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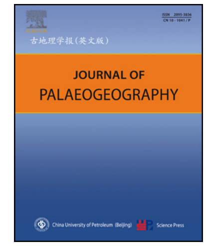

Lithofacies palaeogeography and sedimentology

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

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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

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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.

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-in-cone (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