



# Application of redox sensitive proxies and carbonate clumped isotopes to Mesozoic and Palaeozoic radiaxial fibrous calcite cements



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## ABSTRACT

Ancient marine radiaxial calcite cements are commonly exploited as archives of marine porewater properties based on the argument that they lack metabolic effects often assigned to biogenic carbonates. Here we critically test the significance of conventional versus (with respect to these fabrics) less-conventional proxy data from Pennsylvanian, Triassic, and Cretaceous case examples. Conventional proxies include: cathodoluminescence, carbon and oxygen isotope ratios, main and trace elemental concentrations. Less conventionally applied proxies are: clumped isotope “ $\Delta_{47}$ ”, redox-sensitive, and rare earth elements sampled across a succession of Triassic radiaxial fibrous calcites. Radiaxial calcites are subdivided in three groups based on their luminescence characteristics: non-luminescent, patchy luminescent, and bright luminescent. Luminescence patterns are in fair agreement with isotope ratios, in particular with those of oxygen. The data fall into, or are close to, the range of reconstructed marine seawater values and often plot to the positive end member of the isotopic range. These results disagree with the commonly held view that isotope data from luminescent cements reflect a priori non-marine values. Further evidence for this comes from REE concentration patterns and cerium-anomalies suggesting normal marine porewater values for all except the very last generation of radiaxial calcites. This implies that luminescent radiaxial calcites must not necessarily represent significant diagenetic resetting. Kinetic effects during precipitation and different activator elements must be considered. Marine and earliest burial porewater temperatures of ~12–26 °C are suggested by conventional calcite  $\delta^{18}\text{O}$  thermometry. Conversely, the application of the clumped isotope thermometer to the same radiaxial calcites suggests temperatures of 180–200 °C, reflecting solid-state resetting of fully cemented limestones under a low water:rock ratio. Redox-sensitive elements, particularly Zn, Cd, U, and Cu are affected by kinetic processes overriding fluid Eh. Manganese concentrations and Ce-anomaly data point to gradually decreasing marine porewater oxygen levels from outer to inner cement fringes. Judging from REE patterns and Ce-anomalies, the cement layers in the central portions of the pore filling cement succession witnessed the end of marine precipitation and the onset of shallow marine diagenesis. Consequently, radiaxial calcite precipitation is suggested to continue in the early shallow (marine) burial domain. This study underscores the potential of radiaxial calcite successions as archives of marine porewater to shallow burial diagenetic pathways. The combination of conventional and less conventional proxies is a clear strength of this study and documents that abiogenic carbonate archives are often underexplored.

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## 1. Introduction

Radiaxial fibrous (RFC) and fascicular optical fibrous (FOFC) calcites (Bathurst, 1959; Kendall and Tucker, 1971; Kendall and Tucker, 1973; Kendall, 1976; Mazzullo et al., 1990; Swart, 2015) represent very common (up to 70 vol.%) pore-filling cements in mainly Palaeozoic and Mesozoic marine carbonate buildups. Palaeogene and Neogene

case examples of this marine carbonate fabric are remarkably scarce or perhaps even absent in the rock record (Aissaoui, 1988; van der Kooij et al., 2010). Although it is widely accepted that radiaxial fibrous calcite is an abiogenic precipitate (Richter et al., 2011), other authors, e.g., Lees and Miller (1995) discuss a microbial origin of similar cements but did not find evidence for this themselves.

In many cases, the presence of several stratigraphically overlying fringes of radiaxial and fascicular optical fibrous calcites occluding pore space in reefal carbonates represents a time-resolved archive of fluid properties recording gradual changes from the marine to

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increasingly burial domains. The common view is that these fabrics represent early marine diagenetic stabilization products of a high-Mg radial fibrous calcite precursor phase whereas the controls that lead to the formation of their converging or diverging crystal c-axes are as yet unclear (see review in Richter et al., 2011). Assuming that marine porewater properties represent reasonable analogues of coeval marine waters, numerous workers have exploited their archives (Saller, 1986; Carpenter and Lohmann, 1989; Gray and Adams, 1995; Tobin et al., 1996; Kaufmann and Wendt, 2000; Kim and Lee, 2003; Hasiuk and Lohmann, 2008).

Most previous studies dealing with Palaeozoic or Mesozoic radial fibrous calcites apply standard cathodoluminescence microscopy and conventional stable isotope ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) combined with major and trace elemental (Mg, Mn, Sr, Fe) geochemistry in order to assess the nature and degree of diagenetic overprint (Carpenter and Lohmann, 1989; Mazzullo et al., 1990; Bruhn et al., 1995; van der Kooij et al., 2007, 2009; Hasiuk and Lohmann, 2008). The commonly held opinion is that non-luminescence (black to blue intrinsic) typifies well-preserved material, whilst patchy or bright luminescent (radial) calcites are considered as diagenetically altered and hence not applicable for the reconstruction of past seawater properties (see discussion in van der Kooij et al., 2007, 2009). Only a very limited number of workers exploited these fabrics in a more systematic manner as archives of their diagenetic pathways (e.g., Mazzullo et al., 1990; Kaufmann, 1997). Along these lines, Rare Earth Element (REE) data have the potential to shed light on the nature and properties of pore fluids and their evolution with time (e.g., German and Elderfield, 1990; German et al., 1991; Bodin et al., 2013; Della Porta et al., 2015) but have, to the knowledge of the authors, not yet been applied to these fabrics. The same accounts for the clumped isotopes ( $\Delta_{47}$ ) proxy revealing important information on burial fluid temperatures (e.g., Bernasconi et al., 2011; Huntington et al., 2011; Budd et al., 2013; Huntington and Lechler, 2015; Kluge et al., 2015; Shenton et al., 2015). Acknowledging that the REE proxy is a widely applied tool in geochemistry, we argue that its application to the fabrics studied here is rarely seen. The same accounts for redox sensitive elements and carbonate clumped isotope data. Therefore, referring specifically to radial fibrous calcites, the label “less conventional” for the application of these proxies seems appropriate. The goal is to test if pore fluids from which some of these fabrics precipitated or stabilized might have properties that differed from that of coeval seawater.

The aims of this study are twofold: First, we document a comparison of geochemical and cathodoluminescence features of Pennsylvanian, Triassic and Cretaceous case examples of pore-filling successions of marine radial fibrous calcites. Second, a particularly extensive succession of Upper Triassic radial fibrous calcites was selected as a case example for an in-depth study of the diagenetic pathway recorded in these fabrics. In addition to conventional light stable isotopes and main and trace elements, we here also document clumped isotope, redox sensitive elements, and REE data from a transect across all paragenetic phases of these cements. This is performed with the intention to go beyond previously discussed interpretations of these cement archives and to test the sensitivity of isotopic and elemental proxies for patterns and threshold limits in the diagenetic realm.

## 2. Description of case settings, sample materials and rationale for the selection of study sites

Below we briefly document the main characteristics of three Palaeozoic and Mesozoic case settings investigated here and refer to Table 1 for a summary of the main characteristics of the chosen time slices. The selection of sampling sites has been guided by the need for reasonably well dated, volumetrically significant, stratigraphically thick radial fibrous cement successions in a shallow marine environment. A detailed framework of environmental and diagenetic parameters for all sampling sites exists. Most of the data (about 60%) shown here were obtained from Upper Triassic (Carnian to Norian; ca 227–209 Ma) fibrous cements of Hydra Island (Greece). These are particularly suitable for this study due to their uncommonly thick cement fringes (~5 to 10 cm). Approximately 20% of the samples studied originate from Pennsylvanian (Bashkirian; ca 323–311 Ma) of Northern Spain and approximately 20% from the Late Cretaceous (Cenomanian; ca 99–93 Ma) of Dokos Island (Greece; Table 1). Combining these three sample sets allows for deducing conclusions that go beyond that of a single case study.

### 2.1. Pennsylvanian of Asturias

The carbonate platform sampled in the context of this study, the Sierra del Cuera mountain range, is situated in the province of Asturias, Northern Spain (Fig. 1). This area forms part of the Cantabrian Zone characterized by a wide marine foreland basin during early Pennsylvanian time (Serpukhovian, 328–318 Ma). Nucleation of an extensive carbonate platform took place during Bashkirian (318–312 Ma) and Moscovian times (312–307 Ma; Colmenero et al., 2002; Bahamonde et al., 2007; van der Kooij et al., 2009). Due to tectonic rotation, outcrops of a high-rising margin of the platform are presently exposed in near-vertical position. The Bashkirian part of the margin, the Valdeteja Formation, has a progradational character whilst the Moscovian portions (Picos de Europa Formation) are of aggradational nature (Bahamonde et al., 1997; Della Porta et al., 2004; van der Kooij et al., 2009). The Bashkirian upper-slope sequence, the sampling site of radial fibrous calcites analysed in this study, is characterized by intercalated microbial boundstones, platform-shed grainstones and red-stained limestones with abundant successions of radial fibrous calcites (Fig. 2A). These red intervals in the platform slope represent deepening pulses (van der Kooij et al., 2007).

### 2.2. Triassic of Hydra

The Greek island of Hydra is located offshore the Argolis Peninsula (Fig. 1). Hydra Island extends 18 km in EW and 4 km in NS direction (64.4 km<sup>2</sup>) and forms part of the Subpelagonian Zone, a passive continental margin succession belonging to the Internal Hellenides and has a transitional position to the Pindos zone (Jacobshagen, 1986; Richter, 1999). The geology of Hydra is characterized by three Tethyan neritic carbonate to siliceous hemipelagic successions trusted tectonically on top of each other. The oldest unit (I) is Permian in age and comprises

**Table 1**  
Description of the three different case settings analysed in this study.

Locality	Asturias (Spain)	Hydra (Greece)	Dokos (Greece)
Age	Late Carboniferous (Pennsylvanian (Bashkirian))	Late Triassic (Carnian/Norian)	Late Cretaceous (Cenomanian)
Carbonate platform type	High-rising platform (up to 850 m), progradational geometry	Reef complex, progradational geometry	
Location on platform	Upper slope (150–350 m below platform top)	Platform top, neritic	Platform top, neritic
Host facies	Red-stained microbial boundstone	Reefal limestone	Polymict limestone breccia
Sea-level-mode	Transgressive	Transgressive	Transgressive
Climate-mode	Icehouse	Greenhouse (“Hothouse”)	Greenhouse
Global seawater chemistry	Aragonite-II sea van der Kooij et al. (2007, 2009, 2010)	Aragonite-II sea Richter (1999)	Calcite-II sea Bachmann and Risch (1979) and Clift and Robertson (1990)

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