



# Microbially-mediated fossil-bearing carbonate concretions and their significance for palaeoenvironmental reconstructions: A multi-proxy organic and inorganic geochemical appraisal

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## ABSTRACT

Carbonate concretions are widespread within the geological record. However, the lack of recent known analogues creates a need for novel approaches to unravel the major microbial players involved in concretion formation and establish their suitability as palaeoenvironmental recorders. Here, we used a combination of geochemical and geological techniques to study two pyritiferous calcite concretions and compared the results with their host sediment (Toarcian “Posidonia Shale”, 183 Ma, SW-Germany).

The  $^{13}\text{C}$ -depleted nature of the concretion bodies, with average values of  $\delta^{13}\text{C}_{\text{carb}}$  (−14.8‰),  $\delta^{13}\text{C}_{\text{org}}$  (−32.4‰), and  $\delta^{13}\text{C}_{\text{n-alkanes}}$  (−34.9‰), indicates that sulphate-reducing bacteria (SRB), played a major role in the concretion growth and preservation of the nucleus via the rapid decomposition of organic matter (OM). However, Rock-Eval analyses from both concretions revealed elevated hydrogen indices (HI) in the body and low HI values at the rim. These values suggest that most of the microbial activity did not occur in the concretion body but rather at the rim and at the surface of the nuclei, which generally supports the exceptional preservation of OM in carbonate concretions. Furthermore, enrichment in euhedral pyrite in the concretion rims suggests they were formed through increased activities of iron reducing (FeR) bacteria coupled to a decrease of SRB activity leading towards conditions more favourable to the direct precipitation of pyrite. Despite low  $\delta^{13}\text{C}$  values, the known lipid biomarkers such as acyclic extended isoprenoids or 3 $\beta$ -methyl-hopanes did not reveal evidence of an active methane cycling. The present study emphasises the crucial role of carbonate concretion in OM preservation and highlights their great potential as palaeoenvironmental recorders.

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## 1. Introduction

Subsurface microbial communities decompose organic matter (OM) and trigger carbonate concretion formation in marine and lacustrine environments (Dale et al., 2014; Das and Tripathi, 2009; Marshall and Pirrie, 2013; Martill, 1988, 1989; Raiswell and Fisher, 2000). Carbonate concretions are ubiquitous in the geological record, and often associated with petroleum source rocks (Kiriakoulakis et al., 2000; Lash and Blood, 2004; Zatoń and Marynowski, 2004). They often encapsulate exceptionally-well preserved fossils of different ages and origins (Arua, 1991; Geraghty and Westermann, 1994; Martill, 1989; Wilson and Brett, 2013). Moreover, carbonate concretions can also contain exceptionally well-preserved molecular fossils (Kiriakoulakis et al., 2000;

Marynowski et al., 2007a,b; Melendez et al., 2013a,b; Pearson and Nelson, 2005; Pearson et al., 2005; Zatoń and Marynowski, 2004).

Contemporary analogues are rare and, over the last few decades, several studies have attempted to unravel details about when, where, and how carbonate concretions were formed by analysing their mineral and inorganic geochemical composition (Coleman and Raiswell, 1995; Coleman, 1993; Curtis et al., 1987; Marshall and Pirrie, 2013; Woo and Khim, 2006). Field observations of *in-situ* carbonate concretions, as well as macroscopic observations of internal structures, assisted in characterising the environment of formation. Most calcium carbonate concretions are suggested to form at a very early stage of diagenesis, within the top metres of sediment accumulation (Marshall and Pirrie, 2013; Raiswell and White, 1978; Seilacher, 2001; Sellés-Martínez, 1996). Furthermore, the presence of intact three-dimensional fossils and “card house” clay fabric in many calcium carbonate concretions is concordant with their early formation and highlights the ability of carbonate concretions to resist compaction (Das and Tripathi, 2009; Geraghty and Westermann, 1994; Lash and Blood, 2004; Martill, 1988; Zatoń and Marynowski, 2004).

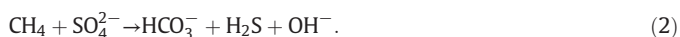
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The association of carbonate concretions with OM-rich pelitic shales reveals a formation under anoxic environmental conditions. In such conditions, OM decays at the sediment/water interface and is controlled by anaerobic micro-organisms. Berner (1968) and Allison (1988) established that microbial OM degradation was responsible for local changes in porewater chemistry. These changes can lead to the formation of a Ca-rich adipocere film playing a pivotal role in the formation of carbonate concretions. Sulphate reducing bacteria (SRB) obtain energy by oxidising organic compounds while reducing sulphate ( $\text{SO}_4^{2-}$ ) to hydrogen sulphide ( $\text{H}_2\text{S}$ ). They are believed to play major role in the formation of calcium carbonate concretions (Coleman and Raiswell, 1980, 1995; Coleman, 1993; Kiriakoulakis et al., 2000; Melendez et al., 2013b) based on the following general reaction:



The role of an active cycling of methane *via* the involvement, in the microbial consortium, of methanogenic archaea, anoxic methane oxidizers (see reaction below) is still poorly understood (Coleman and Raiswell, 1995; Coleman, 1993; Curtis et al., 1987; Kiriakoulakis et al., 2000; Woo and Khim, 2006). Such a consortium has been found in anoxic marine environments, notably gas hydrates (Boetius et al., 2000; Hinrichs and Boetius, 2002), but is yet to be associated with concretions.



Most studies of carbonate concretions have relied on inorganic geochemistry and petrological observations. However, relatively little attention was given to organic geochemical parameters to better understand concretion growth processes (Kiriakoulakis et al., 2000; Melendez et al., 2013b; Pearson et al., 2005; Wolff et al., 1991; Zatoń and Marynowski, 2004; Zatoń et al., 2011) or to establish a thorough comparison with their host rock (Marynowski et al., 2007a,b; Melendez et al., 2013b).

The limited occurrence of known modern analogues for carbonate concretions (Reitner et al., 2005) complicates the use of DNA in the identification of microbial communities. However, work on modern microbialites supports a more complex ecosystem than originally expected (Burns et al., 2009; Edgcomb et al., 2014; Pagès et al., 2014a,b).

In order to obtain further insights into the complex ecosystems involved in subsurface diagenetic environments, multidisciplinary techniques need to be applied. Here we report the first integrative approach, using geological, organic and inorganic geochemistry, to gain a better understanding of concretion growth processes and identify the microbial communities involved in the formation of two carbonate concretions. Furthermore, a systematic comparison of the concretions with their surrounding shale was undertaken to identify geochemical variations between the concretion and the host sediment showing the concretions' potential to be used as a palaeoenvironmental recorder.

More specifically, we aim to i) characterise the timing of formation of the two concretions; ii) identify marker and footprints of microbial activity, iii) establish their significance for palaeoenvironmental reconstruction and iv) investigate the preservation properties of carbonate concretion using bulk OM proxies.

## 2. Palaeoenvironmental settings

During the Jurassic, Europe was located on a broad and shallow continental shelf that deepened towards the South-East of the Tethys Ocean (Jenkyns, 2010; Röhl et al., 2001; Schwark and Frimmel, 2004; Ziegler, 2005). The shallow shelf featured several deeper sub-basins within which episodically restricted water circulation at relatively low sea level occurred (Röhl et al., 2001; Schmid-Röhl et al., 2002; Schwark and Frimmel, 2004). Moreover, global warming and methane release, related to astronomical cycles (Cohen et al., 2004; Hesselbo et al., 2000; Kemp et al., 2005; Ruebsam et al., 2014), as well as tectonic

activity (break-up of the Pangea) led to a major marine transgression during the Early Jurassic. These profound palaeoenvironmental changes led to widespread deposition of OM-rich sediments (Baudin et al., 1990).

A detailed description of the palaeogeographical and palaeoclimatic settings associated with the deposition of the Posidonia Shale of SW-Germany during the Lower Toarcian is presented elsewhere (Cohen et al., 2004; Röhl et al., 2001; Ruebsam et al., 2014; Schmid-Röhl et al., 2002). Here, we provide a short overview of the palaeoenvironment during the deposition of the studied section. The Posidonia Shale of SW-Germany was deposited in the SW-German Basin, a deep sub-basin of the epicontinental basin system of the Western Tethyan Shelf (Ziegler, 2005). The sediment accumulation was mostly controlled by sea-level variations. Enhanced anoxia and subsequent deposition of the OM-rich black shale occurred during intermediate sea level whereas phases of sea level highstand led to increased oxygenation of the water through a better connection to the Tethys Sea (Frimmel et al., 2004; Röhl et al., 2001; Schmid-Röhl et al., 2002). During the deposition of the lower *H. serpentinum* zone (Fig. 1) a warm and humid, monsoonal driven climate (Röhl et al., 2001) was prevalent in SW-Germany. Eutrophication of the epicontinental seas (Cohen et al., 2004; Ruebsam et al., 2014) took place and episodic photic zone euxinia (PZE) in the sub-basins has been previously reported (Berner et al., 2013; Bour et al., 2007; Jenkyns, 2010; Pancost et al., 2004; Röhl et al., 2001; Schouten et al., 2000; Schwark and Frimmel, 2004).

## 3. Material and methods

### 3.1. Study site

The concretions used for this study were collected from the Lower Toarcian Posidonia Shale Formation from the former Rohrbach now HOLCIM Cement quarry of Dotternhausen (SW-Germany) (Fig. 2). Based on the comparison of microfacies, lithology and geochemical signatures with previous analyses of sediments from the same location (Frimmel et al., 2004; Röhl et al., 2001; Schwark and Frimmel, 2004); these concretions derive from directly above one of the major carbonate horizons (the "Unterer Stein"), within the lower *H. serpentinum* zone (Ruebsam et al., 2014; Wignall et al., 2005) also known as *H. falciferum* zone (Frimmel et al., 2004; Seilacher, 2001) although exact stratigraphic position could not be determined after blasting (Fig. 1).

### 3.2. Sample description and preparation

Two concretions (A and B) of ovoidal shape, with a longest diameter nearing the 40 cm, were selected. A slice was cut vertically through the centre of each concretion revealing a "jet" nucleus (Fig. 3A, B) and the presence of sedimentary bedding (Fig. 3A, B, C). Based on morphological features, the slices were further divided into three different zones referred to as i) nucleus (jet), ii) body and iii) rim (Fig. 3C). Subsamples were taken radially from the concretion body to the rim. This mode of sampling was previously performed only in parallel to the bedding plane (Coleman and Raiswell, 1980; Raiswell, 1976, 1982). In this study, additional samples normal to bedding were also taken (Fig. 3D) to perform a more thorough comparison. A further sample was collected from the host *H. serpentinum* zone shale for a detailed mineralogical and geochemical comparison with the two concretions. Sample blocks (5 cm<sup>3</sup>) were sonicated three times in a mixture of dichloromethane: methanol (DCM: MeOH) at 9:1 (v:v) for 15 min to remove surficial organic contaminants. Each analysis corresponds to an average of the sampling area due to the size of each sample.

Most geochemical analyses were performed on samples from both concretions and the host sediment. A detailed description of which analysis techniques have been applied to each individual sample can be found in Table 1. Samples for mineralogy and geochemical analyses were crushed manually and ground using a Zircon mill in a benchtop

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