

**Early overpressuring in organic-rich shales during burial: evidence from fibrous calcite veins in the Lower Jurassic Shales-with-Beef Member in the Wessex Basin, UK**

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**Abstract:** Field, petrographic and geochemical analysis of fibrous calcite veins in the Lower Jurassic Shales-with-Beef Member in the Wessex Basin were conducted to investigate the formation mechanism of the veins. Bedding-parallel fibrous calcite veins, including beef veins and tabular cone-in-cone structures, are widespread in the black shales. The calcite veins consist of sub-vertical fibrous crystals and a dark median zone. The median zone contains scattered clays, pyrite microcrystals, skeletal fragments and amorphous organic matter. The veins exhibit moderate carbon isotope values, ranging from -1.515‰ to 2.732‰. The oxygen isotope composition ranges from -8.872‰ to -4.521‰, which is possibly too negative to reflect the primary pore water oxygen isotope signatures and indicates a pore water modification. It is interpreted that the veins mainly derive carbonates from seawater inorganic carbon and bioclasts. The veins formed as closed-system hydraulic fractures in overpressured cells during sediment degassing in the methanogenic zone. The shale beds with a high TOC could have generated abundant CO<sub>2</sub> which may have resulted in either the cementing of the pores in the matrix or for overpressure buildup. The skeletal fragments provide a control on the spatial distribution of veins as nuclei for calcite precipitation from supersaturated pore fluids.

**Keywords:** overpressure; shale; beef; cone-in-cone; early burial; methanogenesis

Dilation sites of fractures in low-permeability shales are commonly found to be sealed by mineral fillings (Gale et al., 2014; Cobbold et al., 2013; Bons et al., 2012). According to the distinct crystal morphology and arrangement, mineral-filled veins can be subdivided into blocky, elongate-blocky and fibrous veins (Bons et al., 2012; Passchier and Trouw, 1996). Fibrous calcite veins, as a major type of veins in black shales, have been reported in over 110 sedimentary basins worldwide (Cobbold and Rodrigues, 2007; Cobbold et al., 2013). Such veins predominantly occur in marine shales as bedding-parallel structures, whose ages range from Cambrian to Palaeogene (Cobbold et al., 2013). Two types of fibrous calcite veins have been identified, including beef veins and cone-in-cone structures (Cobbold et al., 2013). Calcite beef veins contain parallel-aligned fibres with smooth crystal boundaries and constant widths (Bons and Montenari, 2005; Hilgers and Urai, 2002; Passchier and Trouw, 1996), whereas cone-in-cone structures consist of nested, conical bundles of calcite fibres (Cobbold et al., 2013; Selles-Martinez, 1996; Woodland, 1964).

Calcite beef veins and cone-in-cone structures in fine-grained organic-rich sediments have received great attention from geologists since the 1850s, as they carry much information on fluid and diagenetic conditions, paleostress states and rock deformations (Al-Aasm et al., 1995; Bons et al., 2012; Kowal-Linka, 2010; Marshall, 1982; Passchier and Trouw, 1996; Sorby, 1859; Tarr, 1922). It has been suggested that fibrous calcite veins have a diagenetic origin under favourable physic-chemical conditions, which are evident from ductile distortions in the host shale by the displacive, concretionary growth of the veins (Carstens, 1985; Franks, 1969; Kiriakoulakis et al., 2000; Kowal-Linka, 2010; Marshall, 1982; Tarr, 1922; Woodland, 1964). The high ductility of the surrounding sediments enables clays to be incorporated into veins during the successive growth of calcite fibres (Ábalos and Elorza, 2011; Gilman and Metzger, 1967). Vein genesis has also been attributed to overpressuring in the low-permeability host rocks (Al-Aasm et al., 1995; Cobbold

and Rodrigues, 2007; Conybeare and Shaw, 2000; Parnell and Carey, 1995; Selles-Martinez, 1994; Selles-Martinez, 1996; Zanella et al., 2014). Multiple factors are likely to give rise to overpressure, of which primary hydrocarbon migration has been considered as the dominant origin due to the common appearance of hydrocarbon inclusions within the veins (Cobbold et al., 2013; Parnell et al., 2000; Rodrigues et al., 2009; Stoneley, 1983). Although the origin of fibrous calcite veins remains a subject of debate, these veins provide a snapshot of the early structural diagenesis of organic-rich shales, i.e. the mechanical and chemical processes that lead to vein formation (Ábalos and Elorza, 2012; Laubach et al., 2010).

This paper reports the study of the calcite beef veins and cone-in-cone structures in the Lower Jurassic organic-rich shales in the Shales-with-Beef Member in the Wessex Basin. The study area exposes abundant fibrous calcite veins in the black shales and provides an ideal case for the study of such veins. It has been proposed that the calcite beef veins in the study area formed during diagenesis after the cessation of sulphate-reducing bacterial activity (Kiriakoulakis et al., 2000; Marshall, 1982; Wolff et al., 1992). However, a recent study argued that the beef veins formed between Upper Cretaceous to Tertiary when the source rocks became mature enough to generate hydrocarbons (Zanella et al., 2015). Vein generation has been suggested to be the result of overpressure, which was triggered by hydrocarbon migration and enhanced by tectonic compression, especially during the time of basin inversion in Early Cenozoic (Zanella et al., 2015). Hence, further studies on the vein systems are needed to verify the hypotheses of the mechanism for vein formation.

The paper firstly describes the outcrop features of the fibrous calcite veins, then presents petrographic observations and geochemical data. Finally, the paper discusses several key questions regarding the timing, genetic mechanism, nutrient sources and the controlling factors on vein

development. The aims of the paper are (1) to provide constraints on the timing and diagenetic conditions of vein formation; (2) to determine the geological controls on vein distribution and nutrient sources for vein growth; (3) to refine the current understanding of structural diagenesis in black shales during early burial that caused the generation of bedding-parallel mineral veins. This paper attempts to provide an alternative explanation of fibrous calcite veins in organic-rich shales as immature hydrocarbon-source rocks in sedimentary basins, which reinforces the potential link between early overpressuring and vein genesis.

## **Geological background**

The study area is located on the coast of Charmouth, the southern margin of the Wessex Basin, Southern UK (Fig. 1). The Wessex Basin is a Mesozoic intracratonic basin and forms part of basin network that covers much of NW Europe (Ziegler and Maatschappij's-Gravenhage, 1982). The basin primarily formed during Mesozoic extension and was subsequently modified by Cretaceous uplift and Alpine inversion (Buchanan, 1998; Chadwick, 1986; Karner et al., 1987; Stoneley, 1982; Underhill and Stoneley, 1998).

The Wessex Basin has been intensively studied due to the exceptional exposure of the entire Jurassic succession, which contains all of the potential source rocks for hydrocarbon reservoirs in this region (Chadwick, 1986; Jenkyns and Weedon, 2013; Karner et al., 1987; Stoneley, 1983; Underhill and Stoneley, 1998; Worden et al., 2015). The Lower Jurassic Charmouth Mudstone Group consists of dark grey shales, paler grey blocky mudstone and marls, sporadic limestone concretions and tabular limestone beds (Jenkyns and Weedon, 2013; Simms, 2004), which were deposited in an extensive epicontinental sea during a major global sea level rise (Anderton et al., 1979). Fibrous beef veins and cone-in-cone structures are commonly observed in the black shales

of the Lower Chamouth Mudstone, especially in the Shales-with-Beef Member (Gallois, 2008; Jenkyns and Weedon, 2013; Lang et al., 1923; Zanella et al., 2015).

The Shales-with-Beef Member contains 33 m of laminated black shales with interbedded impersistent limestone beds (Hesselbo and Jenkyns, 1995) (Fig. 2B). The shales are organic-rich and are prominent in the lower and middle parts of the member (Gallois, 2008). The limestones commonly occur as decimetre-scale nodules, which often contain well preserved ammonites (Simms, 2004). The shales consist of numerous thin beds (<10 cm) of fibrous calcite veins, referred to as ‘beef’, which give the member its name (Lang et al., 1923; Tarr, 1933). The Shales-with-Beef Member is overlain by the Black Ven Marl that consists of 43 m dark-grey thinly interbedded and organic-rich mudstone, with a few thin beds of muddy limestone (House, 1989) (Fig. 2).

The black shales are richly fossiliferous, mainly containing ammonites, belemnites, brachiopods and bivalves (Jenkyns and Weedon, 2013). The shales contain a total organic carbon (TOC) up to 10.4%, serving as the source rocks for the hydrocarbons in the Wytch Farm oilfield in Dorset (Buchanan, 1998; Jenkyns and Weedon, 2013). The organic matter is predominantly type II algal material (Underhill and Stoneley, 1998). The shales are highly calcareous, with calcite, dolomite and aragonite. Clay minerals include illite, smectite, kaolinite and chlorite. Mixed illite/smectite has not been detected (Kemp et al., 2005). The non-clay mineral assemblages include carbonates, quartz, feldspar (albite and K-feldspar), pyrite, gypsum and jarosite (Kemp et al., 2005). The equivalent subsurface source rock units encountered the oil window in the Late Cretaceous prior to the basin inversion in Tertiary, with a maximum burial of 2 km and peak paleotemperatures of 75°C (Stoneley, 1992; Kemp et al., 2005). However, the shales exposed at outcrops in the study area are immature, having experienced a maximum burial depth of only 900-1100 m, with an equivalent vitrinite reflectance of 0.35% (Ebukanson, 1985).

## Methods

We observed fibrous calcite veins at three major sites of the Shales-with-Beef Member in the study area, which are not covered with fallen muds due to landslides. Representative veins (30 samples) and their host rocks (29 samples) were sampled for petrographic and geochemical analysis. This permits a comparison of vein and rock features in different horizons. Thin sections with a thickness of 30  $\mu\text{m}$  were cut normal to bedding, and were left uncovered. Optical examination of thin sections of veins and rocks was made in cross-polarized light with a Nikon Optophot Microscope fitted with a high resolution digital camera. Polished thin sections were also examined using a FEI Quanta 650 FEG Scanning Electron Microscope (SEM). Backscattered electron (BSE) images were produced to reveal micro-textures and mineral compositions. Elemental analysis was performed using energy dispersive X-ray spectroscopy (EDS) that is attached to the SEM.

Carbonate content and TOC (total organic carbon) were measured from 15 host rock samples to analyse their control on vein development. The content of carbonate and TOC were measured using a Shimadzu TOC-5000A TOC Analyser, following the principles of the 680°C combustion catalytic oxidation method (Benner and Strom, 1993). Stable isotopes of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of vein and host rock samples were measured. Powdered samples were extracted using a microdrill from both the upper and lower fibres in hand specimens of single veins. Distilled water and high pressure air were used to clean the equipment so as to avoid cross contamination. Concentrated phosphoric acids were added to the samples to produce the  $\text{CO}_2$  to be analysed. The samples were run at the isotope laboratory of the Open University using MAT 253 mass spectrometer. The isotope composition was calculated relative to Pee Dee Belemnite (PDB) standard (Hoefs and Hoefs, 1997).

## Field observations

Calcite beef veins and cone-in-cone structures are widespread in the black shales of the Shales-with-Beef Member (Fig. 3). The veins are white or grey and can be easily distinguished from the black, fissile shales. The occurrence of calcite beef veins is often accompanied by carbonate concretions in the adjacent horizons (Fig. 3A and B). The lenticular concretions are observed to be enveloped with radial cone-in-cone structures in the outer rims, which exhibit different textures from the inner core zones with horizontal laminations (Fig. 3C and D).

Tabular cone-in-cone structures (Fig. 4A) and beef veins (Fig. 4B-E) often appear as vertically clustered arrays. The tabular, sub-horizontal cone-in-cone structures are persistent and thicker than beef veins, with a thickness ranging from 1.8-8.0 cm. Cone-in-cone structures consist of stacks of conical bundles of calcite fibres, and abundant clay inclusions between neighboring cones (Fig. 4A). Calcite beef veins exhibit varied geometries, sizes and textural patterns in different horizons. The beef veins occur either as isolated veins that display tapering tips, or closely spaced veins with blunt tips. The length of single beef veins can vary from one millimeter to tens of meters. The thickness of longer beef veins range from 1-1.5 cm. The short beef veins have a thickness ranging from 0.4-2 cm, and a length less than 40 cm. Beef veins that occur as closely spaced clusters within adjacent horizons commonly exhibit similar sizes and geometries (Fig. 4D-G).

The shale succession between the Table Ledge and the Fish Bed (Fig. 2B) contains abundant calcite veins and was selected for detailed vein observation, logging and sampling at three major sites. Sites 1 and 2 (50°44'01" N, 2°54'44" W) contain vertically clustered vein arrays, whereas Site 3 (50°44'02" N, 2°54'35" W) contains lenticular carbonate concretions with cone-in-cone rims and beef veins in the adjacent horizons. Vein development at the three sites exhibit laterally

consistent features, whereas it varies vertically. The shale successions at these sites exhibit sub-horizontal laminations, with no faults transecting the outcrops.

The shale succession at Site 1 exposes fifteen horizons of calcite beef veins and cone-in-cone structures (Fig. 5). Cone-in-cone structures occur in Horizons 8, 10, 18 and 26, with a maximum thickness of 8, 3, 6 and 1.8 cm respectively. Calcite beef veins occur in the remaining eleven horizons. Horizons 12 and 22 both contain an isolated, persistent calcite beef vein, with a maximum thickness of 0.4 and 0.6 cm respectively. Horizons 20, 22, 28 and 30 consist of four to five closely spaced horizontal beef veins as tightly clustered groups. All of the veins are persistent and can be traced along the outcrop for tens of meters. The vertical spacing of veins in a single group is between 1-2 cm. Vein thickness ranges between 1-1.5 cm. Horizon 6 contains two types of beef veins. The first type are 200-300 cm long, with a maximum thickness of 1cm, whereas the second type are 10-15 cm long, with a maximum thickness of 0.4-1 cm. Other horizons contain numerous small veins that exhibit similar geometries and sizes. Vein size varies from 1 to 40 cm in length, and 0.4 to 1.4 cm in thickness. The veins are closely clustered with a vertical spacing commonly less than 1 cm.

## **Petrographic characterization**

### **Veins**

The fibrous calcite veins consist of a blocky median zone and two fibrous zones on either side of the median zone, exhibiting characteristic features of antitaxial veins (Bons et al., 2012; Bons and Montenari, 2005). The fibres are oriented sub-vertically and are parallel-aligned, with a high aspect ratio. The median zone, which has been suggested as the seed vein for subsequent fibre nucleation and growth (Bons, 2000), has a finite width (up to 4 mm), containing host rock fragments, equant



179 calcite crystals, pyrite framboids and spheres, skeletal fossil fragments and amorphous organic  
180 matter (Fig. 6A).

181 Skeletal fragments are widely dispersed within the median zones. The morphologies of the  
182 skeletons are preserved to varying degrees. Chambers of the skeletal fragments are mainly filled  
183 with both calcite and pyrite, whereas some of the chambers are completely filled with pyrite (Fig.  
184 6B and C). Many pyritised tabular skeletons are juxtaposed with vertical calcite fibres either on  
185 one side (Fig. 6D) or on both sides (Fig. 6E-G).

186 Pyrite is one of the major components within the calcite veins, occurring as homogeneous fillings  
187 of skeletal fragments, single microcrystals of framboids, or as spherical aggregates of framboids.  
188 Individual pyrite framboids are regularly shaped, with a diameter ranging from 0.8 to 10  $\mu\text{m}$ . The  
189 pyrite spheres exhibit a spherical morphology, consisting of densely packed aggregates of  
190 uniformly sized and shaped framboids. The diameter of the spheres varies from 9 to 80  $\mu\text{m}$ . Pyrite  
191 framboids and spheres are commonly associated with skeletal fragments, clay flakes and AOM,  
192 and localized to the sites with those components. This indicates diagenetic modifications of the  
193 sediments by sulphate reduction (Berner et al., 1985).

194 Organic matter appears commonly within the calcite veins as amorphous organic matter 'AOM'  
195 (Fig. 7) (AOM is here defined as structureless particulate organic components at the scale of light  
196 microscopy) that corresponds to degraded phytoplankton or bacterially-derived AOM, higher plant  
197 resins, and amorphous products by the diagenesis of macrophyte tissues (Tyson, 1995). AOM  
198 occurs as scattered patches in varied shapes, and sizes ranging from 10 to 500  $\mu\text{m}$ . AOM is widely  
199 disseminated in the median zone, which is intimately associated with clay particles, skeletal  
200 fragments and pyrite crystals (Fig. 7E and F). The AOM appears either as isolated patches that are

enveloped by calcite, or as thin, curvy bands with varied width (4-26  $\mu\text{m}$ ) and embedded clay flakes and pyrite framboids. Similar features of AOM preserved in beef veins have been also reported by Kiriakoulakis et al. (2000) and Franks (1969).

#### **Host rock**

The petrographic characterization of the non-clay mineral compositions within the host rock focuses on pyrite, AOM, detrital and authigenic carbonates within the clay matrix, which allows a comparison with the composition of the solid inclusions within the calcite veins, and provides insights into shale diagenesis.

Pyrite is prevalent within the clay matrix in the form of single framboids or aggregates as spheres (Fig. 8). Pyrite spheres are often concentrated within skeletal fragments. The shales contain abundant AOM, whose distribution is commonly associated with calcium sulphate that was not consumed during bacterial sulphate reduction (Curtis, 1980). AOM is also enriched in the zones with abundant bioclasts of calcite skeletons and peloids (Fig. 8A and B).

Authigenic carbonate occurs as pore-filling cements in the clay matrix (Fig. 8C-F), with the longest dimension up to 200  $\mu\text{m}$ . Their distribution is often associated with AOM. Elongate-fibrous calcite is observed to develop along pyritised skeletal fragments on one side (Fig. 8F). The crystal length reaches up to 500  $\mu\text{m}$ .

Detrital carbonates are mainly skeletal fragments of aragonitic fossils and non-skeletal grains of peloids. The peloids are spherical, and silt sized with a diameter of 10-20  $\mu\text{m}$  (Fig. 9). They occur in clusters within multiple horizons, exhibiting flattened, elongate features on the scale of 200-800  $\mu\text{m}$ . The peloids are generally white and grey, containing a thin, darker outer rim of micritic

components (Fig. 9A and B). The cores of the peloids are structureless and symmetrical. EDS data demonstrates that the peloids are mainly composed of carbonate (Fig. 9C and D). AOM patches in the sizes ranging from 10 to 200  $\mu\text{m}$  are developed in the clays adjacent to the peloids. Microcrystals of pyrite framboids are widely disseminated throughout the same horizons as AOM. Such peloids are likely to have a fecal origin, produced by a variety of organisms fine carbonate mud while feeding on organic-rich sediments (Flügel, 2004). The environment is likely low-energy, in a quiet marine water with muddy bottoms. It has also been suggested that rounded peloids could have formed as micritized bioclastic grains by alteration of skeletal fragments by microboring microbes and recrystallization (Samankassou et al., 2005).

## **Geochemical characteristics**

### **Site 1**

The carbonate concentration in different horizons of shales at Site 1 ranges from 8.25% (Horizon 27) to 36.17% (Horizon 29) by weight (Fig. 5), with an average value of 17.58%. TOC in shales of site 1 varies from 1.78% (Horizon 19) to 4.70% (Horizon 9), with an average value of 3.18%.

The  $\delta^{13}\text{C}$  values of the fibrous calcite veins at site 1 range from -1.180‰ to 2.462‰, with an average value of 0.353‰ (Fig. 5). The  $\delta^{13}\text{C}$  values are predominantly positive. The  $\delta^{13}\text{C}$  values in the beef veins with ammonites on vein surfaces range from 0.156‰ to 0.726‰. In contrast to the calcite veins, the shale beds all reveal negative  $\delta^{13}\text{C}$  values, excluding Horizon 19 (0.092‰). The negative  $\delta^{13}\text{C}$  values range from -0.232‰ to -1.708‰, with an average value of -0.686‰. The shales with the lowest  $\delta^{13}\text{C}$  values are in Horizon 27, which contains discrete carbonate concretions.

The  $\delta^{18}\text{O}$  composition of calcite veins at Site 1 are all negative, ranging from -8.872‰ to -4.521‰ (Fig. 5). Most  $\delta^{18}\text{O}$  values are between -6.5‰ to -4.5‰. The  $\delta^{18}\text{O}$  values of the host rocks reveal a narrower range from -6.616‰ -4.224‰, mostly between -6‰ and -5‰.

#### Site 2

The  $\delta^{13}\text{C}$  values are similar at Site 2 (Fig. 10). The  $\delta^{13}\text{C}$  values of the closely spaced calcite veins are all positive, ranging from 0.244‰ to 0.888‰. The upper and lower parts in single veins exhibit different values. The  $\delta^{13}\text{C}$  values of the upper parts of two veins are smaller than their lower parts respectively, whilst the value of the upper part is higher in the other vein. In contrast, the shales between these three veins all exhibit negative values in  $\delta^{13}\text{C}$ , ranging from -0.232‰ to -0.587‰.

The measurement of calcite veins at Site 2 reveals  $\delta^{18}\text{O}$  values ranging from -7.921‰ to -5.547‰. The samples from the three shale horizons exhibit  $\delta^{18}\text{O}$  values of approximate -6‰ that is higher than most vein  $\delta^{18}\text{O}$  compositions.

#### Site 3

The  $\delta^{13}\text{C}$  values revealed in the core of the carbonate concretion range from -8.783‰ to -7.117‰, which are much lower than the surrounding cone-in-cone structures and beef veins (Fig. 11). The cone-in-cone structures in the lower rim of the concretion exhibit a negative  $\delta^{13}\text{C}$  value of -1.515‰, whilst those in the upper rim exhibit positive values. A  $\delta^{13}\text{C}$  measurement of 2.723‰ is revealed in a beef vein above the concretion. The  $\delta^{13}\text{C}$  values of dark shales above and below the concretion are 0.461‰ and -0.063‰ respectively.

The core of the concretion exhibit  $\delta^{18}\text{O}$  values from -5.705‰ to -4.772‰, which are higher than the surrounding cone-in-cone structures and beef veins. Compared to the concretion and the host

shales, the  $\delta^{18}\text{O}$  composition of cone-in-cone structures in the upper rim of the concretion exhibits the lowest values.

Plots of carbon versus oxygen isotope compositions of samples demonstrate the covariations of oxygen and carbon isotope signatures in the calcite veins, especially in the samples from Site 3 (Fig. 12). A lower  $\delta^{18}\text{O}$  value commonly corresponds to a higher  $\delta^{13}\text{C}$  value.

## **Discussion**

The discussion focuses on the source of carbonates, diagenetic conditions, formation mechanism and controls on vein development, and is based on the petrographic observations and the stable isotope signatures of fibrous calcite veins and their host rocks at the studied sites of the Shales-with-Beef Member.

### **Source of carbonates**

The fibrous calcite beef veins and cone-in-cone structures are ubiquitous throughout the succession of thinly bedded organic-rich shales in the Shales-with-Beef Member in the Wessex Basin. The question arises as to what is the source of the carbonate involved in the precipitation of vein fills. It has been suggested that carbon isotope signatures revealed in calcite beef veins could provide an important clue for sources of carbonate (Al-Aasm et al., 1995; Astin and Scotchman, 1988; Kiriakoulakis et al., 2000; Kowal-Linka, 2010).

Given the isotopic zonation of the carbonate concretion in Site 3, with the core presenting the most negative  $\delta^{13}\text{C}$  values (Fig. 12C), it is suggested that the light carbon has been mainly derived from in situ decomposition of organic matter during bacterial reduction in an anaerobic environment (c.f. Wolff et al., 1992; Kiriakoulakis et al., 2000). Bacterial sulphate reduction produces

284 carbonate with depleted  $^{13}\text{C}$  of -20‰ to -25‰ (Hudson, 1978; McLane, 1995). This idea has been  
285 verified by the presence of biomarkers of abundant unsaturated fatty acid in the Birchi Bed in the  
286 Shales-with-Beef Member (Kiriakoulakis et al., 2000). The commencement of concretion  
287 formation has been suggested to be early during burial, possibly at the first tens of metres, which  
288 is synchronous with the onset of bacterial activity (Marshall, 1982). The early timing is also evident  
289 from the preservation of labile organic matter and uncrushed ammonites within the concretions,  
290 which have been protected from decomposition and crushing during burial (Allison and Pye, 1994;  
291 Marshall and Pirrie, 2013; Stewart, 1986).

292 Importantly, the shift in carbon isotope signatures from the concretion core to the enveloping cone-  
293 in-cone indicates the weakening of the role of bacterial sulphate-reduction in providing carbonate  
294 materials during later calcite precipitation. The moderate  $\delta^{13}\text{C}$  values found in cone-in-cone  
295 structures and beef veins are similar to that of marine seawater and the skeletal remains of aragonite  
296 fossils. The dissolution of fossil shells with a  $\delta^{13}\text{C}$  value of  $\sim 0\text{‰}$  has been considered as  
297 volumetrically important components of the calcite veins (Rukin, 1990). It is conceivable that  
298 bioclasts have provided carbonates for the calcite veins in the Shales-with-Beef Member as the  
299 main source for two reasons: (1) skeletal fragments commonly occur in the median zones of beef  
300 veins; and (2) invertebrate fossils of ammonites, bivalves and gastropods are widespread in the  
301 shales (Simms, 2004). However, biomarkers of bacterial activities, which resemble those of  
302 carbonate concretions, have also been observed in the calcite veins, though they are less abundant  
303 (Kiriakoulakis et al., 2000; Pearson et al., 2005). This indicates that bacterial activity has at least  
304 contributed to some of the precipitated carbonate in the calcite veins; however, the organic matter-  
305 derived carbonate with depleted  $^{13}\text{C}$  are much less volumetrically significant.

306 CO<sub>2</sub> produced in the methanogenic zone that usually underlies the sulphate-reducing zone in the  
307 sediment column has been suggested to result in heavy carbon isotope signatures ( $\delta^{13}\text{C} \approx 0\text{‰}-15\text{‰}$ )  
308 (Raiswell, 1987; Wolff et al., 1992). Hence, the precipitation of the methanogenic carbonate results  
309 in authigenic carbonates with positive carbon isotope compositions (Krylov et al., 2008; Whiticar,  
310 1999), and they could have been an important source of CO<sub>2</sub> for the precipitation of the calcite  
311 beef veins (Kiriakoulakis et al., 2000). This is possible because of the high TOC in the host  
312 sediments, which could release abundant methanogenic CO<sub>2</sub> when the sediments entered the  
313 methanogenesis zone. The positive  $\delta^{13}\text{C}$  values exhibited in some of the beef veins could have  
314 resulted from the precipitation of methanogenic bicarbonate that is thought to contribute to an  
315 overall heavier carbon isotope signature. An example is from the beef veins in Horizon 2 (Site 1)  
316 with higher  $\delta^{13}\text{C}$  values and lower  $\delta^{18}\text{O}$  values than the encasing host rocks and other veins. Their  
317 isotopic compositions could possibly have resulted from a greater component of CO<sub>2</sub> derived from  
318 methanogenesis than other veins formed at a deeper burial depth and at a higher formation  
319 temperature.

320 Another possible source of carbonate is the CO<sub>2</sub> generated by oxidation of CH<sub>4</sub> above the  
321 methanogenesis zone. However, this process gives rise to carbonate with extremely light carbon  
322 isotope compositions ( $\delta^{13}\text{C} \approx -70\text{‰}-60\text{‰}$ ) (Gautier and Claypool, 1984). Hence, this hypothesis  
323 can be ruled out as an important source of CO<sub>2</sub>.

324 It has been suggested that antitaxial veins derive materials for crystal growth from the adjacent  
325 wall rocks (Bons et al., 2012). In this case, the upper parts and lower parts in single, antitaxial  
326 calcite veins could have derived carbonates from the overlying and underlying shales respectively,  
327 which could possibly explain the slightly different  $\delta^{13}\text{C}$  values they exhibit.

In summary, the fibrous calcite veins derived their carbonate largely from seawater inorganic carbon and bioclasts, whilst microbial decomposition of organic matter provides a minor component.

### **Diagenetic fluids**

The oxygen isotope composition of carbonate minerals is a function of primary isotope composition and the specific temperature of the water in which the carbonates are precipitated (Boggs, 2009; Grossman and Ku, 1986). However, the  $\delta^{18}\text{O}$  values of the black shales do not reveal the primary  $\delta^{18}\text{O}$  composition due to the resetting of oxygen isotope values during burial and diagenesis in the sediments (Worden et al., 2015). Hence, the oxygen isotope signatures of calcite veins can provide information on the source of formation fluid and the clues to physical and chemical processes that may have affected the original fluid composition (Conybeare and Shaw, 2000; Longstaffe, 1986).

The oxygen isotope composition of the calcite veins fall within a narrow range (ca. -7‰ - -5‰), which is similar to or slightly below the range of host shales (Fig. 12A and B). Such an oxygen isotope signature is too negative to reflect carbonate precipitation in equilibrium with the early Jurassic marine pore waters at shallow burial temperatures (Marshall, 1982), and suggests that the veins grew in pore waters of modified compositions (MacKenzie, 1972; Marshall, 1982). The negative shift of the oxygen isotope compositions is mainly ascribed to several mechanisms, including the influence of isotopically light meteoric waters (Carpenter et al., 1991),  $\delta^{13}\text{C}$  depleted waters generated by the decomposition of organic matter (Sass et al., 1991) or by water-rock interactions (Longstaffe, 1986; Zheng and Hoefs, 1993), and an increase of pore water temperatures (Al-Aasm et al., 1995; Longstaffe, 1986).



350 One possible explanation for the negative shift of  $\delta^{18}\text{O}$  value in the calcite veins is the influence  
 351 of meteoric waters with depleted  $^{18}\text{O}$ . However, there is a limitation on how much meteoric waters  
 352 could have been mixed with original sea water to deplete the  $\delta^{18}\text{O}$  values (Al-Aasm et al., 1995).  
 353 In addition, the narrow variations of carbon and oxygen isotope values indicate a minor influence  
 354 of meteoric waters which could have generated a range of water compositions between two end  
 355 member fluids that have distinct  $^{18}\text{O}$  and  $^{13}\text{C}$  signatures (Zheng and Hoefs, 1993).

356 It has also been suggested that the decomposition of organic matter can produce  $\delta^{18}\text{O}$  depleted  
 357 fluids by sulphate reduction (Sass et al., 1991). However, this model is based on very organic-rich  
 358 sediments (TOC>50%) and the induced  $\delta^{18}\text{O}$  shift is relatively small, which may not be applicable  
 359 to sediments with a moderate or a low TOC such as those in the present study.

360 Water-rock interaction during shallow to deep burial diagenesis of shales is another possible  
 361 mechanism for causing oxygen isotope fractionation in pore waters and thus influence  $\delta^{18}\text{O}$   
 362 signatures of authigenic carbonates (Longstaffe, 1986; Zheng and Hoefs, 1993). It has been  
 363 suggested that the gradual pore water evolution with burial can contribute to a systematic  $^{18}\text{O}$   
 364 depletion in successive precipitates (Dickson and Coleman, 1980; Hodgson, 1966; Marshall, 1982).  
 365 Hydration and carbonatization that occur in the sediments could lead to a negative shift in  $\delta^{18}\text{O}$   
 366 values of pore waters (Al-Aasm et al., 1995). This model is especially applicable when the  
 367 sediments contain volcanic or volcanoclastic materials (Morad and De Ros, 1994).

368 The dissolution of the abundant aragonitic fossil shells in the shales would introduce abundant  
 369 bicarbonate with  $\delta^{18}\text{O}$  of approximately zero (Marshall, 1982) which are different from the pore  
 370 waters with modified oxygen isotope signatures. Hence, the  $\delta^{18}\text{O}$  values of precipitated calcite  
 371 could exhibit a shift from those of pore waters.

Isotopic variations can also be induced by an ultrafiltration process in shales during compaction, which results in residual waters being enriched in  $^{18}\text{O}$  (Coplen and Hanshaw, 1973). However, it is difficult to assess the magnitude and validity of this explanation simply from the observed isotope signatures.

In summary, the calcite of vein fills precipitated from pore waters of modified compositions from the original sea water, which results in a more negative oxygen isotopic signature than that in equilibrium with the Jurassic sea water during early burial.

### **Formation mechanism of veins**

Horizontal fibrous beef veins and cone-in-cone structures in black shales are widely considered as natural hydraulic fractures due to overpressure during primary oil migration (Rodrigues et al., 2009; Stoneley, 1983). This hypothesis is evident from the frequently observed hydrocarbon inclusions in the median zones of the veins that mark the primary crack opening (Dobes et al., 1999; Lash and Engelder, 2005; Suchy et al., 2002; Zanella et al., 2014). For this model, vein formation commences along bedding planes when the shales enter the oil window and release abundant oil and gas (Cobbold et al., 2013; Lash and Engelder, 2005; Parnell et al., 2000; Rodrigues et al., 2009). This explanation is possibly viable for shales when they have acted as mature source rocks. This model does not seem applicable to the veins in the study area for two main reasons. Firstly, the outcrop shales are too immature to have produced oil (Ebukanson and Kinghorn, 1986; Kemp and McKerverey, 2001; Kemp et al., 2005), and secondly no oil has been found as inclusions in the veins.

As discussed above, the calcite veins likely owe part of their authigenic carbonate materials to methanogenic  $\text{CO}_2$  with positive carbon isotope values. Previous studies have demonstrated that

394 the degassing of organic-rich shales is an important or even the principle cause of overpressure  
395 during early burial (Flemings et al., 2003; Hedberg, 1974, 1980; Lacazette and Engelder, 1992;  
396 Osborne and Swarbrick, 1997). The biogenic gas generated in the megthanogenic zone would  
397 readily migrate upward by buoyancy, which could result in a decrease in fluid pressure and the  
398 solubility of CO<sub>2</sub>. This would conceivably be accompanied by a volume expansion in the relatively  
399 impermeable medium (Lacazette and Engelder, 1992). Meanwhile, the gas bubbles dispersed in  
400 pore waters will reduce the permeability of the bulk rock for either a liquid phase (pore water) or  
401 a gas phase (methane) (Hedberg, 1974). Under such conditions, a substantial increase in fluid  
402 pressure may occur with minor changes in composition in a fixed pore-volume rock mass,  
403 especially when given the low-permeability nodular carbonate beds above as seals. The free gas  
404 can produce three orders of magnitude more fracture volume than brines for a given pressure drop  
405 due to its greater compressibility (Lacazette and Engelder, 1992). Overpressure triggered by  
406 generation of biogenic gas is possibly able to exceed the sum of the least stress and tensile strength  
407 of the sediments and may yield abundant tension failure that vents overpressured gas (Flemings et  
408 al., 2003; Liu and Flemings, 2007; Tréhu et al., 2004) (Fig. 13).

409 It has been suggested that rapid deposition of sediments on top of under-compacted shales could  
410 give rise to overpressure in the shales (Gaarenstroom et al., 1993; Leynaud et al., 2007; Potter et  
411 al., 2005). The Dyrham Formation (Middle Lias), which overlies the Shales-with-Beef Member  
412 and Black Vein Marl Member and contains abundant, intact ammonite fossils as one of the major  
413 ammonite subzones, has a quick sedimentation rate at which the fossil assemblages remained a  
414 short time at the sediment-water interface before burial and received little erosion and crushing  
415 (Hallam, 1975; Simms, 2004). The rapid influx of sediments could lead to overpressuring in the  
416 Shales-with-Beef member when the rich organic content produced CO<sub>2</sub> during methanogenesis

(Simms, 2004). The poor development of beef veins in the Blue Lias Formation and other formations of the Charmouth Mudstone Group can be attributed to the lower organic-carbon contents than the Shales-with-Beef Member, which does not provide enough gas essential for triggering overpressure (Simms, 2004).

The increase in pore pressure may have also influenced the chemical equilibrium in the aqueous system by increasing the solubility of minerals. It has been suggested that as pore pressure increases, more  $\text{CaCO}_3$  is dissolved in the pore fluid, reaching a maximum when the pore pressure reaches its maximum (Shemesh et al., 1992). When hydraulic fracturing occurs, pore pressure drops drastically (Oliver and Bons, 2001), leading to the supersaturation of the pore fluids. This results in a rapid precipitation of calcite in the fracture systems, giving rise to the vein filling.

Hence, the sediment degassing in the methanogenesis zone and the rapid deposition of the overlying rocks are suggested to be responsible for the overpressuring and subsequent hydraulic fracturing in the shales, whose commencement also gave rise to the supersaturation of pore fluid and rapid calcite precipitation in fractures.

### **Controls on vein development**

The TOC in the shales at Site 1 exhibits a positive correlation to vein thickness in multiple horizons, especially in Horizons 8, 10 and 18 that are adjacent to organic-rich shales (Fig. 5). This indicates that the veins derived their carbon at least partially from organic matter. This is evident from the covariations in the carbon and oxygen isotope compositions of these calcite veins, revealing the significance of  $\delta^{13}\text{C}$  enriched methanogenic  $\text{CO}_2$  for the precipitation of authigenic carbonates at a relative deeper burial depth. The degassing by shale beds with a greater TOC may also favor the

precipitation of inorganic-sourced carbonates on vein surfaces in the adjacent horizons by supersaturating the pore fluid with respect to carbonates.

However, the TOC in the host rock is not well correlated to vein thickness in all cases, e.g. the vein in Horizon 28. The TOC values in Horizon 27 and 29 are both low-moderate; however, the vein thickness is even higher than several other veins whose host rocks exhibit higher TOC values (Fig. 5). It is notable that the bed 27 has the highest carbonate concentration (36.17%) among all shale horizons. Such a high carbonate content may have resulted from the precipitation of authigenic carbonates in the pore spaces of the host sediments. This is evident from the occurrence of carbonate concretions in this horizon that have been largely sourced from the decomposition of organic matter during sulphate reduction.

The abundant, pyritised skeletal fragments in the median zones of single veins suggest that the veins follow the site of fossil preservation, where the shells act as a nucleus for calcite precipitation. It has been suggested that bicarbonate derived from the dissolved aragonitic fossils that exhibit similar range of carbon isotope compositions to calcite veins are highly likely to be responsible for the majority of vein fills (Hendry, 2002; Hendry et al., 1995). Hence, the fossil skeletons in the median zones of veins are thought to provide significant nutrient for calcite precipitation, especially during the early stages of vein development. As nuclei for calcite precipitation, the skeletons could have largely determined the spatial distribution of calcite veins. The carbonates would have preferentially precipitated on skeleton surfaces rather than the pore spaces from the supersaturated pore fluid.

In summary, a high TOC is critical not only for triggering overpressure in the sediments, but also promoting pore fluid supersaturation with respect to bicarbonates. Fossil skeletons in the sediments

provide carbonates as important material sources for vein fills and serve as nuclei for calcite precipitation.

## **Conclusions**

(1) Fibrous calcite veins that exhibit antitaxial patterns are well developed in the organic-rich shales of the Lower Jurassic Shales-with-Beef Member in the Charmouth area. The sub-horizontal veins contain skeletal fragments, pyrite and amorphous organic matter in the median zones that represent the sites of initial fractures.

(2) The veins exhibit moderate carbon isotope values, indicating a deeper formation depth than carbonate concretions and a major component from seawater inorganic carbon and bioclasts, with a minor input of bicarbonate from bacterial decomposition of organic matter.

(3) The veins formed as hydraulic fractures in shales in the methanogenic zone. Overpressure is caused by sediment degassing and/or rapid deposition of the overlying sediments.

(4) The degassing of shales with a high TOC led to overpressuring in the sediments and pore fluid supersaturation with respect to bicarbonates. The aragonitic skeletal fragments not only provide carbonates for vein fills, but also serve as nuclei for calcite precipitation.

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## Figure Captions

Figure 1 Geological map of the study area in southern Dorset, southern UK.

Figure 2 (A) General stratigraphy of the Early Jurassic exposed on the Dorset coast. Adopted from Jenkyns and Weedon (2013). (B) Simplified stratigraphic column of the Shales-with-Beef Member in the regions of Lyme Regis and Charmouth. Modified from Gallois (2008). (C) Cross-section of the outcrop between Lyme Regis and Charmouth. Modified from Simms (2004).

Figure 3 Outcrop photographs showing carbonate concretions and fibrous calcite veins in the black shales of the Shales-with-Beef Member. (A) Calcite beef veins in the upper layers of a concretion horizon. (B) Multiple horizons of beef veins below a concretion horizon. (C) A lenticular carbonate concretion with an outer rim of cone-in-cone structures. (D) A carbonate concretion enveloped by cone-in-cone structures and beef veins in the adjacent horizons. Note the textural differences between the core and the rim of the concretion.

Figure 4 Outcrop photographs showing tabular cone-in-cone structures (A) and beef veins (B-H) in the black shales in the study area. (B) An isolated beef vein. (C) Multiple persistent beef veins. (D) A close shot of four closely spaced beef veins. (E) A group of persistent beef veins above a carbonate concretion. (F) A swarm of small beef veins below a thick cone-in-cone structure. (G) A small beef vein below a cone-in-cone structure. (H) A discrete beef vein with identifiable tapering tips. The diameter of the lense cap and the coin as the marker is 52 mm and 22.5 mm respectively.

Figure 5 Stratigraphic column showing the distribution and thickness of beef veins and cone-in-cone structures, carbonate concentration and TOC of the host shales, carbon and oxygen isotope compositions of the veins and shales at site 1. The dashed lines mark the average values.

Figure 6 (A) Backscattered electron image showing the composition of the median zone of a representative fibrous calcite veins. (B) A pyritised fossil skeleton. (C) EDS spectrum showing the elemental composition of the circular area in figure 6B. (D) Fibrous calcite developed on one side of pyritised skeletal fragments. (E) Calcite fibres developed on both sides of a lenticular aggregate of pyrite crystals. (F) Fully pyritised skeleton enclosed by calcite. (G) A partially pyritised skeleton in the median zone.

Figure 7 (A) Photomicrograph showing the distribution of AOM. Reflected light. (B) Backscattered electron image showing the same area as figure 7A. (C) EDS spectrum showing the elemental composition of the circular area in figure 7B. (D) A patch of AOM enclosed by calcite. (E) A skeleton filled with pyrite spheres and AOM along the margins. (F) The association of AOM and pyrite crystals in the median zone.

Figure 8 (A) EDS image showing the mineral composition of the host shales that are enrich in peloids, gypsum and organic matter. (C) EDS image showing the host shales with calcite cement. (B) and (D) The elemental composition of Ca, S, C and O in the same area as figures 8A and 8C respectively. (E) Authigenic carbonate in the clay matrix. (F) Calcite developed on one side of skeletal fragments that are filled with pyrite.

Figure 9 Calcitic peloids in the black shales under reflected light (A) and SEM (B). The arrow in figure 9B marks the dark rim of a peloid. (C) EDS image showing the mineral composition of peloid-enriched shales in the study area. (D) The elemental composition of Ca, C, Fe and Al in the same area as figure 9C.

Figure 10 Carbon and oxygen isotope compositions of three closely spaced, persistent beef veins at site 2. See field photograph in figure 4D.

Figure 11 Carbon and oxygen isotope compositions of a carbonate concretion and the veins and shales in the adjacent areas at site 3. See field photograph in figure 3D.

Figure 12 Plot of carbon versus oxygen isotope values of calcite veins and the host rocks at site 1 (A), site 2 (B) and site 3 (C).

Figure 13 Schematic sketch illustrating the formation mechanism of bedding-parallel calcite veins in the methanogenic zone during burial of organic-rich clays. OM = organic matter; SRB = sulphate reducing bacteria.



































