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First description of Phanerozoic radiaxial fibrous dolomite

D.K. Richter, F. Heinrich, A. Geske, R.D. Neuser, H. Gies, A. Immenhauser*

Ruhr-University Bochum, Institute for Geology, Mineralogy and Geophysics, Universitätsstrasse 150, 44801 Bochum, Germany

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ABSTRACT

The petrographic analysis and crystallographic analysis of concretionary carbonate cements ("coal balls") from Carboniferous paralic swamp deposits reveal the presence of (length fast) radiaxial fibrous dolomite (RFD), a fabric not previously reported from the Phanerozoic. This finding is of significance as earlier reports of Phanerozoic radiaxial fibrous carbonates are exclusively of calcite mineralogy. Dolomite concretions described here formed beneath marine transgressive intervals within palustrine coal seams. This is of significance as seawater was arguably the main source of Mg²⁺ ions for dolomite formation. Here, data from optical microscopy, cathodoluminescence, electron backscattered diffraction, X-ray diffraction and geochemical analyses are presented to characterize three paragenetic dolomite phases and one calcite phase in these concretions. The main focus is on the earliest diagenetic, non-stoichiometric (degree of order: 0.41–0.46) phase I, characterized by botryoidal dolomite constructed of fibres up to 110 µm wide with a systematic undulatory extinction and converging crystal axes. Petrographic and crystallographic evidence clearly qualifies phase I dolomite as radiaxial fibrous. Conversely, fascicular optical fabrics were not found. Carbon-isotope ratios ($\delta^{13}C$) are depleted (between -11.8 and -22.1%) as expected for carbonate precipitation from marine pore-fluids in organic-matter-rich, paralic sediment. Oxygen isotope (δ^{18} O) ratios range between -1.3 and -6.0%. The earliest diagenetic nature of these cements is documented by the presence of ubiquitous, non-compacted fossil plant remains encased in phase I dolomite as well as by the complex zoned luminescence patterns in the crystals and is supported by crystallographic and thermodynamic considerations. It is argued that organic matter, and specifically carboxyl groups, reduced thermodynamic barriers for dolomite formation and facilitated Mg/CaCO₃ precipitation. The data shown here reveal a hitherto unknown level of complexity with respect to radiaxial fibrous carbonates and are of importance for those concerned with dolomite and carbonate petrography in general.

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1. Introduction

Radiaxial-fibrous (RFC) and fascicular-optic fibrous (FOFC) calcites (first described by Bathurst in, 1959; see also Kendall, 1985; Sandberg, 1985: review in Richter et al., 2011) are widespread and volumetrically important calcite cements in marine carbonate platform deposits of Palaeozoic and Mesozoic age (Lohman and Meyers, 1977; Videtich, 1985; Davies and Nassichuk, 1990; Tucker and Wright, 1990; Wilson and Dickson, 1996; Reinhold and Kaufmann, 2010; Van der Kooij et al., 2010). Radiaxial (length slow) fibrous dolomite, along with (length slow) fascicular optic dolomite, was first documented by Tucker (1983) in the Upper Precambrian Beck Spring Dolomite (~850 Ma). Recently, Hood and Wallace (2012) described marine radiaxial dolomite cement (fascicular slow dolomite = FSD; radiaxial slow dolomite = RASD) from the Neoproterozoic (Cryogenian; \sim 650 Ma) Oodnaminta Reed Complex in southern Australia. It is of interest that the fascicular and radiaxial marine dolomite cements described in Tucker (1983) and Hood and Wallace (2012) are length slow, not length fast as in radiaxial calcites. The widespread marine dolomite

E-mail address: adrian.immenhauser@rub.de (A. Immenhauser).

cementation in Cryogenian reefal settings is arguably related to the rather specific chemico-physical properties of these ancient oceans. In particular, the occurrence of "saline giants" in the Neoproterozoic (Knauth, 2005) is indicative of very specific geographical, geological, climatic, oceanographic and depositional boundary conditions that might have no genuine counterpart in the Phanerozoic world.

In contrast to Palaeozoic and Mesozoic oceans, radiaxial fibrous calcite is scarce in Paleogene and near-absent in Neogene and Quaternary marine carbonates (Saller, 1986; Kim and Lee, 2003). The cause of this intriguing secular pattern in frequency distribution, however, is enigmatic. It is crucial, then, to assess the origin and controlling mechanisms of the c-axis anomalies that characterize these fabrics. Moreover, RFC and FOFC fabrics have been described from Holocene meteoric-vadose calcitic stalagmites in dolomite host-rock caves and in Jurassic and Cretaceous biogenic endoskeletons (belemnite guards; Neuser and Richter, 2007; Richter et al., 2011; Wassenburg et al., 2012). Thus far, however, a mechanistic understanding of the formation and potential alteration of radiaxial cements is lacking (Richter et al., 2011).

The presence of these fabrics in marine reefal settings, in continental cave carbonates and in marine biominerals provides evidence that RFC and FOFC fabrics are primary feature and far more widespread than previously expected. Nevertheless, most previous reports of RFC and

^{*} Corresponding author. Tel.: + 49 234 32 2825.

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FOFC fabrics referred to a calcite mineralogy with variable Mg content (Richter et al., 2011). Here, for the first time, evidence is presented that the radiaxial fibrous fabric is also present in Phanerozoic nonstoichiometric, early diagenetic dolomite concretions from paralic settings in Germany and Belgium ("coal balls" sensu Scott et al., 1996). This is of significance because previous work suggested that increasing fluid Mg/Ca ratios during calcite precipitation and the related increasing incorporation of Mg^{2+} ions in the calcite crystal lattices represent a possible mechanism of the c-axis anomalies that characterize radiaxial calcite (Richter et al., 2011). Analogous to the term "radiaxial fibrous calcite", the fabric described here is referred to as "radiaxial fibrous dolomite" (RFD).

Radiaxial fibrous dolomite cements are common as concretionary carbonates in Upper Carboniferous palustrine (paralic swamp) coal seams in NW Germany (Fig. 1). Similar to other Carboniferous occurrences of calcitic coal balls in Belgium (Scott and Rex, 1985), Great Britain (Scott et al., 1996) and the USA (Evans and Amos, 1961), as well as Permian examples from China (Tian et al., 1996), the stratigraphic association with marine horizons in an otherwise paralic setting to the coal balls is significant. Exceptions include sideritic coal balls in the Stellarton basin in Nova Scotia, Canada that might have formed in a meteoric diagenetic environment (Zodrow and Cleal, 1999).

Previous reports of Carboniferous dolomite concretions from Germany ("Torfdolomite") go back to the 19th century (see compilation in Kukuk, 1938). Carboniferous calcitic "coal balls" from Great Britain were first described by Hooker and Binney (in Scott et al., 1996). As a result of the uncommonly well-preserved plant material in these concretions (Fig. 2) and their systematic occurrence beneath coastal marine sequences, alternating with palustrine/paralic facies (Fig. 1), Teichmüller et al. (1953) and Eckhardt and v. Gaertner (1955) suggested that these peculiar dolomites represent a very early diagenetic precipitate. This view is generally shared with the majority of workers suggesting that, in some cases, the formation of coal balls was contemporaneous with the living vegetation in the mire (Scott and Rex, 1985; Scott et al., 1996; Zhou et al., 2008). The influence of marine fluids in coal ball formation is indicated by the presence of well-preserved high-Mg calcite in mid-Carboniferous coal balls from the Donets basin



Fig. 2. Thin-section image of dolomite concretion (Sample 4, Table 1) depicting wellpreserved, uncompacted plant (P) remains. Dolomite portions of thin-section appear translucent; plant remains and pyrite are opaque.

(Zodrow et al., 2002) and Upper Carboniferous examples from the Kalo Formation in Iowa (Raymond et al., 2012).

The aims of this paper are to (i) document the mineralogy, petrography, crystallography and geochemistry (δ^{13} C, δ^{18} O, 87 Sr/ 86 Sr; Ca, Mg, Mn and Sr elemental abundances) of radiaxial fibrous dolomite and (ii) place these findings in a process-oriented diagenetic and paragenetic context. The work shown here is of significance for those concerned with carbonate petrography and dolomite in general and sheds new light on a poorly understood fabric.

2. Geological context and material

Stratigraphically, the dolomite concretions described here belong to the Upper Carboniferous coal seams "Finefrau Nebenbank" and "Katharina" situated near the SW-border of the sub-Variscian foredeep of western Germany (Fig. 1). Similar fabrics are also present in the seam "Katharina of Bouxhannout" in Belgium (Table 1). Füchtbauer et al. (1991), Süss et al. (2000) and Wrede et al. (2005) have provided a sedimentological and stratigraphical overview of the rock units



Fig. 1. Palaeogeographic map for the Late Carboniferous (Westphalian) time interval depicting the southern edge of sub-Variscan fore-deep. Sampling locality of palustrine dolomite concretions near the village of Essen is indicated. Westphalian stratigraphy indicating position of coal seams Finefrau Nebenank and Katharina beneath transgressive intervals. Map modified after Ziegler (1990). Stratigraphy according to Menning et al. (2000).

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