For that factory to have operated in response to a large-scale input of dissolved inorganic carbon from ocean acidification processes, a thick continuous layer of B-CIC calcite would be expected associated with the extinction level. However, Wignall and Bond (2008) and Mander et al. (2008) demonstrated the sparsity of B-CIC in these beds, which is confirmed in our fieldwork at Lavernock Point. Mander et al. (2008) drew attention to the energetic shallow water environments in which both the upper Westbury Formation and

overlying Cotham Member (of Lilstock Formation) formed, including rip-up clasts at the base of the Cotham Member, indicating contemporaneous erosion of the sediments. Gallois (2008) noted the Cotham Member has a basal pebble bed on the eastern Devon coastline. Warrington and Ivimey-Cook (1995) noted that the boundary between the Westbury and Lilstock Formations is locally erosional. Hesselbo et al. (2004) noted that the boundary is gradational in some places, erosional in others, also affected by physical disruption of the beds that may be due to an extraterrestrial impact. Thus, although it is possible that contemporaneous erosion removed previous B-CIC beds, there is little preserved evidence of B-CIC layers associated with the extinction.

Regarding the chronology of the T/J boundary sequence, Hesselbo et al. (2004) noted that the Central Atlantic Magmatic Province (CAMP) volcanism (interpreted to have raised carbon dioxide to acidify the oceans for the subsea carbonate factory model) ranges stratigraphically from the upper Rhaetian to the top of the Hettangian, thus terminating around the Hettangian-Sinemurian boundary. Dates given in Fig. 1 are from Gradstein et al. (2005). More recent high-precision dating from sections in North America places the oldest and youngest dates of the CAMP as being 201.9 Ma and 199.25 Ma respectively, with the T/J extinction dated as 201.564 Ma (Blackburn et al., 2013). The dates of boundaries stated on Fig. 1 may not precisely match these new dates by Blackburn et al. (2013), but even with imprecision of dating, the top of the Westbury Formation is within the time period of the CAMP volcanism, where B-CIC is rare, but the Shaleswith-Beef Member in South Dorset, where B-CIC is abundant, is entirely within the Sinemurian, thus post-dating the CAMP episode. Overall, evidence that the Upper Triassic Westbury Formation beef beds can be reasonably related to environmental processes associated with the extinction, and with the period of volcanism expected to provide raised carbon dioxide levels, is very weak.

Thirdly: CIC calcite reported in P/T boundary microbialites in Iran by Heindel et al. (2015) is the only site so far known at this horizon; this is not recorded in the database of Cobbold et al. (2013). It is not likely that occurrences of B-CIC calcite have been missed in other P/T boundary microbialites; there has been intense study of these facies in similar shallow marine settings globally in recent years by numerous authors (e.g. Baud et al., 2005 in Turkey; Baud et al., 2007 in Iran; Hips and Haas, 2006 in Hungary; Yang et al., 2011 and Kershaw et al., 2012b in China). If B-CIC calcite can indicate a global oceanic precipitation of sub-seafloor calcite, it is surprising that this one Iran site is the only report of its presence, noting also that there are numerous P/T boundary sites in Iran. Certainly, calcite cements are described in some locations in facies associated with the P/T extinction in Iran (Baud et al., 2007), but these are sea-floor deposits, not associated with the subsediment redox boundary and are not widespread, nor B-CIC form. Sea floor cements are also rare across all the Chinese P/T extinction sites (Kershaw et al., 2012b). Thus, if Heindel et al. (2015) are correct in their interpretations, then the process is localized to that one site, not representing a global pattern of rapid response to Earthsurface conditions.



Fig. 10 — Polished vertical sections of the basal part of the Shales-with-Beef limestone Member (Lower Jurassic), Lyme Regis, West Dorset, southern England. Growth of CIC calcite was upwards in these photographs, which are from only part of a bed. The lowermost 40% of each picture is fossiliferous limestone with pyritized and calcitic shells. A pyritized glauconitic nodule is shown in A. The uppermost 60% of each picture is cone-in-cone (CIC) calcite. Note the undulous layers and approximately flat lines parallel to bedding, all representing boundaries between units of CIC calcite growth. Some entrapped clay can be seen as thin dark lenses and lines in the contacts between CIC calcite layers. The apparent sharp contact (red arrows) between the CIC calcite and sedimentary material is in fact a gradational contact when seen in thin section in Figs. 11 and 12.

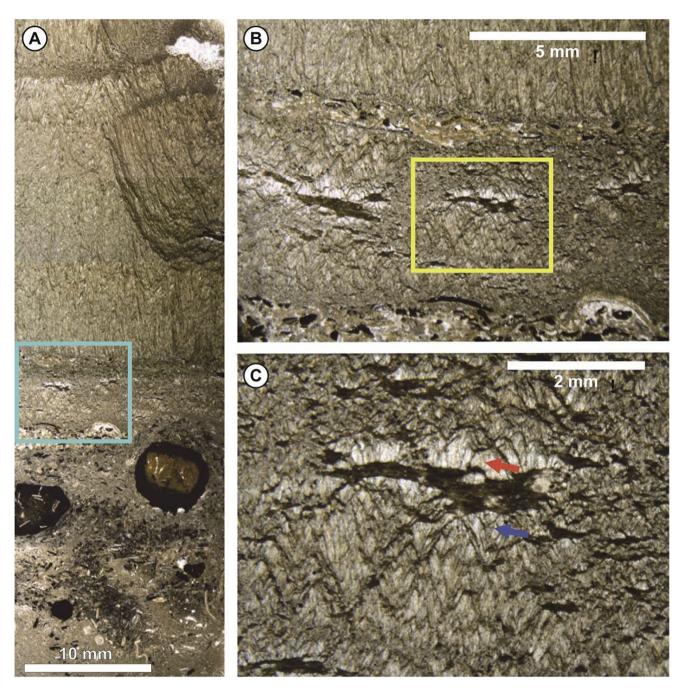


Fig. 11 — Vertically-orientated thin section of CIC calcite from a loose block, basal part of Shales-with-Beef beds of the Lower Jurassic, Lyme Regis, West Dorset, southern England. Growth of CIC calcite was both upwards and downwards in this sample. A—CIC calcite overlies a fossiliferous section containing pyritized nodules; B—Detail of blue box in A, showing clay fragments entrapped in developing CIC calcite. Note the geopetal shelter cavity in the shell, lower right, indicating way up; C—Detail of yellow box in B, showing downward (red arrow) and upward (blue arrow) growth of small CIC calcite crystals pervade the sediment, which may have replaced the limestone with CIC calcite crystals and compressing the insoluble clay component into small lens-shaped areas. Note that the crystals develop in the direction opposite to the taper direction, so they are relatively flat-topped crystal masses composed of small needle-shaped crystals. This form was reported by Richardson (1923) and is consistent with descriptions of CIC calcite by Heindel et al. (2015) in a P/T boundary sequence in Iran, discussed in the text. Compare these photos with Fig. 13, which shows the largest cones we observed.

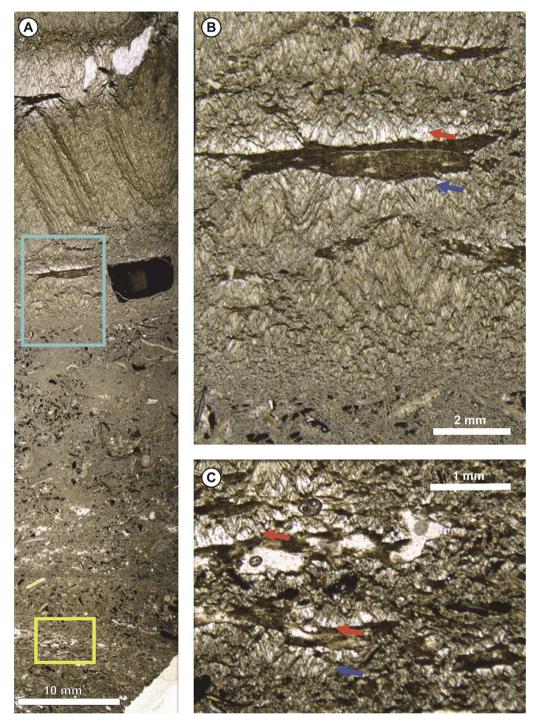


Fig. 12 — Vertically-orientated thin section of CIC calcite in a loose block, basal part of Shales-with-Beef Member of the Lower Jurassic, Lyme Regis, West Dorset, southern England. Growth of CIC calcite is both upwards and downwards in this sample. A—CIC calcite overlies a fossiliferous section containing pyritized nodules; B—Detail of blue box in A, showing shale fragments entrapped in developing CIC calcite; and the increase in size of CIC calcite crystals upwards from almost unaltered sediment at the base to well-developed CIC crystals near the shale fragment upper centre. Note also that CIC calcite crystals above and below the shale fragment are orientated towards each other (red and blue arrows). Although the established view that these crystals are displacive (e.g. Marshall, 1982), the possibility exists that they could be replacing the carbonate fraction of the sediment, leaving the clay fraction to be compacted between layers of growing CIC crystals; C—Detail of yellow box in A, showing downward growth (red arrows) and upward growth (blue arrow) of small CIC calcite crystals. Here, the CIC calcite crystals may be displacing or replacing a small area of the limestone. Note the white areas and air bubbles due to areas of thin section damage during preparation in this soft material.





Fig. 13 — Very large cone-in-cone fabrics in a loose block from the Shales-with-Beef Member of the Lower Jurassic, Lyme Regis, West Dorset, southern England. Growth of CIC calcite was upwards in these photographs. A and B—Side views of the cones; C and D—Vertical cut faces; note small angular pieces of clay entrained in steps in the margins of the cones, interpreted as the insoluble clay fraction of the limestone entrapped as the CIC calcite crystals grew, and compressed into small areas between crystal ends; E—Surface view of a cone broken out of the sample, from which entrapped clay was removed. Steps show the three-dimensional expression of the cones where clay was trapped in elongated triangular patches. Horizontal thin sections (not illustrated) show the trapped clay actually forms concentric rings, as horizontal sections through cones.

5.2. Beef and cone-in-cone (B-CIC) calcite formation processes

The novel carbonate factory is proposed by Greene et al. (2012) as being composed of upward-growing crystals, presumably because upward growth in soft sediment a short distance below the sea floor is less constrained by a small amount of overlying sediment than attempting to push downwards into sediment below. Tarr's (1933) study of the Lower Jurassic Shales-with-Beef observed that the "beef" was thicker on the tops of beds, and interpreted this as due to downward flow under gravity of leached calcium carbonate that reprecipitated in the sediment. Nevertheless, both Greene et al. (2012) and Heindel et al. (2015) reported upward and downward growing crystals, and Greene et al. (2012, p. 1044) noted the occurrence of sideways-orientated crystals, as part of crystal development radiating from existing crystals. Heindel et al.

(2015, their Fig. 7) in particular, drew attention to the substantial development of both upward and downward growing crystals. Furthermore, all the examples studied in fieldwork for our study show approximately equal upward and downward growing CIC crystals. Marshall (1982) and Franks (1969) recorded the antitaxial character of these forms of fibrous calcite, and although thicker upward-growing portions do exist, there was clearly no barrier to downward growth in beef and CIC calcite and preferential upward growth is not common.

In our Upper Triassic samples from Lavernock Point, we have not been able to determine whether or not the sediment was unconsolidated when the CIC crystals grew. Similarly, our thin sections of CIC calcite from the Lower Jurassic Shaleswith-Beef illustrated in Figs. 8, 9, 11 and 12 do not allow clear distinction between development of CIC calcite crystals in soft sediment from those in lithified sediment, because the structure of the sediment is pervasively affected by CIC crystal growth. However, it is clear that ammonites were crushed by compaction prior to growth of CIC calcite (Fig. 8), demonstrating that, at least in those beds, the CIC calcite post-dated compaction. We make the same interpretation for the coneshaped patch of limestone entrapped in CIC calcite in Lulworth Cove (Fig. 14D and E). It is possible that some of the B-CIC calcite was formed by recrystallization of the carbonate fraction of argillaceous limestones and may not necessarily be entirely attributable to new addition, derived from either the ocean above or from later porewaters. Our recognition of micro-B-CIC calcite in the central portions of limestone beds is not accompanied by fracturing that would be expected by expansion of the sediments if calcite was added throughout the rock volume. Thus we suggest the possibility that some of the CIC crystals were formed by recrystallization of existing limestone and not necessarily all of it was additive. Overall, the view that the crystals grew in unconsolidated sediment can be rejected for our samples at Lyme Regis, because of ammonites crushed prior to being encased in B-CIC calcite. In illustrations in other published cases we have not been able to identify unequivocally whether or not the sediment was consolidated when beef and CIC calcite formed. Because the theory of a novel carbonate factory a short distance below the sea floor demands growth of crystals in unconsolidated sediment, then that aspect of the theory remains problematic.

An additional component of the arguments relating to the end-Triassic extinction lies in a recent interpretation by Ibarra et al. (2014) that the Cotham Marble stromatolites (formed just after the extinction, see Wignall and Bond, 2008) were postextinction disaster taxa, reflecting raised carbonate saturation of the oceans. Mayall and Wright (2015) discussed several problems of interpreting the Cotham Marble as a disaster biota, concluding that it is at best an equivocal indicator of the Late Triassic mass extinction. The stromatolite unit is discontinuous and very thin (20 cm thick), it has limited geographic distribution and is associated environmentally with lagoons of non-normal salinity (Mayall and Wright, 1981; Wright and Mayall, 1981). In comparison with microbialites after the Frasnian/Famennian extinction (e.g., Whalen et al., 2002) and the end-Permian extinction (Kershaw et al., 2012b), the Cotham Marble stromatolite is a very poor indicator of a post-extinction disaster biota. Nevertheless, the Late

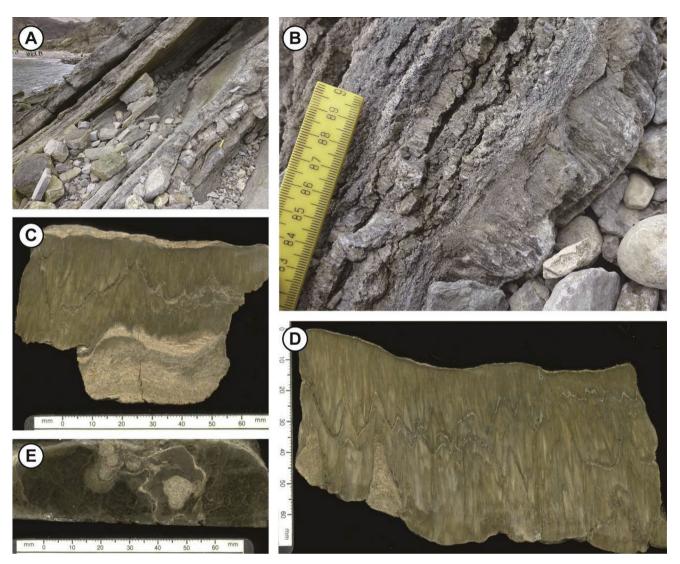


Fig. 14 — CIC calcite in upper Purbeck limestones (Lower Cretaceous) on the east side of Lulworth Cove, southern England. A—Field photo showing layered CIC calcite interbedded with limestones, detail in B; way up to left. Note the bed-parallel layers of fibrous calcite interbedded with limestone; C—Vertical section of polished block of CIC calcite showing undulating contact with pale-colored limestone, in which the layering of the sediment matches the bedding lines in the CIC calcite, which may be due to the CIC calcite recrystallizing limestone that has undulating bedding; D—Vertical section of polished block showing CIC calcite with cone-shaped patches of limestone entrapped in the structure, interpreted here as remnants of limestone that has been recrystallized, leaving unaltered cone-shaped limestone; E—Horizontal section showing similar to D, with the entrapped cone of limestone revealed as an approximately circular patch in tangential cross-section. See text for discussion.

Ordovician extinction has a poor record of disaster biota, and the end-Cretaceous extinction has no microbial deposits, thus highlighting continuing problems of interpretation of post-extinction disaster facies (Kershaw et al., 2007, 2009).

6. Conclusions

Our study of beef and cone-in-cone (B-CIC) calcite in Late Triassic, Early Jurassic and Early Cretaceous sedimentary rocks in southern UK, leads us to the following conclusions: 1) Most samples cannot provide proof of formation of B-CIC calcite before lithification, but crushed ammonites encased in B-CIC calcite prove these fibrous calcite cements formed after compaction. Thus it is problematic to demonstrate that crystal growth occurred in unconsolidated sediment (critical to the proposal of a novel carbonate factory) in the shallow sea floor soon after deposition, prior to lithification. The novel carbonate factory is proposed as being composed of upward-growing crystals of such fibrous calcite in soft sediment, but downward growing crystals are as common.

2) The Upper Triassic material at Lavernock Point formed in relatively shallow marine to lagoonal conditions, the Lower Jurassic material at Lyme Regis was in a deep shelf setting, and the Lower Cretaceous deposits were in non-marine carbonates, emphasizing that ocean processes are not required for B-CIC formation and depositional environments seem to have little or no influence on B-CIC calcite formation. B-CIC calcite occurs in the Lower Triassic outcrops as stratigraphically scattered thin beds and lenses, not consistent with an intense ocean acidification event following mass extinction; and is much more abundant in the Early Jurassic Shales-with-Beef Member, significantly later than the T/J extinction and therefore unrelated to it.

Published work reported in this paper shows that B-CIC calcite is not clustered around mass extinctions, and is interpreted to have formed in burial at higher pressures and temperatures than are found at the Earth's surface. CIC calcite reported by other authors in P/T boundary microbialites in Iran is the only site so far known at that time, despite worldwide study of similar shallow marine settings, demonstrating localized formation. There is no evidence of a global link between CIC calcite and the end-Permian extinction. Overall, we consider that the existence of a subsea carbonate factory associated with the T/J and P/T mass extinctions is highly unlikely.

Acknowledgements

We thank Prof. Zeng-Zhao Feng and three anonymous reviewers for helpful comments on an earlier version of this paper. This paper is a contribution to IGCP630.

REFERENCES

- Barton, C.M., Woods, M.A., Bristow, C.R., Newell, A.J., Westhead, R.K., Ecands, D.J., Kirby, G.A., Warrington, G., Riding, J.B., Freshney, E.C., Highley, D.E., Lott, G.K., Forster, A., Gibson, A., 2011. Geology of South Dorset and South-East Devon and its World Heritage Coast. Special Memoir of the British Geological Survey. Sheets 328, 341/342, 342/343, and parts of 326/340, 327, 329 and 339 (England and Wales).
- Baud, A., Richoz, S., Marcoux, J., 2005. Calcimicrobial cap rocks from the basal Triassic units: western Taurus occurrences (SW Turkey). Comptes Rendus Palevol 4 (6–7), 569–582.
- Baud, A., Richoz, S., Pruss, S., 2007. The Lower Triassic anachronistic carbonate facies in space and time. Global and Planetary Change 55 (1-3), 81-89.
- Blackburn, T.J., Olsen, P.E., Bowring, S.A., McLean, N.M., Kent, D.V., Puffer, J., McHone, G., Rasbury, E.T., Et-Touhami, M., 2013. Zircon U—Pb geochronology links the end-Triassic extinction with the Central Atlantic Magmatic Province. *Science* 340 (6135), 941—945.
- Cobbold, P.R., Rodrigues, N., 2007. Seepage forces, important factors in the formation of horizontal hydraulic fractures and bedding-parallel fibrous veins ('beef' and 'cone-incone'). *Geofluids* 7 (3), 313–322.

- Cobbold, P.R., Zanella, A., Rodrigues, N., Løseth, H., 2013. Beddingparallel fibrous veins (beef and cone-in-cone): worldwide occurrence and possible significance in terms of fluid overpressure, hydrocarbon generation and mineralization. *Marine and Petroleum Geology* 43, 1–20.
- Franks, P.C., 1969. Nature, origin, and significance of cone-in-cone structures in the Kiowa formation (Early Cretaceous), north-central Kansas. *Journal of Sedimentary Petrology* 39 (4), 1438–1454.
- Gallois, R.W., 2008. The stratigraphy of the Penarth Group (Late Triassic) of the east Devon coast. Geoscience in South-West England Proceedings of the Ussher Society 11, 287—297.
- Gradstein, F.M., Ogg, J.G., Smith, A.G., 2005. A Geologic Time Scale 2004. Cambridge University Press, New York.
- Greene, S.E., Bottjer, D.J., Corsetti, F.A., Berelson, W.M., Zonneveld, J.P., 2012. A subseafloor carbonate factory across the Triassic-Jurassic transition. *Geology* 40 (11), 1043—1046.
- Heindel, K., Richoz, S., Birgel, D., Brandner, R., Klügel, A., Krystyn, L., Baud, A., Horacek, M., Mohtat, T., Peckmann, J.R., 2015. Biogeochemical formation of calyx-shaped carbonate crystal fans in the subsurface of the Early Triassic seafloor. Gondwana Research 27 (2), 840–861.
- Hesselbo, S.P., Jenkyns, H.C., 1995. A comparison of the Hettangian to Bajocian successions of Dorset and Yorkshire.
 In: Taylor, P.D. (Ed.), Field Geology of the British Jurassic.
 Geological Society, London, pp. 105–150.
- Hesselbo, S.P., Robinson, S.A., Surlyk, F., 2004. Sea-level change and facies development across potential Triassic—Jurassic boundary horizons, SW Britain. *Journal of the Geological Society, London* 161 (3), 365–379.
- Hillebrandt, A.v., Krystyn, L., Kürschner, W.M., Bonis, N.R., Ruhl, M., Richoz, S., Schobben, M.A.N., Urlichs, M., Bown, P.R., Kment, K., McRoberts, C.A., Simms, M., Tomāsových, A., 2013. The global stratotype sections and point (GSSP) for the base of the Jurassic system at Kuhjoch (Karwendel Mountains, Northern Calcareous Alps, Tyrol, Austria). Episodes 36 (3), 162—198.
- Hips, K., Haas, J., 2006. Calcimicrobial stromatolites at the Permian—Triassic boundary in a western Tethyan section, Bükk Mountains, Hungary. Sedimentary Geology 185 (3–4), 239–253.
- Ibarra, Y., Corsetti, F.A., Greene, S.E., Bottjer, D.J., 2014. Microfacies of the cotham marble: a tubestone carbonate microbialite from the Upper Triassic, southwestern U.K. *Palaios* 29 (1), 885–899.
- Kershaw, S., Li, Y., Crasquin-Soleau, S., Feng, Q.L., Mu, X.N., Collin, P.Y., Reynolds, A., Guo, L., 2007. Earliest Triassic microbialites in the South China block and other areas: controls on their growth and distribution. Facies 53 (3), 409–425.
- Kershaw, S., Crasquin, S., Collin, P.Y., Li, Y., Feng, Q., Forel, M.B., 2009. Microbialites as disaster forms in anachronistic facies following the end-Permian mass extinction: a discussion. Australian Journal of Earth Sciences 56 (6), 809—813.
- Kershaw, S., Crasquin, S., Li, Y., Collin, P.Y., Forel, M.B., 2012a. Ocean acidification and the end-Permian mass extinction: to what extent does evidence support hypothesis? *Geosciences* 2 (4), 221–234.
- Kershaw, S., Crasquin, S., Li, Y., Collin, P.Y., Forel, M.B., Mu, X.N., Baud, A., Wang, Y., Xie, S., Maurer, F., Guo, L., 2012b. Microbialites and global environmental change across the Permian–Triassic boundary: *a synthesis Geobiology* 10 (1), 25–47.
- Lang, W.D., Spath, L.F., Richardson, W.A., 1923. Shales-with-'beef', a sequence in the Lower Lias of the Dorset Coast. Quarterly Journal of the Geological Society, London 79, 47–66.
- Le Breton, E., Cobbold, P.R., Zanella, A., 2013. Cenozoic reactivation of the Great Glen Fault, Scotland: additional

evidence and possible causes. *Journal of the Geological Society, London* 170 (3), 403–415.

- Mander, L., Twitchett, R.J., Benton, M.J., 2008. Palaeoecology of the Late Triassic extinction event in the SW UK. *Journal of the Geological Society*, London 165 (1), 319—332.
- Marshall, J.D., 1982. Isotopic composition of displacive fibrous calcite veins: reversals in pore-water composition trends during burial diagenesis. *Journal of Sedimentary Petrology* 52 (2), 615–630.
- Mayall, M.J., Wright, V.P., 1981. Stromatolites from the Upper Triassic of south-west England. *Palaeontology* 24, 655–660.
- Mayall, M.J., Wright, V.P., 2015. Comment to Ibarra et al. Microfacies of the Cotham Marble: a tubestone microbialite from the Upper Triassic, southwestern U.K. Palaios 30 (11), 802–805
- Penman, D.E., Hönisch, B., Zeebe, R.E., Thomas, E., Zachos, J.C., 2014. Rapid and sustained surface ocean acidification during the Paleocene–Eocene thermal maximum. *Paleoceanography* 29 (5), 357–369.
- Richardson, W.A., 1923. Petrology of the shales-with-'beef'. Quarterly Journal of the Geological Society, London 79 (1-4), 88-99.
- Tarr, W.A., 1933. Origin of the "beef" in the Lias shales of the Dorset coast. Geological Magazine 70, 289—294.

- Warrington, G., Ivimey-Cook, H.C., 1995. The Late Triassic and Early Jurassic of coastal sections in west Somerset and south and mid-Glamorgan. In: Taylor, P.D. (Ed.), Field Geology of the British Jurassic. Geological Society, London, pp. 9–30.
- Whalen, M.T., Day, J., Eberli, G.P., Homewood, P.W., 2002. Microbial carbonates as indicators of environmental change and biotic crises in carbonate systems: examples from the Late Devonian, Alberta basin, Canada. Palaeogeography, Palaeoclimatology, Palaeoecology 181 (1–3), 127–151.
- Wignall, P.B., Bond, D.P.G., 2008. The end-Triassic and Early Jurassic mass extinction records in the British Isles. *Proceedings of the Geologists' Association* 119 (1), 73–84.
- Wright, V.P., Mayall, M., 1981. Organism-sediment interactions in stromatolites: an example from the Upper Triassic of south west Britain. In: Monty, C. (Ed.), *Phanerozoic Stromatolites*. Springer-Verlag, Berlin, pp. 74–84.
- Yang, H., Chen, Z.Q., Wang, Y.B., Tong, J.N., Song, H.J., Chen, J., 2011. Composition and structure of microbialite ecosystems following the end-Permian mass extinction in South China. Palaeogeography, Palaeoclimatology, Palaeoecology 308 (1–2), 111–128.