Isotope and elemental geochemistry of black shale-hosted fossiliferous concretions from the Cretaceous Santana Formation fossil Lagerstätte (Brazil)

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ABSTRACT

Carbonate concretions hosted within organic carbon-rich shale sequences represent unique archives of often exceptionally preserved fossil biota. Besides providing high-fidelity preservation, their geochemical signatures can provide insight into the physical and chemical processes during early and later-stage concretion growth. Here, two fossiliferous carbonate concretions of the late Early Cretaceous Santana Formation (Araripe Basin, NE Brazil) are analysed with an integrative geochemical approach including μ -XRF scanning, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and Δ_{47} (clumped-isotope thermometry). Individual concretions show a concentric internal zonation with the outermost layer being composed of mm-thick cone-in-cone calcite. A strong covariance of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the fine-crystalline concretion body indicates mixing of two different carbonate phases and supports a scenario of temporally separated pervasive growth stages. Microbially-mediated formation of an

early porous calcite framework was controlled by the combined processes of fermentation and methanogenesis around the decaying carcass, forming localized environments within a zone of sulfate reduction. Microbial sulfate reduction is indicated by the concentric enrichment of pyrite in the outer part of the concretion body and by high pyrite abundance in the surrounding shale. Information on the later-stage diagenetic processes affecting the Santana concretions can be derived from the outermost fringing cone-in-cone calcite. The carbonate precipitating fluid was characterized by a more or less marine $\delta^{18}\text{O}$ composition (calculated $\delta^{18}\text{O}_{\text{porewater}} = -1.0$ to -1.8 ‰) and by radiogenic Sr-isotope ratios (up to $0.713331 \pm 7.0 \cdot 10^{-6}$), the latter probably reflecting modification due to interaction with the surrounding shale or, alternatively, with underlying evaporitic sulfate deposits influenced by strong continental inflow or with crystalline basement rocks. The Δ_{47} -derived temperature estimates range between $37\text{--}42^\circ\text{C} \pm 5$, indicating precipitation of the cone-in-cone calcite at a depth of 650 – 850 m, which is only half as much as the maximum burial depth derived from existing fission-track data. Overall, the study of fossiliferous carbonate concretions in organic carbon-rich sedimentary sequences can reveal a complex growth history spanning incipient microbially influenced precipitates as well as later-stage burial diagenetic phases.

Keywords Carbonate concretion, inorganic geochemistry, pervasive growth, clumped isotopes, cone-in-cone, Santana Formation,

INTRODUCTION

Concretions represent a common feature in many sedimentary successions and are considered as unique archives of the physical and chemical processes during sediment diagenesis. Carbonate concretions may record the geochemical evolution of pore waters and changes in temperature during progressive carbonate precipitation, hence providing information on the conditions during early and later-stage burial (Irwin *et al.*, 1977; Buchardt & Nielsen, 1984; Mozley & Burns, 1993; De

Craen *et al.*, 1999; Raiswell & Fisher, 2000; Hudson *et al.*, 2001; Hendry *et al.*, 2006). Fossil-bearing carbonate concretions, often hosted within bituminous shale, are of particular interest due to the frequent preservation of uncrushed and frequently delicate skeletal remains and/or phosphatized soft-tissue (e.g. McCoy *et al.*, 2015). Famous examples include the Cambrian phosphatized arthropods preserved in the so-called “Orsten” concretions of Sweden (Müller, 1985; Maas *et al.*, 2006) or the unique early fish and crustacean invertebrate fauna derived from concretions of the Upper Devonian Gogo Formation of Western Australia (Long & Trinajstić, 2010; Melendez *et al.*, 2013; Trinajstić *et al.*, 2013). Similar exceptional preservation is also seen in the carbonate concretions of the Early Cretaceous Santana Formation, which yields a rich and diverse fish fauna (e.g. Brito & Gallo, 2003) as well as turtles, crocodiles and pterosaurs (Martill, 1993; Hirayama, 1998; Fara *et al.*, 2005). Despite a wealth of studies dealing with their paleontological content, the growth mechanism and diagenetic evolution of the Santana concretions have never been subject to detailed investigations.

The growth of fossiliferous carbonate concretions is generally explained with the concentration of highly metabolizable organic material causing a microenvironment of enhanced carbonate supersaturation (“local-equilibrium model” of Raiswell & Fisher, 2000). According to these authors, carbonate precipitation around a decaying organism is expected to result in an early phase of pervasive cementation given the high degree of local supersaturation and associated calcite nucleation. As pointed out by McCoy *et al.* (2015), initial pervasive growth of individual crystals across the entire concretion volume allows for limited oxidant diffusion, a prerequisite for microbially-mediated soft-tissue replication as described from the Santana concretions (Martill, 1988; Martill, 1993). More recently, Bojanowski & Clarkson (2012) highlight the role of organic remains in creating isolated microenvironments of methanogenesis within the sulfate reduction zone, resulting in pervasive concretions without concentric zoning. Besides the undisputed importance of a significant microbial contribution during early growth of fossiliferous concretions (Raiswell, 1976; Irwin *et al.*, 1977), however, the role of later-stage cementation of an initially retained porosity may often be underestimated (Mozley, 1996; Raiswell & Fisher, 2000). Later-stage

processes during burial can result in a significant diagenetic overprint of earlier geochemical signatures and result in long-lasting and complex growth histories for mudrock-hosted concretions. Having new state-of-the-art geochemical tools at hand, such as high resolution X-ray fluorescence (μ -XRF) scanning, computer-controlled micro-milling and clumped stable isotope analysis, the growth of fossiliferous carbonate concretions is revisited for the Santana Formation as an exemplary case. In order to decipher the role of early microbially-controlled versus later-stage burial processes, two concretion specimens are studied with an isotope-geochemical approach. This includes high-resolution elemental and stable carbon and oxygen isotope analyses in combination with Sr-isotope measurements. In addition, carbonate clumped-isotope thermometry is applied as a tool for assessing temperatures of carbonate precipitation independently of pore-water $\delta^{18}\text{O}$ composition (Loyd *et al.*, 2012; Dale *et al.*, 2014; Loyd *et al.*, 2014). Based on this multi-proxy approach the diagenetic history of the fossil-bearing Santana concretions is reconstructed, and the different controlling factors evaluated.

GEOLOGICAL SETTING

The studied concretions were collected from the Romualdo Member of the Early Cretaceous Santana Formation cropping out on the flanks of the Chapada do Araripe, in the Araripe Basin of northeastern Brazil. The Araripe Basin is a fault-bounded interior basin located in the border region of the states of Ceará, Pernambuco and Piauí (Figs. 1A and 1B). The formation of this basin and its sedimentary infill history are linked to the crustal extension accompanying the opening of the Atlantic Rift System (Chang *et al.*, 1988; De Matos, 1999). During the post-rift stage of basin development, low subsidence resulted in the deposition of deltaic to lacustrine sediments (Rio da Batateira and Crato formations) overlain by evaporites (Ipubi Formation), deltaic to marginal marine sandstones, organic carbon-rich shales (Santana Formation) and fluvial siliciclastics (Exu Formation) (Martill, 1993; Ponte & Ponte Filho, 1996) (Figs. 1B and 1C). The stratigraphic assignment of the different units is essentially based on terrestrial palynomorphs and ostracods. For the concretion-

bearing Santana Formation, a latest Aptian to Early Albian age is suggested (Coimbra *et al.*, 2002; Heimhofer & Hochuli, 2010; Rios-Netto *et al.*, 2012).

Figure 1

(A) Map of Brazil showing location of the Araripe Basin. (B) Simplified geological map showing the outcrop of the Santana Formation around the Chapada do Araripe. (C) Schematic lithological log of the Early Cretaceous Santana Formation with the concretion-bearing horizon of the Romualdo Member marked by an arrow.

The Romualdo Member of the Santana Formation consists of an 8 to 15 m thick sequence of finely laminated organic carbon-rich shale with abundant fossiliferous carbonate concretions. The Santana concretions occur preferentially in two stratigraphic horizons located in the lower part of the Romualdo Member (Fara *et al.*, 2005). Typically, concretions range in size between 20 and 40 cm on average and frequently contain remains of fossil fish with *Tharrhias*, *Vinctifer* and *Rhacolepis* being the most common taxa (Fara *et al.*, 2005). Larger concretions (up to 1 m length) containing large

predator fish or remains of terrestrial vertebrates are rarer (Martill, 1993). At the Sobradinho locality, the bituminous shale unit hosting the concretions is characterized by low carbonate content (CaCO_3 ; 2.9 to 7.3 wt. %), whereas high total organic carbon contents (TOC; up to 10.8 wt. %) and high hydrogen indices (HI; up to 810 mg HC g^{-1} TOC) indicate a predominantly autochthonous, lipid-rich algal and/or microbial OM source (Heimhofer *et al.*, 2008). Based on findings of the *Chlorobia*-derived biomarker isorenieratane the latter authors proposed the occurrence of photic-zone euxinia during deposition of the Romualdo Member. The sedimentary OM is considered as being thermally immature with respect to hydrocarbon generation based on biomarker data and palynological observations (Baudin & Berthou, 1996). These observations are in line with apatite fission-track data indicating minor burial of the succession of less than 1.5 km (Morais Neto *et al.*, 2009), excluding deep burial alteration and strong recrystallization.

MATERIALS AND METHODS

Sampling methodology

Following visual inspection of several fossiliferous Santana Formation concretions, two non-weathered, dark-grey/blue-grey concretions (weathered concretions are buff colored) were selected for further analyses (CON-1, CON-7). Additional stable carbon and oxygen isotope data of cavity-filling spar are derived from CON-5. For studying the internal structure and composition, concretions were cut into slabs perpendicular to bedding. Petrographic thin-sections covering different parts of the concretions were studied using transmitted light as well as cathodoluminescence (CL) microscopy using a "hot cathode" CL microscope (type HC1-LM) operated at 14 kV and 9 $\mu\text{A}/\text{mm}^2$ located at the Ruhr-University Bochum. High-resolution sampling for geochemical analyses was performed using a computer-controlled Merchantek Micromill system equipped with tungsten drill bits ($\varnothing = 0.4$ mm). To cover the full range of geochemical variability, sampling transects for stable isotopes were orientated from center towards the edge both perpendicular and parallel to bedding (Fig. 2). Powder samples for $^{87}\text{Sr}/^{86}\text{Sr}$ -isotope and Δ_{47} analyses were taken from different positions across both concretions using a hand-held micro-drilling device.

Figure 2

Transverse section of concretion CON-1 cut normal to bedding plane. The centre is formed by fossilized fish remains. Differential compaction is indicated by deflection of sedimentary laminae towards the edge. Dark bluish-green colour indicates non-weathered state of concretion. Traces in horizontal and vertical direction result from micromill sampling. Extent of zones I to IV is marked.

Element and isotope geochemistry

Qualitative elemental composition was obtained on selected samples at a micrometre resolution (4 data points/mm) using an EAGLE III μ -XRF scanner under vacuum conditions with a 50 μ m diameter beam at the University of Geneva, Switzerland. For details of the applied μ -XRF scanning technique see Dulski *et al.* (2015). Two selected slabs were measured for light (Mg, Al, Si, S, Ca, Ti, Mn, Fe) and heavy (Cu, Zn, Sr) elements. The data are expressed as elemental intensities in counts per second (cps). Only Ca, S and Fe are presented here.

Measurement of stable carbon and oxygen isotopes of carbonates was performed on a total of 161 powdered bulk samples (~0.5 mg). A Thermo Fisher Scientific Gasbench II carbonate device connected to a Finnigan MAT Delta S isotope ratio mass spectrometer, available at the Ruhr-University Bochum, Germany, was used for the stable isotope analyses. Repeated analyses of certified carbonate standards show an external reproducibility ± 0.1 ‰ for $\delta^{18}\text{O}$ and ± 0.07 ‰ for $\delta^{13}\text{C}_{\text{carb}}$. Values are expressed in conventional delta notation relative to the Vienna-Pee Dee Formation belemnite (VPDB) international standard, in per mil (‰).

Strontium isotope compositions of 7 sample powders were processed and measured at the stable isotope laboratory at Ruhr-University. Strontium was separated with standard ion-exchange methods

(e.g. Geske *et al.*, 2012) and loaded onto a rhenium filament, then measured with a thermal ionization mass-spectrometer (Finnigan MAT 262) in dynamic mode. The long-term standard mean ratios for reference materials (USGS EN-1, NIST NBS 987) are 0.709170 ($n=17$; 2σ mean= $2.0 \cdot 10^{-6}$) and 0.710246 ($n=29$; 2σ mean= $2.0 \cdot 10^{-6}$), respectively. Strontium-isotope ratios were adjusted to a USGS EN-1 value of 0.709175.

Carbonate clumped isotope measurements

All clumped isotope analyses were performed at ETH Zurich following the methodology of Schmid and Bernasconi (2010) incorporating improvements described by Meckler *et al.* (2014). The sample powders were measured as 6–10 individual aliquots of 150–200 μg , by reaction with 104% phosphoric acid at 70°C using a Kiel IV-MAT 253 system. The raw data were corrected offline for pressure baseline (PBL) effects (Bernasconi *et al.*, 2013; Meckler *et al.*, 2014) and transferred to the absolute reference frame (Dennis *et al.*, 2011) by means of an empirical transfer function (ETF) based on heated and equilibrated gases measurements (Meckler *et al.*, 2014). An acid fractionation correction of +0.064‰ was then applied to the Δ_{47} , which results from a linear interpolation of the observed offset between 25°C and 90°C acid temperature (Henkes *et al.*, 2013) to our reaction temperature of 70°C. The long-term reproducibility of the method based on our internal standards is ± 0.012 – 0.016 ‰ (1 SD) (Meckler *et al.*, 2014). Masses 48 and 49 were monitored to check for possible contamination according to Affek and Eiler (2006).

Carbonate clumped isotope measurements determine the excess abundance of ^{13}C – ^{18}O bonds in carbonate minerals, compared to a calculated stochastic distribution. The excess is expressed with the parameter Δ_{47} that is defined as:

$$\Delta_{47} (\text{‰}) = [(R^{47}/R^{47*} - 1) - (R^{46}/R^{46*} - 1) - (R^{45}/R^{45*} - 1)] * 1000,$$

where R^i is the abundance of the minor isotopologues relative to the most abundant isotopologue with mass 44, and the expected stochastic ratios R^{i*} are calculated based on the measured

abundances of ^{13}C and ^{18}O in the sample (Wang *et al.*, 2004; Eiler, 2007). The Δ_{47} values are reported in the absolute reference frame (Dennis *et al.*, 2011). Temperatures were calculated using the calibration of Kele *et al.* (2015) which is based on measurements on the same instruments as the data reported in this study, thus ensuring internal consistency of the calculated temperatures.

RESULTS

Petrography

Both concretions exhibit a long flat ellipsoidal shape with the long axis parallel to bedding. Macroscopically, the concretions show a concentric internal structure with different zones arranged around a central fossil (Fig. 2). The fossil specimen (zone I) is surrounded by a 1-2 cm thick pale-grey finely crystalline carbonate layer (zone II and inner zone III), which forms the dense and indurated body of the concretion. Outward, this part is surrounded by a greenish, clay-rich layer with interspersed white calcite aggregates (outer zone III). The outermost friable rim of the concretion is composed of a thin (up to 5 mm thick) layer of calcite spar (zone IV). Concretions show internal bedding composed of thin laminae. Lamination is more or less parallel in zones II and inner zone III with laminae deflection and convergence occurring towards the concretion edge.

Petrographic inspection of sections cut perpendicular to bedding supports the macroscopically observed zonation. The centre of the concretion (zone I) is formed by the fossilized specimen typically comprising internal cavities of variable sizes and irregular shapes. Cavities are surrounded by bone material (scales), preventing infill of soft sediment. Most internal cavities show a zonation of the infilling calcite cement indicative of successive growth towards the centre (Figs. 3A and 3B). The cavities are typically filled by a coarse (up to 100 μm), inclusion-rich, equant calcite spar. The remaining cavity is cemented by a thin (< 30 μm wide) seam of microcrystalline calcite spar, which is overgrown by an inclusion-poor blocky calcite spar (50 to 200 μm). Zone II is composed of fine-grained and indurated, pale-grey calcite with minor contribution of silt-sized quartz and mica. In this zone, the finely laminated bedding is well preserved as it can be observed in Fig 2. In general, the lamination is undulating and discontinuous with individual laminae being between 0.5 and 1 mm

thick and composed of pale, microsparitic layers alternating with grey micritic layers. Microsparitic layers are composed of small sparite crystals showing a distinct increase in size towards the centre of each layer. In contrast, grey micritic layers are more dense and composed of a patchwork of elongate and spherical structures of varying sizes, which can show a filamentous or tube-like form. In zone II, pyrite is rare and occurs predominantly in form of finely disseminated particles. Zone II shows an overall dull reddish luminescence; bright orange luminescence within zone II is restricted to interspersed silt-sized skeletal fragments, spar filled voids and microcracks (Fig. 3B). Zone III represents a transitional zone essentially characterized by the increasing abundance of pyrite. Individual pyrite crystals occur in the form of finely dispersed framboids of a few microns diameter as well as larger aggregates (up to 500 μm). The latter type often occurs in the form of irregular-shaped aggregates between larger calcite crystals. Increasing pyrite enrichment is observed towards the outer rim of zone III. The outermost zone IV is composed of a fibrous calcite rim enveloping the entire concretion. Remnants of the organic carbon-rich clay-rich host sediment can be found squeezed in between the calcite crystals. Individual calcite fibres are oriented perpendicular to the concretion surface and diverge towards its outside, resulting in the formation of cones with inward pointing apices (cone-in-cone structures) (Fig. 3C). The cone-in-cone calcite is characterized by a uniform bright orange and luminescence, indicating a high Mn- and low Fe-content (Fig. 3D).

Figure 3

Paired cross-polarized light (right) and cathodoluminescence (left) photomicrographs from a transverse section across concretion CON-1. Scale bar in CL images also applies to cross-polarized images. (A) and (B) Assembled photomicrograph showing characteristics of zones I and II under cross-polarized light and CL. Within the spar-filled body cavity (zone I), at least three successive generations of calcite spar are distinguished under CL (1 = oldest, 3 = youngest). Black arrow marks open pore space in the centre. Note the overall dull reddish-orange luminescence visible in the dense fine-grained matrix of zone II. Vertical microcrack cutting the fish bone is healed with a bright orange luminescent calcite (white arrows). (C) and (D) Close-up of cone-in-cone calcite (zone IV) under cross-polarized light and CL. Individual calcite fibres are oriented perpendicular to the concretion surface. Note the absence of internal zonation under CL within individual calcite fibres indicating unchanged pore fluid composition during growth.

Elemental composition

Qualitative elemental results derived from μ -XRF analyses shows a very similar elemental distribution for both concretions measured in transects perpendicular to bedding. Strongest intensities, in the order of $\sim 10,000$ cps, are shown for Ca, clearly reflecting the high abundance of calcite forming the bulk of the concretions. All other elements show intensities in the range of at least one (Fe), or several (Mg, Al, Si, Ti, Sr), orders of magnitude less than Ca. Intensity curves of Fe and S show distinct fluctuations in a geochemical profile from concretion core (base of zone II) to margin (top of zone IV)

(Figs. 4 and 5). The two elements display a very similar behavior ($R^2 = 0.81$ for CON-1) that is mostly opposite to variations in total Ca counts. Whereas zone II is characterized by low Fe and S concentrations, zone III displays a pronounced increase with peak values in the upper part of this zone. The outermost zone IV displays a return to comparatively low S and Fe contents.

Figure 4

Stable isotope and μ -XRF data from the upper half of concretion CON-1 plotted against height (in millimetres): S, Fe and Ca intensities are shown (in counts per second, cps). Stippled line in the photomicrograph shows transect analysed using μ -XRF. Roman numbers correspond to lithological zonation. Horizontal grey bar marks pyrite-rich interval; cps = counts per second.

Figure 5

Stable isotope and μ -XRF data from the upper half of concretion CON-7 plotted against height (in millimetres). See Fig. 4 for details; cps = counts per second.

Carbon and oxygen isotopes

In high-resolution geochemical profiles from core (base of zone II) to margin (top of zone IV), both concretions show distinct trends in C and O stable isotope values (Figs 4 and 5). In CON-1, $\delta^{13}\text{C}$ varies between -2.4 and -7.1 ‰. Zone II shows relatively stable values for $\delta^{13}\text{C}$ (-11.2 to -13.8 ‰; avg. -11.9 ‰) with only minor divergence. In zone III, $\delta^{13}\text{C}$ values show a trend to more negative values (from -11.9 to -14.5 ‰; avg. -12.8 ‰) with the most negative values in the middle part of zone III. The transition from zone III to zone IV shows a strong positive shift in $\delta^{13}\text{C}$ with highest values of -9.1 ‰. In contrast, the outermost cone-in-cone calcite of zone IV is characterized by negative $\delta^{13}\text{C}$ signatures (as low as -19.7 ‰) with a decreasing trend towards the concretion margin. The $\delta^{18}\text{O}$ values vary between -2.4 and -7.1 ‰ within the innermost zone II showing relatively stable values (-3.6 to -5.0 ‰; avg. -4.6 ‰). In zone III, a trend towards less negative $\delta^{18}\text{O}$ can be observed (reaching -2.4 ‰) followed by a shift to consistently negative and stable $\delta^{18}\text{O}$ signatures between -6.1 and -6.9 ‰ (zone IV). Zones II and III are characterized by a very distinct anti-correlation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (R^2 of 0.91). Cavity-filling spar derived from zone I (CON-5) shows $\delta^{13}\text{C}$ values of -13.1 to -13.7 ‰ and $\delta^{18}\text{O}$ values of -6.7 to -7.6 ‰.

The distinct isotope shift from zone III to zone IV has been reproduced in CON-1 at three different positions (Fig. 2) and confirms the spatial stability of the measured isotope pattern within the same concretion. Concretion CON-7 shows an almost identical stable isotope trend across the concretion (Fig. 5) with a similar strong anti-correlation of carbon and oxygen (R^2 of 0.94; Fig. 6). The overall consistency of the stable isotope variations within different concretions of the Santana Formation indicates a characteristic signature and excludes small-scale influences or weathering effects.

Figure 6

Cross-plot of carbon versus oxygen isotope compositions of carbonate powders from sample transects covering three different concretions (CON-1, CON-5 and CON-7). Note the similarity of measured values in concretions CON-1 and CON-7.

Strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$)

Strontium isotope ratios vary between $0.709915 (\pm 8.0 \cdot 10^{-6})$ and $0.713331 (\pm 7.0 \cdot 10^{-6})$ for concretion CON-7 and between $0.710416 (\pm 6.0 \cdot 10^{-6})$ and $0.712465 (\pm 7.0 \cdot 10^{-6})$ for concretion CON-1 (Figs. 7 and 8). In both specimens, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios show a trend towards higher ratios from centre to concretion rim. The lowest ratios have been measured in the microcrystalline matrix (zone II). In contrast, the fibrous calcite spar forming the cone-in-cone rim (zone IV) is characterized by comparatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Bulk Sr-isotope signatures from different zones within the Santana concretions are all significantly more radiogenic compared to late Early Cretaceous (Albian) marine calcite (between 0.707289 and 0.707387; McArthur et al. 2001).

Figure 7

Clumped isotope temperatures ($^{\circ}\text{C}$), calculated $\delta^{18}\text{O}_{\text{porewater}}$, Sr, C and O isotopic composition of CON-1 plotted against distance from fossil debris. Roman numbers correspond to lithological zonation.

Figure 8

Clumped isotope temperatures ($^{\circ}\text{C}$), calculated $\delta^{18}\text{O}_{\text{porewater}}$, Sr, C and O isotopic composition of CON-7 plotted against distance from fossil debris. See Fig. 7 for details.

Carbonate clumped isotopes (Δ_{47})

Mean Δ_{47} values of the calcites range from $0.659 \pm 0.008 \text{ ‰}$ ($n = 7$) to $0.616 \pm 0.011 \text{ ‰}$ ($n = 10$) for samples derived from CON-7 and from $0.654 \pm 0.010 \text{ ‰}$ ($n = 8$) to $0.605 \pm 0.020 \text{ ‰}$ ($n = 8$) for

333 samples from CON-1. Using the new ETH temperature calibration (Kele *et al.* 2015), this corresponds
334 to precipitation temperatures ranging between $26 \pm 2^\circ\text{C}$ and $37 \pm 3^\circ\text{C}$ for CON-7 calcite and between
335 $26 \pm 3^\circ\text{C}$ and $42 \pm 5^\circ\text{C}$ for CON-1 calcite (Figs. 7 and 8). Reconstructed $\delta^{18}\text{O}_{\text{porewater}}$ values vary
336 between +0.3 and -1.7 ‰ for CON-7 and +0.9 and -1.8 ‰ for CON-1 with the cone-in-cone calcite
337 (zone IV) showing lowermost $\delta^{18}\text{O}_{\text{porewater}}$ values. All results are shown in Table 1.

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Table 1. Concretion petrographic and geochemical data including stable isotope and clumped isotope composition

Sample	Type*	Distance [†] (mm)	<i>n</i>	$\delta^{13}\text{C}_{\text{cc}}$ (‰, VPDB)	$\delta^{18}\text{O}_{\text{cc}}$ (‰, VPDB)	$\delta^{18}\text{O}_{\text{cc}}$ (‰, SMOW)	Δ_{47} (‰)	St Err	$\Delta_{47}\text{-T}$ (°C) [‡]	$\Delta_{47}\text{-T}$ St Err	$\delta^{18}\text{O}_{\text{porewater}}$ (‰, SMOW)
*M, matrix; FS, fringing spar. †Distance measured from top of central fossil debris. ‡ETH calibration slow precipitates.											
Con1-C1	FS	17.5	8	-19.30	-6.86	23.84	0.605	0.020	42	5	-1.0
Con1-C2	FS	15.5	8	-16.55	-6.87	23.83	0.618	0.016	38	4	-1.8
Con1-C2a	M	11.5	8	-13.91	-3.38	27.42	0.654	0.010	26	3	-0.4
Con1-C3	M	8.0	8	-12.21	-4.43	26.34	0.615	0.012	39	3	0.9
CON1-C4	M	2.5	8	-11.82	-4.55	26.22	0.617	0.011	39	3	0.7
Con7-C4	FS	17.5	10	-16.97	-6.72	23.98	0.616	0.011	37	3	-1.7
Con7-C3	M	14.5	10	-13.67	-2.90	27.93	0.654	0.010	27	3	0.3
Con7-C2	M	7.0	7	-12.81	-3.91	26.88	0.659	0.008	26	2	-1.1
Con7-C1	M	0.5	8	-11.90	-4.57	26.20	0.649	0.016	28	4	-1.3

DISCUSSION

Assessing concretion growth style

Understanding the growth mode of carbonate concretions is of major importance for the interpretation of geochemical signatures derived from the concretion matrix (Mozley, 1996; Raiswell & Fisher, 2000; Bojanowski & Clarkson, 2012). Traditionally, concretion growth was suggested to occur via concentric growth from the centre towards the edge by the radial addition of fine-grained carbonate cement as indicated by centre-to-edge textural and geochemical trends. This view was challenged by the observation of zoned crystallites occurring across the entire volume of concretions, indicative of a concurrent and pervasive growth mode (Mozley, 1989; Fisher *et al.*, 1998). Incomplete early cementation may result in high initial porosity, which is subsequently filled by later-stage diagenetic carbonate during burial (Coleman & Raiswell, 1995; Mozley, 1996; Raiswell & Fisher, 2000). Such a pervasive mode of cementation complicates any geochemical interpretation due to the difficult spatial separation of individual carbonate phases formed under differing diagenetic regimes. Macroscopically, the Santana concretions provide evidence for concentric growth as indicated by the changes in color and texture in centre-to-edge transects (Fig. 2). The occurrence of a radial zone of pyrite enrichment (zone III) and an outermost fringing spar (zone IV) may suggest spatially and/or temporally separated phases of growth (Coleman & Raiswell, 1995). However, a concentric growth style contrasts with the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ patterns observed across the concretion body (zones II and III). The strong anti-correlation of C- and O-isotopes within zones II and III is interpreted to result from continuous mixing of two different carbonate phases. This becomes particularly evident in a C/O-isotope cross-plot, where a well-defined mixing line is observed (Fig. 6). Here, one component is characterized by comparatively low $\delta^{13}\text{C}$ (-15‰) and high $\delta^{18}\text{O}$ (-2.5‰) values, the other component shows significantly higher $\delta^{13}\text{C}$ (-7‰) and lower $\delta^{18}\text{O}$ signatures (-7‰). Concretionary carbonates showing a negative carbon isotopic composition in combination with high oxygen isotope values may indicate formation close to the sediment-water interface. The negative $\delta^{13}\text{C}$ signature most probably reflects a significant contribution from OM-derived carbon metabolized by microbial processes during the early stages of diagenesis at shallow depth (Claypool & Kaplan,

1974). Based on the carbon isotope signature alone, a more specific assignment to a particular microbial process is hampered by the broad range of $\delta^{13}\text{C}$ observed from dissolved inorganic carbon produced during the various OM mineralization processes (Raiswell & Fisher, 2000). The other component characterized by a less negative carbon and more negative oxygen isotope composition represents a diagenetic carbonate phase formed during subsequent burial. This phase may correspond to fine-grained cement filling the remaining porosity during burial. The comparatively high carbon-isotope signature may be controlled by the dissolution of bioclastic carbonate particles of marine origin, probably mixed with DIC derived from OM oxidation. A potential source is represented by the calcite carapaces of ostracods, which occur in high abundances within the surrounding organic carbon-rich shales.

The strong anti-correlation observed in the carbon and oxygen isotope trends of zones II and III is best explained by the pervasive cementation of an early porous carbonate framework by later-stage cement, resulting in the dense finely crystalline concretion body. Following the view of Mozley (1989), the observed isotopic variations within zones II and III are to a lesser extent the result of compositional variations in pore-waters but rather reflect changing contributions of the different carbonate phases precipitated during different stages of pervasive growth of the Santana concretions. This interpretation contrasts somewhat with the view of Bojanowski & Clarkson (2012), who interpreted centre-to-edge isotopic trends in pervasively grown siderite concretions to reflect growth in spatially separated microenvironments. The analysed siderite concretions show a strong positive correlation of carbon and oxygen isotope values interpreted to reflect the effects of the differing microbial metabolic processes rather than temporally displaced cementation events. However, compared to the pronounced centre-to-edge trends observed by Bojanowski & Clarkson (2012), the variations in zones II and III of the Santana concretions are of rather small amplitude, thus supporting a pervasive growth mechanism (McCoy *et al.*, 2015).

A third end-member composition characterizes the cone-in-cone calcite of zone IV and shows the most negative $\delta^{13}\text{C}$ values (-20‰) coupled with low $\delta^{18}\text{O}$ values (-7‰). Here, a phase of uninterrupted calcite precipitation during burial is indicated by the invariable negative oxygen

isotope composition, indicating more or less similar burial temperatures. A potential source for the depleted carbon in the cone-in-cone calcite might be OM remineralization in the surrounding bituminous shale or in the deeper subsurface (e.g. within the underlying Rio da Batateiras or Crato formations). A similar formation during burial is indicated from the innermost cavity-filling spar occurring in zone I (CON-5). The negative $\delta^{18}\text{O}$ signatures (reaching -7.6 ‰) and relatively low $\delta^{13}\text{C}$ values (-13.5 ‰) point towards a late burial cementation event under conditions of increased temperatures.

Early onset of concretion formation

The Santana concretions provide unequivocal physical evidence for very early growth at shallow depth in non-lithified sediment. The early formation of a carbonate framework prior to significant mechanical compaction is indicated by the preservation of delicate fossils and associated taphonomic structures. Macro- and microfossils derived from Santana concretions often exhibit three-dimensional preservation with very limited signs of crushing (Martill, 1997; Hirayama, 1998; Smith, 2000; Kellner & Campos, 2002). Studies on fossil fish specimen reveal delicate taphonomic features such as bloated carcasses, collapse and gas escape structures, witnessing an early phase of partial cementation surrounding the fossil specimen (Martill, 1988; Maisey, 1991; Martill, 1997). In sections cut normal to bedding plane, the studied concretions show parallel lamination in the inner part (zone II and inner zone III) with convergence of individual laminae at the edge, indicating differential compaction between host sediment and concretion (Fig. 2). This is a widely observed phenomenon of many concretions and taken as evidence for early resistance to compaction due to early, albeit incomplete, cementation (Raiswell, 1971; Mozley, 1996).

Geochemical evidence for microbial activity during the early phases of concretion growth is given by the distinct distribution of Fe and S intensities along centre-to-edge transects (Figs 4 and 5). The elemental pattern traces the distribution of pyrite forming a well-defined concentric ring of enrichment (zone III). This contrasts with the low abundance of pyrite in the finely crystalline carbonate directly surrounding the fossil (zone II). Concentric enrichment of pyrite has previously

426 been reported from carbonate concretions hosted in organic-carbon-rich mudrocks, typically
427 associated with fossil debris in the centre (Coleman & Raiswell, 1995). In general, high abundances of
428 pyrite in concretions are thought to reflect the activity of sulfate-reducing bacteria, metabolizing OM
429 within the zone of sulfate reduction (Raiswell, 1976; De Craen *et al.*, 1999; Hudson *et al.*, 2001). For
430 the Santana Formation, the presence of *Chlorobiaceae*-derived biomarkers point to an extension of
431 the sulfate reduction zone into the overlying water column reaching the photic zone (Heimhofer *et*
432 *al.*, 2008). During sediment accumulation, high rates of microbial sulfate reduction within the TOC-
433 rich deposit (up to 11.6 wt. %) may have resulted in sulfate depleted pore-waters. Under such
434 conditions, remaining sulfate may have been consumed rapidly by enhanced sulfate reduction
435 around a local concentration of highly metabolizable OM, eventually resulting in a sulfate-depleted
436 halo (zone II) around the decaying fossil. In absence of sulfate reduction, fermentation and
437 methanogenesis would have been the only OM degrading pathways within and around the fish
438 carcass. The amount of OM available would have been sufficient to produce methane-filled
439 interstices. Physical evidence for the formation of gas filled internal cavities is given by findings of gas
440 escape structures, ruptured body walls and by fish fossils showing bloated bodies (Martill, 1988,
441 1997). Anaerobic oxidation of methane (AOM) would then have occurred in a concentric ring around
442 the fossil. Furthermore, to allow the formation of pyrite, a source of iron must have been available.
443 Reduced iron (Fe^{2+}) is soluble in the absence of sulfide and could have been diffusing outwards from
444 a sulfide free methanogenic zone and precipitated at a concentric sulfide front, now visible in the
445 pyrite enrichment of zone III. Under reducing and slightly acidic conditions (due to CO_2 production
446 during methanogenesis) iron could have been leached and reduced from iron oxides or clay minerals.
447 Subtle differences in pH and alkalinity would have induced slow precipitation of carbonate cement
448 around the buried fish. However, carbonate precipitation must have occurred very slowly, i.e. slow
449 enough that the alkalinity and pH drop caused by the precipitation could have been compensated by
450 diffusion from the surrounding pore-water. The moderately negative $\delta^{13}\text{C}$ values in the early phase
451 component most likely represents a mixed signal including ^{13}C -enriched DIC from methanogenesis
452 diffusing outwards from the center of the concretion and ^{13}C -depleted DIC from sulfate reduction

and AOM in the surrounding sediment. Such mixed values are commonly observed in diagenetic carbonates forming in proximity to a sulfate-methane transition zone (e.g. Meister *et al.*, 2007). The comparatively low $\delta^{13}\text{C}$ and high $\delta^{18}\text{O}$ values in the pyrite-enriched zone III are consistent with the precipitation of a larger volume of early phase calcite compared to the inner part (zone II). In addition, ammonium production from the degradation of OM contributes to an increase in alkalinity. The combined processes result in an excess of alkalinity and induce precipitation in a concentric zone around the central cavity. A similar scenario of early concretion growth within localized microenvironments of methanogenesis/AOM occurring within a sulfate reduction zone has recently been proposed by Bojanowski & Clarkson (2012). The scenario for the Santana concretions contrasts with model of Coleman & Raiswell (1995), where carbonate precipitation is triggered by local sulfide generation (via enhanced sulfate reduction) within the concretion core. Here, the absence of pyrite in the concretion center is explained with the limited inward diffusion of reduced Fe from the surrounding shale. However, for the Santana concretions, euxinic conditions and the associated sulfide concentrations in water column and porewaters hamper the establishment of widespread iron-reduction outside the concretion. Thus, a precipitation near the sulfate-methane interface is a more suitable model for the Santana concretions.

Constraining temperatures of carbonate precipitation

Providing reliable precipitation temperatures for diagenetic carbonates based on oxygen isotope palaeothermometry is hampered by the lack of information on pore-water $\delta^{18}\text{O}$ composition, a parameter necessary for the calculation of reliable oxygen isotope-derived temperatures. A multitude of processes can alter the $\delta^{18}\text{O}_{\text{porewater}}$ composition, often resulting in a significant offset from the original marine isotopic signature (Loyd *et al.*, 2012). Recently, clumped isotope thermometry has been successfully applied to concretion carbonate, providing information on both, carbonate precipitation temperature and $\delta^{18}\text{O}_{\text{porewater}}$ (Loyd *et al.*, 2012; Dale *et al.*, 2014; Loyd *et al.*, 2014). The few existing studies show a broad range of temperatures between $\sim 20^\circ\text{C}$ and $\sim 70^\circ\text{C}$ for

the concretion matrix and an equally broad range of pore-water compositions between -5‰ and +2.5‰.

Clumped isotope thermometry from the Santana Formation shows consistent Δ_{47} -derived temperatures for both studied concretions. Calculated temperatures for the fine-crystalline body matrix are on average lower (26-39°C) compared to temperatures derived from the cone-in-cone calcite spar (37-42°C). This difference is more pronounced in CON-7 (~10°C) compared to CON-1 (~5°C) and indicates that the concretions were not affected by high-temperature recrystallization.

Precipitation temperatures for the fine-crystalline concretion body range between 26-28°C for CON-7 whereas CON-1 shows somewhat increased temperatures between 26-39°C. Given that the body of the concretions is interpreted to have formed via pervasive cementation of an early porous calcite framework, any powder sample taken from the inner part (zones II and III) will integrate multiple carbonate phases formed under varying temperatures during growth. Hence, calculated temperature estimates for zones II and III can be considered to represent a mixture of temperature signals acquired during initial near-surface and early-stage burial cementation. In consequence, the observed difference in Δ_{47} -derived body temperatures between the two analyzed concretion specimens (but also between different parts within a single concretion) may be interpreted to reflect differing amounts of early vs. late cement rather than overall different growth temperatures.

Due to the small size of individual crystals in the concretion body, sampling of early carbonate phases for assessing temperature conditions during early growth is not possible. However, a first tentative approximation of precipitation temperatures for early calcite phases can be achieved via regression analysis from a Sr-isotope vs Δ_{47} diagram (Fig. 9). Based on the assumption that early carbonate phases did precipitate from marine pore waters with a typical Early Albian $^{87}\text{Sr}/^{86}\text{Sr}$ signature between 0.707289 and 0.707387 (McArthur *et al.*, 2001), back-calculated near-surface pore-water temperatures vary in the range of 20°C. These comparatively high estimates for marine bottom-water and near-surface pore-water temperatures from the equatorial Araripe Basin are in good agreement with the general view of exceptionally warm mid-Cretaceous ocean waters. Based on TEX₈₆ measurements, sea-surface temperature reconstructions for the tropical proto-Atlantic in

excess of 33°C are proposed for Albian times (Forster *et al.*, 2007). For the same area, $\delta^{18}\text{O}$ analyses of benthic foraminifera indicate intermediate to bottom water temperatures >20°C (Friedrich *et al.*, 2012).

Figure 9

Strontium isotope ratios plotted against clumped isotope-derived temperatures from concretion carbonate (CON-1 and CON-7).

In contrast to the polygenetic nature of the concretion matrix, which complicates specific geochemical interpretations, the fringing spar (zone IV) can be considered as a single phase. Individual elongate sparite crystals show no signs of change in pore-fluid composition during crystal growth as evidenced by bright and uniform luminescence colors and the lack of internal zonation pattern (Figs 3C and 3D). Calcite fibres are arranged in the form of conical structures referred to as “cone-in-cone” (Selles-Martinez, 1994; Cobbold *et al.*, 2013). Besides occurring as bedding-parallel veins, cone-in-cone calcite has been reported to form mm- to cm-thick layers around carbonate

concretions hosted within OM-rich mudstones (Gilman & Metzger, 1967; Raiswell, 1971; Marshall, 1982; Buchardt & Nielsen, 1984). Cone-in-cone calcite (zone IV) shows Δ_{47} -derived temperatures ranging between $38\text{--}42^\circ\text{C} \pm 5$ for CON-1 and $37^\circ\text{C} \pm 3$ for CON-7. Temperatures derived from traditional $\delta^{18}\text{O}_{\text{cc}}$ temperature estimates (assuming Cretaceous $\delta^{18}\text{O}_{\text{pw}}$ of -1.2‰) are only slightly higher and range between 42.8°C (CON-7) and 43.6°C (CON-1) for the cone-in-cone cement. These estimates are in accordance with thermal maturity estimates based on biomarkers. The sterane isomerization pattern of CON-1 shows a relative proportion of $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ steranes of less than 0.1 indicative of a strong predominance of steranes with their original biological configuration preserved and hence, very low thermal maturity (Schwark, pers. com).

The mechanisms leading to the formation of cone-in-cone have long been debated. Early studies proposed formation due to displacive crystal growth during conditions of shallow burial within unconsolidated or only partly lithified sediment (Raiswell, 1971). More recently, formation caused by tensile fracturing and dilation due to fluid overpressure under considerable overburden is suggested (Selles-Martinez, 1994; Cobbold & Rodrigues, 2007; Cobbold *et al.*, 2013). For the cone-in-cone associated with the Santana concretions, the good agreement between clumped- and traditional-derived temperature estimates supports precipitation from a pore fluid with a more or less marine composition. However, formation temperatures of the zone IV cone-in-cone of $\sim 40^\circ\text{C}$ are considerably lower than estimates for calcite ‘beef’, which typically range between 70° and 120°C (Cobbold *et al.*, 2013).

Fluid source and burial history

Additional information on the origin of the fluids can be obtained from Sr-isotope values. In both studied concretions, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are highest in the cone-in-cone spar and reach values of up to $0.713331 (\pm 7.0 \cdot 10^{-6})$. All measured ratios are significantly higher than typical values for Albian seawater, which vary between 0.707289 and 0.707387 (McArthur *et al.*, 2001). The high ratios in the cone-in-cone calcite point to contribution from a continental, more radiogenic source. Similarly increased $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (compared to contemporaneous seawater) have been reported from calcite

spar in septarian concretions from the Oxford Clay (Hudson *et al.*, 2001). Here, enrichment in radiogenic Sr has been attributed to spar precipitation in the presence of meteoric-derived fluids (Hudson *et al.*, 2001), a view recently confirmed by clumped-isotope analyses and reconstructed $\delta^{18}\text{O}_{\text{porewater}}$ compositions as low as -6‰ (Loyd *et al.*, 2014). For the Santana cone-in-cone calcite, back-calculated $\delta^{18}\text{O}_{\text{porewater}}$ values vary between -1.0 and -1.8‰ and are close to an estimated Cretaceous seawater signature of -1.2 ‰ (Shackleton & Kennett, 1975). This observation points to a fluid with a more or less unaltered marine $\delta^{18}\text{O}$ composition and does not support strong meteoric influence of the cone-in-cone precipitating fluid. The radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of the Santana concretions may reflect fluid contribution originating from fluid/rock interaction between the pore-water and the silicate component of the surrounding shale. During pressure solution, clay diagenesis and K-feldspar dissolution, pore-fluids with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be generated (Teichert *et al.*, 2005; Nollet *et al.*, 2009). However, the Sr-isotope values measured in the cone-in-cone cements are very radiogenic, requiring substantial leaching from the terrigenous fraction. Alternatively, the radiogenic Sr-isotope composition may originate from the underlying strata. In fact, marine sulfate-rich evaporite deposits of the Ipubi Formation represent a potential source for radiogenic Sr-isotope ratios. As reported by Peryt & Anczkiewicz (2015) based on analyses of Miocene evaporites, substantial inflow of continental waters during brine formation has the potential to shift the Sr-isotope ratio of marine gypsum and anhydrite towards non-marine, more radiogenic values. Alternatively, ascending fluids may have been modified by interaction with terrigenous siliciclastics and/or continental crust (Meister *et al.*, 2011; Kuznetsov *et al.*, 2012). In the Araripe basin, the concretion-bearing deposits are superimposed on a heterogeneous lithological succession made up of terrigenous and marginal marine siliciclastics, which cover a complex suite of Proterozoic crystalline basement (Martill, 1993). The basement includes Neoproterozoic granitoids and gneisses located within the transversal zone of the Borborema structural province (Archanjo *et al.*, 2002), which represent a potential source for high radiogenic Sr ratios.

The depth of the basement rocks varies substantially across the Araripe Basin as indicated e.g. by the unconformable contact of the Aptian Crato Formation with the metamorphic basement in the

marginal area of the basin (Ponte & Ponte Filho, 1996). Fluid temperatures in the range of ~40°C for the cone-in-cone spar can be used to assess the burial depth of its formation. Assuming bottom-water temperatures between 15°C and 20°C and a geothermal gradient of 30°C/km, deposition of 670–830 m of sediment would be required to account for the calculated temperatures of ~40°C. Today, the Romualdo Member is overlain by a ~30 m thick succession of grey to greenish shales, which form the upper part of the Santana Formation (Martill, 1993; Heimhofer *et al.*, 2008). The topmost unit is represented by the sandstones and conglomerates of the Albian-Cenomanian Exu Formation, which varies in thickness from east to west and accounts for some 280 m on average (Martill, 1993). Sedimentary deposits postdating the Exu siliciclastics are not preserved in the Araripe Basin.

Estimates of erosion of the former sediment cover overlying the Araripe plateau can be inferred from apatite fission-track analysis. For the Araripe and neighboring Borborema plateaus of northeastern Brazil, two dominant palaeothermal events can be identified, which were associated with post-Albian and Neogene uplift (Morais Neto *et al.*, 2006; Morais Neto *et al.*, 2009). Fission-track results from the Rio da Batateiras Formation (which is located ~100 to 150 m below the Santana Formation) show an earlier event with palaeoheating not in excess of 100°C indicating minor burial of the succession during the Late Cretaceous (Morais Neto *et al.*, 2006). According to the latter authors, the present relief results from subsequent erosion of post-Albian deposits with an estimated thickness of eroded strata of ~1.5 km across the Araripe area. This estimate is twice as large as compared to the Δ_{47} -derived overburden. The higher fission-track burial estimates may be explained by the fact that the cone-in-cone spar does not correspond to the maximum burial depth of the concretion-bearing strata, but a conflict with preliminary biomarker data is also implied.

CONCLUSIONS

The diagenetic history of fossiliferous carbonate concretions hosted in black shales of the late Early Cretaceous Santana Formation (Araripe Basin, NE Brazil) is documented by geochemical signatures preserved in concentrically arranged internal zones. The geochemical inventory is in accordance with

sedimentological and taphonomic observations and supports a scenario with a decaying fossil carcass being surrounded by semi-lithified sediment due to early calcite precipitation as a result of alkalinity increase driven by OM degradation. An early microbially-driven precipitation stage is supported by concentric pyrite enrichment in the outer part of the concretion body. During the subsequent early burial stage, the inner part of the concretion was pervasively cemented with calcite from a fluid showing normal marine $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures. The outermost fringing cone-in-cone calcite formed as the last step of concretion growth. Combined $^{87}\text{Sr}/^{86}\text{Sr}$ and Δ_{47} data point to precipitation at elevated temperatures ($37\text{--}42^\circ\text{C} \pm 5$) from a radiogenic pore-fluid under moderate burial depth of 650 – 850 m. Overall, the multiproxy approach reveals that concretion growth occurs in several steps over a range of different depth intervals, resulting in the complex entanglement of geochemical signatures formed during very different diagenetic regimes.

ACKNOWLEDGEMENTS

We thank D. Buhl and U. Schulte (Ruhr-University Bochum) and M. Jaggi and S. Bishop (ETH Zürich) for laboratory assistance. Financial support from DFG project HE 4467/5-1 and by the Nordrhein-Westfälische Akademie der Wissenschaften und Künste to UH is gratefully acknowledged. Dr. Artur Andrade (DNPM Crato) assisted our field work in Brazil. We thankfully acknowledge M. Gutjahr and an anonymous reviewer for critical comments that improved an earlier draft of the manuscript.

REFERENCES

- Affek, H.P. and Eiler, J.M.** (2006) Abundance of mass 47 CO₂ in urban air, car exhaust, and human breath. *Geochimica et Cosmochimica Acta*, **70**, 1-12.
- Archanjo, C.J., Trindade, R.I.F., Bouchez, J.L. and Ernesto, M.** (2002) Granite fabrics and regional-scale strain partitioning in the Serido belt (Borborema Province, NE Brazil). *Tectonics*, **21**.
- Baudin, F. and Berthou, P.-Y.** (1996) Depositional environments of the organic matter of Aptian-Albian sediments from the Araripe Basin (NE Brazil). *Bulletin des Centres de Recherches Exploration-Production Elf-Aquitaine*, **20**, 213-227.
- Bernasconi, S.M., Hu, B., Wacker, U., Fiebig, J., Breitenbach, S.F.M. and Rutz, T.** (2013) Background effects on Faraday collectors in gas-source mass spectrometry and implications for clumped isotope measurements. *Rapid Communications in Mass Spectrometry*, **27**, 603-612.
- Bojanowski, M.J. and Clarkson, E.N.K.** (2012) Origin of siderite concretions in microenvironments of methanogenesis developed in a sulfate reduction zone: an exception or a rule? *Journal of Sedimentary Research*, **82**, 585-598.
- Brito, P.M. and Gallo, V.** (2003) A new species of Lepidotes (neopterygii: Semionotiformes: Semionotidae) from the Santana Formation, Lower Cretaceous of northeastern Brazil. *Journal of Vertebrate Paleontology*, **23**, 47-53.
- Buchardt, B. and Nielsen, A.T.** (1984) Stable isotope composition of lower paleozoic limestones from Bornholm - evidence for deep burial diagenesis. *Geologiska Foreningens I Stockholm Forhandlingar*, **106**, 383-384.
- Chang, H.K., Kowsmann, R.O. and de Figueiredo, A.M.F.** (1988) New concepts on the development of East Brazilian Marginal Basins. *Episodes*, **11**, 194-202.
- Claypool, G.E. and Kaplan, I.R. (1974) The origin and distribution of methane in marine sediments. In: Kaplan, I.R., (ed) *Natural Gases in Marine Sediments*. Plenum Press, New York, 99-139.
- Cobbold, P.R. and Rodrigues, N.** (2007) Seepage forces, important factors in the formation of horizontal hydraulic fractures and bedding-parallel fibrous veins ('beef' and cone-in-cone). *Geofluids*, **7**, 313-322.
- Cobbold, P.R., Zanella, A., Rodrigues, N. and Loseth, H.** (2013) Bedding-parallel fibrous veins (beef and cone-in-cone): Worldwide occurrence and possible significance in terms of fluid overpressure, hydrocarbon generation and mineralization. *Marine and Petroleum Geology*, **43**, 1-20.
- Coimbra, J.C., Arai, M. and Carreno, A.L.** (2002) Biostratigraphy of Lower Cretaceous microfossils from the Araripe Basin, northeastern Brazil. *Géobios*, **35**, 687-698.

- 661 **Coleman, M.L. and Raiswell, R.** (1995) Source of carbonate and origin of zonation in pyritiferous
 662 carbonate concretions - evaluation of a dynamic model. *American Journal of Science*, **295**,
 663 282-308.
- 664 **Dale, A., John, C.M., Mozley, P.S., Smalley, P.C. and Muggeridge, A.H.** (2014) Time-capsule
 665 concretions: Unlocking burial diagenetic processes in the Mancos Shale using carbonate
 666 clumped isotopes. *Earth and Planetary Science Letters*, **394**, 30-37.
- 667 **De Craen, M., Swennen, R. and Keppens, E.** (1999) Petrography and geochemistry of septarian
 668 carbonate concretions from the Boom Clay Formation (Oligocene, Belgium). *Geologie en*
 669 *Mijnbouw*, **77**, 63-76.
- 670 **De Matos, R.M.D.** (1999) History of the northeast Brazilian rift system: kinematic implications for the
 671 break-up between Brazil and West Africa. *In: Cameron, N.R., Bate, R.H. and Clure, V.S., (eds)*
 672 *The oil and gas habitats of the South Atlantic*, Volume 153, London, 55-73.
- 673 **Dennis, K.J., Affek, H.P., Passey, B.H., Schrag, D.P. and Eiler, J.M.** (2011) Defining an absolute
 674 reference frame for 'clumped' isotope studies of CO₂. *Geochimica et Cosmochimica Acta*, **75**,
 675 7117-7131.
- 676 **Dulski, P., Brauer, A. and Mangili, C.** (2015) Combined μ -XRF and microfacies techniques for lake
 677 sediment analysis. *In: Croudace, I.W. and Rothwell, R.G., (eds) Micro-XRF studies of sediment*
 678 *cores*, Volume 17. Springer, Dordrecht, Heidelberg, New York, London.
- 679 **Eiler, J.M.** (2007) "Clumped-isotope" geochemistry - The study of naturally-occurring, multiply-
 680 substituted isotopologues. *Earth and Planetary Science Letters*, **262**, 309-327.
- 681 **Fara, E., Saraiva, A.A.F., de Almeida Campos, D., Moreira, J.K.R., de Carvalho Siebra, D. and Kellner,**
 682 **A.W.A.** (2005) Controlled excavations in the Romualdo Member of the Santana Formation
 683 (Early Cretaceous, Araripe Basin, northeastern Brazil): stratigraphic, palaeoenvironmental
 684 and palaeoecological implications. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **218**,
 685 145-158.
- 686 **Fisher, Q.J., Raiswell, R. and Marshall, J.D.** (1998) Siderite concretions from nonmarine shales
 687 (Westphalian A) of the Pennines, England: Controls on their growth and composition. *Journal*
 688 *of Sedimentary Research*, **68**, 1034-1045.
- 689 **Forster, A., Schouten, S., Baas, M. and Damsté, J.** (2007) Mid-Cretaceous (Albian-Santonian) sea
 690 surface temperature record of the tropical Atlantic Ocean. *Geology*, **35**, 919-922.
- 691 **Friedrich, O., Norris, R.D. and Erbacher, J.** (2012) Evolution of middle to Late Cretaceous oceans - A
 692 55 m.y. record of Earth's temperature and carbon cycle. *Geology*, **40**, 107-110.
- 693 **Geske, A., Zorlu, J., Richter, D.K., Buhl, D., Niedermayr, A. and Immenhauser, A.** (2012) Impact of
 694 diagenesis and low grade metamorphism on isotope ($\delta^{26}\text{Mg}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) and

- 695 elemental (Ca, Mg, Mn, Fe and Sr) signatures of Triassic sabkha dolomites. *Chemical Geology*,
 696 **332**, 45-64.
- 697 **Gilman, R.A. and Metzger, W.J.** (1967) Cone-in-cone concretions from western New York. *Journal of*
 698 *Sedimentary Petrology*, **37**, 87-&.
- 699 **Heimhofer, U., Hesselbo, S.P., Pancost, R.D., Martill, D.M., Hochuli, P.A. and Guzzo, J.V.P.** (2008)
 700 Evidence for photic-zone euxinia in the Early Albian Santana Formation (Araripe Basin, NE
 701 Brazil). *Terra Nova*, **20**, 347-355.
- 702 **Heimhofer, U. and Hochuli, P.A.** (2010) Early Cretaceous angiosperm pollen from a low-latitude
 703 succession (Araripe Basin, NE Brazil). *Review of Palaeobotany and Palynology*, **161**, 105-126.
- 704 **Hendry, J.P., Pearson, M.J., Trewin, N.H. and Fallick, A.E.** (2006) Jurassic septarian concretions from
 705 NW Scotland record interdependent bacterial, physical and chemical processes of marine
 706 mudrock diagenesis. *Sedimentology*, **53**, 537-565
- 707 **Henkes, G.A., Passey, B.H., Wanamaker, A.D., Grossman, E.L., Ambrose, W.G. and Carroll, M.L.**
 708 (2013) Carbonate clumped isotope compositions of modern marine mollusk and brachiopod
 709 shells. *Geochimica et Cosmochimica Acta*, **106**, 307-325.
- 710 **Hirayama, R.** (1998) Oldest known sea turtle. *Nature*, **392**, 705-708.
- 711 **Hudson, J.D., Coleman, M.L., Barreiro, B.A. and Hollingworth, N.T.J.** (2001) Septarian concretions
 712 from the Oxford Clay (Jurassic, England, UK): involvement of original marine and multiple
 713 external pore fluids. *Sedimentology*, **48**, 507-531.
- 714 **Irwin, H., Curtis, C. and Coleman, M.** (1977) Isotopic evidence for source of diagenetic carbonates
 715 formed during burial of organic-rich sediments. *Nature*, **269**, 209-213.
- 716 **Kele, S., Breitenbach, S.F.M., Capezzuoli, E., Meckler, A.N., Ziegler, M., Millan, I.M., Kluge, T., Deak,**
 717 **J., Hanselmann, K., John, C.M., Yan, H., Liu, Z.H. and Bernasconi, S.M.** (2015) Temperature
 718 dependence of oxygen- and clumped isotope fractionation in carbonates: A study of
 719 travertines and tufas in the 6-95°C temperature range. *Geochimica et Cosmochimica Acta*,
 720 **168**, 172-192.
- 721 **Kellner, A.W.A. and Campos, D.D.** (2002) The function of the cranial crest and jaws of a unique
 722 pterosaur from the Early Cretaceous of Brazil. *Science*, 389-392.
- 723 **Kuznetsov, A.B., Gorokhov, I.M., Melezhik, V.A., Mel'nikov, N.N., Konstantinova, G.V. and**
 724 **Turchenko, T.L.** (2012) Strontium isotope composition of the lower proterozoic carbonate
 725 concretions: The Zaonega Formation, Southeast Karelia. *Lithology and Mineral Resources*, **47**,
 726 319-333.
- 727 **Long, J.A. and Trinajstić, K.** (2010) The Late Devonian Gogo Formation lagerstätte of western
 728 Australia: exceptional early vertebrate preservation and diversity. *In: Jeanloz, R. and*

- 729 Freeman, K.H., (eds) *Annual Review of Earth and Planetary Sciences, Vol 38*, Volume 38, 255-
730 279.
- 731 **Loyd, S.J., Corsetti, F.A., Eiler, J.M. and Tripathi, A.K.** (2012) Determining the diagenetic conditions of
732 concretion formation: Assessing temperatures and pore waters using clumped isotopes.
733 *Journal of Sedimentary Research*, **82**, 1006-1016.
- 734 **Loyd, S.J., Dickson, J.A.D., Boles, J.R. and Tripathi, A.K.** (2014) Clumped-isotope constraints on
735 cement paragenesis in septarian concretions. *Journal of Sedimentary Research*, **84**, 1170-
736 1184.
- 737 **Maas, A., Braun, A., Dong, X.-P., Donoghue, P.C.J., Mueller, K.J., Olempska, E., Repetski, J.E.,**
738 **Siveter, D.J., Stein, M. and Waloszek, D.** (2006) The 'Orsten' - more than a Cambrian
739 Konservat-Lagerstätte yielding exceptional preservation. *Palaeoworld*, **15**, 266-282.
- 740 **Maisey, J.G.** (1991) *Santana Fossils: An illustrated atlas*, Tropical Fish Hobbyist Publications, New
741 Jersey, USA.
- 742 **Marshall, J.D.** (1982) Isotopic composition of displacive fibrous calcite veins: reversals in pore water
743 composition trends during burial diagenesis. *Journal of Sedimentary Petrology*, **52**, 615-630.
- 744 **Martill, D.M.** (1988) Preservation of fish in the Cretaceous Santana Formation of Brazil.
745 *Palaeontology*, **31**, 1-18.
- 746 **Martill, D.M.** (1993) *Fossils of the Santana and Crato Formations, Brazil*, Palaeontological
747 Association, London, UK.
- 748 **Martill, D.M.** (1997) Fish oblique to bedding in early diagenetic concretions from the Cretaceous
749 Santana formation of Brazil - Implications for substrate consistency. *Palaeontology*, **40**, 1011-
750 1026.
- 751 **McArthur, J.M., Howarth, R.J. and Bailey, T.R.** (2001) Strontium isotope stratigraphy: LOWESS
752 Version 3. Best-fit line to the marine Sr-isotope curve for 0 to 509 Ma and accompanying
753 look-up table for deriving numerical age. *Geology*, **109**, 155-169.
- 754 **McCoy, V.E., Young, R.T. and Briggs, D.E.G.** (2015) FACTORS CONTROLLING EXCEPTIONAL
755 PRESERVATION IN CONCRETIONS. *Palaos*, **30**, 272-280.
- 756 **Meckler, A.N., Ziegler, M., Millan, M.I., Breitenbach, S.F.M. and Bernasconi, S.M.** (2014) Long-term
757 performance of the Kiel carbonate device with a new correction scheme for clumped isotope
758 measurements. *Rapid Communications in Mass Spectrometry*, **28**, 1705-1715.
- 759 **Meister, P., Gutjahr, M., Frank, M., Bernasconi, S.M., Vasconcelos, C. and McKenzie, J.A.** (2011)
760 Dolomite formation within the methanogenic zone induced by tectonically driven fluids in
761 the Peru accretionary prism. *Geology*, **39**, 563-566.

- 762 **Meister, P., McKenzie, J.A., Vasconcelos, C., Bernasconi, S., Frank, M., Gutjahr, M. and Schrag, D.P.**
 763 (2007) Dolomite formation in the dynamic deep biosphere: results from the Peru Margin.
 764 *Sedimentology*, **54**, 1007-1031.
- 765 **Melendez, I., Grice, K., Trinajstić, K., Ladjavardi, M., Greenwood, P. and Thompson, K.** (2013)
 766 Biomarkers reveal the role of photic zone euxinia in exceptional fossil preservation: An
 767 organic geochemical perspective. *Geology*, **41**, 123-126.
- 768 **Morais Neto, J.M., Hegarty, K.A. and Karner, G.D.** (2006) Preliminary constraints on
 769 paleotemperature and landscape evolution in and around Araripe Basin, northeastern Brazil,
 770 using apatite fission track analysis. *Boletim de Geociências da Petrobras*, **14**, 113-119.
- 771 **Morais Neto, J.M., Hegarty, K.A., Karner, G.D. and Alkmim, F.F.** (2009) Timing and mechanisms for
 772 the generation and modification of the anomalous topography of the Borborema Province,
 773 northeastern Brazil. *Marine and Petroleum Geology*, **26**, 1070-1086.
- 774 **Mozley, P.S.** (1989) Complex compositional zonation in concretionary siderite - implications for
 775 geochemical studies. *Journal of Sedimentary Petrology*, **59**, 815-818.
- 776 **Mozley, P.S.** (1996) The internal structure of carbonate concretions in mudrocks: A critical evaluation
 777 of the conventional concentric model of concretion growth. *Sedimentary Geology*, **103**, 85-
 778 91.
- 779 **Mozley, P.S. and Burns, S.J.** (1993) Oxygen and carbon isotopic composition of marine carbonate
 780 concretions - an overview. *Journal of Sedimentary Petrology*, **63**, 73-83.
- 781 **Müller, K.J.** (1985) Exceptional preservation in calcareous nodules. *Philosophical Transactions of the*
 782 *Royal Society of London Series B-Biological Sciences*, **311**, 67-&.
- 783 **Nollet, S., Koerner, T., Kramm, U. and Hilgers, C.** (2009) Precipitation of fracture fillings and cements
 784 in the Buntsandstein (NW Germany). *Geofluids*, **9**, 373-385.
- 785 **Peryt, T.M. and Anczkiewicz, R.** (2015) Strontium isotope composition of Middle Miocene primary
 786 gypsum (Badenian of the Polish Carpathian Foredeep Basin): evidence for continual non-
 787 marine inflow of radiogenic strontium into evaporite basin. *Terra Nova*, **27**, 54-61.
- 788 **Ponte, F. and Ponte Filho, F.** Evolução tectônica e classificação da Bacia do Araripe, in Proceedings
 789 Boletim do 4º Simpósio sobre o Cretáceo do Brasil UNESP, Campus de Rio Claro, São Paulo,
 790 1996, p. 123-133.
- 791 **Raiswell, R.** (1971) Growth of Cambrian and Liassic concretions. *Sedimentology*, **17**, 147-171.
- 792 **Raiswell, R.** (1976) The microbiological formation of carbonate concretions in the Upper Lias of NE
 793 England. *Chemical Geology*, **18**, 227-244.
- 794 **Raiswell, R. and Fisher, Q.J.** (2000) Mudrock-hosted carbonate concretions: a review of growth
 795 mechanisms and their influence on chemical and isotopic composition. *Journal of the*
 796 *Geological Society of London*, **157**, 239-251.

- 797 **Rios-Netto, A.M., Regali, M.S.P. and Carvalho, I.S.** (2012) Palinoestratigrafia do intervalo Alagoas da
 798 Bacia do Araripe, Nordeste do Brasil. *Revista Brasileira de Geociências*, **42**, 331-342.
- 799 **Schmid, T.W. and Bernasconi, S.M.** (2010) An automated method for 'clumped-isotope'
 800 measurements on small carbonate samples. *Rapid Communications in Mass Spectrometry*,
 801 **24**, 1955-1963.
- 802 **Selles-Martinez, J.** (1994) New insights in the origin of cone-in-cone structures. *Carbonates and*
 803 *Evaporites*, **9**, 172-186.
- 804 **Shackleton, N.J. and Kennett, J.P.** (1975) Paleotemperature history of the Cenozoic and the initiation
 805 of Antarctic glaciation: oxygen and carbon isotope analyses in DSDP Sites 277, 279, and 281.
 806 *Initial reports of the deep sea drilling project*, **29**, 743-755.
- 807 **Smith, R.J.** (2000) Morphology and ontogeny of Cretaceous ostracods with preserved appendages
 808 from Brazil. *Palaeontology*, **43**, 63-98.
- 809 **Teichert, B.M.A., Torres, M.E., Bohrmann, G. and Eisenhauer, A.** (2005) Fluid sources, fluid
 810 pathways and diagenetic reactions across an accretionary prism revealed by Sr and B
 811 geochemistry. *Earth and Planetary Science Letters*, **239**, 106-121.
- 812 **Trinajstić, K., Sanchez, S., Dupret, V., Tafforeau, P., Long, J., Young, G., Senden, T., Boisvert, C.,**
 813 **Power, N. and Ahlberg, P.E.** (2013) Fossil musculature of the most primitive jawed
 814 vertebrates. *Science*, **341**, 160-164.
- 815 **Wang, Z.G., Schauble, E.A. and Eiler, J.M.** (2004) Equilibrium thermodynamics of multiply
 816 substituted isotopologues of molecular gases. *Geochimica et Cosmochimica Acta*, **68**, 4779-
 817 4797.
- 818
- 819